THORPE'S DICTIONARY
OF
APPLIED CHEMISTRY
VI

THORPE'S DICTIONARY
OF
APPLIED CHEMISTRY

BY
(the late)

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AND

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ASSISTED BY EMINENT CONTRIBUTORS

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VOL, VI

With an index to Vols. I—VI by Dr. J. N. Goldsmith

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FOREWORD.

The first volume of the original edition of this Dictionary was published in 1890 under the editorship of Professor T. E. (later Sir Edward) Thorpe (Professor of Chemistry in the Normal School of Science and Royal School of Mines, South Kensington), who explained in the preface that the work is "*essentially a Dictionary of Chemistry in its Applications to the Arts and Manufactures*; *hence it deals but sparingly with the purely scientific aspects of Chemistry, unless these have some direct and immediate bearing upon the business of the technologist.*" The first edition occupied three volumes; the second and third editions, in five and seven volumes respectively, were also edited by Sir Edward Thorpe, but the third edition was still in course of publication at the time of his death in 1925. Seven years after its completion this edition was brought up to date by the publication, in 1934-36, of two supplementary volumes, together with a glossary and index. These were jointly edited by Professor J. F. (later Sir Jocelyn) Thorpe (Professor of Organic Chemistry and Director of Organic Chemistry Laboratories, Royal College of Science, Imperial College of Science and Technology, South Kensington) and Dr. Martha A. Whiteley (Assistant Professor of Organic Chemistry at the same college), thus maintaining the association of the Dictionary with the Chemistry Staff of the Royal College of Science.

The publication of a supplement was in itself insufficient to keep the Dictionary in line with the modern trend of applied chemistry, for the last one or two decades have shown clearly that pure science and technology, so tacitly distinguished in Sir Edward Thorpe's original preface, cannot be divorced. This changed attitude is reflected in the present edition of the Dictionary, of which Volumes I to VI inclusive have now been published under the above editorship. * This edition is wider in scope than the preceding ones, and is intended to be a general work of reference for all who are concerned with various branches of chemistry and chemical industry.

The death of Sir Jocelyn Thorpe again made new editorial arrangements necessary. In order to maintain a balance between the various branches of chemical science an Editorial Board has been formed, comprising Professor Sir Ian M. Heilbron (Professor of Organic Chemistry and Director of the Laboratories for Organic Chemistry at the Imperial College) (Chairman), Dr. H. J. Emeléus (Professor of Inorganic Chemistry in the University of Cambridge), Professor H. W. Melville (Professor of Chemistry in the University of Aberdeen), and Professor A. R. Todd (Professor of Organic Chemistry in the University of Cambridge). This Board will determine the general editorial policy in conjunction with the publishers. Dr. Whiteley continues as Editor, and Dr. A. J. E. Welch (Lecturer in Inorganic Chemistry at the Imperial College) becomes Assistant Editor.

It is proposed to complete the current edition with seven further volumes, which it is hoped to publish at yearly intervals. Although the Board, do not consider any major modification is called for in the general character of the work, they are of the opinion that certain changes in the scope of the articles will enhance its value.

Nowadays a great and growing part of applied chemistry involves a fundamental knowledge of physical chemistry. It is, therefore, felt desirable to increase the proportion of articles in this field. In the view of the Board this important addition can be achieved without increase in the number of volumes by the judicious selection of the subject matter, and the pruning of historical material. Twenty articles on physico-chemical subjects are included in this volume and, so far as is possible, other articles in this category, supplementing those which have appeared in Volumes I to V, will be included in later volumes under modified titles.

Each subsequent volume will contain an index. An index of the first six volumes is included in the present volume: this has been prepared by Dr. J. N. Goldsmith, to whom thanks are due also for valuable assistance in proof-reading.

The editorial work of the Dictionary continues to be carried on in Cambridge, and grateful acknowledgment is made to the Management Committee of the University Chemical Laboratory for the accommodation and library facilities afforded for this purpose.

M. A. WHITELEY.

CAMBRIDGE,
February, 1943.

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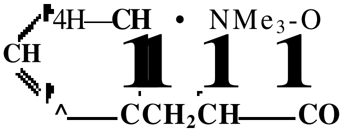
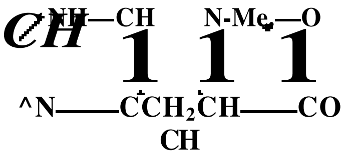
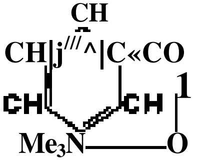
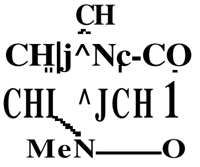
I	686(2	*(above 16*)*		
I	686d	*(bottom)*		
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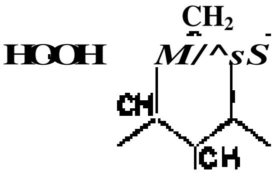
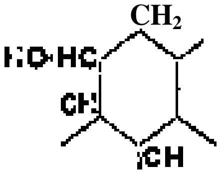
II	529c	(Formula A.)		
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A DICTIONARY OF APPLIED CHEMISTRY.

G—*continued.*

GLAUBERITE (v. Vol. II, 233c).

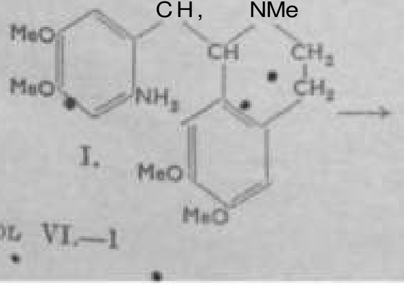
GLAUCANIC ACID (v. *Vol.* **V,** 566).

GLAUCIC ACID (v. Vol. **V,** *56b).*

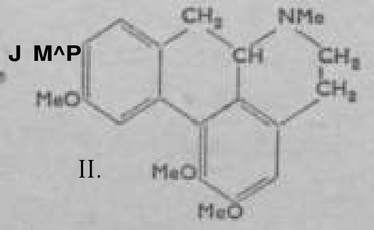
GLAUCINE, $C_{21}H_{25}O_4N$, occurs in several plants of the Pupuveracca? and FiimiiriacesB femiliea. It was first isolated from *Qiaudum luteum* by Probst {Annalen, 1839, 31, 241) and from the same plant along with protopine by R. Fischer (Arch. Pharm. 1901, 239, 426). Since then glaucine has been isolated from *Corydalis tuberosa* (Gadamer, *ibid.* 1911, 249, 25:4), *Dicznlra eximia,* D. *formosa* and *D. oregana* (Manske, Canad. J. Res, 1933, 8, 592: 1 tm, 10,521,7155; 1937; 15, B, 274). Ordinary glaucine is dextrorotatory; Go (J. Pharm. Soc. Japan, 193t), 50, 122 or Cheni. Zentr. 1931, I, '1)1} claims to have obtained *l-glaucine* from a Korean corydalis.

Extraction of glaucife from *Glaucium luteum, see* Barger and Silberschmidt, J.C.S. 1928, 2923. The base was first prepared in a pure state and characterised by II. Fischer *(IA).* It crystallises in colourless rhombic prisms or bundles of needles, m.p. 119-120°, $[\alpha]_D$+m° (in EtOH). The base is soluble in the usual organic solvents, as a non-phenolic aporphine base (for definition, see Gadamer *et al.,* Arch. Pharm. 1925, 283, 81); it is also soluble in light petroleum. The salts are crystalline, although they may precipitate as jellies (especially the hydrochloride). Apart from its natural source, glaucine has been obtained from *laurotetani* «e. N •*vietkyllauTOtetani-iic, boldine.* and *glaucentrine* by methylation (Barger and 'SiJljerschmidt, ?c.; Spath*and Straubal, **Ber. 1828,** 61 [B], 2398; Spatb and Suominen, *ibid.* 1933, » Li*], 1344; Warnat, *ibid.* 1925, 58 [B], 2768; ***Hid.*** 192fi, 59 [B], 85).

Glaucine has been synthesised by Gadamer (Arch. Pharm? 1911, 249, 680) by treating a diazotised solution of aminolaudanosine (I) with copper powder, when |jlifii.i)itlirfno-N-methyU ^ranydropapaverine (U), identical with **(B-glati** *"-- formed (*see also* PBohorr, Ber. 1904, 37, 1926):



I.



II.

Like all racemic aporphine bases, dl-glaucine can easily be resolved into the optically active compounds by means of the *d-* and *l*-tartaric acids.

Glaucidine, m.p. 238-239° (decomp. starting at 209-210°) has been isolated from *Papavtr orientate* (Klee, Arch. Pharm. 1914, 252, 274); it is believed to be closely related to glaucine.

Glaucentrine, $C_{17}H_{13}N(OH)(OMe)_3$, m.p. 148° has been isolated from *Dicentra eximia* (Manske, Canad. J. Res. 1938, 16, 81). By methylation with diazomethane glaucine is obtained. Glaucine is said to induce narcosis accompanied by some tetanising action.

Schl.

GLAUCOBILIN (v. Vol. T, 691c).

GLAUCONIC ACID ***(v.*** Vol. **V,** 566). •

GLAUCONITE. *[Okmeonk,* Fr.; %«-*konit,* Ger.) Hydrated silicate of iron, potassium, etc., of variable composition, found as small rounded grains in sedimentary rocks. It was named in 1828, from *yXavws,* bluish-green, on account of its characteristic colour, which is of various shades of dark green. The **typical** occurrence of the mineral is the **Gnensand** formation {below the Chalk) of tho Cretaceous system, but it is also met with in sands, sandstones, marls and limestones of all ages from the Cambrian, and is forming at the present day on the floor of the ocean. The granules measure about J to 1 mm. in diameter. Under the microscope they show a clear green or yellowish-green, slightly pleojhroic and birefringent material embedded in a network of black, optically isotropic, organic matter, the latter having the composition of humic acid. The mineral is decomposed by hot concentrated hydrochloric acid, and before the blowpipe it is fusible with difficulty to a black magnetic slag.

Analysis I is of grains isolated from a calcareous sandstone in the Upper Greenland at **Woodbnxn, Camckfergn*,** Co. Antrim '.\. I, Hoskins. QML Mag. 1895). II, from the Cambridge (Jrrcnsand (G. D. Liveing, Geol. Mag.

. 1866). Ill gives the extreme values shown in ten analyses of glauconite grains isolated from Eocene, Cretaceous, and Jurassic sandstones and from Lower Silurian limestone from various Russian localities; sp.gr. 2-40-2-87, varying like the colour—yellowish-green and dark green —with the percentage of iron (K. D. Glinka, 189(5). IV, grains forming 83% of a sandy deposit dredged at a depth of 556 fathoms from the Pacific off Panama (W. A. Caspari, Proc. Roy. Soc. Edin. 1910, 30, 364). V, similar material dredged at 110 fathoms from the AguL has Bank, South Africa (W. A. Caspari, J.&). Numerous analyses of glauconite are quoted by C. K. Leith, Monographs, U.S. Geol. Survey, 1903,53,240. Analyses of Swedish glauconites, by N. Sahlbom, Bull. Geol. Inst. Univ. Upsala, 1916, . 15, 211; A. Hadding, Lunds Univ. Arsskrift, 1932, 28, No. 2.

	I.	II.	III.		IV.	V.
			Slin.	Max.		
SIO_8. .	40-00	51·09	41·02	52-96	49·12	51·15*
AI2O3 .	13·00	9·00	5-84	22-19	7·09	7-61
&^{Or} .	16-81	—	8-17	23-43	25-95.	18-83
&. .	10-17	19-54	1-32	5-95	0-8f	2-78
MgO .	1-97	3-37	0-69	4·11	3·10	c4-54
CaO . .	1-97	0-30	—	8-37	—	—
Na_2O .	2·16	3-56	0-30	0-98	—	—
K_2O. .	8*21	2-47	5-74	9-54	7·02	7-80
H;O. .	6·19	10-80	4-45	7-88	7·12	7-56
	100-48	100-13	—	—	100-29	100-27

The chemical composition has been discussed and a variety of formulae deduced by A. F. Hallimond, Min. Mag. 1922, 19, 330; C. S. Ross, Proc. U.S. Nat. Mus. 1926, 69, art. 2; H. Schneider, J. Geol. 1928, 13, 589; A. Hadding, *I.e.;* J. W. Gruner, Amer. Min. 1935, 20, 699; K. Smulikowski, Arch. Min. Soc. Sci. Varsovie, 1936, 12, 145. Closely allied to glauconite are the minerals celadonite (green-earth) and greenalite (this vol., p. 135<£).

The Greensand of England, consisting mainly of sandy beds with quartz grains intermixed with glauconite, is developed in the Wealden area, the Isle of Wight, and extends from Berkshire and Oxfordshire to Norfolk and Lincolnshire. Some of the limonitic iron-ores of these districts may possibly, likr those of the Lake Superior region, have been derived by the alteration of glauconite. The same formation has also a wide distribution on the Continent. In America, greensand and glauconitic marls of Cretaceous and Tertiary age are developed in New Jersey, Virginia, Kentucky and Tennessee. The glauconite marls of New Jersey contain K_8O 1-54-7-08% with P_aO_5 019-6-87%, and have been extensively used in the raw state as an agricultural dressing (*v.* Ann. Rep. State Geologist New Jersey, 1886,1892,1893). Those from Virginia have been used in the preparation of commercial fertilisers. Attempts have been made to extract potash from greensands (U.S. Geol. Survey, Min. Res. for 1911, 1912, ii, 901).

The frequent association of phosphatic nodules with glauconite deposits has some bearing on the origin of glauconite. The terrigenous deposits of green mud and sand formed on the floor of the ocean at depths of i'^bout <£03 to 1000 fathoms, and found by the'"' Challenger^' Expedition to be of wide distribution, particularly off continental coast lines composes of igneous rocks, contain this mineral in considerable amount. The potash set free by the weath jring of the felspars < and micas of these rocks and carried into the sea is conserved by the formation of glauconite, but apparently only through organic agencies, which &t the same time give origin to the phosphatic nodules. Grains of glauconite are frequently found filling the chambers of foraminifera and other organisms ; and in the artificial production of the mineral the presence *of* an .organic acid seems to be essential (W. A. Caspari, *I.e.).* E. W. Galliher (Bull. Geol. Soc. Alner. 1935, 46, 1351) gives analyses showing the gradual alteration of biotite to glauconite in Monterey Bay, California, and suggests that the alteration is due to sulphur bacteria in the black mud and alkaline sea-water.

L. J. S.

GLAZES AND^RITS. In the ceramic industry the term " glaze " is intended to convey a vitreous coating fixed by heat on the underlying pottery body.

Pottery bodies cover a very wide range of articles made from clay, whicfc when fired give a hard mass, but, except in the case of clays which of themselves giye, when fired, a perfectly vitreous surface,- remain of a porous nature and readily absorb moisture, and consequently are unsuited to domestic requirements.' It becomes necessary, therefore, after the first fire, when the ware is in what is termed the " biscuit state," to affix to it a coating which, on being again subjected to heat, will render it impermeable to moisture and impart a smooth and glossy surface.

The term "glaze," however, while being understood to refer to this vitreous coating, is also applied to the mixture of ground materials used in the compounding of such glaze, and which mixture may be either in the form of a dry powder or an emulsion of these materials suspended in water. The terms used for these two varieties are " dry glaze " and " slop daze " and these are often supplied to potters by millers "specially equipped for their manufacture. The pottery thus avoid the trouble of makuig small quantities in their own works.

Glazes broadly may be divided into three classes, viz., transparent, opaque arid coloured, but all must fulfil certain conditions, viz.:

(1) Must be sufficiently hard to resist abrasion.

(2) For domestic use should be resistant to the action of ordinary acids.

(3) Must be sufficiently fusible to adhere firmly to the body without subjecting this to any undue risk of warping during fire, but sufficiently infusible to prevent running off the biscuit ware during the firing of the glaze.

(4) Must have approximately the same co- . to prevent the

nun v* W»VMWA w*. vuv v n\j [illegible] of glaze,

viz., crazing and peeling.

(6) Must hold dissolved, without unsightly e^rafons, metalhc oxides that have been added to impart colour.

(6) Must not exGrt too strong a solvent action on the colours \$ed in painting and decoration of the ware.

Ti^ difficulties attending the fulfilment of such varied conditions therefore ^necessarily involve much careful study and research work by tEg} potter, and having regard to the many varieties of bodies used £nd the conditions appertaining to the methods* of compounding both the body and also the glaze, and the methods of firing, the published recipe* of any glaze is of y^ry little practical service unless accompanied by an accurate description of the body on which it is applied, and the many other factors involves. Much general information may, however, be obtained by a knowledge of the fundamental principles involved and the materials available to produce the desired result.

At first sight glass seems to haye some of the required properties, but when &red on the body it yields a devitrified mass scarcely sintered together. It becomes evident then, that what is required is something which, while stilhof a glassy nature, needs additions of other materials to render it of servi<&. Ordinary flint glass consists of silica, soda, lime and lead, and using these materials as a basis of experiment, the necessary additions and alterations can be made to bring about the desired result.

The composition of glazes varies within very wide limits according to the maximum temperature required to mature them, the duration of the firing and the nature of the body on which they are* fired. The -fusion point of a glaze depends on the nature of the ingredients used as well as on the relative quantities employed. All glazes may be looked upon as glasses, and their fusing points will depend largely on the ratio of the basic compounds to the acidic content in the formation of silicates or borosilicates and also on the alumina content.

A convenient method of expressing the composition is in terms of the chemical formula which shows at a glance the relative molecular proportions of the different oxides present, the alumina being kept separate-and the silica and boric acid being classed as the acidic content.

Usually the bivalent basic oxides are collectively classed as RO, the whole being taken as one molecular proportion, then the alumina being placed as intermediary, followed by the acids (silica and be *Y;* acid). S«ch method enables easy comparison of the large number of recipes in existence which themselves give little indication of the true properties, and also enables the potter to see at a glance the possibility of substituting other materials for th&se called for in the recipe with tksassurance of maintaining the necessary equilibrium of the finished glaze. A simple example will illustrate the application of this principle.

A Fecipe for a glaze is given as white lead 258, china clay 52 and flint 81 parts.

Assuming all the materials to be pure and having the formulae :

		Mol. wt.
Wh2telead,	$Pb(OH)_2,2PbCO_3$	.775
China clay,	$Al_2O_3,2SiO_2,2H_2O$	. 258
Flint,	SiO_2	.60

I * simple calculaticn gives the formula of the glaze as **PbO**: 0-2 Al_2O_3, 1-75 SiO_2. Such a glaze would mature at a relatively low temperature, approximately 900°C.

Generally speaking, the maturing point of a glaze may be said to be governed by:

(1) The equivalent proportion between acids and bases.

(2) The proportion of alumina in relation to the bases and acids.

(3) The ratio between the silica and boric acid. The higher the silica content of the glaze, the less fusible it becomes, therefore the modification of the proportion of silica in a glaze affords an easy means of regulating its fusibility.

Expressed in the foregoing manner, the whole range of glazes in common use fall within the following limits:

Common Pottery.

nQ: J-5 SiO_2 to RO : 3 SiO_2

EartXenware, Bone China and Stoneware.

RO: 0-25 Al_2O_3, 2-5 SiO_2
to RO: 0-40 Al_2O_3, 4-5 SiO_s

Porcelain.

RO:0-5 Al_2O_3, 5'0 SiO_2
to RO: 1-25 Al_aO_3, 120 SiO_2

with firing temperatures ranging from 900-1,450°C.

Glazes fall conveniently into four groups according to composition, viz.:

(1) *Alkaline,* which are mainly silicates of the alkalis or of alkalis and lime.

(2) *Felspathic,* consisting of silica, alumina and alkalis and containing a large proportion of felspar or felspathic rock.

(3) *Lead,* consisting mainly of silicates and borosilicates, of alkali? and alkaline earths with some alumina and softened by addition of lead oxide and boric acid.

(4) ***Enamels or opaque glazes,*** **which are usually,** of similar composition to lead glazes, but rendered opaque by the addition of opaojfying agents such as tin oxide, arsenious oxide, zirconia, etc.

Alkaline Glazes.—The simplest example of the first type of glaze, *i.e.* the alkaline, is the well-known *salt gkize* used extensively on stoneware, but also formerly applied to earthenware which, when fii*^, is essentially an alkali-alumina silicate. It is produced in practice by the introduction of common salt into the kiln when the ware is near its vitrifying point. The vapour of the salt accompanied by steam decomposes the salt into sodium oxide and hydrochloric acid, the former entering into combination with the silica, alumina and basic compounds of the clay to form, a sodium alumina glass very rich in silica. A very good salt glaze, after firing, approximates to the formula :

RO: 0-5 Al_2O_3, 4*0 to 80 SiO_2

As £he salt gives only the #ne constituent, viz.: Na_2O to the RO content, it is evident that the remainder of the formula must be taken up from the body.

It is also essential that the body shall possess the alumina and silica in such a ratio as to give the most stable glaze. The body also must contain sufficient fluxing material to become vitreous at a reasonable heat, for if the body be still porous when the alkali fumes are introduced in the kiln, these will be absorbed by the clay ware without glazing the surface.

Much research work has been done with a view to finding the best relations between the constitution of a clay and its ability to form a good salt glaze. L. *E.* Barringer (Trans. Amer. Ceram. Soc. 1902, 4, 211) proves that, contrary to some expressed opinions, it is essential that the clay shall have a certain alumina-silica ratio to be capable of giving a good salt glaze. He gives the analysis of the clay used, and also of the glaze, taken from fired specimens of what is known as a first class salt-glaze product.

Clay analysis.

SiO_2	63·11
Al_2O_3	23·30
Fe_2O_3	2·83
CaO	[illegible]
MgO	0·970
Na_2O	0·490
K_2O	0·930
SO_3	0·240
H_2O	7·810
	99·810

corresponding to the formula:

$$\left.\begin{matrix} 0{\cdot}050\ CaO \\ 0{\cdot}108\ MgO \\ 0{\cdot}034\ Na_2O \\ [illegible]\ K_2O \end{matrix}\right\} \left.\begin{matrix} 1{\cdot}00\ Al_2O_3 \\ 0{\cdot}06\ Fe_2O_3 \end{matrix}\right\} 4{\cdot}005\ SiO_2$$

$$+ 1{\cdot}95\ H_2O$$

and the glaze gave

SiO_2	55·475
Al_2O_3	21·340
Fe_2O_3	2·640
CaO	3·500
MgO	0·041
Na_2O	17·210
K_2O	0·080
	100·285

corresponding to the formula:

$$\left.\begin{matrix} 0{\cdot}812\ Na_2O \\ 0{\cdot}002\ K_2O \\ 0{\cdot}182\ CaO \\ 0{\cdot}002\ MgO \end{matrix}\right\} \left.\begin{matrix} 0{\cdot}615\ Al_2O_3 \\ 0{\cdot}048\ Fe_2O_3 \end{matrix}\right\} 2{\cdot}704\ SiO_2$$

RO = 0·998

It will be noticed that for the clay, Al_2O_3 is taken as unity, while in the glaze the sum of the bases RO is taken as unity, following the practice usually adopted in ceramic calculations. This particular clay is thus seen to have an Al_2O_3 : SiO_2 ratio of [illegible].

From further experiments recorded in the same work the author still got a good salt glaze, by the addition of free silica to the original clay up to the ratio Al_2O_3 to SiO_2 1:10.

Knell (Tonind-Ztg. 1896, 20, 495) assumed that the salt vapour attacked a double silicate of aluminium and iron in the body; the sodium of the salt displaced the iron of the [illegible] silicate; and the salt glaze remained behind as a double silicate of aluminium and sodium. The iron was supposed to be liberated as ferric chloride which, in contact with water vapour in the oven, was transformed into ferric oxide and hydrogen chloride. He gives the reactions occurring as:

$$(AlFe)_2O_3+SiO_2+6NaCl \rightarrow [illegible] + Fe_2Cl_6,$$

$$Fe_2Cl_6+3H_2O \rightarrow Fe_2O_3+6HCl$$

But this view meets with little approval, as the quantity of iron present in the clay body exposed to the action of the salt fumes is too small to account for the amount of glaze formed.

It is quite evident, however, *that* the salt vapour, in attacking the silica and alumina of the body, will have its effect on the iron content of the clay according to the amount of iron present, and also to the nature of the fire just prior to salting, as in the event of this being "reducing," the iron will be reduced to the ferrous state and give to the finished glaze a much darker colour than if an oxidising atmosphere had been maintained throughout the firing and glazing. While salt glaze is mainly used in the stoneware industry, it is interesting to note that in the early eighteenth century much fine earthenware of a good white colour was glazed by this process, but it was entirely abandoned with the advent of lead glazes.

The chief advantage of salt glaze is its high resistance to the action of acids and this property has led to its extensive use in the manufacture of articles for the chemical industry.

In applying the salt glaze the ware is placed in the kiln with the surfaces to be glazed exposed to the kiln atmosphere. When the temperature corresponding to the vitrifying stage of the clay ware is reached and a clear fire maintained, a quantity of salt is thrown in the fire-holes; this decomposes in the kiln with a lowering of the temperature inside the kiln of about 100°C. The fires are then fed to restore the temperature to the desired level and a further batch of salt introduced; the same procedure may be repeated three or four times according to the quantity of salt used in each application and the composition of the body. After the last salt application, the reheating is repeated until the maximum temperature is reached, approximately 1,250°C., when the kiln is allowed to cool.

It has been suggested (Everhart, J. Amer. Ceram. Soc. 1930, 13, [illegible] salt, instead of being ap[illegible] method, can be utilised [illegible] a glaze when embodied in a slip and dipped on the ware in the usual [illegible] clay slip made from the same material [illegible] body often the ideal medium [illegible] the salt. A mixture of [illegible] together and applied either by dipping [illegible] ground [illegible] spraying and fired to about [illegible] C. [illegible] a [illegible] smooth surface. This [illegible] does not seem to have passed the experimental stage, but the results so far obtained are quite satisfactory. Coloured slips may also be used with good effect.

Feisptathic Glazes.—This type covers the range uausflly twined Bristol Glazes which are ofN febpathic type and maturing atfla high temjWa/ure, I,'250-L,300°C. They are of two varitties^-tranaparent and opaque—and mainly us^d on stoneware and glazed bricks. In this type a representative formula, for a transparent glaze would be: (N. D. Wood, Trans. Cerara. 'Sue. 1935, 34, 279)

$$\left.\begin{array}{l}0{\cdot}18\ K_2O\\0{\cdot}38\ CaO\\0{\cdot}44\ ZnO\end{array}\right\}0{\cdot}21\ Al_2O_3,\ 1{\cdot}95\ SiO_2$$

.the raw materials usuallj adopted being felspar, whiting, zinc oxide, ehinj clay and flint, whereas the opaque variety is produced by varyiifg the proportions of the sanftj raw materials and adding an opacifying agent such as tin oxide, zirconia, arseuious oxide, bona fish, etc. Such glazes approximate to the formula:

$$\left.\begin{array}{l}0{\cdot}50\ K_2O\\0{\cdot}40\ ZnO\\0{\cdot}10\ CaO\end{array}\right\}0{\cdot}50\ Al_2O_3,\ 3{\cdot}00\ SiO_2$$

Dheso glazes possess the advantage of elf ap-ness, no i'rittijij: being required, but they do not give a very brilliant surface, so that for the better classes of stoneware (domestic and art ware) a Fritted icadless-glnze is usually adopted with the approximate formula as follows :

Frit

$$\left.\begin{array}{l}0{\cdot}14\ K_2O\\0{\cdot}10\ Na_2O\\0{\cdot}09\ CaO\\0{\cdot}67\ ZnO\end{array}\right\}0{\cdot}41\ Al_2O_3\left\{\begin{array}{l}2{\cdot}01\ SiO_2\\0{\cdot}13\ B_2O_3\\0{\cdot}006\end{array}\right.$$

Glaze containing 3% of above frit

$$\left.\begin{array}{l}0{\cdot}157\ K_2O\\0{\cdot}0\text{[illegible]}\ Na_2O\\0{\cdot}537\ CaO\\0{\cdot}133\ BaO\\0{\cdot}082\ ZnO\end{array}\right\}0{\cdot}567\ Al_2O_3\left\{\begin{array}{l}\text{[illegible]}{\cdot}025\ SiO_2\\0{\cdot}037\ B_2O_3\\0{\cdot}053\ SnO_2\end{array}\right.$$

A folspathie glaze, as used in the production of **hard** porcelain, both Continental and English, with which the body is first fired at a low temperature, about SO0°C.. ami then glazed, and fired at a very high temperature (1,45O-1,55O°C0, would approximate to the formula:

$$\left.\begin{array}{l}0{\cdot}62\ K_2O\\0{\cdot}38\ CaO\end{array}\right\}1{\cdot}33\ Al_2O_3,\ 15{\cdot}60\ SiO_2$$

The third <;rmip of glazes comprises those consisting mainly of tiilicates and boro-silicates with sucue alumina and softened by the addition of lead oxide; such include all **ordinary** English earthenware transparent glaze and also moat of the English porcelains.

The best glazes in this group approximate to the **formula** i

$$\left.\begin{array}{l}0{\cdot}30\ KNaO\\0{\cdot}40\ CaO\\0{\cdot}30\ PbO\end{array}\right\}0{\cdot}18\ Al_2O_3\left\{\begin{array}{l}2{\cdot}10\text{–}3{\cdot}00\ SiO_2\\0{\cdot}40\ B_2O_3\end{array}\right.$$

and give *a* good clear transparent glaze when fired to about 1,150°C.

These glazes are visually compounded from a frit consisting of borax, whiting, Hint, felspar and china flay, to which is added on grinding white lead, felspar or Cornish atone, china clay and flint.

A typical example of such a glaze, is :

Frit

Borax	37·7
Whiting	18·8
Cornish stone	18·8
Flint	18·8
China clay	5·6
	99·7

Glaze

Frit	36·8
Cornish stone	31·8
Flint	10·2
White lead	21·2
	100·0

giving formula:

Frit

$$\left.\begin{array}{l}0{\cdot}370\ KNaO\\0{\cdot}630\ CaO\end{array}\right\}\text{[illegible]}\left\{\begin{array}{l}1{\cdot}90\ SiO_2\\0{\cdot}64\ B_2O_3\end{array}\right.$$

Glaze.

$$\left.\begin{array}{l}0{\cdot}30\ KNaO\\0{\cdot}40\ CaO\\0{\cdot}30\ PbO\end{array}\right\}0{\cdot}30\ Al_2O_3\left\{\begin{array}{l}3{\cdot}10\ SiO_2\\0{\cdot}36\ B_2O_3\end{array}\right.$$

FRITTKIO.—The, limitations of raw glozea are so great by reason of the small number of materials available that in order *tq* widen the **field** it is essential to resort to the process of fritting which accomplishes threo objects;

(1) Makes a soluble substance insoluble.

(2) Drives out volatile and useless substances in the **original materials** which otherwise would have to be done when the glaze is on the surface of the ware.

(3) Enables small amounts of colouring oxide* to be introduced into a glaze which if brought in as the raw oxides would not be disseminated evenly in the whole moss of glaze.

Certain rules should be observed in fritting:

(1) The ratio between acids and bases in *the* frit **should** be wituin the range of easy fusion, i.e. the acid molecules should not fall below the base molecules nor exceed them three times. The low limit is exemplified by the formula:

$$\left.\begin{array}{l}0{\cdot}3\ Na_2O\\0{\cdot}3\ K_2O\\0{\cdot}4\ CaO\end{array}\right\}0{\cdot}1\ Al_2O_3\left\{\begin{array}{l}0{\cdot}7\ SiO_2\\0{\cdot}3\ B_2O_3\end{array}\right.$$

and the high limit by :

$$\left.\begin{array}{l}0{\cdot}3\ Na_2O\\0{\cdot}3\ K_2O\\0{\cdot}4\ CaO\end{array}\right\}0{\cdot}1\ Al_2O_3\left\{\begin{array}{l}2{\cdot}\text{[illegible]}\ SiO_2\\0{\cdot}6\ B_2O_3\end{array}\right.$$

(2) The two substances most commonly requiring fritting are the alkalis, nearly alt salts of which are soluble, and boric aeid which is itanlf soluble and also forms some soluble salts.

The alkalis are remarkable in that they form soluble silicates; therefore it is not enough to fuse a soluble alkali compound with silica, as this would not produce an insoluble silicate. For instance, $K_2O:2SiO_2$ when fritted is soluble, but $0{\cdot}5K_2O:0{\cdot}5CaO:2{\cdot}0SiO_2$ is insoluble. A base which forms an insoluble silicate, *e.g.* lime, lead, zinc, alumina, etc., may reduce or inhibit the solubility of the alkaline silicates. Boric acid also requires crossing to make its products safe for use. A common practice years ago among some potters was to frit boric acid and flint together without any basic matter. Such a frit, however, is not insoluble.

A good rule to follow is to use at least two bases other than the alkalis, one of which shall be Al_2O_3, if the glaze formula allows of this.

(3) The ratio between the alkalis and boric acid in the frit formula should be the same as in the completed glaze, otherwise some other source of alkali or B_2O_3 will need to be introduced in the glaze, and to avoid this is the object of fritting.

(4) The ratio between the alkalis and the other elements of the frit must not fall below that existing in the glaze for the same reason as in (3). It may exceed this ratio, as additions of the insoluble bases are readily made in *the* glaze.

Preparation of Frit.—Any extra time spent on the preparation of and the thorough mixing of the ingredients of the frit is a very distinct advantage as usually the materials are purchased ready ground, and only need mixing in the desired proportions. The practice of mixing in a box by means of shovelling cannot be too strongly condemned. The method is inefficient and raises an injurious dust. A simple means of effecting efficient mixing is by means of a cylinder with paddle instead *of* pebbles, or a wooden barrel, preferably with an eccentric motion. A well-mixed frit should be readily fusible, and time is saved..

Frit Kiln.—The kiln in general use is of the type of the ordinary horizontal reverberatory furnace. The hearth of the furnace is composed of fireclay blocks and slopes to a central hole at the side. The fire gases coming from the grate pass over a firebridge, and thence over the hearth on which the charge has been filled through an opening in the top, and then passes on over another bridge at the end to the chimney.

The exit from the kiln is sealed with a fireclay block or a lump of china clay, and when the fused mass is ready for running off, this is withdrawn and the frit allowed to run into a tank of water placed underneath the opening. The water is then drained off and the frit taken to store ready to be ground with the other constituents of the glaze.

Where only small quantities of frit are required, such as frits for coloured glazes, the fusion may be conveniently carried out in a crucible furnace, many types of which are capable of being used either intermittently or continuously, the crucible being emptied into water as the frit is fused. Another method of making a small batch is by firing the crucible in the ordinary oven at the required temperature, but in this case the frit naturally sets to a hard mass on the cooling of the oven, and, is more difficult to break up for grinding.

In the typical glaze mentioned in the third group the lead is introduced in a raw state, viz., as white lead.

Some 40 years ago the Government appointed a commission to inquire into the prevalence of lead poisoning in the Potteries with a view to doing away with the use of lead in the glazes used. It quickly became recognised that it would be impossible to prohibit the use of lead compounds altogether, but suggestions for minimising the risks took the form of fritting the lead with other constituents of the glaze to render it insoluble in the gastric juices of the workers, and eventually the following restrictions were laid down as Special Rules by the Government (" Home Office Circular, December 14th, 1889):

" No glaze into the composition of which lead or a compound of lead, other than galena; enters, shall be regarded as satisfying the requirement as to insolubility which yields to a dilute solution of hydrochloric acid more than 4% of dry weight of a soluble lead compound calculated as lead monoxide when determined in the following manner: 'A weighed quantity of dried material is to be continuously shaken for one hour, at the common temperature, with 1,000 times its weight of an aqueous solution of hydrochloric acid containing 0·25 of HCl. This solution is thereafter to be allowed to stand for one hour, and to be passed through a filter. The lead salt in an aliquot portion of the clear filtrate is then to be precipitated and weighed as lead sulphate.' "

The general results of the application of these regulations to the pottery industry during the last 30 or 40 years has been the practical elimination *of* the grave risk of plumbism amongst the operatives.

While the general rule laid down seemed to be simple, many factors in the method of preparing the lead frits exert their influence on the final solubility of the product.

T. E. Thorpe in his evidence to the Lead Commission stated that " the insolubility of the lead depends not upon any one oxide or group of oxides with which it may be associated, but upon the maintenance of a certain ratio between the whole of the basic oxides on the one hand and the whole of the acidic oxide on the other • the acidic oxides in this case being silica and boric oxide." Thorpe therefore proposed an empirical rule which gives a very fair indication of the " low solubility » of a frit or glaze.

The rule may be stated thus:

$$\frac{\text{Sum of bases (including } Al_2O_3) \times 223}{\text{Sum of acids (including } B_2O_3) \times 60} = 2 \text{ or less,}$$

where 223 is the molecular weight of PbO and 60 the molecular weight of SiO_2.

[illegible] a guide for [illegible] compounding a [illegible] certain fac[illegible] [illegible] which are likely to affect the [illegible]

(1) The proportion of B_2O_3 to SiO_2 for it the former is unduly high, [illegible] no. conform to the Government test, although

Thorpe's ratio gives a figure below the calculated limit of solubility.

The effect of B_2O_3 on the solubility of a lead frit is illustrated as follows, by the work of G. D. Htifley (Trans. Ceram. Soc. 1935, 34, 166):

Frit composition

$$\left.\begin{matrix}0·3\ K_2O\\0·3\ CaO\\0·4\ PbO\end{matrix}\right\}0·2\ Al_2O_3\left\{\begin{matrix}2·8\ SiO_2\\n\ B_2O_3\end{matrix}\right.$$

boric oxide being the only variable

n	0	0·1	0·5	0·8
PbO solubility	0·19	0·91	1·07	5·89%

while the effect of alumina in counteracting the deleterious effect of boric oxide is shown in the following tests by the same investigator:

Frit composition :

$$\left.\begin{matrix}0·3\ K_2O\\0·3\ CaO\\0·4\ PbO\end{matrix}\right\}n\,Al_2O_3\left\{\begin{matrix}2·8\ SiO_2\\0·8\ B_2O_3\end{matrix}\right.$$

where alumina is the only variable

n	0	0·05	0·16	0·30
PbO solubility	11·38	9·64	5·56	5·46%

Another suggestion to overcome the action of increased solubility is the substitution of borocalcite or colemanite (both insoluble calcium borates) as the source of B_2O_3.

(2) Another factor affecting the solubility of a lead frit is the fineness of grinding. W. Jackson and E. M. Rich (Mem. Manchester Phil. Soc. **1900,** 45, No. 2) showed that the solubility of a frit varies with its degree of fineness. Their results obtained on elutriation in Schöne's apparatus gave;

Gauge reading	1	5	50	100 cm.
Solubility . .	17·5	8·7	4·0	1·5% **PbO**

While then it is evident that the fineness of subdivision has an influence on the degree of solubility, the effect is too small to be of serious moment within the limits of fineness occurring in actual practice.

The observations on the solubility of lead frits are important, but it must be remembered that the Government restrictions are applicable to the glaze as a whole and not to the lead frit contained in it. The amount of lead frit in a **standard** glaze rarely exceeds one-third of **the whole, and** it is quite possible that while **the** lead frit itself would not conform to the Thorpe ratio, the glaze as a whole might be well **within** the limits of the Government requirements, the remaining two-thirds of the glaze mixture being composed of entirely insoluble material.

In practice, it is usual to adopt the bisilicate of lead or even more complex silicates in order to keep the solubility as low as possible, and the preparation of low.solubility glazes was considerably simplified by the introduction of lead silicates of a definite composition by the suppliers, the most general being the so-called bisilicate of lead.

A word of caution should, however, be given to those changing from a raw lead to a fritted lead glaze. The composition of a bisilicate of lead ($PbO,2SiO_2$) is approximately **PbO** 65 and SiO_2 35%, but a typical analysis of the market product shows that, while being of a composition tending to keep the solubility at a low figure, it can hardly be considered as a true bisilicate and, unless allowance is made for the other ingredients introduced, the final result of the glaze may be disappointing.

Analysis of commercial bisilicate of lead:

SiO_2	31·60
Al_2O_3	2·73
Fe_2O_3	0·11
MgO	0·11
CaO	0·04
K_2O	0·28
Na_2O	0·62
PbO	64·30
Loss on ignition	0·20
	99·09

with approximate formula:

$$\left.\begin{matrix}0·04\ KNaO\\0·01\ CaO\\0·95\ PbO\end{matrix}\right\}0·09\ Al_2O_3,\ 1·73\ SiO_2$$

The change in composition from a glaze, containing raw lead compounds, to one of fritted lead for a good class earthenware body is indicated in the following example from actual experience.

The analysis of the original glaze gave:

SiO_2	51·40
Al_2O_3	0·95
CaO	6·20
K_2O	1·90
Na_2O	3·02
PbO	17·59
B_2O_3	8·06
Loss on ignition	3·90

Approximate formula:

$$\left.\begin{matrix}0·3\ KNaO\\0·4\ CaO\\0·29\ PbO\end{matrix}\right\}0·25\ Al_2O_3\left\{\begin{matrix}3·16\ SiO_2\\0·40\ B_2O_3\end{matrix}\right.$$

The recipe:

Frit		*Glaze*	
Borax . . .	38·0	Frit . . .	37·0
Whiting . .	19·0	White lead ,	21·0
Cornish stone .	19·0	Cornish stone	32·0
Flint . . .	19·0	Flint . . ,	10·0
China clay .	5·0		
	100·0		100·0

Approximate formula of frit:

$$\left.\begin{matrix}0·37\ KNaO\\0·63\ CaO\end{matrix}\right\}0·175\ Al_2O_3\left\{\begin{matrix}1·90\ SiO_2\\0·64\ B_2O_3\end{matrix}\right.$$

The low-solubility glaze was made up from : ^

Borax frit (as above) . . .	44-5
Lead frit[1]	30·0
Cornish stone	25-0
Flint	0·5
	100·0

This change gave practically the same chemical formula and at the same time brought the glaze well within the Home Office requirements, while the appearance and durability were not affected.

Another very popular composition for a lead frit and largely used by potters making their own frits is red lead 50, Cornish stone (china stone) 25, flint 25 parts with approximate formula:

$$\left.\begin{array}{l}0{\cdot}082\ KNaO\\ 0{\cdot}008\ CaO\\ 0{\cdot}908\ PbO\end{array}\right\}0{\cdot}178\ Al_2O_3, 3{\cdot}008\ SiO_2$$

Such a frit is found in practice to be more insoluble than the previously mentioned bisilicate.

Lead Glazes.—The great variety of pottery bodies made from such different clays and admixtures necessitates such a range of glares, that to set a standard to suit all requirements would be impossible. The numerous published recipes, however, when calculated out to the suggested formula, can be reduced to a few main types which may be classified according to their lead content.

Red Ware.—This is the simplest and cheapest type of glazed pottery formed often from natural clay alone, such as is used for common bricks, but washed before use. Such clays are fired at relatively low temperature, approximately 900°C. The products in this grade consist of such articles as milk crocks, common bowls, teapots, etc. The glaze for such bodies is of the basic type and is often applied on the clay ware; it sometimes consists solely of a wash of litharge or galena, and depends on the adsorption of sufficient alumina and silica from the body during firing to form the glaze. An approximate formula of such glaze after firing is:

$$PbO\left\{\begin{array}{l}0{\cdot}08\ Al_2O_3\\ 0{\cdot}03\ Fe_2O_3\end{array}\right\}1{\cdot}4\ SiO_2$$

Naturally, such a basic glaze is very liable to the action of acids and not to be recommended for use on vessels intended for domestic purposes.

A higher grade of Red Ware is that known as " Rockingham " which consists of better class red clays and often mixed with a proportion of ball clay or china clay and flint, the desired tone of colour being given by the addition of ochre. This class of body'is usually given a biscuit fire at approximately 1.100°C. before being glazed, although at the present time considerable quantities are being completed in one fire only. The glaze for this class is usually of the raw-lead type consisting of white lead, Cornish stone, china clay and flint/' to which is added manganese dioxide.

An approximate formula is:

$$\left.\begin{array}{l}0{\cdot}80\ PbO\\ 0{\cdot}20\ KNaO\end{array}\right\}0{\cdot}20\ Al_2O_3,\ 20\ SiO_2$$

with approximately 10% MnO_2 addt'd.

Closely allied to the Rockingham grade is the one known as " Jet Glaze." This is applied to the same red body as used for Rockingham, but to give the jet-black coloured glaze, cobalt oxide is substituted for the manganese dioxide used in the Rockingham glaze. During the last few years considerable progress has been made with a view to substituting glazes of a low-solubility nature for this grade of ware in order to be free from the restrictions* imposed on users of ^aw-lead glazes. One such low-solubility glaze approximates to the formula:

$$\left.\begin{array}{l}0{\cdot}20\ KNaO\\ 0{\cdot}30\ CaO\\ 0{\cdot}50\ PbO\end{array}\right\}0{\cdot}160\ Al_2O_3\left\{\begin{array}{l}2{\cdot}20\ SiO_2\\ 0{\cdot}30\ B_2O_3\end{array}\right.$$

with the addition of 10% MnO_8 and compounded from borax frit, lead frit, Cornish stone, china clay and manganese dioxide.

Another type of high-lead glaze, formerly extensively used, is that termed " Majolica Glaze." This grade of earthenware was in great demand years ago in the manufacture of ornamental goods such as flower pots, umbrella stands, pedestals, etc., the body being made from a cheap earthenware recipe, fired biscuit at a relatively low temperature and covered with a soft glaze often made up by the addition of colouring oxides to a standard white glaze.

A typical glaze of this type would correspond to the formula:

$$\left.\begin{array}{l}0{\cdot}25\ Na_2O\\ 0{\cdot}25\ CaO\\ 0{\cdot}50\ PbO\end{array}\right\}0{\cdot}20\ Al_2O_3\left\{\begin{array}{l}2{\cdot}5\ SiO_2\\ 0{\cdot}5\ B_2O_3\end{array}\right.$$

prepared from a frit of the formula:

$$\left.\begin{array}{l}0{\cdot}50\ Na_2O\\ 0{\cdot}50\ CaO\end{array}\right\}\left\{\begin{array}{l}2{\cdot}0\ SiO_2\\ 1{\cdot}0\ B_2O_8\end{array}\right.$$

with the addition of white lead, china clay and flint. The colouring agent would then be added in the desired proportion during the grinding of the glaze.

As will be seen from the formulæ, the foregoing four types of glaze are all of high lead-content, approximating to betwt Jn 40 and 50% PbO, but are used on common clay bodies of uncertain colour. Lead glazes are also used for what are termed " white-ware bodies " and these cover a wide range from the common earthenware to the highest class efcrni-porcelain and china.

While the materials used in the various bodies are practically the same for all types the W portions and qualities vary widely; a few typical examples will furnish a fair idea of the g e S range.

Common Earthenware, formerly designated by the term C.C. or cream colour. Here thTbod^ is usually composed 5f the cheaper varietieTof china and ball clays with the addition 07 Cornish stone and flint. The clay content iS higher than in better-class wares, to ensure easy

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[1] Commercial bisilicate.

working properties} and the fineness of texture, etc., required do not demand so much preparation of the clay body. The percentage composition of a typical cream-colour body is ball clay 34, china clay 26, flint 25 and Cornish stone 15, but the glaze used is practically the same in both cases. A simple glaze largely used for this type before the introduction of the low-solubility variety had the recipe, white lead 59·0, Cornish stone 31·7 and flint 9·3 parts, corresponding to the formula:

$$\left.\begin{array}{l} 0{\cdot}10\ KNaO \\ 0{\cdot}05\ CaO \\ 0{\cdot}85\ PbO \end{array}\right\} 0{\cdot}20\ Al_2O_3,\ 2{\cdot}2\ SiO_2$$

but since the introduction of fritted glazes a more general formula has been;

$$\left.\begin{array}{l} 0{\cdot}33\ KNaO \\ 0{\cdot}33\ CaO \\ 0{\cdot}38\ PbO \end{array}\right\} 0{\cdot}25\ Al_2O_3 \left\{\begin{array}{l} 2{\cdot}50\ SiO_2 \\ 0{\cdot}33\ B_2O_3 \end{array}\right.$$

made up from a borax frit with Cornish stone, china clay and white lead added.

The bodies for the higher grade of earthenware and semi-porcelain and the type formerly known as " Granite " are usually compounded from better class clays and Cornish stone; the clay content is lower and the flint and stone content higher, thus giving a better colour and increased vitreousness. A body of this type will approximate to the recipe, ball clay 30, china clay 20, flint 33 and Cornish stone 17%, and to give extra whiteness a small proportion of cobalt oxide stain is added, approximately 1 in 12,000 parts. The working clay is prepared with extreme care to ensure as clean a body as possible.

The body of china is distinguishable from earthenware by reason of its translucence, and is compounded from calcined bone, Cornish stone and china clay with the addition of a small quantity of ball clay to increase plasticity, although this detracts somewhat from the perfect colour.

A typical bone-china body has the following percentage composition : bone 46, Cornish stone 29, china clay 23 and ball clay 2, varying slightly according to quality required.

The glaze usually adopted for both the better class earthenware and the china is now the low-solubility type composed of borax frit, lead frit and mill mixture, being mainly Cornish stone, flint and china clay.

A typical formula would be:

$$\left.\begin{array}{l} 0{\cdot}066\ K_2O \\ 0{\cdot}260\ Na_2O \\ 0{\cdot}383\ CaO \\ 0{\cdot}28S\ PbO \end{array}\right\} 0{\cdot}29\ Al_2O_3 \left\{\begin{array}{l} 2{\cdot}80\ SiO_2 \\ 0{\cdot}50\ B_2O_3 \end{array}\right.$$

Such glazes represent a lead content of approximately 18% PbO.

Other white-ware glazes in which lead is used are those for white tiles, in which the body contains a very high proportion of flint, sometimes as high as 45% owing to the necessity of freedom from warping during firing. The glaze for such bodies is usually much higher in lead content than the other white-ware bodies, varying from 25 to 40% PbO.

A typical formula is:

$$\left.\begin{array}{l} 0{\cdot}28\ KNaO \\ 0{\cdot}29\ CaO \\ 0{\cdot}43\ PbO \end{array}\right\} 0{\cdot}24\ Al_2O_3 \left\{\begin{array}{l} 2{\cdot}70\ SiO_2 \\ 0{\cdot}35\ B_2O_3 \end{array}\right.$$

maturing at a temperature of 970°C, compounded from borax frit, Cornish stone, china clay and white lead.

Leadless Glazes.—The restrictions on the use of lead have led to much research to find a satisfactory glaze entirely free from that substance, with the result that many lead-free glazes are now in use; these, while giving very good results, do not quite reach the brilliance obtained when using lead; nor is the palette of the decorator so unlimited, as many colours are affected both in tint and brilliance by the absence of lead.

One of the first such *leadless glazes* used some 50 years ago was composed of a frit as follows:

Felspar.	47·0
Borax.	30·0
Sand.	6·5
China clay.	5·5
Nitre.	5·5
Soda ash.	5·5

5% calcined borax added during grinding.

Corresponds to formula:

$$\left.\begin{array}{l} 0{\cdot}42\ K_2O \\ 0{\cdot}58\ Na_2O \end{array}\right\} 0{\cdot}42\ Al_2O_3 \left\{\begin{array}{l} 2{\cdot}50\ SiO_2 \\ 0{\cdot}80\ B_2O_3 \end{array}\right.$$

Such a glaze was found to have a marked effect on the colours used in decoration, and owing to high content of B_2O_3, and to being all fritted, difficulty was experienced in keeping the glaze in suspension during the dipping process. At the present time, the practice conforms to the use of a glaze approximating to the formula:

$$\left.\begin{array}{l} 0{\cdot}57\ CaO \\ 0{\cdot}43\ KNaO \end{array}\right\} 0{\cdot}45\ Al_2O_3 \left\{\begin{array}{l} 3{\cdot}50\ SiO_2 \\ 0{\cdot}55\ B_2O_3 \end{array}\right.$$

compounded from a frit consisting of:

Borax.	27·0
Flint.	20·0
Whiting.	12·0
Felspar.	22·5
China clay	18·5

with 2½% china clay added during grinding.

Such a glaze in practice gives a very satisfactory result.

Other leadless glazes, apart from those covered by the first class, are those termed :

Slip Glazes.—These are mainly used in connection with once-fired stoneware; in some cases they may be simply a very fusible clay giving of itself a good even glaze when fired. The best example of such a clay glaze is the one known as "*Albany Slip*," largely used in the United States and having the formula:

$$\left.\begin{array}{l} 0{\cdot}1954\ K_2O \\ 0{\cdot}4502\ CaO \\ 0{\cdot}3464\ MgO \end{array}\right\} \left.\begin{array}{l} 0{\cdot}608\ Al_2O_3 \\ 0{\cdot}810\ Fe_2O_3 \end{array}\right\} 3{\cdot}905\ SiO_2$$

giving when fired to approximately 1,250°C. a good dark brown colour.

The colour is, however, a drawback for some purposes, and to meet the demand for a cleaner looking lining for the ware, potters resort to a whitish semi-opaque glaze composed of felspar or Cornish stone, whiting and flint with sometimes a little barytes and, if required, softened by a small proportion of a soft frit.

Such a glaze taken from practice has the following formula:

$$\left.\begin{array}{l}0{\cdot}26\ KNaO\\0{\cdot}58\ CaO\\0{\cdot}16\ BaO\end{array}\right\}0{\cdot}56\ Al_2O_3\left\{\begin{array}{l}4{\cdot}41\ SiO_2\\0{\cdot}05\ B_2O_3\end{array}\right.$$

A very simple slip glaze may be compounded from Cornish stone 75, felspar 15 and whiting 10% and maturing at approximately 1,250°C, giving the formula:

$$\left.\begin{array}{l}0{\cdot}40\ KNaO\\0{\cdot}60\ CaO\end{array}\right\}0{\cdot}70\ Al_2O_3,\ 6{\cdot}6\ SiO_2$$

Coloured Glazes.—This term is mainly used to describe those bodies covered entirely with a glaze in which is incorporated a certain proportion of a colouring oxide, and does not refer to the colouring obtained by the use of a printed or painted decoration on the biscuit ware.

Such glazes are usually confined to majolica ware and to tiles, but sometimes they are also used in stoneware. In the case of majolica and tiles, it is essential that the firing temperature be relatively low, approximately 960°C, consequently the lead content is high. To give the necessary colour, it is usual to grind a percentage of colouring oxide with a portion of the glaze and then mix well with the whole batch. A more satisfactory method, however, is to use (1) a batch of transparent glaze, (2) a batch of coloured glaze too high in colouring oxide for the purpose required. By using suitable proportions of each, any desired blend can be obtained. Much time is saved by adapting this method and the inconvenience of storing a large number of blends is avoided. A simple example will illustrate the procedure:

Transparent glaze No. 1, formula 1-00 PbO: 0-15 Al_2O_3, 1-75 SiO_2, and with this as base a series of majolica glazes are to be made with cobalt oxide as colouring agent.

For this purpose a glaze No. 2 is made up, having the formula:

$$\left.\begin{array}{l}0{\cdot}80\ [illegible]\\0{\cdot}20\ [illegible]\end{array}\right\}0{\cdot}15\ Al_2O_3,\ 1{\cdot}75\ SiO_2$$

This glaze will be black in colour and can be used with No. 1 in any desired proportion.

If glaze No. 3 is required to contain 0-02 mol. parts of CoO, the difference between the CoO content of glaze No. 2 and the required CoO content of glaze No. 3 is 0-18 mol. parts. Dividing the difference in the CoO content of the desired glaze and one extreme by the total difference between the two extremes gives a fraction expressing the proportion of the opposite extreme to be used in the mixture, thus:

$$\frac{\text{Desired difference}}{\text{Total difference}}=\frac{0{\cdot}18}{0{\cdot}20}=0{\cdot}9$$

Therefore glaze No. 3 requires:

0-9 molecular parts glaze No. 1
0-1 „ „ „ „ 2.

This method has the advantage that the glazes Nos. 1 and 2 can be kept in the slop state and thus readily mixed without the necessity of drying; the only precaution being that the dry content per unit volume of the slop glazes be known.

A more perfect mixture is, however, obtained if the colouring oxide in glaze No. 2 is embodied in a fritted form.

Matt Glazes.—Of recent years, such glazes have received much attention owing to their decorative possibilities and are largely used in the tile and ornamental trades. Many of these glazes are compounded by the addition to a transparent glaze of a so-called matt mixture, depending for its composition on the type and colour of the surface required. The matt effect is produced by the addition of either alumina, lime or magnesia, with the addition of zinc oxide to give the desired sheen. These glazes may also be made direct as raw glazes. A typical raw matt-glaze has the composition: red lead 42-0, whiting 6-4, felspar 16-0, china clay 21-5, flint 10-6 and zinc oxide 3-5%, corresponding to the formula:

$$\left.\begin{array}{l}0{\cdot}10\ KNaO\\0{\cdot}20\ CaO\\0{\cdot}57\ PbO\\0{\cdot}135\ ZnO\end{array}\right\}0{\cdot}35\ Al_2O_3,\ 1{\cdot}60\ SiO_2$$

and matures at 1,080°C.

Many examples of such glazes are quoted by C. F. Binns (Trans. Amer. Ceram. Soc. 1903, 5, 50).

A type of lime matt-glaze is produced by the addition of approximately 25% whiting to an ordinary low-solubility transparent glaze. Coloured matt-glazes may be produced by using any of the usual coloured glazes with the addition of a matt mixture, this being either added to the transparent glaze or sometimes dipped on the top of the glazed piece before firing. One such matt mixture used in practice has the percentage composition: SiO_2 36-97, Al_2O_3 9-36, TiO_2 9-90, MgO 19-27 and CO_2 23-47, corresponding to the formula:

$$MgO:0{\cdot}2\ Al_2O_3\left\{\begin{array}{l}1{\cdot}28\ SiO_2\\0{\cdot}26\ TiO_2\end{array}\right.$$

Care must be taken in the selection of a suitable matt mixture as this will exercise considerable influence on the final colour. As an instance, if the above matt mixture be superimposed on a blue glaze, the resultant colour instead of being a matt blue will be of a dark plum colour, owing to the action of the magnesia on the cobalt oxide in the base glaze.

Fireclay Glazes.—The usual colour of fireclay when fired is a deep buff, and if glazed with a same colour is naturally as cheap cane sanitary-ware, this colour is not considered. case of better-class ware demands a white appearance. This effect can be produced on theSbuff coloured body by the use of an *tngobtq* which is an intermediary between body and glaze and is usually majie by mixinx part of the buff body with a proportion of a white&burning clay. In the higher class of fireclay sanitary-ware, it is necessary to have several coats of the engobe to mask thoroughly the colour of the body, and ea<& succeeding coat should have a higher proportion o|the white body, thus gradually correcting any differences in the contraction of the original body and that«of the white engobe. ^ The composition of the white engobe usually approximates to that of an ordinary earthenware bfjdy. The glaze then applied on the Engobe' will ^approximate to formula:

0-24 KNaCK
0-54 CaO I 0166 Al_2O_3 /4-5 SiO_a
0-13 BaO f \<?>05 $Sn6_2$
OlOZnO J

and will mature at about l,250°C.

A similar procedure will be followed in the production of glazed bricks with possibly the addition of colouring oxicfes as required.

The composition of the glaze will, of course, depend on that of the body and this will vary according to the grade of the fireclay used, but the quoted example is one taken from practice end used on a second-class fireclay and gives a fair indication of the composition of such glazes.

Decorative Glazes.—Many varieties of glaze are used for the purpose of decoration. The beautiful effects of many of the art potteries and also of the studio potters are examples of what can be done by the blending of coloured glazes in producing* pleasing effects. Such glazes are usually of the majolica type, and the effects are produced by superimposing one glaze on the other before firing, as instanced by dipping a turquoise glaze on the top of a blue one. Mottling can also be introduced with good effect by dabbing one colour with a sponge on the ware and then dipping the pfece in a glaze of another colour.

From an academic standpoint, the outstanding example of a decorative glaze is the one known as crystalline glaze. The application to ceramics of super-saturation, so usual in pure chemistry, has long exerted a fascination on ceramic chemists whose object was to introduce substances into the glaze which, d" Ting the eooling process, would separate out as crystals. Up to the present time zfhc oxide has been found to give the most satisfactory results in the production of crystals of zinc silicate. Various colouring oxides can be added in small proportions to enhance the effect of the crystallisation. The earliest work on the subject was done by Lauth and Dutailly and reported in their work " La Manufacture Nationale de Sèvres," 1879-87; Paris, Libraire I. B. Bailliere et Fils, 1889, in which they give the following recipe for producing the best crystals whon fired to a temperature of l,350°C.: SiO, 57-49, $AI_2O_3$11-68, CaO 6-72, NaKO 6-12 and ZnO 18*00%, corresponding to the formula:

0-28 CaO ^
0-19 NaKO > 0-277 AI_2O_3, 2*629 SiO_8
0-52 ZnO J

Outstanding pieces *qf* these productions are to be seen in the showrooms of the Royal Works at Sèvres.

The Royal Copenhagen factory has also specialised in crystalline glazes, but their results are obtained by two fires. The first glaze is of the hard porcelain type, approximating to the formula:

0·6 K_2O }
0·4 CaO } 1·33 Al_2O_3, 15·6 SiO_2

maturing at approximately l,450°C, and on this a softer glaze high in zinc oxide is applied having the formula:

0-2 K_2O }
0-8 ZnO } 0-80 Al_2O_3, 10·0 SiO_2

and fired to approximately l,350°C.

Softer Crystalline glazes can be compounded by the substitution of boric acid for part of the silica.

A simple low temperature glaze maturing at l,150°C. has the following recipe: leadless glaze 100, zinc oxide 20, rutile 10 and cobalt oxide 1 part, gf formula:

0-56 CaO \ /3-40 SiO_2
0-44 NaKO/ 0·47 Al_2O_3 \0-62 B_2O_3

Many other examples of such glazes are included in a paper by Purdy and Krehbiel (J. Amer. Ceram. Soc. 1907, 9, 319).

Crackled Glazes.—One of the chief defects of glazes, viz., crazing, has been utilised, originally by the Chinese ancTJapanese potters, as a means of decoration under the term " Craquèje." This effect has also been developed in the researches of Lauth and Dutailly (Bull. Soc. chim. 1888, [ii], 49, 948) who found that by modifying the composition of an ordinary stable glaze, by increasing the silica and alkali content and decreasing the lime and alumina, very handsome crackled glazes can be produced on soft porcelain, and they give the following recipes:

	Ordinary glaze.	Crackled glaze. No. 1.	No. 2.
SiO. . . .	[illegible] ·18	79-42	69-92
. .	14-55	11-89	18-13
CaO . . .	15-90	2-88	—
Alkalis . .	3-55	5-81	11-90

corresponding to the formula?:

Ordinary glaze:

0·85 CaO
0.15KNao}$^{0'4}$26AI_2O_3,3.28SIO_a

Crackled No. 1:

0·26 CaC
0-74 KNa"o} 0-09 Al_2O_3, 10-40 SIO_a

Crackled No. 2:

1-00 KNaO ; 0-11 AI_2O_3, 7-60 SiO,

The temperature required for the firing of the crackled glaze is higher than the ordinary glaze. Some very pretty effects are produced by filling up the fine cracks (crazes) with a very fusible coloured frit and firing again at a low temperature.

Aventurine Glaze.—This is another example of a type of crystals produced at a low temperature, approximately 980°C., showing, **when** properly matured, golden spangles or crystals in a red ground. Usually the best results are obtained in glazes free from lead and with about 25% of iron oxide, of which a great part separates out in a crystalline state on cooling. Anon., **Sprechsaal**, 1906, **39,** 2«4, gives the following recipe:

Frit

Sand	444
Borax	330
Ferric oxide	148
Felspar	14
Potassium nitrate	38
Barium carbonate	27

corresponding to the formula:

$$\left.\begin{matrix} 0{\cdot}929\ NaKO \\ 0{\cdot}071\ BaO \end{matrix}\right\} \left\{\begin{matrix} 0{\cdot}013\ Al_2O_3 \\ 0{\cdot}479\ Fe_2O_3 \end{matrix}\right\} \left\{\begin{matrix} 3{\cdot}91\ SiO_2 \\ 1{\cdot}[illegible]\ B_2O_3 \end{matrix}\right.$$

Oxidising conditions are essential to produce the desired result.

Red Glaze.—A good red glaze without crystals can be produced from the above recipe, by the addition of 33⅓% bisilicate of lead and firing to a temperature **of** 1,100°C.

Rouge Flambe, Chinese Red or Sang de Bœuf.—This glaze, originally the work **of the** Chinese, has been the subject of much **research** work, mainly by Lauth and Dutailly (Bull. **Soc.** Chim. 1888, [ii], 49, 501) and Seger (" Seger's Collected Works," 1902, II, 708).

The colouring agent is undoubtedly **copper,** but the results obtained, are due **to the** nature of the glaze and its mixing and application, and more especially to the method of firing.

An analysis of a piece of glaze from a Chinese vase gave the following results: SiO_2 73·90, Al_2O_3 6·00, Fe_2O_3 2·10, CaO 7·30, K_2O 3·00, **Na_2O** 3·10 and CuO 4·60%.

A glaze made up from this recipe and applied to a porcelain body and fired in a reducing fire in a special kiln gave the first satisfactory results produced in Europe. The great **difficulties** attending the production of the true Chinese Flambe have led to many attempts to simplify the method, and a very popular one is that of coating the already glazed piece with a mixture of china clay and copper carbonate or acetate and firing at a low temperature, approximately 800°C, in a reducing atmosphere; on drawing from kiln, the clay is washed off, **leaving the** original glaze impregnated with a deposit of copper and, if properly compounded and **fired,** giving a rich Sang de Bœuf effect.

Defects of Glazes.—The two principal defects to which glazes on pottery are subject are (1) " crazing " and (2) " peeling."

Crazing is the defect appearing on the surface of the ware in the form of a network of line-cracks, while peeling takes the form of the glaze " chipping " or " scaling " off the surface of the ware, usually at the edges.

Broadly speaking, both faults are attributed to the same cause, viz., a difference in the coefficients of expansion of the body and the glaze. If the glaze, during cooling, contracts more than the body, strains are set up and crazing will result, while if the glaze during cooling contracts less than the body, the glaze peels or scales off. Such statement appears on the face very simple, but there are so many other factors to be considered that those interested in the subject should consult the voluminous survey of the literature up to 1934 compiled by J.W. Mellor (Trans. Ceram. Soc. 1935, 34, 1-112) as well as recent work on various aspects of crazing by H. W. Webb (*ibid.* 1939, 38, 75) and F. T. Wood and S. H. Hind (*ibid.* 1939, 38, 435).

While the actual principles involved are still the subject of much discussion, the practical potter has at hand ready means of controlling the fault. The usual remedy adopted to prevent crazing is to increase the silica content of the body, while to remedy peeling, the lowering of the silica content is the method adopted. The altering of the body is usually preferred to any interference with the glaze, as it is inferred that the body materials are more liable to fluctuation than those of the glaze. If, however, the latter be adopted, the silica content of the glaze must be raised to lower the tendency to **crazing,** while to remedy peeling the silica content must be reduced.

Seger, whose pioneer work on the subject has been the main guide for succeeding **workers,** formulated a series of rules which, while not universally applicable to all conditions existing in pottery bodies, forms a very serviceable basis on which to work, but as mentioned above, the practical potter does not concern himself much with the academic issue involved while he has a ready and simple means of overcoming the trouble.

Full details of Seger's Rules may be found in " Seger's Collected Works," 1902, II, 557 [illegible]

Enamels.—This term is usually applied **to** glosses rendered opaque by the addition of colouring oxides, but in ceramics is understood to mean soft glazes with which are **incorporated** **colouring** oxides and applied to the ware in what is known as " on glaze " decoration, and **therefore** commonly called " enamel colours."

These colours consist of colour base and flux. The colour base may be metallic oxides alone or **silicates,** borates or aluminates of the metals. In **some cases the colour base** and flux are simply ground together while in other cases they are **fritted** together, thus ensuring [illegible] form product. The [illegible] enamel colours varies **between** [illegible] The composition **of the** flux must necessarily be considered in its relation to the [illegible] oxide and **also to** the [illegible] as the [illegible] colour produce [illegible] nent of the two, so that the [illegible] varies very widely.

Three [illegible] properties of the finished colour are:

(1) Must adhere strongly to the glaze.

(2) Must be fusible enough to penetrate to the desired depth.

(3) Must have a correct coefficient of expansion to prevent seeing or peeling.

The commonest flux used in this country is known as No. 8 flux and is made by fritting, at approximately 900°C, red lead 30, borax 20 and flint^{10} parts, corresponding to the formula:

0-285 Na_2O } /0·[illegible] SiO_2
0-715 PbO } L0-57 B_2O_3

A typical recipe is as follows :

White Enamel.—Tin oxide 20, felspar 10 and No. 8 flux 20 parts, ground together.

Coloured enamels may be produced by the addition to the flux of the various oxides thus: cobalt for blues; chromium or copper for greens; manganese for browns; antimony or uranium for yellows; iron for reds; and iridium or a mixture of cobalt and manganese for black.

Under-Glaze Colours.—These colours are used on what is termed biscuit ware and are developed by the covering glaze during firing. The colour itself will be influenced by:

(1) The temperature of the kiln.
(2) The atmosphere of the kiln.
(3) To some extent by the composition of the body.
(4) The composition of the glaze.

The high temperature necessary to fuse the glaze naturally limits to some extent the variety of colours used for under-glaze decoration.

The general colours in use are blue, black, brown, green, yellow and pink, and are made up from colouring oxides with the addition of fluxing material.

A typical recipe is: *Blue.*—Cobalt oxide 1, zinc oxide 4 and flint 2 parts, calcined at approximately 1,250°C. and finely ground. Any desired shade may be obtained by the addition of flux consisting of approximately: flint 12, Cornish stone 12, whiting 5 and borax 4 parts, fritted at 1,000°C.

Blacks are usually prepared from mixtures of iron, chrome and cobalt, and a typical recipe is: Fe_2O_3 80, Cr_2O_3 76-2 and Co_2O_3 10 parts, fritted at 1,250°C.

Greens are obtained from chromium or copper oxides;

Pinks from tin oxide, whiting and potassium dichromate;

Browns from manganese and mixtures of manganese and chromium oxides ;

Yellow from uranium and antimony oxides.

A. H.

GLESSITE (*v.* Vol. I, 302d).

GLIADIN (*v.* Vol. II, 85a).

GLIMMERTON (*v.* Vol. III, 19Cc).

" *GLOBUK* " (*v.* Vol. II, 480a).

GLOBULINS. General term for proteins which are coagulated by heat, are insoluble in water but dissolve in dilute solutions of neutral salts, acids and alkalis. They are precipitated in half-saturated ammonium sulphate or in fully saturated sodium chloride or magnesium sulphate solutions.

GLOBULOL. The sesquiterpene alcohol, (*globulol, h*\\ 283°/755 mill., $[a]_D$ -35-29°, occurs in the essential oil from the leaves of *Eucalyptus globulus* (Schimmers Report, 1904, 1, 46; Scmmler and Tobias, Bcr. 1913, 46, 2030; R'jzioka, Pontalti and Balas, Helv. Chim. Acta, 1923, 6, 861). On dehydrogenation it yields cadalene *(q.v.)* but its structure has not been determined.

J. L. S.

GLONOINE OIL (v. Vol. IV, 491d).

GLORIOSINE (*v.* Vol. III, 276c).

GLUCAL (*v.* Vol. II, 294c).

GLUCINUM *(Beryllium).* Be. At. no. 4. At. wt. 9·02. Two isotopes (8), 9. This fourth member of the atomic series was first detected in beryl by L. N. Vauquelin (Ann. Chim. Phys. 1798, [i], 26, 155), and from this source he isolated the oxide " la terre du beril " and prepared some of its salts; in a footnote *(l.c.* 169) the editors of the Annales proposed the name glucine for the oxide on account of the alleged sweet taste of the salts. The metal was not isolated until 30 years later when Wöhler obtained it by heating the chloride with potassium. He called it *beryllium,* the name by which it is best known, and which will be adopted throughout this article. The name still used in France is glucinium.

There are several beryllium minerals, such as euclase, $Be(AlOH)SiO_4$; phenakite, Be_2SiO_4; chrysoberyl, $BeAl_2O_4$; beryllonite, $NaBePO_4$; and hambergite, $Be_2(OH)BO_3$; but beryl, $Be_3Al_2Si_6O_{18}$, is still the only practical source of the metal although its refractory nature has led to much effort in devising suitable methods for its decomposition. Usually some modification of Copaux's method is adopted (Compt. rend. 1919, **168,** 610) in which the finely ground mineral is fused with sodium silicofluoride at about 700-800°C. Aluminium and magnesium form insoluble fluorides, ferric iron is unattacked while the soluble double fluoride, $NaBeF_3$, is extracted with water. Air is blown through the solution to oxidise any ferrous iron, which is then removed, and the filtrate is evaporated to yield crystals of the double fluoride. From this product pure beryllium compounds may be obtained by one of the following methods:—

(a) A solution of the double salt is treated with a slight excess of lime and the precipitate of CaF_2, $Be(OH)_2$ and excess $Ca(OH)_2$ is extracted with hydrofluoric acid; evaporation of the filtrate at 100° yields the hydrated fluoride or basic fluorides which, when heated to 300°, produce the oxyfluoride, $2BeO\text{-}5BeF_2$ (Illig *et* al., Wiss. VeröffeW. Siemens-Konzern, 1929, 8, [il, 34).

(b) The double salt solution is allowed to react with silica and silicofluoric acid according to the equation

$$6NaBeF_3+2H_2SiF_6+SiO_2=6BeF_2+3Na_2SiF_6+2H_2O$$

After removing the insoluble sodium silicofluoride the filtrate is worked up as in (a) *(see also* Gadeau, Rev. Met. 1935, 32, 627, and F.P. 742619).

(c) The double fluoride is converted to sulphate by heating with conc. sulphuric acid, any alkaline earth sulphate being removed, and the filtrate oxidised with hydrogen peroxide. A quarter of the resulting solution is treated with ammonia, the crude beryllium hydroxide filtered off and a part of it added to the remaining solution thereby'causing precip?tat'*on of much of the impurity. The process is repeated and the final filtrate acted on with hydrogen sulphide to remove traces of the heavy metals. Dilution of the solution with 8-8-5 times its volume of water induces precipitation of the hydroxide; the basic sulphate (about 10% SO_3) which it contains is decomposed by heating with carbon black at 700° (Sloman, J.S.C.I. 1929, 48, 309T).

More recently it has been found that beryl which has been heated to its melting-point and then quenched in water is easily attacked by strong sulphuric acid. The solution of beryllium, aluminium and alkali sulphates is then concentrated, the removal of aluminium being facilitated by adding ammonium sulphate so that an alum crystallises out. The resulting beryllium sulphate is decomposed to the oxide at 1,450° (Sawyer and Kjellgren, Ind. Fng. Chem. 1938, 30, 501).

PREPARATION OP THE METAL.—Large-scale production of the metal is carried out by electrolysis of fused salts, a procedure which was first successfully employed by Lebeau, (Gompt. rend. 1898, **126,** 744) who electrolysed a fused mixture of sodium and be-yllium fluorides at 300° in a nickel crucible vhich served as the cathode and upon which the metal was deposited in flakes. For coherent deposits the bath temperature must exceed the melting point of beryllium and in order to achieve this barium fluoride is added; even so there is always a notable volatilisation of beryllium fluoride. Usually a graphite pot is employed with graphite anodes, the cathode being a water-cooled iron or steel rod tipped with beryllium (Stock and Goldschtaidt, G.P. 375824; B.P. 192970; Vivian, Trans. Faraday Soc. 1926, **22,** 211). Later work has shown that it is preferable to use mixtures of beryllium oxyfluoride with sodium or barium fluoride. The process is made continuous by adding oxyfluoride from time to time; volatilised salts are recovered by means of absorption towers (G.P. 467247 ; B.P. 278723).

Fused mixtures of beryllium and alkali chlorides have also been electrolysed at temperatures between 370 and 400°C. The metal separates as spangles which are rendered coherent by pressing into rods and melting under fused barium chloride (B.P. 377858, 434338).

Beryllium produced elect! 61ytically is contaminated with oxide, nitride and carbide; a surface skin of the last-named is always noticeable but may be removed by dipping the metal in molten sodium hydroxide. Impurities may also be got rid of by melting the crude metal either *in vacuo* in a high-frequency induction furnace or under a mixture of alkali and alkaline-earth halides when the dross rinks to the bottom. Further purification can be achieved by subliming the metal in a higli vacuum (Vivian, *I.e.;* G.P. 443944, 465525; Sloman, J. Inst. Metals, 1932, 49, 365; Loeana, Alluminio, 1939, 8, 67).

NUCLEAR REACTIONS.—Beryllium is[11] apparently a simple dement in that the mass spectrograph fails to reveal any lines other than that corresponding to a mass of 9; nevertheless, the isotope of mass 8 has been frequently postulated in transmutation reactions. Thus Laaff (Ann. Physik, 1938 [vj, 32,743) rtates that the 4Be nucleus is produced in the process $^{ll}B(p,$''a)^{8}Be but that it disintegrates info two a-particles. On the other hand Gliickauf and Paneth (Pn3c. Roy. Soc. 1938, A, **165,** 229) irradiated ^{9}Be with y-rays from radon and &om the quantity of telium produced they concluded that the reaction produced two a-particles an,d a neutron in preference to ^{8}Be and a neutron. By tfris transformation is most probably produced the helium which is often found in beryl and in amounts related to the age of the mineral (Rayleigh, *ibid.* 1933, A, **142,** 370; Burkser *el al.,* Compt. rend. Aoad. Sci. U.R.S.S. 193J, 15,. 193). The mass difference of **jBe** and **jBe** is 1.0072 while the stability of **JBe** with respect to two a-particles is given as 0-3 m.e.v. (Allison *etal,* Physical Rev. 1939, [2], **55,** 107 624; Collins *et>al., ibid.* 172).

PHYSICAL PROPERTIES.—Beryllium to a hard, brittle, steel-grey metal possessing a low Bp.gr. (1*84 at 20°) and high melting-point (1,285°C). It crystallises in hexagonal plates, the crystal lattice being a hexagonal close pack with lattice constants, o=2-268, c=3-594, axial ratio 1-585. The work of Jaeger and his collaborators indicates that beryllium exhibits allotropy, a metastable form at 600° being interesting in possessing a super-lattice containing some 60 atom' Although normally brittle the metal does acquire some ductility on heating while, according to Sloman, pure beryllium is ductile at room temperature. Other physical properties are tabulated below:

***Atomic volume,* 5.**

Hardness, 130 BrinelKfor 99-8-99-9% metal and 60-65 for 99-99%.

***Young's modulus of elasticity,* 30,000 kg./sq.** mm., a calculated value (Schwerber Metallbörse, 1928, 18, 706).

Vapour pressure, 5 mm. at 1,530°C.f 760 mm. at approximately 3,040°.

***Heat of fusion*-. 345-5 g.-cal.**

Heat conductivity, 0-3847 at 0° and increases regularly with temperature as expressed by the equation K=0-3847+00$_8$751M)-0$_a$468<*.

Specific heat. Presumably as a result of allotropic modification this property varies with the thermal treatment accorded to the metal. Constant values are said to be given by powdered ben/Ilium (Jwger and Rosenbohm, Rec. trav. chim. i934> 84f 451. proc. K. Akad. Wetensch. Amsterdam, 1&34, 37, 67].

***Linear coefficient of expansion,* (20-100°C.)** 123 x 10-«; (20-300°C.), 14-S x lV«

Specific resistance. Like many of, the other properties this varies with the thermal history of the specimen. After heatine to 700° and cooling slowly, fairly reproducible values **are obtained of about 6-6 WrohnJ * 3r** (Lewis, Physical Rev. 1929, [ii], 88, 284)

SPECTRA.—The chief lines in the emission

[illegible] ionised beryl-

Jtf SSk JSS: 2E2- S »

332101, 301960, 301951 3019-34 SSe-el

298644, 298609, **265078;** ^O-'t ££

2650-61, ,2650-57, 265047, 2494-59, 2494-55, 2494-44, 2&0-83* 2350-69, 2348-61, 217507, 2174-94.

Be*II. 5270-84, 5270-32, 4673-46, 436103, 4360-69, 3274-64, 3241-84, 3241*65, 3197-16, 31$L-06, 3046-68, 3046-52 (Paschen and Kruger, Anm. Physik, 1931, [v], 8, l#05). The wavelengths in bold type are important in the analysis of alloys by arc spectra^F. Twyman and D. M. Smith, " Wave Length Tables," A. Hilger, London, 1931).

For lines corresponding to Be III and Be IV and also for series relationships, *see* Robinson (Physical Rev. $36, [ii* 50, 99), Kruger and Cooper *(ibid.* 1933, [ii], 44, 418), Edlén *(ibid.* 778), Paton *et al. (ibi&.* 1929, [ii], 33*16, 1093), Selwyn (Proc. Physical Soc. 1929, 41, 392).

CHEMICAL PROPERTIES.—As th* first member of the second group of the Periodic Table beryllium exhibits bivalency, while in its properties it is more nearly related to the zinc sub-group than to that of the alkaline earths. Possessing a strong affinity for oxygen, the freshly polished inetal soon tarnishes in air and when finely divided it burns brilliantly on heating in air or oxygen. Combination with the appearance of flame also occurs if the metal is heated in the halogens, in sulphur vapour or if melted with ^elenium. Hydrogen does not attack it, but nitrogen, ammonia or cyanogen react with the heated metal to form a nitride. Combination with carbon at high temperatures produces a carbide.

Beryllium is resistant to attack by hot or cold water and cold cone, nitric acid although the diluted acid affects dts slightly. Warm nitrfe acid dissolves the metal, but addition of the chloride of a noble metal, *e.g.* $PtCl_4$, increases its resistance. Both hydrochloric, and sulphuric acid readily attack beryllium, which also dissolves in cone, alkalis in the cold and in dilute alkalis on warming.

ALLOYS.—Although it might have been expected that additions of beryllium with its high modulus of elasticity would lead to an improvement in the mechanical properties of other light metals the results have been disappointing. It does not alloy with magnesium and while small additions to aluminium increase the hardness and resistance to wear, the effects are not so good as th^Se produced by silicon or magnesium. With aluminium beryllium forms a eutecflc at 644° containing 1-1% of the latter the solubility at room temperature is very small.

More interesting results have been obtained by the addition of small amounts of beryllium to the hnavy metals and much attention has been given to the beryllium bronzes and nickel beryllium alloys. The bronzes containing about 2-25-2-5% beryllium, when heated at 800° for 1 hour and quenched in water, are softer than copper and easier to work, while heat treatment produces great hardness and elasticity. As such alloys possess considerable resistance to wear and fatigue they make excellent springs and are also recommended for moulding dies, hypodermic syringes, electric switches, clock bearings etc. The inclusion of small amounts of manganese, cobalt and many other metals has been egg&ted to increase the electrical conductivity of the bronzes and to decrease the amount of beryllium necessary to produce such excellent mechanical properties. For a general description of these alloys, *see* Gadeau, Rev. Mét. 1935, 32, 627; Hessenbruch, Metallwirts. 1938, 17, 541; Sawyer and Kjellgren, i.e.; Met. and Alloys, 1940, 11, 163).

BERYLLIUM AND HYDROGEN.

No hydride of beryllium has been isolated, but the arc produced between beryllium electrodes in dry hydrogen gives a spectrum containing two band systems, one between 4800A and 5120A due to the BeH molecule and the other between 1882A and 3600A produced by the ionised molecule BeH+. Similar bands have been observed for the deuteride (W. W. Watson *et al.,* Physical Rev. 1928, [ii], 31, 1130; 32, 600; 19^9, [ii], 34, 372; 1931, [ii], 37, 167; 1937, [ii] 52,^318; Koontz, *ibid.* 1935, [ii], 48, 707).

BERYLLIUM AND OXYGEN.

Beryllium Oxide, BeO.—Formed when the finely divided metal, sulphide or iodide burns in air or oxygen. It is more conveniently prepaid by dehydrating the hydroxide at 300-400° or igniting the carbonate at 1,100°. The nitrate or sulphate may also be employed, but long heating is necessary to remove the last traces of oxides of nitrogen or sulphur. Beryllium oxide is a white, amorphous powder which may be obtained crystalline, as hexagonal pyramids isomorphous with zinc oxide, either by dissolving it at red heat in alkali sulphates or by fusion or sublimation (Zachariasen, Z. physikal. Chem. 1926,119,204; Mallard, Oompt. rend. 1895,105, 1267). Although the melting-point is about 2,500° the oxide begins to volatilise slowly above 320° while at 2,000° the loss is rapid. The density varies between 2-86 and 304, depending on the previous history of the specimen. The heat of formation is 135-9 kg.-cal. and the mean index of refraction 1-723.

Beryllium oxide remains unchanged when heated in chlorine, bromine or iodine; with fluorine a fluoride is formed. It is not easily, reduced on heating with metals although reduction seems easier if there is present a metal with which beryllium alloys readily. Ease of attack by acids and alkalib depends on the temperature to which the oxide has been subjected; it dissolves easily in fused alkalis or alkali carbonates or pyrosulphates.

Beryllium Hydroxide.—White, voluminous, gelatinous precipitate formed when alkali hydroxides, ammonia, amines or ammonium sulphide act on solutions of beryllium salts; alkali carbonates produce mixtures* of carbonate and hydroxide. The moist precipitate readily absorbs CO_2 from air and must, therefore, be washed and dried in an atmosphere free from this gas. Dried at ordinary temperature the hydroxide has an indefinite water content, but heating to 150° gives a product corresponding to $Be(OH)_2$. The amorphous material slowly changes into a denser and more granular crystalline, but metastable, form on standing in air or under water; this is known as the a-hydroxide.

It is more readily obtained from the gelatinous product by electrodialysis or by heating in solutions of alkalis, alkali carbonates .or ammonia. A quantitative precipitation is achieved by heating a neutral solution of a beryllium salt with ammonium nitrate and methyl alcohol, air being simultaneously passed through the mixture (Haber and van Oordt, Z. anorg. Chem. 1904, 38, 380; Havestadt and Fricke, *ibid.* 1930, **188,** 357; Moser and Singer, Monatsh. 1927, 48, 676).

In contact with bases and in the cold the metastable a-form changes into a stable, crystalline j3-form which also results when a hot saturated solution of the amorphous hydroxide in 10JV·NaOH is slowly cooled (Fricke, Z. anorg. Chem. 1927,166, 245; 1929, 178, 400).

As might be expected, the amorphous product is more reactive than the crystalline forms. Unlike them it absorbs CO_2 from the air,^s soluble in alkali carbonates, dilute mineral and organic acids and in certain beryllium salts, fhe crystalline modifications • require higher concentrations of alkalis to dissolve them and the solutions contain beryllates of the type **M'_2Be<O,** (**M'=Na** or K); the amorphous form under like conditions partly yields beryllatey. and partly gives a colloidal solution (Hantzschai Z. anorg. Chem. 1920, 30, 303, 319; Mohanlal and Dhar, *ibid.* 1928,**174,**1; Fricke *et al.,* *ibid.* 1932, 205, 127, 287).

BERYLLIUM AND HALOGENS.

Beryllium Fluoride, BeF_2.—Formed by heating the carbide or oxide in fluorine or hydrogen fluoride, it is usually made by slowly heating dry ammonium beryllofluoride, $(NH_4)_2BeF_4$, to a red heat in a current of CO_2 (Lebeau, Ann. Chim. Phys. 1899, [vii], 16, 484). The product is a transparent, vitreous mass, d;*?=l-98, which shows no regular structure but has a " random network " (Wa*ren and Hill, Z. Krist. 1934, 89, 481). It has no definite melting-point but is fluid at 800° and begins to volatilise at that temperature giving a white crystalline sublimate ; the molten product is a poor conductor bf electricity. The fluoride dissolves in water with hydrolysis so that, like the other halides, it cannot be produced from aqueous solution. It is slightly soluble in absolute alcohol and more so in a mixture of ak/bjhol and ether. No combination occurs with anhydrous hydrofluoric acid so that the acid, H_2BeF_4, corresponding to the beryllofluorides is apparently not produced. With liquid or gaseous ammonia A monammine, **BeF_2-NH_3,** is formed (Biltz and Rahlfs, Z. anorg. Chem. 1927,**166,** 351,355, 361, 367). The fluoride differs from the other beryllium halides in that-addition of sodium hydroxide docs not precipitate the hydroxide but yields a sparingly soluble double salt.

Evaporation of an aqueous solution of beryllium fluoride and heating the product to 300-800° gives a whiter mass of the • oxyfluovide, $2BeO*5BeF_2$, which* is an important intermediate in the production of the metal from its ores; it is completely soluble in water.

Beryllofluorides.—Numerous double compounds of the type M'_2BeF_4 and $M''BeF_4$ have been obtained and are interesting in that many of them are isomorphc^is with the corresponding sulphates. They are usually made by one of the following methods: (a) concentrating a solution containing the two fluorides in the correct proportions; (6) dissolving • stoicfciometric amounts of beryllium oxide and the metal carbonate or hydroxide in a slight excess of hydrofluoric ackl; (c) from ammonium or silver beryllofluoride by double decomposition. LUie the corresponding sulphates the alkaline earth and lead salts are sparingly soluble but the silver salt is very soluble in water. Acid salts of the type $M'HBeF_4$..ind more complex double compounds, including amminoberyUofluorides', hav~ been prepared wiiile by fusion methods the compounds $M'BeF_3$ 'M'=Na or K) have been obtained (Marignac, Ann. Chim. Phys. 1873, [iv], 30, 55;, N. Ray, Z. anorg. Chem. 1931, 201, 289; 1932, 205, 257; 206, 209; 1936, 227, 32, 103; 1939, **241,** 165; HulUren, Z. Krist. 1934, **88,** 233).

Beryllium Chloride.—Beryllium ignites on gently heating in chlorine and the resulting chloride is deposited "as a sublimate of white needles. It is also produced by heating the carbide or intimate mixtures of the oxide and sugar charcoal in chlorine or hydrogen chloride at 1,000°. Phosgene readily reacts with beryllium oxide at 900°, but below 500° the reactior. is so slow that it is possible to remove alumina and ferric oxide by heating the crude beryllia in this gas at 450° since aluminium and ferric chlorides are volatile at this temperature.

Beryllium chloride melts at 405° and begins to volatilise near this temperature; the Loiling-point is given an 488°. The vapour pressure at the boiling point indicates about 50% association to Be_2CI_4. The molten chloride is practically a non-conductor of electricity but additions of alkali chlorides rapidly increase the conductivity (Fischer and Rahlfs, ?Ao E lek; rochem 1932, **, 592 ,* Z. anorg. Chem. 1933, 211, 321).;, Beryllium chloride is very hygroscopic and is easily hydrolysed in aqueous solution. It is insoluble in benzene, carbon disulphide, chloroform or carbon tetrachloride although it is soluble in many other organic media (*e.g.* MeOH, EtOH), often with combination (*e.g.* o-toluidine) to produce molecular compounds of the type $BeCl_a$-nY where Y is the solvent molecule fcnd *n* is usually 2 or 4 (R. Fricke *et al.,* Z. anorg. Chem. 1925,146, 103, 121; 1926,152, 347; 1927,**163,** 31; 192&, **170, 257).**

Thermal analysis indicates that double compounds of the type M'_2BeCI_4 or $M''BeCL$ are formed with alkali and barium chlorides respectively ; thallous chloride forms $Tl\,Be_2CI$. Complex formation also occurs with certain other r ^ ^ / W * ' ? 1 ^ Bull. Soc. chim. 1926, [iv], 39, 1086; Ann. Chim. 1929, M; 35 / Prytz (Z. anorg. Chem. 1937, 231, 8) was unable to secure evidence of any complex formation m aqueous solutions of beryllium chloride containing potassium chloride. cm<>nae

When an aqueous Solution of .eryllium chloride is evaporated over sulphuric acid and are deposited colourless crystals of the hydrated chloride' ^$BeCl_2,4h_2O$. The tetrahydrate is extremely hygroscopic and readily loses HCl in damp air; it is more stable in dry air and can be kept over phosphorus pentoxide without losing water of crystallisation (Debray, Ann. Chim. Phys. 1855, [iii], 44, 22; Mieleitner and Steinmetz, Z. anorg. Chem. 1913, 80, 73; Fricke and Schützdeuer, *ibid.* 1923, 161, 130; Cupr and Salanský, *ibid.* 1928, 176, 241). Mieleitner and Steinmetz state that the hydrated chloride is formed when hydrogen chloride is led into the aqueous solution mixed with ether, but Cupr and Salanský on repeating this work obtained, instead, white needles of the^compound $[Be(H2O)_3(C_2M_6)_2O]Cl$.

Numerous oxychlorides of beryllium have been described, but there is some doubt whether they are definite chemical compounds. The view of Parsons and his collaborators (J. Amer. Chem. Soc. 1904-06) is that all basic salts of beryllium are merely solid solutions of the normal salt in the hydrated hydroxide; *see, however,* beryllium sulphate.

Dry beryllium chloride, cooled in a freezing mixture, reacts with ammonia in the absence of air to form the hexammine $BeCl_2*6NH_3$ as a white voluminous powder which deliquesces slowly in air. At 0° the tetrammine is produced, and this is also obtained when ammonia is passed into an ethereal solution of the chloride. Thermal decomposition of the tetrammine above 210° and *in vacuo* yields a diammine which also results from the action of ammonia on beryllium chloride at room temperature (Ephraim, Ber. 1912, 45, 1323; Z. physikal. Chem. 1913, 81, 532; Mieleitner and Steinmetz, *l.c.;* Fricke and Havestadt, Z. anorg. Chem. 1925,146, 126? W. Biltz *et al., ibid.* 1925, 148, 158; 1927, 166, 341; Bergstrom, J. Amer. Chem. Soc. 1928, 50, 657).

Beryllium Perchlorate, $Be(ClO_4)_2,4H_2O$.—Obtained as fine, colourless, deliquescent crystals by double decomposition of barium perchlorate and beryllium sulphate and concentrating the filtered solution with excess of perchloric acid (Cupr, Coll. Czech. Chem. Comm. 1929, 1, 377). The solubility of the anhydrous salt at 25° is 59-5% (Sidgwick and Lewis, J.C.S. 1926,1290).

Beryllium Bromide, $BeBr_2$.—Obtained as long white needles by methods analogous to those used for the chloride which it resembles closely in properties. The melting-point is 487° although sublimation begins at 473°; the density at 25° is 3-465. The fused bromide is a non-conductor of electricity.

With liquid hydrogen sulphide at -78-5° the bromide forms a compound $BeBr_2*2H_2S$ while with ammonia it forms ammines containing 10, 6 and 4 mol. NH_3; the tetrammine alone is stable at room temperature.

Beryllium bromide tetrahydrate is produced similarly to the chloride and forms hygroscopic cubic crystals. A trihydrate-etherate, $BeBr_2,3H_2O,(C_2H_5)_2O$, is also known.

Beryllium Iodide, BeI_2.—M.p. 480°; b.p. [illegible]; sublimation temp. 488°; d^{*}\=4-325.

Prepared by similar methods to the chloride and bromide, but higher reaction temperatures are needed. It sublimes to form white needles which are very sensitive to moisture, deliquescing and losing hydrogen iodide in moist air. The iodide is more susceptible to oxidation than the other halides and takes fire if heated to red heat in air or oxygen; it is safer, therefore, to sublime it in a high vacuum (Messerknecht and Biltz, Z. anorg. Chem. 1925, 148, 152). The other halogens convert the iodide into the respective halides although with fluorine an iodofluoride is also produced. Heated in hydrogen sulphide or sulphur vapour beryllium sulphide is formed while with liquid hydrogen sulphide at —83° the double compound BeI_2*2H_2S is obtained (W. Biltz and Keunecke, *ibid.* 1925, 147, 185, 174).

Beryllium iodide is soluble in water but no hydrate has been isolated apart from a dihydrate-dietherate, $BeI_2,2\,H_2O,2\,(C_2H_5)_2O$ (Cupr and Salanský, *l.c.).* Solution in organic media is often accompanied by combination.

Ammines containing respectively 13, 6, 4 and 1} mol. of ammonia per mol. of iodide have been reported (W. Biltz *et al., ibid.* 1925, 148, 152; 1927,166,341; Bergstrom, *l.c.).*

Beryllium Periodate.—Evaporation of an aqueous solution of basic beryllium carbonate with periodic acid leads to the separation of thick plates of $Be_?(IO_5)_2,11\,H_2O$; the salt is decomposed on boiling with water (Atterberg, Bull. Soc. chim. 1875, [ii], 24, 358).

BERYLLIUM AND SULPHUR.

Beryllium Sulphide, BeS.—Formed as a grey, amorphous mass when the halides are heated in hydrogen sulphide or sulphur vapour or when finely divided beryllium is burned in sulphur vapour. It is best prepared by heating the powdered metal, covered with sulphur, in a current of hydrogen in a porcelain tube for 10-20 minutes at 1,000-1,300°. The grey, partly sintered mass is, apparently more stable in air than products obtained by other methods (Tiede and Goldschmidt, Ber. 1929, 62~>[B], 758). This material also develops a blue phosphorescence if heated in a high vacuum at 1,300° and then exposed to an arc lamp; this is attributed to the presence of traces of iron.

Beryllium sulphide, *d* 2-36 (Zachariasen, Z. physikal. Chem. 1926,119, 201) possesses a faint odour of hydrogen sulphide, this gas being easily liberated on treatment with dilute acids. Lebeau states that it is attacked by water, but according to Mieleitner and Steinmetz it is only slowly decomposed even by boiling water. Heated in air or oxygen the sulphide burns, yielding sulphur dioxide and beryllia in the former gas and beryllium sulphate in the latter. Hydrogen does not attack it but chlorine and bromine convert it at a red heat into the respective halides.

Beryllium Sulphite, $BeSO_3$.—When freshly precipitated beryllium hydroxide, freed from water by washing with alcohol, is dissolved in alcohol saturated with sulphur dioxide, the solution on evaporation *in vacuo* over sulphuric acid and sodium hydroxide deposits small, colourless, hexagonal crystals of beryllium sulphite. The product is only slightly soluble in alcohol or water but the latter medium soon hydrolyses it, forming more soluble baric salts (Krüss and Moraht, Ber. 1890, 28, 734).

Beryllium Sulphate, $BeSO_4$.—Prepared by dissolving the oxide or hydroxide in excess of hot conc. sulphuric acid and cooling; the excess acid is decanted from the fine microcrystalline powder which separates; this is washed with alcohol and dried. Removal of excess acid by evaporation leads to slight decomposition and the formation of a little beryllium oxide. This is evident, too, when the sulphate is made by dehydrating the di- or tetrahydrate by heating to 400°.

Beryllium sulphate is very hygroscopic and although not appreciably soluble in cold water it is slowly converted into the soluble tetrahydrate; this process proceeds more rapidly on heating. The density of the salt is 2·443. With dry ammonia there is formed a diammine which passes into a monoammine on heating to 234°.

Hydrates of Beryllium Sulphate.—Considerable attention has been given to the system $BeSO_4$-H_2O and numerous hydrates have been reported, but the only ones about which there appears to be no doubt are the tetra- and di-hydrates (Parsons and Fuller, Science, 1906, 24, 202; Taboury, Compt. rend. 1914, 159, 180; Britton, J.C.S. 1921, 119, 1967; F. Krauss and Gerlach, Z. anorg. Chem. 1924, 140, 61; Schreiner and Sieverts, *ibid.* 1935, 224, 167; Schröder, *ibid.* 1936, 228, 129; Novoselova and Levina, J. Gen. Chem. Russ. 1938, 8, 1143).

The tetrahydrate is prepared by dissolving beryllium oxide, hydroxide or carbonate in warm dilute sulphuric acid (*d* 1·07), filtering and concentrating the solution; the crystals which separate on cooling are washed with alcohol. Britton and Allmand also obtained it by treating a strong solution of the nitrate with excess of conc. sulphuric acid and pouring the mixture into alcohol when the tetrahydrate separates (J.C.S. 1921, 119, 1464). It may be recrystallised from hot dilute sulphuric acid or even hot water. The crystals belong to the tetragonal holohedral class and their density is 1·712. The tetrahydrate is readily soluble in water, 100 g. of the solution containing 29·94 g. $BeSO_4$ at 25° (Sidgwick and Lewis, *l.c.*); the solution reacts acid, the salt being appreciably hydrolysed.

Heating the tetrahydrate to 120° or maintaining it at 93° until a constant weight is attained causes the loss of 2 mol. of water; the resulting dihydrate has a similar crystalline form to that of the tetrahydrate. It partly melts on heating to 158° and gradually loses water above 100°. Like the tetrahydrate it is stable at room temperature.

Double Salts.—Beryllium sulphate yields double salts with potassium and ammonium sulphate of the type $BeSO_4,M_2SO_4,2H_2O$. Fused potassium and beryllium sulphates are readily miscible, and from the melt containing 33-60 mol. per cent, of the latter there can be crystallised the double salt $K_2SO_4{\cdot}2BeSO_4$.

A study of the isotherms of the system $BeSO_4$-Na_2SO_4-H_2O between 0° and 100° reveals the existence of the compound $BeSO_4 3Na_2SO_4$ which is stable above 42° (Grahmann, Z. anorg. Chem. 1913, 81, 265; Marchal, J. Chim. phys. 1925, 22, 516; Schröder, Z. anorg. Chem. 1938, 239, 39, 225; 1939, 241, 179).

Basic Beryllium Sulphates.—Parsons and his collaborators hold the view that all basic salts of beryllium consist of solid solutions of the salt in hydrated beryllium hydroxide, but Sidgwick and Lewis (J.C.S. 1926, 1298), finding that approximately 4 mol. of the oxide will dissolve in 1 mol. of beryllium sulphate, suggest that beryllia may replace water in $[Be{\cdot}4H_2O]SO_4$. There will thus be formed the complex $[Be{\cdot}4BeO]SO_4$ although, actually, the replacement may take place in stages. Such basic salts have not, however, been obtained crystalline, but only as syrupy masses when solutions of beryllium hydroxide or carbonate in aqueous solutions of the normal salts are concentrated.

BERYLLIUM AND SELENIUM.

Beryllium Selenide, BeSe.—Grey crystalline mass obtained by leading hydrogen carrying selenium vapour over the heated metal. The product is soluble in water but the solution soon decomposes with deposition of selenium (Zachariasen, Z. physikal. Chem. 1926, 124, 278, 437; Pauling, J. Amer. Chem. Soc. 1927, 49, 787).

Beryllium Selenite, $BeSeO_3,2H_2O$.—Obtained as a precipitate on adding a solution of neutral sodium selenite to one of beryllium sulphate. The salt, after filtering and washing, is treated with selenious acid until neutral and dried at 60°. The acid salts $BeSeO_3$-H_2SeO_3 and $BeSO_3$-$2H_2SeO_3$ are also known (Nilson, Ber. 1875, 8, 655).

Beryllium Selenate.—Treatment of an aqueous solution of basic beryllium carbonate with the requisite amount of selenic acid and evaporation of the solution gives rise to colourless rhombic crystals of $BeSeO_4,4H_2O$ from which the anhydrous salt may be obtained by heating to 300°. At 100° 2 mol. of water are removed and the dihydrate produced. These compounds closely resemble the corresponding sulphates, the tetrahydrates being isomorphous (Topsoë, Ber. Wien Akad. 1872, [ii], 66, 6; Atterberg, Bull. Soc. chim. 1873, [ii], 19, 498; Sidgwick and Lewis, l.c.).

BERYLLIUM AND TELLURIUM.

The telluride is obtained in a like manner to the selenide and is a grey powder, *d* 5·09. It is slowly decomposed by moist air and readily by water with evolution of hydrogen telluride.

Beryllium tellurite and tellurate are stated to form white precipitates on treating solutions of beryllium salts with alkali tellurite or tellurate respectively (Berzelius, Ann. Chim. Phys. 1836, [ii], 58, 244, 259). These are probably basic salts, for M[illegible] ([illegible] Soc. Chim. 1935, [v], 2, 864) assigns to the tellurate the formula $BeTeO_4{\cdot}7Be(OH)_2$.

BERYLLIUM AND NITROGEN.

Beryllium Nitride, Be_3N_2.—Beryllium combines with [illegible] above 900°, but even at 1100° the reaction is slow and the product contains appreciable amounts of metal; a better result is obtained when ammonia is substituted for nitrogen. The nitride formed in these methods is a grey powder, but a white product is matte to passing cyanogen over the metal at 800°. Heating beryllium carbide in nitrous oxide or with ammonium nitrate yields an equally pure material.

Beryllium nitride melts at about 2,200° and begins to dissociate above ^his temperature. The melt, on cooling, solidifies to colourless cubic Crystals which scratch glass, arastable in air and only slowly decomposed by boiling water; dilute acids and concentrated alkalis readily dec&npose it. When mixed with alumina the nitride develops a strong phosphorescence after exposure to a mercury vapour lamp (Fichter and Brunner, Z. anorg. Chem. 19*5, 93, 89; Neumann *et al.y ibid.* 1932, °204, 81; Vourngsos, Bull. Soc. chim. 1917, [ivl 21, 282; Satoh, Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 29,41; 1938,34,888; Stackelbegg and Paulus, Z. physikal. Chem. 1933, B, 22,-«05).

Beryllium Nitrate.—The anhydrous salt has not yet been isolated, but hydrates containing 4 and 3 mol. of water have been prepared while the existence of a mono- and dihydrate has been inferred from Sensimetric data. The tetrahydrate is obtained either by dissolving beryllium hydroxide in nitric acid *(d 1-52)* at 0° and allowing the solution to evaporate in air or by repeated evaporation of the basic acetate with cone, nitric acid, adding fuming acid and seeding the solution. It forms deliquescent crystals which melt at 61°. If crystallisation takes place from a solution more dilute in nitflc acid, colourless prisms of the trihydrate are obtained. Attempts to dehydrate these products result in loss of oxides of nitrogen (Parsons, Science, 1907, 25, 409; Haase, Z. Krist. 1927% 65, 537; Sieverts and Petzold, Z. anorg. Chem. 1933, 212, 49; Novoselova and Nagorskaja, Bull. Soc. chim. 1935, [v], 2, 967).

No double compounds with alkali nitrates have been reported, but the existence of such compounds in solution has been inferred by Chauvenet (Compt. rend. 1939*208, 194; 1940, 210, 250).

BERYLLIUM AND PHOSPHORUS.

Beryllium Phosphide.—Formed when beryllium is heated in phosphorus vapour. Both Wöhler and Lebeau state that it is obtained when phosphinp acts en heated beryllium chloride, but Höltje and Meyer (Z. anorg. Chem. 1931, •197, 93) could not induce combination even at high temperature and pressure.

Beryllium Phosphates.—According to F. Travers and -Perron (Ann. Chim. 1924, [x], 1, 318) the hydrated orthophosphate,

$$Be_3(PO_4)_2,nH_aO,$$

is formed as a dense, white, microcrystalline precipitate by adding a dilute aqueous solution of disodium phosphate to one of beryllium sulphate until a faint turbidity appears and then heating the solution. Excess of the sodium phosphate solution produces an amorphous, white precipitate also stated to be tKe orthophosphate; the tetrahydrate is said to separate on crystallising from dilute acetic acid. Heating the tetrahydrate at 100° produces a trihydrate while iquch higher temperatures are needed for complete dehydration.

Primary Beryllium Hydrogen Phosphate, $BeH_4(PO_4)_2$, separates as hygroscopic, colourless plates on evaporating a solution of the oxide in a slight excess of the calculated amount of phosphoric acid. The *secondary phosphate,* $BeHPO_4$, is apparently incapable of existence and disproportionates readily into the primary and tertiary salts. The ammonium salt, NH_4-$BePO_4,H_2O$, is, however, known and is the precipitate obtained on treating neutral or slightly acid solutions of beryllium salts with ammonium phosphate. It is sufficiently insoluble to provide a method of estimating the metal, the precipitate being converted into the pyrophosphate, $Be_2P_2O_7$, by ignition (Travers and Perron, *I.e.).* A beryllium metaphosphate has also been reported (Bleyer and Mtiller, Z. anorg. Chem. 1913, 79, 273).

BERYLLIUM AND ARSENIC.

When beryllium is heated in arsenic vapour a grey product is formed which is probably the arsenide, for it liberates arsine with water.

Beryllium Arsenate, $Be_3(AsO_4)_2,15H_2O$, is prepared by adding an aqueous solution of the sulphate to one of disodium hydrogen arsenate acidified with acetic acid and air-drying the precipitate.

The acid salts $BeH_4(AsO_4)_2$ and $BeHAsO_4$ have also been made as well as numerous basic salts (Bleyer and Miiller, *ibid.* 1912, 75, 288; Ephraim and Rossetti, Helv. Chim. Acta, 1929, 12, 1033).

BERYLLIUM AND CARBON.

Beryllium Carbide, Be_2C—Beryllium possesses considerably affinity for carbon, particularly at high temperatures, and a carbide is readily formed on heating the metal at 1,300-1,400° with carbon 07 in CO or CO_2. The usual method of preparation is to heat, in an electric furnace, intimate mixtures of b^yllia and sugar charcoal bonded together with an agent such as dextrin. The product is cleaned by treating with hot dilute hydrochloric acid to remove adhering oxide and carbon. It forms regular, brick-red, octahedral or hexagonal crystals hard enough to scratch glass and of density 1-9. Moist ~ir and water slowly decompose it with liberation of methane. The carbide suffers only a superficial attack when heated in oxygen, nitrogen, phosphorus or iodine vapour, but the other halogens as well as their hydrides decompose it fairly readily at 800° as also docs sulphur vapour at 1,000°. Hot aqueous mineral acid solutions attack it more easily when dilute, while with hot caustic alkali there is a rapid evolution of methane (Lebeau, Compt rend. 1895,121, 496; Fichter and Brunner, Z. anorg. Chem. 1915, 93, 91; Messerknecht and Biltz, *ibid.* 1925, 148, 153} Schmidt, Bull. Soc. chim. 1928? [iv], 43, 49; Stacketyerg and Quatram, Z. physikal. Chem. 1934, T$, 27, 50).

Beryllium Acetylide, BeC_2.—Produced when acetylene is led over powdered beryllium at 450°; it differs from the carbide in regenerating acetylene when treated with water or dilute hydrochloric acid (Durand, Rull. Soc. chim. 1934, [iv], 35, U41).

Beryllium Carbonate.—Freshly precipitated beryllium hydroxide readily absorbs atmospheric carbon dioxide, while if an aqueous suspension of the hydroxide is saturated with the gas there is formed the basic carbonate $3Be(OH)_2{,}BeCO_3$. Basic salts of somewhat indefinite composition are also produced as white precipitates on adding aqueous sodium or ammonium carbonate to solutions of beryllium salts. If carbon dioxide is passed for a long time into a suspension of one of these basic carbonates and the solution filtered and evaporated over H_2SO_4 in an atmosphere of CO_2, white hexagonal crystals are obtained which are said to be the tetrahydrate of the normal salt $BeCO_3{,}4H_2O$ (Jahrcsber. 1868, 203). The crystals effloresce in air, are not very soluble in water and lose carbon dioxide as well as water on drying at 100°; the residual basic carbonates do not begin to decompose until about 200°. Beryllium carbonates are soluble in excess of alkali or ammonium carbonate and from the solutions alcohol precipitates crystalline compounds of the type

$$3BeM_2(CO_3)_2Be(OH)_2$$

(M=alkali metal or NH_4). The amount of hydroxide seems to vary in different preparations so that possibly it is merely an impurity in the true double salts $M_2CO_3{,}BeCO_3$. Heating the solutions redeposits the basic beryllium carbonate (Klatzo, J. pr. Chem. 1869, [i], 106, 227; Debray, Ann. Chim. Phys. 1855, [iii], 44, 32; Atterberg, Svenska Akad. Handl. 1873, 12, 31; Parsons, J. Amer. Chem. S0c. 1904, 26, 721; Venturello, Gazzetta, 1939, 69, 73).

BERYLLIUM SALTS OF ORGANIC ACIDS.

Numerous beryllium salts of organic acids have been made; in some cases, for example with oxalic acid, the normal salt is known while with other acids only basic salts have been obtained. The most important of these is the basic acetate, for its ready solubility in chloroform provides a means of separating beryllium from many other metals, including iron and aluminium.

Basic Beryllium Acetate,

$$(CH_3\cdot CO_2)_6Be_4O$$

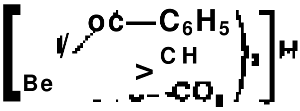
Separates as octahedral crystals on cooling a solution of the hydroxide in excess of hot, strong acetic acid. The crude product is recrystallised from chloroform until the melting-point is 286-287° or it may be purified by sublimation *in vacuo* (Urbain and Lacombe, Compt. rend. 1901,133, 874; 1902,134, 772; Tanatar, J. Russ. Phys.-Chem. Soc. 1904, 36, 82; Haber and van Oordt, Z. anorg. Chem. 1904, 40, 465; Kling and Gelin, Bull. Soc. chim. 1914, [iv], 15, 205).

The physical and chemical properties of the salt indicate that £ is a non-ionised covelent complex, while X-ray^xamination demonstrates that the four beryllium atoms occupy the apices of a regular tetrahedron in the centre of which is the single oxygen atom; the acetate radicals span the six edges (W. Bragg and Morgan, Proc. Roy. Soc. 1923, A, 104, 437; Morgan and Astbury, *ibid.* 1926, A, 112, 4,'4; Pauling and Sherman, Proc. Nat. Acad. Sci. 1934, 20, 340).

The basic acetate is stable to air and is insoluble in, and unaffected by, cold water; warm water dissolves it with decomposition. It is soluble in many organic solvents.

Normal beryllium acetate is said to be formed when the basic rait is heated at 140° in a sealed tube with acetic acid and acetic anhydride; it is insoluble both in cold water and organic solvents (Tanatar, *l.c.;* Steinmetz, Z. anorg. Chem. 1907,54,219).

Most of the mono!aaic organic acids give definite basic salts analogous to the acetate, but witk di- and tribasic'acids the more indefinite types experienced with inorganic acids are obtained. With the monobasic organic acids, however, nor/nal salts are also known. The beryllium derivative of benzoylpyruvic acid,



has been resolved into two forms with opposite and fugitive mutarotations (Mills and Gotts, J.C.S. 1926, 3121).

Beryllium Acetylacetone, $Be(C_6H_7O_2)_2$.—Prepared cither by the action of acetylacetone on aqueous or boiling alcoholic suspensions of beryllium carbonate or by treating aqueous beryllium chloride solution with an ammonical solution of the dikctone followed *i*y* further careful addition of ammonia (Jaeger, Rec. trav. chim. 1914, 33, 394; Parsons, Z. anorg. Chem. 1904, 40, 412; W. Biltz', Annalen, 1904, 331, 336). It may be purified by sublimation or by crystallisation from alcohol. Slightly soluble in cold water it dissolves readily in the hot medium, but with gradual decomposition and deposition of the hydroxide; it is soluble in many organic solvents. The acetylacetone docs not form an additive compound with ammonia although with SO_2 a 1:1 compound is formed. The ethylacetoacetate behaves similarly (Booth and Smiley, J. Physical Chem. 1933, 37, 171).

ORGANOMETdLUC DERIVATIVES OF BERYLLIUM.

Few such derivatives are knoum, none of them being analogous to the Grignard reagents produced with magnesium.

Beryllium dimethyl, diethyl and *dibutyl* have been prepared from beryllium chloride and the appropriate Grignard reagent; the first-named is also formed when mercury dimethyl acts on beryllium. The diethyl and dibutyl compounds are liquids while the dimethyl is a hiirh-meltine solid subliming at 200°

Beryllium diphenyl and *di-p-lolyl* have been obtained (Schulze, Iowa State Coll. J. Sci. 1933, 8, 225).

For the detection and estimation of beryllium, *v.* CHEMICAL ANALYSIS, Vol. II, 580a and 587 6, c, *d.*

GLUCOCHLORAL *(v.* Vol. III, 3&).

GLUCONIC ACID *{v.* Vol. II, 297a).

GLUGOSANS (*v.* Vol. II, 2956).

GLUCOSE (*in* Vol. II, 284a).

GLUCOSEEN-5:6 (*v.* Vol. II, 284d).

GLUCOSIDASE (*v.* Vol. IV, 3136, 3146).

GLUCOSIDES (v. GLYCOSIDES).

GLUCOXYLOSE (*v.* Vol. II, 300c).

GLUCURONIC ACID (*v.* Vol. II, 297c).

GLUE AND GLUE TESTING. Glue or gelatin adhesives are materials which have the property of gelatinising in aqueous solution and drying to form a hard strongly adhesive layer. They are obtained from the collagenous parts of animals and fish, chiefly hide and skin trimmings, bones, cartilage and tendons, by extraction with water. Keratinous materials such as muscles, horns and hoofs contain little, if any, glue-yielding material, but horn-piths give ossein.

Other preparations which possess this adhesive property are also loosely termed glues, *e.g. marine glue,* a mixture of rubber and asphaltum, gluten and casein glues, mineral and vegetable glues, blood and albumin glues, phenol-formaldehyde condensation products, etc, but, strictly speaking, these have no claim to that name, as they contain no gelatin.

Gelatin is the principal constituent of a glue, and therefore many of the properties of the latter depend on those of the former. This, however, is not always the case; highly purified gelatin is distinctly weaker, as an adhesive, than a commercial gelatin or a high grade glue. The superior adhesive power of the latter may be due to the presence of other soluble products which in themselves possess no adhesive properties, but which modify those of the gelatin by altering its state of Aggregation.

Glue and gelatin do not exist, as such, in the animal organism but are the products of the hydrolysis of various nitrogenous components brought about by boiling water.

These components may be classed as follows:

(1) *Collagens.*—The organic materials of hides, skins, bones, tendons and cartilage. Hofmeister regarded collagens as anhydrides of gelatin. According to Grassmann (J. Soc. Leather Trades' Chem. 1938, 22, 473) the fibres exist in different forms, dependent on the stretching or folding of the polypeptide chains. Kiintzel (Magyar Timar, 1938, 1; J. Soc. Leather Trades' Chem. 1938, 22, 410) regards the formation of gelatin as a type of mating process. In the molten or gummy condition the individual molecules are unstable and pass from the stretched into the coiled-up condition.

(2) *Keratins.*—Found in the hard structure of the nails, hair, horns, hoofs, whale-bone, etc. They are unaffected by boiling water except under pressure, yield products which have little gelatinising power and are not used in glue manufacture.

(3) *Elastins.*—Mainly derived from tendons and ligaments. They are similar to the keratins in behaviour in water but are acted on by trypsin and other enzymes. Liming with arsenic limes swells and breaks these tissues (W. T. Roddy and F. O'Flaherty, J. Amer. Leather Chem. Assoc. 1938, 33, 257).

(4) *Reticulin.*—The collagen fibres of hides are held together by a meshwork of reticulin and elastin fibres. Collagen fibres are covered with a fine sheath of reticular tissue, which is stronger in young skins than in old ones. It is very susceptible to bacteria, broken by hydrochloric acid solutions of $Pn<2$, weakened by sodium hydroxide or sodium sulphide and more slowly by calcium hydroxide.

(5) *Mucins and Mucoids.*—A class of glycoproteins, insoluble in water but easily soluble in dilute alkalis, which is present to a small extent in tendons, connective tissue of hides and skins, cartilage and bones.

(6) *Chitin.*—Found in the hard sheaths of beetles, locusts, shrimps, crabs, etc. It can be converted into a gelatinous form by treatment with acids but is of no utility.

For convenience the products obtained from collagens by the action of water may be classed into gelatin, chondrin and mucin, the properties of which will be described later. During the extraction of glue, or gelatin, two reactions take place: (a) hydrolysis of ossein or collagen to form gelatin; (6) hydrolysis of gelatin giving harmful degradation products.

The extraction process appears to be, therefore, a very simple one. In practice it is not so because, unless properly controlled, the second reaction, although slower than the first, will tend to produce larger quantities of those materials which impair the properties of the finished product and especially the adhesiveness. It follows therefore that, whatever the glue-yielding material used, the following precautions should be observed:

(a) The extraction should be carried out as rapidly and at as low a temperature as is consistent with economic working.

(6) The acids or alkalis used in the preliminary treatment of the bones or hide trimmings should be removed as completely as possible.

(c) The extracting water should be as nearly neutral as possible. Distilled water is always to be preferred, and for the gelatin maker it is almost a necessity.

Many other factors influence the properties of glue, but will be considered later, as they relate to processes which follow the extraction.

Of the materials mentioned, tannery by-products and bones are those most commonly used; horn-piths are used for the production of special glues in which great adhesiveness is not necessary.

MANUFACTURE: *(a)* **Hide and Skin Glues.**—While the epidermis of the hide yields little or no glue, the *corium* or inner skin, consisting mainly of collagen fibres, gives a high grade glue. Hides and skins are, however, only used for this purpose when unfit for leather manufacture. The following are the raw materials in decreasing order of quality[1]: hide pieces of calf, goat, deer, etc., including ear and face clippings; low grade de-woolled sheepskins; sheep " spetches "; hand and machine trimmings and fleshings from hides and skins; foreign sheep " spetches "; and foreign hide and skin fleshings. Good tannery pieces (" spetches ") yield about 45% of glue while fleshings only give 20-30%. Rabbit skins yield a pale coloured glue which has a good adhesive power, but a weaker jelly strength than best hide glue. Glues from the skins of young an& small animals' coAtain more *chondrin (q.v.)* and are weaker in jelly strength than glues from older and larger animals. The pieces and trimmings may be unlimed or limed. Many patents exist for making glue from tanned leathers, but the cost of the previous de-tanning is considerable. In the manufacture of high class glues, much discretion is required in blending the raw materials.

The unlimed raw materials are obtained from the tannery or from the animals at the slaughterhouse. If not used immediately they must be washed and salted, salted and dried, or limed to prevent putrefaction. Before liming, they are washed in a machine to remove blood and dirt, which would either produce a highly coloured glue or reduce its adhesive properties, and they are often run through shredding or cutting machines to ensure a more uniform action of the lime.

The limed raw materials are ciSt from hides which have been laid flat in pits in liquors containing about 4% lime and 0-2-0-5% sodium sulphide (which contains iron and turns the hides a bluish-green) for 7-21 days, with about 4 liftings. The object is to loosen the hair by softening the bottom layer of the epidermis. Mucins and mucoids are also dissolved Out. The hair is then removed by a machine with a blunt knife, the hides are trimmed and the surplus flesh scraped off. The hair thus obtained finds use in plastering work and felt making, etc.

Skins are painted on the flesh side with a 2% sodium sulphide solution thickened with lime, de-woolled or imhaired the next day, trimmed, fleshed, well washed and limed further in a lime liquor containing arsenic sulphide.

The *first process* in the manufacture of glue is the liming and the quality of the product depends upon the thoroughness of this treatment. It is necessary to avoid hydrolysis of the collagen and the extent of this liming therefore depends upon the'condition of the raw material, and with already limed stock reduced liminf; 'is usually desirable. For unlimed stock, saturated lime-water has been recommended, but in practice this has to be changed at frequent intervals. It is necessary to construct the whole plant so that it can be kept absolutely clean without excessive labour. It is best to employ several changes of a lime suspension in wooden or concfete vats using about 10% of lime on the weight of the stock, or less if caustic soda is used. The total time varies from 30-60 days, but is considerably less if caustic soda is present, and the stock is then firm and free from a greasy feel. If it is frequently turned over no bacterial action occurs, Bleaching agents, such as bleaching powder or sodium peroxide, 'and preservatives, such as phenolic compounds, are sometimes added, but may cause coagulation during evaporation.

The *second process* is carried out in the washing mills with running water until the washings are clear. As the remo/al of the lime is incomplete, acid is added to tte next wash-water. The most commonly used are sulphurous and hydrochloric acids. The former has the advantage of being both a bleaching and antiseptic acid, but it has the disadvantage that appreciable! quantities of sulphur dioxide or sulphites may be left in the finished product. Commercial hydrochloric acid is used more frequently in the manufacture of glues where the presence of traces of iron or arsenic would not be considered as objectionable. After the acid treatment, the materiel must be in a nearly neutral condition with a p_E value of about 5-0. Stock containing rancid fats would yield turbid glue because of the emulsifying power of the oxidised acids. " Such material can be improved by calbonation, that is blowing carbon dioxide through them in water until phenolphthalein is no longer reddened. In any cast, the materials are then either used immediately or dried and stored read/ for future use. "•

The *third process* is the extraction of the glue by " boiling " with a large quantity of water, The word " tailing" does not imply actual ebullition, but gentle cooking at a temperature of about 60°C. to convert the collagens Lito glue and allow the fat to rise without emulsifying with the gelatinous matter. This is the most important process of the manufacture, and the quality of the finished product depends upon a number of factors which are very difficult to control. It is necessary, for instance, to avoid as far as possible the formation of degradation products by prolonged heating. Very frequently, however, degradation products are present in certain portions of the skins, owing to overtiming. These dissolve first, and the " first run " of glue is then of inferior quality compared with the second extraction.

Generally, the extraction of glue is carried out in open aluminium or wooden vats, 3 or 4 ft. deep and 6-8 ft. in dianr ter. Copper heating coils are placed at the bottom of the vats and covered with a perforated false bottom usually made of iron or copper. By this arrangement the materials do not come in contact with the coils, while the perforated false bottom is used as a support for a coarse filtering medium. The steam for heating, comes from a vertical pipe in the centre surrounded by a wooden casing or " eye " passing through the false bottom so that when the liquor boils it rises through the casing and flows out at the top of the vat, passing down through the glue-stuff. For dry material, the vat is fitted with a " curb" in which the spetches can be piled and sink down gradually as they soften.

The" vat is filled with the treated materials and enough water is allowed to run in to* cover them, and steam passed through the coils, the temperature being maintained at about 60°C (140°F.) for 6-8 hours or until a Sample of the liquor forms a firm jelly on cooling. As much of the fat as possible is skimmed off and the due liquor is then drawn off through a valve at the bottom of the vat, run into a tank, allowed to cool somewhat, and a further portion of fat allowed to separate.

More water is then added, and the " boiling " is continued until the necessary concentration has been reached. This second liquor will yield the best glue, but a large quantity will still be left in the hide stock, which is extracted by reDeatin* the " boiling " 3 or 4 times, the temperature of the extracting water being increased if necessary.

The gpue liquors must be filtered and concentrated, ftit as*these processes are similar to those employed for bone glues they ^{f}AU be described later.

(b) **Bone Glue.**—For this purpose, bones of alV kinds are used and vary, therefore, so much in composition that it is useless to give any detailed analysis. Apart from the marrow, Blood-vessels, etc., they contain the main ingredients of the ash, calcium phosphate and carbonate, fat and the gelatin-forminf substance ossein. The inorganic portion is so intimately blended and incorporated with the ossein that it is^nly b£ drastic treatment as, for instance, by the action df strong mineral acids, that they can be separated.

In many respects the 'processes used in the manufacture of bone glue differ from those described for hide glues. These differences do not refer to the extraction of* the glue itself, but to*the preliminary treatment of the raw material in order to obtain a number of very valuable by-products.

The ossein, the collagen of bones, may be isolated from degreased T>ones by a prolonged^ and somewhat expensive and troublesome treatment with dilute acids. The number of acidB suitable for this purpose is limited, as some of them, e.g. nitric and acetic acids, have an injurious effect on the gelatin-yielding material. Hydrochloric acid is by far the most commonly used; the strength of the solution varies between 2 and 5%.

Ossein f»n be limed and treated in a manner similar to hides, but owing to the expense and the time required, this treatment is only used for the manufacture Cf gelatin.

In order to extract glue from untreated bones, the following process is adopted.

The green bonus are first passed through a crusher, and then over a belt in order to remove by means of a magnet any metallic objects which may be present. In many cases the bones are thoroughly washed before crushing.

The crushed bones are then treated for the removal of fat. Fresh bones comprising the heads, ribs, shoulder-blades, etc., contain 12-13% while the large thigh bones (" marrows ") yield 17-18%. Marine store bones$_4$ which have generally been used for making soups, Indian and South American bones rarely contain more than 12% of fa J>

There are three methods of extracting fat from *bones: (1) by heating the bones with water in a tank provided with a steam coil; (2) by heating with steam in a digester under pressure; (3) by extracting with a volatile solvent (t? BONE FAT).

By the first of these processes the yield of fat is small, but it is of good colour and finds ready use in many subsidiary industries such as soap-making.

The second process will extract more fat, but at the same time also a certain amount of the glue.'

The solvent extraction process will remove practicafiy the whole of the fat without injury to the glue-yielding material and is the one used in most modern factories. The usual solvents are benzine, benzol and trichlorethylene; benzine w&s Commonly used, but trichlorethylene and other modern solvents are rapidly taking its place owing to non-inflammability and lower cost of degreasing.

The idea that in order to obtain a good extraction of fat the bones must not contain more than 10% of moisture has been proved incorrect, as the presence of water will not hinder the extraction of the fat and will not cause loss of glue, especially if the solvent used has a low boiling-point, *e.g.* if trichlorethylene (b.p. 87°C.) is employed.

A modern fat-extracting plant consists generally of 6 cylindrical vertical extractors, each of a capacity of 5 or 10 tons, worked in sets of 3 units, one lot extracting while the other set is being emptied. The extractors are provided with wet and dry ste&m coils placed under a perforated false bottom.

After sorting, the crushed unscreened bones are filled intcPthe extractors, the manholes are tightly closed, and sufficient solvent to cover them is allowed to run in from the storage tank. Steam is then admitted to the dry coils and the solvent is distilled over through a pipe placed at the top of each extractor and connected with suitaMe condensers often situated outside the buiJding.

By formation of an azeotropic mixture the solvent carries off all the water contained in the bones; the mixture is passed, after condensation, into a separator which allows the solvent to be recovered and returned to the storage tank, and thence, automatically, to the extractor.

The heating is continued in this way until the condensed solvenjj is free, or practically free, from water, when extraction is assumed to be complete. The steam is then turned'off, and the fat, together with the remaining solvent, is drawn off from the bottom of the extractor into a still for the recovery of the solvent.

The bones are then washed once or twice with the solvent, to remove from them as much as possible of the adhering fat. These washings are also drawn into the still, and high pressure steam from the wet steam coils is then blown into the extractors to completely expel all the solvent. This is continued until the condensate is all water, when the extractors are opened to admit a circulation of air for drying the bones. The whole operation takes about 12 hours.

The fat obtained by this method is, as a rule, highly coloured, and is known commercially as " benzine bone grease." It is freed from dirt, if necessary, by heating with hot water, and settling, and is then run into barrels. It contains about 98% of fatty matter and is used for soap, candle, glycerin, and if made from fresh bones, for margarine making?

The bones are raked out, conveyed to a cleanser, consisting of a rotating cylindrical wire gauze sifter, where they are " polished " and all small particles of adhering tissues removed. The*' polished " bones shodd be free from smell and not contain more tN,n 0-25% of fat. In many works the extraction of the glue is carried out without subjecting them to any further preliminary treatment; in others they are subjected to maceration either in dilute alkali or dilute acids. The acid tisatment, for which dilute solutions of sulphurous acid are used, is supposed to facilitate the extraction of the glue, by causing a slight decalcification on the surface of the bone, while an alkaline treatment, either with milk of lime or dilute soda, has for its object the removal of substances which by their presence impair the properties of the glue. These substances occur always in the connective tissue of various organs, and belong to the chondroproteins; in the case of bones this chondroprotein is called osseo-mucoid and was isolated in notable quantities for the first time by Hawk and Gies (Amer. J. Physiol. 1901, 5, 388).

The extraction of glue from the " polished " bones is carried out in pressure tanks, commonly called "digesters." These are steel cylinders with convex ends, having a large manhole at the bottom for the removal of the spen£ material and a hinged lid for the charge.

Before the extraction, steam is blowri through the bones in order to further clean them and to remove any trace of adhering solvent. When the digester is filled with steam, the steam outlet is closed and the pressure allowed to increase to the desired extent. Both the pressure and the time for which it is maintained vary in diffetent works; in some, pressure and vacuum are applied alternately in order to ensure better penetration of the water and thus give more concentrated liquors.

When the pressure in the "digester" has been released, water preheated to 100-110°C. (212-230°F.) is run in to effect the extraction of the glue. As in the case oxhide glues, several " runs" are made, each yielding glue of a different grade.

TREATMENT OF GLUE LIQUORS.—The liquors, either from hides or from bones, contain suspended fine materials. Several methods have been suggested for their elimination. In many works glue liquors are clarified by standing in tanks, kept warm by steam coils, here the dirt settle 3 and the grease that comes to the surface is skimmed off. Not all glue liquors can be filtered bright; the protective action of the gelatin itself is a hindrance to a good filtration. Fuller's earth, charcoal and alumina have been recommended as filtering media, but the best results are obtained with cellulose. Cellulose, being slightly electronegative to water, holds the electropositive particles without adsorbing the glue, but in order to obtain a good filtration it is necessary to pack the cellulose loosely. Filter presses therefore prove to be useless and gravity filters should be used instead.

Many manufacturers prefer precipitating the euspended material by producing a colloidal coagulation in the glue liquor, which can collect and hold the suspended particles; albumin is added, for instance, to a comparatively cool liquor, and the temperature gradually raised until coagulation takes place. The liquor is then allowed to stabd for the separation *oY* the coagulum, and the clogr portion siphoned off and filtered. Instead of albumin, blood is frequently used, or, in many cases, inorganic precipitants such as alum or acids which form insoluble salts with the alkaline earths.

The clarified glue liquors are then, evaporated to the necessary concentration in vacuum pans, *e.g.* thM Yaryan evaporator (v. Vol. IV, 409d).

Many glues have a strong tendency to foam when heated* *in vacuo*; the addition of soaps (*e.g.* aluminium soap) or of tallow will, by altering the surface tension, decrease very markedly this tendency, but at the same time render the finished product useless for certain purposes.

After evaporation, the glue liquors before settling are bleached, if necessary, by treatment with sulphur dioxide, which is introduced through perforated pipes into the liquors contained in lead-line^ tanks and kept liquid by steam coils." When the required shade has' been reached, the liquors are ready for jellying and are run 'into wooden or galvanised iron troughs about 5 ft. long by 9 in. deep and \&y in. wide and allowed to cool. Great care is taken to keep these coolers free from putrefactive bacteria and they 'are frequently washed with sulphurous acid solution or frefth milk of lime. When set, the mass is removed and cut by a " wire knife " into sheets of suitable thickness, or the liquors may be run into shallow trays and the slabs cut to the required size. In modern practice many glues are prepared in the form of beads or flakes by running the glue liquor into a suitable liquid and a preservative is generally incorporated.

The drying operation which follows requires very great care ; artificial heat cannot be used, since the melting-point of the jelly is frequently not above 25°C. and in hot, and especially in thundery weather, it sometimes melts. Bacterial contamination often causes bubbles in the interior of the cakes. *VQT* these reasons the glue is often concentrated in the Yaryan or " Climbing Film " type of evaporator until it will set to a firm cake when run on to glass plates previously waxed or rubbed with ox-gall to prevent adhesion. Otherwise, the glue slices or " cakes " are laid out upon frames of galvanised wire ai.d transferred to the drying tunnels, so constructed as to receive trucks each stacked with a number of frames.

The tunnels are of varying length, and air is blown through them in counter-current flow to the direction of the progress of the trucks. This exposes the first trucks carrying nearly dry glue to the driest air, while trucks with cakes from successive batches of glue and therefore only partially dry are exposed to cooler air practically saturated with water vapour. By this method the too rapid drying of the surface of the glue cake is avoided (case-hardening).

Steam coils and humidifiers are provided at the intake of the air duct and the temperature and relative humidity are carefully controlled by wet- and dry-bulb thermometers, or automatically in modern plant, throughout the drying; if possible, the air blown into the drying tunnels should be filtered, as even under'the best conditions the amount of dust and accompanying bacteria deposited on the glue by the air-current is considerable.

A properly dried glue should contain from 12 to 18% of moisture. Many properties of the finished product depend on this hygroscopic moisture; a dehydrated glue has a low t»n«ili» strength,* while a damp glue has bad keeping qualities.

Ossein.—This is a preparation obtained by treating the fat-freed bones with dilute mineral acids, when the phosphates, carbonates and soluble salts are removed. The residue consists of the glue-forming ingredients and is put on the market in a dry state for the manufacture of gelatin.

(c) Fish Glue.—The waste products of the fish industry give fish glue, which is the most important liquid glue. The raw materials are the skins (especially those of soles and plaice), the bladders of various fish and, chiefly, all varieties of fish offal. The quality of the glue prepared from ground fish such as cod, haddock, hake, etc., is higher and the yield is greater than in the case of glue made from most other fish, *e.g.* menhaden. Fish such as mackerel and herring contain large quantities of oil. The offal is carried by conveyors to a series of washing tanks placed overhead and thoroughly washed until the water contains a low percentage of chlorides. It then falls by gravitation into the digesters and is covered with water and heated with live steam. The length of the cooking varies with the nature of the glue stock. Usually the liquor formed by cooking the stock is drawn off when it becomes sufficiently concentrated and a second run of inferior glue liquor is obtained. The oil is skimmed off and 0-5-3-0% of preservative such as phenol, cresol or boric acid is added because bacterial growth would cause rapid decomposition. After straining, the liquors are evaporated to a uniform viscosity, and a sufficient quantity of some essential oil, dissolved in ethyl alcohol, is added to prevent mould-growth and to mask the fishy odour. Some fish glues are made opaque by means of a white pigment, such as zinc white, whilst others are bleached with sulphurous acid.

Fish glue is usually marketed as a liquid glue, which differs from hide and bone glues in consisting chiefly of proteoses and peptones and being soluble in water at 18°C. It is very adhesive but should not contain more than 0-2% of sodium chloride as otherwise it gives joints which will weaken in humid weather. It should be slightly acid to phenolphthalein* The best way of comparing different samples is to compare the times of drying^ and the hardness of the dried films produced in a room at 20°C. and 2(J% relative humidity.

Isinglass.—*See under* GELATIN.

Glue Size may be considered as a by-product, since it usually consists of the crude glue liquors which are the product of the third or fourth extraction^of the raw material, and, if dried, would yield a glue of inferior quality.

Size is usually treated with sulphur dioxide to improve its colour and its keeping power. Zinc sulphate or boric acid is often added as a preservative, and when sold it usually contains about 25-38% of glue.

Concentrated Size consists of ground glue, prepared from cakes of inferior shade and quality.

Coloured or Opaque Glues are made by the addition of a small quantity of some pigment, or finely ground chalk or whiting.

CHEMISTRY AND PROPERTIES OF GLUE.

The products yielded by the hydrolysis of collagens may be divided into three groups :

(1) Gelatin *(q.v.).*—This is the first hydrolytic product. The commercial varieties are flexible and horny in the air-dry condition, when they contain 8-15% of water. When precipitated from alcohol or by salts, gelatin is pure white and nearly water-free. It is soluble in glacial acetic acid (such solutions being made use of in the familiar "*Diamond Cement*" and "*Seccotine*"). In cold water it swells to a transparent jelly which melts at temperatures from 30 to 40°C. giving a solution of gelatin which sets again on cooling if the concentration is above 1%. To avoid further hydrolysis in dissolving gelatin, the temperature must not exceed 50°C. and a solution heated above 70°C. will not return to its original state. The melting-point varies very considerably with the quality of the gelatin, but is little affected by concentration between 5 and 10%. A 10% jelly of best hard gelatin melts at about 38°C. but the melting point is raised by various salts, such as alum, chrome alum and basic chromium salts, which react with it chemically.

Commercial gelatins contain gelatoses and peptones, often in considerable quantities, and the protein chondrin is probably also present. Even the best French gelatin contains peptone. Bague ("Chemistry and Technology of Gelatin and Glue," New York, 1922, p. 28) gives the following percentages:

	Protein nitrogen.	Proteose nitrogen.	Peptone nitrogen.	Amino-acid nitrogen.
Russian isinglass.	91·0	4-4	4-5	0·1
Edible gelatin .	87-8	11:3	0-7	0-2
Hide glue. . .	84-43	12-4	2-6	0-4
,, ,, . . .	52·0	38-6	8-4	0-9
Bone glue. . .	73-5	1(3-4	8·1	2·0
,, ,, . . .	31-5	50-6	14-8	3·0
Peptone . . .	0·0	33-2	48-5	18-3

The chemical distinction between gelatin and glue is merely one of purity. Commercially a gelatin differs only from a glue in that the former is a very high grade product, is of high jelly strength, is light in colour, gives solutions that are reasonably clear and contains relatively less degradation products, *see* table.

Dry distillation of gelatin yields water and a dark thick oil, similar to Dippel's Oil, containing pyridine bases, aniline, etc. Formaldehyde, when added to gelatin in solution, solidifies it and renders it insoluble even in hot water. 8% of formaldehyde gives the maximum effect. This property has been utilised in waterproofing and in the production of the long extinct Vandura silk (*v.* Vol. V, 115ft).

(2) Chondrin (v. GELA^N, Vol. V, 509d).—This hoi^iy substance, very similar to gelatin, is contained in most glues, but differs in being precipitated from its solutions by nearly all acids, though usually soluble in excess. It is

distinguished by giving, like mucin, a precipitace with acetic acid. It may be detected by adding a saturated solution of chrome alum to a 10% solution of the suspected gelatin, which will gelatinise while still hot if chondrin is present in injurious quantity. Many salts, such as alum, lead acetate and iron salts also precipitate it. Its gelatinising and adhesive powers are weaker than those of gelatin.

(3) Mucin.—This name covers a number of slimy substances, which* swell, but do not dissolve in water. They are soluble in lime-water and are usually removed in the liming operation. They dissolve in 10% salt solutions, but are precipitated by more concentrated solutions. They are detected in glue by the addition of acetic acid which causes a precipitate. They are also thrown down by aium. .If left in the glue, they give rise to " foaming," and have little or no adhesive or gelatinising properties.

USES OF GLUE.—A great variety of industries employ glue in some form or other, *e.g.* in sizing textiles, papers, walls, canvas, etc., and in bookbinding. It is also largely employed in joiner's work, veneering, box-making, the making of matches, distempers, etc.

Mixed with glycerin, treacle or glucose it forms the compositions used as substitutes for rubber and for printing rollers, stamps, etc. Mixed with treacle or glycerin it is employed in making the familiar " jellygraph."

It is also used in photography, and as gelatin it forms part of the raw materials of cookery.

GLUE TESTING.

The facts that commercial glue is not a pure substance and that traces of impurities materially affect its properties make its testing difficult.

The physical and chemical properties of glue depend on the nature of the raw material and on the methods of processing. It is not possible to draw up any simple tests which will evaluate completely the quality of a glue, or its suitability for » particular trade. If, however, the glue is made from a specific type of raw material by a standard method of manufacture, then the British Standard Methods for testing Joiners[1] Glues (British Standard No. 745—1937) and Bone, Skin and Fish Glues (British Standard, No. 647—1938) provide indications of the behaviour of the glue in use and may be taken as reliable criteria of quality. When more stringent specifications are required reference should be made to British Standards, Nos. 4 V11, Dry Gelatine Glue; 5 V 10, Liquid and Jelly Gelatine Glues, Glues for Aircraft Purposes.

The relative importance of the tests to be employed depends very largely on the purposes for which the glue is intended. For veneering and general joiner'B work, for book-binding and the like, a glue should have good joint-strength, little foam and gooo\ keeping qualities. It should also show a good jelly strength and be free from grease, or it may give uneven joints. The gummed paper and carton manufacturers are particularly intelested in viscosity and foam, etc. The glue for use in the sizing of canvas and the like should show a good jelly strength and good tensile strength: foaming power and grease are of less importance. For preparing distempers, the grease content should'be low as it may; give rise to flecks; the keeping power shoula'be high, but the tensile strength and jelly strength are of less importance. It is not necessary in any "particular case to employ all the tests. In practice the consumer usually knows from his experie: ce the most suitable type of glue for his purpose. The problem then reduces itself to checking those properties which are relevant.

In testing glue the appearance should always be noted and the odour of a freshly prepared hot solution, which should not be objectionable. Jelly or liquid glues should be in the form of a jelly or viscous liquid, which, at the temperature stated by the maker, should, as supplied or after dilution with water, be of satisfactory consistence. The tests may be divided into two classes: ph^si^al tests upon some property, and chemical analysis for some constituent. The physical tests most commonly used are: (1) Jelly Strength, (2) Viscosity, (3) Melting-point, (4) Adhesive Strength, (5) Tensile Strength, (6) Keepin? Quality, (7) Water Absorption, and (8) Foam Test. The chemical analysis includes the determination of the following: (1) Moisture Content, (2) Reaction *(Pa)*, (3) Grease, (4) Ash, (5) Chloride, and (6) Sulphur Dioxide.

' The question of the sampling is one of prime importance. It is necessary to sample each container in a delivery if this consists of 5 or less. For larger deliveries of 6-50, 51-100, 101-500, and 501-1,000 the numbew are 5, 10, 15 and 20 respectively. The liquid sample is taken by a sampling tube, scoop or similar tool. Pieces are broken up or ground by hand in an iron mortar, and quartered to give a final 2 1b. sample.

(1) *Jelly Strength.*—As a general index to quality the jelly strength and/or viscosity are usually included. In testing the former, the glue solutions are arranged in order of merit by comparing the iSsiliency of their jellies as ascertained by the pressure of the finger tips. In the British Standard method, the sample is compared with an agreed standard sample under similar conditions. According to the grade of the powdered sample 5, 7-5 or 10 g. are weighed into a 150 c.c. beaker and 50 c.c. of cold dtatfibd water added. The glue is allowed to soak until completely swollen, "the beaker heated on a water-bath for 10 minutes during which the glue is all dissolved at not above 60°C by constantly stirring. The glue liquor is' poured immediately into a Chinese ointment-jarTnternal measurements 1J in. x 2J in.) and the celluloid cap put on after 2 minates It fc kept for 18 hours at 10°C. «* the jell/is compared with that of the agreed sample by pressure with the finger.

The testing of the [illegible] «« »P»tt™ consistencies of [illegible] by [illegible] their [illegible] for bearing [illegible] tested by Lipowitz (fleue Chem.-Tech. Unters. Berlin 1861 .171

[illegible] be mJittnn $A^{YA1,,andw}$ (U.S.P. 882731) may be mentioned ae they tend to overcome the error which always attends the breaking or compression of a jelly, due to the formation of a "skin" at the surface.

Sheppard, Sweet and Scott (Ind. Eng. Chem. 1920, 12, 1007; J. Amer. Chem. Soc., 1921, 43, 53?; at the laboratories of the Eastman Kodak Co. have developed an apparatus in which cylinders of gelatin jelly are submitted to torsional stress. This method is scientific and capable of giving absolute results, but has not been adopted in industrial practice.

Another method, whereby reliable comparative results may be obtained, consists in determining the jelly strength by means of a balance provided with a pan at one end of the beam and a counterpoise at the other. At the bottom of the pan is soldered a rod on which is fixed a steel ball of standard diameter. The glue jelly is prepared by weighing 1-5 g. of the glue to be tested in a small glass cylinder (10-15 mm. diameter) graduated to 15 c.c. at 15°C. Water is added and the glue allowed to soak overnight. The volume is then made up to 15 c.c, the glass cylinder gradually warmed on a water-bath, and the contents stirred until all the glue goes into solution. A few drops of toluene are added to prevent the formation of a "skin" and the solution is allowed to cool slowly. The cylinder is then placed in a cold chamber the temperature of which should not go below 1° or 2°C. After the lapse of 3 or 4 hours the cylinder is placed under the plunger and the balance adjusted to zero by means of the counterpoise, while the steel ball just touches the jelly. The height of the plunger can be adjusted if necessary. Weights are then slowly added to the pan until a pointer has indicated an arbitrarily fixed deflection. A comparison is made with a jelly prepared at the same time with purified gelatin or an accepted standard glue.

Where there is no agreed sample glue for comparison the B.S.I, have adopted the Bloom jelly strength tester (Ind. Eng. Chem. [Anal.], 1930, 2, 34; British Standard No. 4B47—1938). An extra-wide-mouthed test bottle is used of 155 c.c. capacity, 59 mm. internal diameter and 66 mm. outside diameter and 85 mm. height overall. A tapered rubber stopper with a base diameter of 42-45 mm. is cut in half and the upper portion centrally perforated by means of a red hot 2-5 cm. brad. The upper half of the stopper is used to obtain a snug fit in the neck of the bottle and the air vent prevents the stopper from being blown out during the melting and heating of the sample. 15 g. of the sample are put in the test bottle and 105 c.c. of distilled water at 15°C. added whilst stirring. It is allowed to soak overnight at 10-15°C. The bottle is placed for a few minutes in water at 20-30°C. to prevent cracking before putting it into the melting bath below 70°C, where it is brought to 62°C. in less than 15 minutes. After closing the bottle with the stopper, now carrying a thermometer, and before reaching 62°C, the solution is made uniform by swirling the bottle. The bottle is then kept at 10±1°C. for 16-18 hours. The determination of jelly strength is made with the Bloom gelometer, adjusted to give a 4 mm. depression and to deliver shot at the rate of 200 g. per 5 seconds. The results are expressed in grams required to produce the 4 mm. depression.

(2) *Viscosity.*—This has always been considered, by both manufacturers and users, as an important test in the evaluation of a gelatin or glue. In the British Standard method, 105 c.c. of cold, distilled water are added to 15 g. of the glue in a corked flask. After standing 2 hours, it is placed for 10 minutes in a water-bath at 65°C, dissolution being aided by gentle stirring. The flask is cooled to 40°C. and placed in a thermostat at 40±1°C. for ½ hour. The liquid is then poured through a funnel, loosely plugged with cotton wool, into a British Standard U-Tube Viscometer (B.S. 188—1937) and allowed to stand for ½ hour before taking the measurement. It is essential that the time of efflux should be within the accurate range of the instrument chosen, which will be usually No. 2 or No. 3, and that the instructions given in the Specification be adhered to. In making up a solution, and in order to obtain comparable results, the percentage of moisture contained in the sample must be taken into consideration. The percentage composition of the solution should always refer to the dry weight of glue. The results are expressed as the viscosity in centipoises of the glue at a concentration of 12-5% by weight and a temperature of 40°C.

The viscosity of a gelatin (or glue) solution varies with keeping: the change in viscosity which takes place when a gelatin solution is kept at a lower temperature after being heated for a short time at 100° is shown by the following figures (water = 1):

Viscosity at:	After heating for:				
	5 mins.	10 mins.	15 mins.	30 mins.	60 mins.
21° . .	1-83	2-10	2-45	4-13	13-76
24-8° .	1-65	[illegible]	1-74	1-80	1-30
31° . .	1-41	[illegible]	1-42	1-43	1-42

If the heating is prolonged, as would be the case in commercial practice, the viscosity reaches a minimum and constant value. This is due to an irreversible change, that is, to a decomposition of the gelatin.

It follows that the temperature at which the viscosity of a gelatin solution is determined is of very great importance. Von Schroeder, in his important work on the viscosity of gelatin solutions (Z. physikal. Chem. 1903, 45, 75), showed that at a temperature of 31°C. (*see* table) the viscosity does not alter over a period of 1 hour, thus indicating the approach to some kind of equilibrium. C. R. Smith[1] (J. Amer. Chem. Soc. 1919, 41, 135) and, later, Bogue (*ibid.* 1922, 44, 1313) found that at a temperature of 32-35° the gel form could not exist, and that no evidence of plastic flow could be observed above this temperature, which should therefore be used for viscosity readings of a*0% gelatin (or glue) solution.

(3) *Melting-Point.*—The melting-point of a glue is intimately correlated with its jelly strength and viscosity. It depends upon the

percentages of pure gelatin and gelatin degradation products it contains. The greater the concentration of gelatin the higher will be the melting-point; the greater the amount of degradation products the lower will be the value found.

Many methods have been suggested for the measurement of the melting point, but most of them will only give approximate results. The method described by Cambon (J.S.C.I. 1907, 26, 703) has been used in the British Standard No. 647, 1938. The apparatus consists of a brass bowl 22 mm. in height, 17 mm. external diameter at the top and 15 mm. at the bottom. It should weigh exactly 7 g. Into this fits loosely a glass rod 40 mm. long and 3 mm. in diameter, which is flattened at one end to a disc of 9 mm. diameter and fashioned at the other end into a hook. 15 g. of the powdered sample are placed in a beaker with 105 c.c. of cold, distilled water, allowed to stand for 2 hours, placed on a water-bath and maintained at 50°G. for 10 minutes, dissolution being aided by gentle stirring. The glue liquor is then poured into the bowl, the rod inserted to the base of the bowl and maintained in an upright position for 16 hours in a thermostat at 10°C. The cup is then totally immersed and suspended by the glass rod in a beaker of water at 15°C. placed in a water-bath at 20°C. The water in the latter is heated so that the temperature of the water in the beaker rises at the rate of exactly £°C. per minute. The temperature of the water in the beaker at which the bowl falls from the rod is taken as the melting-point.

References to other methods which have been suggested are Chercheffski's (Chem.-Ztg. 1901, 25, 413); Kissling's (Z. angew. Chem. 1903, 17, 398); Smith's (J. Amer. Chem. Soc. 1919, 41, 146), and the one described by Sheppard and Sweet (Ind. Eng. Chem. 1921, 13, 423), which is very accurate, but necessitates the use of a complicated apparatus. The Aeronautical Inspection Directorate, however, have suggested another method, which is simpler and equally accurate. A 20% glue solution is poised into a U-tube, which is then placed in cold water to allow the glue or gelatin to set properly. One end of the U-tube is connected through a T-piece to a gauge and suitable means to obtain a pressure head of 6 in. of water, the connections being air-tight? The U-tube is then immersed in a beaker of water which is heated gradually by means of a micro-burner. The temperature at which the glue melts is indicated by the fall of the meniscus in the pressure gauge.

(4) *Adhesive Strength.*—If a glue has to be used as a binding agent in joint or veneer work, the main test is its adhesive strength.

This property of glues has been studied extensively by Douglas and Pettifor on behalf of the Adhesives Research Committee and their valuable work is summarised in Appendix 1 of the Third Report of the Committee (H.M.S.O. 1932). They recommend the use of the simple lap joint, already suggested in 1916 by the Aeronautical Inspection Directorate, and give the procedure to be followed in order to obtain the minimum of variation in the test results. Their work leads to the conclusion that the strength of a common glued wood joint depends upon two factors: (1) Mechanical embedding,** and (2) Specific adhesion. Of these the greater emphasis should be laid on (1). The British Standard defines joint strength in shear as the load required to break a walnut overlap joint, when determined by the specified Method. This value should not be less than 1,000 lb. per sq. in. for joiner's glues whether cake, powder, liquid or jelly. For the determination, the glue liquor is prepared by soaking 10 g. of the sample in 15 c.c. of cold, distilled water in a beaker for 2 hours and melting on a water-bath for 10 minutes at not above 60°C. Liquid and jelly glues are tested at the original concentration. The test pieces are made from two slips of carefully selected, straight-grained, dry black American walnut and are 4£ in. x f in. x 1 in. The 1 in. face must lie in a tangential direction to the grain and the 4J in. length must be approximately parallel to the longitudinal direction, but shall preferably make a small angle of 3° with the grain. The two parts of the test-piece are assembled so that the grain tends to run through the joint from one piece of wood to the other. The overlapping surfaces are toothed by hand with a sharp, fine toothing-plane having 20-25 teeth per inch. The glue is applied with the finger, avoiding air bubbles, to one surface of each of two test slips at ordinary air temperature, which must not be below 10°C. When the surface of the glue has become tacky, the surfaces are placed together without rubbing, so as to produce a 1 in. overlap joint. Six of these test-pieces are made. They are clamped immediately after closure of the joint in a suitable press under a pressure of $00 lb. per sq. in. for 16-20 hours, and are then conditioned at 12-24°C. at 50-75% R.H. for 72 hours. The pieces are put into an approved testing machine with the grips 4 in. apart and arranged so that the load is applied in the plane of the unstrained joint. The load is applied uniformly at the rate of about 1,500 lb. per minute. The total load required to break a joint is regarded as the strength of the joint and the average of six is taken, an experimental error of 5% being allowable in the mean figure.

(5) *Tensile Strength.*—It has been shown by McBain and Hopkins (Second Report Adhesives Research Committee) that it is possible to obtain a measure of the strength of the glue itself by tensile strength measurements and to study other properties such as adaptation to volume change consequent upon setting, shrinking, ability to withstand impact or actual bending, the effect of humidity, etc.

Uniform glue films are obtained (Lee, Ind Eng Chem. 1930, 22, 778) by pouring the necessary amount of a 20 or 30% glue solution on a highly polished Bakelite plate accurately levelled. The film, when dry, can be easily removed and cut into the required shape of test-piece. McBain and Hopkins (*l.c.*) state that it is necessary to rehumidify the film before cutting in order to prevent it from splitting. The approved type of test-piece consists of a straight strip, the long sides of which can be cut with one stroke of the scissors, thereby minimising the possibility of snipping the edges. The ends of the test-piece are reinforced with paper and fixed in the grips of a Schgpper dynamometer of the pendulum type. The grips we supported on a horizontal knife edge, and the load is applied uniformly and at$_a$a rate which can be determined.

The 'test strip should be bent backwards and forwards several times before the tensile strength is inpasured, and the result compared with that of another test strip which has not been subjected to previous bending.

(6) *Keeping Quality.*—This is intended simply as* an index of the behaviour of the gibe *in* practice and is not to be taken as a substitute for a more complete bacteriological examination. The cake or powdered varieties of joiner's glues should retain their properties*for at least 12 months when stored in a ^ool, dry place. The period with jelly or liquidities is agreed on by the purchaser and vendor. In the British Standard method of determination, 5 g. of the powdered sample are soaked in <20 c.c. of cold distilled^water until completely swollen. It is then heated on a water-bath until dissolution is completed, and, transferred to a B.S. Petri I)i»h (B.S. 611), 94 mm. diameter. It is covered and placed in an incubator maintained at 40°C, taken out after each 24 hours and cooled for inspection. The periods are noted when liquefaction, ,putrefaction or moulds occur.

(7) *Water Absorption.*—The behaviour of glue fyhen immersed in water at 18-20°C. for 24 hours is a useful criterion of its quality. Generally speaking, the greater the water absorption the better the glue, provided that the cake docs not break and remains firm. Fine bone and skin glues increase in weight about 8-11 times, common glues about 5 times, but a bad glue will pass entirely into solution. In the British Standard Specification, water absorption is defined as the proportion of water absorbed by a powder retained on a •& in. B.S. test sieve and passing through a & in. B.S. sieve. 10 g. of the powder are weighed into a 300 c.c. squat beaker containing 100 c.c. cold distilled water. It is kept for 16 hours at 10°C. with occasional stirring. The supernatant water is then poured off through a funnel fitted with a strainer of stretched damp muslin of about •& in. mesh. The quantity of water passing through the funnel in 5 minutes is measured. The difference between this figure and 100 is the wate*r absorbed by 10 g. of the glue.

(8) ***Foam Determination?—The*** **peptones present** m glue increase its tendency to foam and this test is of interest when the glue is to be Q?!fdJ by 8Pecial machines. In the British Standard method for foam determination, 5 g. ot the powdentt sample are allowed to soak in < C'oi' ? f d di8tillcd Wfttcr in a beaker until completely swollen. The beaker is heated in a water-bath to not above 60°C. until dissolution is completed. 50 c.c. is poured into a 100 c.c. stoppered cylinder (diameter 32 mm.±2 mm.) The internal height to graduation mark is 15±U-5 cm. and to the shoulder is 23±0-5 cm., and the air space above the graduations corresponds to CO c c ±2 c.c. This is placed in a water-batl? at 45°C. for 1 "hour. The cylinder is then shaken vigorously with a throw of about 12 in. at a rate of 3 shakes per second for 1 minute. It is replaced in the water-bath at 45*C.< and left until* the height of the liquor corresponds to 45 c.c. The time taken for this 45 c.c. meniscus to form and the volume in c.c. of the foam above the liquid are reported.

Chemical Analysis.—The following points and further determinations may be added to those described under GELATIN *(q.v.).*

(1) *Moisture Content.*—Glues contain 12-18%, and a figure of 18% is the limit with cake or powder joiner's glues. A very low result is not desirable, as it shows that the glue has been over-dried and has little tenacity, while a high result throws doubt on its keeping quality.

(2) *Reaction* (p_E).—This should be from 6-0 to 8-5 for cake or powder glues and between 4-0 and 8-0 for jelly or liquid glues. Free acid can be determined directly by titrating to phenolphthalein.

(3) *Grease.*—Only a negligible amount should be present^

(4) *Ash.*—The ash content of good glues varies from 1*5* to 3-0%. Some bone glues contain considerable quantities of calcium phosphate, while hide glues arc apt to contain calcium sulphate or chloride resulting from the neutralisation of the lime used in preparing the stock, and an? frequently alkaline, due to the presence of li&c. Various whitening agents, such as zinc oxide, lead sulphate or carbonate, chalk, clay, etc., may be present. Glues weighted with barytes, etc., and some coloured glues also yield high ash weights.

(5) *Chloride.*—The chloride content is one index of the behaviour under various atmospheric conditions. It should not exceed 2% (as **NaCI**) in joiner's solid glues. 5 g. of the powdered sample are weighed into a nickel or platinum basin and 10 c.c. of cold, * distilled water added. After soaking for 1 hour, it is heated on a water-bath until dissolved and 5 g. of pure lime added. After drying on a steam-bath and ignition so that the sample is completely ashed, the residue is extracted by boiling rapidly with small quantities of water and the salt determined by neutralising with acetic acid and titrating with JV/10 **$AgNO_3$.**

(6) *Sulphur Dioxide.*—This is important when the glue is being used for sizing coloured paper, textiles or artificial silk. 27-5 g. of the powdered sample are weighed into a 1-litre round-bottomed distillation flask. 300 c.c. of distilled water containing 5g. of phosphoric acid *(d* 1*7) are added and the flask is connected by a bent glass tube fitted with 2 bulbs to a glass condenser, to the exit of which a " B.A.R." bubbler is fixed. 25 c.c. of *N/2* iodine solution are placed in a receiving flask. Pure CO_2 is bubbled through the contents of the distillation flask throughout the determination. The distillation flask is surrounded by a water-bath and ^heated until the glue is dissolved. The flask is then heated directly until 200 c.c. of distillate have been collected. The distillate is acidified with 5'c.c. cone. **HCI,** evaporated to 75 c.c. and filtered. The filtered solution is heated to boiling, 10 c.c. of 0-5A'$BaCI_2$ solution addH slowly and allowed to stand overnight. It is then filtered through an ashloRs filter-paper, which is washed with hot distilled water and ashed. The percentage SO_2 is calculated from the weight <f Wi

sulphate. Blank determinations should bfc nude on the chemicals used with the same rubber stoppers and CO_2 apparatus.

(7) *Gelatin.*—Many tests have been devised for determining the gelatin contents of glues, such as precipitation with zinc sulphate and estimating the nitrogen in the precipitate, precipitation with tuimie acid, etc., but they are all untrustworthy. Possibly the formaldehyde til.r:dinn (*see* GBLATIN, Vol. V_f 507a) **gives** the most reliable information.

Bibliography,—Lambert, " Glue, Gelatine and their Allied Products," London, 1905; Fernbaeh, "Glues and Gelatine," New York, 1907; Rideal. " Glue and Glue Testing/[1] London, 1914 ; Reports of Adhcsives Research Committee, London, 1922-32; Bogue, " Chemistry and Technology of Gelatine and Glue," New York, 1922; Thiele, **"Lam** und Gelatine," Leipzig, 1922; Procter, " Principles of Leather Manufacture," 2nd ed. London, 1922; Alexander, "Glue and Gelatine," New York, 1923; Sheppard,'" Gelatin in Photography," **New** York, 1923; Cambon, " Fabrication dea colics efc gelatines," Paris, 1923; GerngroBS und Gocbel, " Chemie und Tecbnologie der Lcim- und Gelatine-fabrikation," Dresden and Leipzig, 1931; Stadlingeib " **Die** Leimfibel," Berlin, 1929; Saner, "Leinitiund Gelatine," Steinkopff, 1927 j Smith, " Glue and Gelatine," London, 1929.

Extensive bibliographies on glue are given by R. Ditmar (KolJoid-Z. 1906. 1, 80), R. II. Bogue (Chem. Met. Eng. 1920, 23, No. 5), and W. Simon (*ibid.* Ift38, 84, 101),

D. B.

" *GLUSIDE* " (*v.* Vol. IV, ^*U).*

GLUTACON1C ACID. Propene-ay-diciiiboxyh'c aoid, $HO_2CCH{:}CHCH_2CO_2H$, w beet prepared by one of two methods. In the first of them, due to Conrad and Guthzeit (Annalen, 1883, 222, 249), chloroform is condensed with ethyl disodiomalonate and the resulting yellow sodium compound decomposed with dilute hydrochloric acid, yielding ethyl *ay*-dicatbethoxyglutaeonate, which is then hydrolysed and decarboxylated to **glutaconio** acid by means of strong hydrochloric acid ;

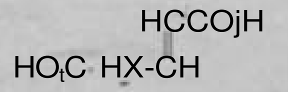
$$CHCl_3+2CH_2(CO_2Et)_2 \xrightarrow{NaOEt} (CO_2Et)_2CH{\cdot}CH{:}C(CO_2Et)_2$$

$$(CO_2Et)_2CH{\cdot}CH{:}C(CO_2Et)_2 \xrightarrow{HCl} HO_2CCH_2CH{:}CHCO_2H$$

In the second, more recent, method (Gruhdniann, Ber. 1937, 70 [B], 1148) oxalocrotonic acid (readily obtained by hydrolysis of the condensation product of ethyl oxidate and ethyl crotonale) is oxidised with warm 3% hydrogen peroxide:

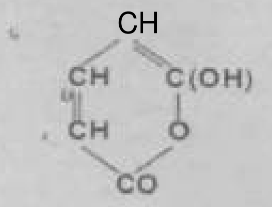
$$CO_2H{\cdot}CH{:}CHCH_2COCO_2H + H_2O_2 \rightarrow CO_2HCH{:}CHCH_2CO_2H + CO_2 + H_2O$$

The acid obtained'Jjy both of these **msthc** Js haa m.p. 138° and is row known to be the (raws-acid ;



$$\begin{array}{c} HCCO_2H \\ HO_2C{\cdot}H_2C{\cdot}CH \end{array}$$

ThiB acid, on treatment with aCety'. chloride **yielda,** not a normal anhydridr, but'the hydroxy-anhy^ride (m.p. 87-88°):



hydrolysis of which, under ordinary conditions, yields only the (ran^acid. Malachowski, however (*ibid.* 192ji, 62 [B], 1323) succeeded in preparing the ci's-ad*i,

$$\begin{array}{c} HCCO_2H \\ HCCH_2CO_2H \end{array}$$

by very careful hydrolysis of the aydroxy-anhydride. The cw-acid, BO obtained, melts at 1&6°, but shows a considerably depression on admixture with the *Jrans&cid* and also differs from the latter in the rate with which it undergoes isotopic exchange with deuterium oxide (Evans, Rydon and BriBCoe, J.C.S^1939, 1673); there is thus no doubt of the reality of the two stereoisomcrie forms.

lamneriam of the Qlutaconic Acids.—TL. elucidation of the isomerism phenomena displayed by glutaconio acid and its alkyl derivatives has played a great part in the development of modern views on tautoraerkm.

Rogerson and Thorpe (*ibid.* 1905, 87, 1669, 16K5) showed that the *two* distinct eaters

$$EtO_2CCMe(CN){\cdot}CMe{:}CHCO_2Et$$

and

$$EtO_2CCH(CN)CMe{:}CMe{\cdot}CO_2Et$$

gave, on hydrolysis, the *same,* dimctbylglutaconic iacid. This they interpreted as proving the identity of the two possible acida :

$$HO_2CCHMeCMe{:}CHCO_2H$$

/Jy-dimethylBtutacouie acid.

and

$$HO_2CCH_2CMe{:}CMeCO_2H$$

ap-dimcthy]glutacoiijc acid.

A similar identity was found In the cases of a- and y-roethyl- and the a-methyl-yethyl- and a-ethyl-y-mcithyl-glutauonic acids. These observations were taken to **imply the** equivalence of the o- and ypoutiuns in glutaconic acid *I_cf* the equivalence of the two o-posjtions ***in***'. mono-substituted benzene derivative.

In addition to this peculiarity, the glutaconic acids showed other anomalous proj viz. DO stereoisoincric forms were knowrT^rif J05), geometrical laomers having been sought for witliout success ; they also showed anomalous addition reactions, and they formed hydroxy-anhydrides instead of normal anhydrides. These anomalies were found to disappear completely when the mobile hydrogen atom was blocked by substitution, *e.g.* in

$$HO_2C{\cdot}CH{:}CH{\cdot}CMe_2{\cdot}CO_2H.$$

Thorpe himself (J.C.S. 1923, 123, 3343) expressed his point of view as follows: " All experiments on the glutaconic acids . . . combine to show that there is something in the constitution of these substances which conventional symbols do not explain, and that this 'something' is connected with the mobile hydrogen atom of the system, because it disappears when that atom is absent; we assume, therefore, that this structural peculiarity is connected with the mode of "attachment of the mobile hydrogen atom to the rest of the molecule." On the basis of such reasoning Thorpe, in 1905, put forward his well-known " normal" formula:

$$CO_2H\cdot\dot{C}H\cdot CH[H]\cdot\dot{C}H\cdot CO_2H$$

Feist (Annalen, 1909, 37$, 41) had prepared a second, labile, form of a-methylglutaconic acid which he regarded as a stereoisomeride of the stable acid. Thorpe, however, was of opinion that the stable acid possesses the " normal " structure while Feist's and the other labile acids which were later isolated have the conventional unsaturated structure:

$$HO_2CCH{:}CH\dot{C}H_2CO_2H$$

In 1931, McCombes, Packer and Thorpe (J.C.S. 1931, 647; *cf.* Bull, Fitzgerald, Packer and Thorpe, *ibid.* 1934, 1653) succeeded in resolving the stable form of αγ-dimethylglutaconic acid; thus showing that this acid has the " unsaturated" structure B, which contains the essential asymmetric carbon atom, absent in the " normal " structure A:

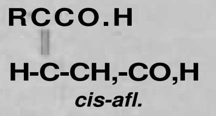
$$CO_2H\cdot\dot{C}Me\cdot CH[H]\cdot\dot{C}Me\cdot CO_2H$$

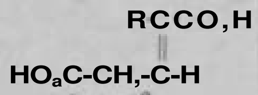
" Normal."
A.

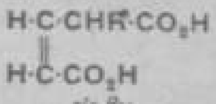
$$CO_2HCHMeCH{:}CMeCO_2H$$

" Unsaturated."
B.

A reinvestigation of the whole subject was undertaken by Kon and collaborators, working in Thorpe's laboratories at South Kensington (Kon and Nanji, *ibid.* 1931, C6O; 1932, 2426, 2657; Kon and Watson, ***ibid,*** 1932, 1, 2434; Gidvani, Kon and Wright, *ibid.,* p. 1027; Gidvani and Kon, ***ibid.,*** p. 2443). This fresh attack was much benefited by the experience gained in the work on three-carbon tautomerism which had been carried out at South Kensington in the nineteen-twenties. It may now be concluded, as a result of these investigations, that the isomerism of the glutaconic acids and their derivatives is due to the simultaneous occurrence of three-carbon tautomerism and *cis-trans* isomerism. On this view it will be seen that an unsymmetrically substituted glutaconic acid can give rise to four isomers, *e.g.:*


cis-αβ.


trans-αβ.


cis-βγ.

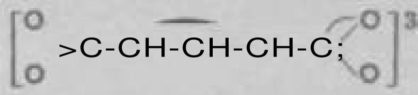

trans-βγ.

Usually only two forms are encountered in practice, viz. the *cis-αβ* and the *trans-βγ* isomers, but Kon and Watson *(l.c.)* were able to prepare all the four possible α-benzyl-β-methylglutaconic esters and three out of the four possible corresponding acids. The absence of anomalous behaviour in glutaconic acid derivatives with no mobile hydrogen atom also receives an explanation, since such compounds will show only normal *cis-trans* isomerism, three-carbon tautomerism being structurally impossible in such compounds. The following articles should be consulted for **further** information on this subject: Thorpe, ***ibid.*** 1931, 1011; Kon, Annual Reports, 1932, 29, 140; Linstead, J.C.S. 1941, 457.

It is evident that the tautomerism of glutaconic acid itself

$$(CO_2H\cdot CH{:}CH\cdot CH_2\cdot CO_2H \rightleftharpoons CO_2HCH_2CH{:}CHCO_2H)$$

is not susceptible of study by ordinary means. Nevertheless an estimate of the very high mobility of this " crypto-tautomeric " system has been made by Evans, Ryder and Briscoe *(l.c.)* by a study of the exchange reaction between glutaconic acid and deuterium oxide. These authors point out that the isomerisation takes place through a common mesomeric ion :



which is a resonance hybrid of the two possible canonical structures:

and

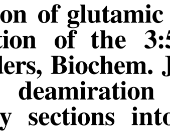
This common mesomeric ion is, in fact, the modern successor of Thorpe's " normal" formula. There can be little doubt that the resonance energy set free in the formation of this ion is responsible for the " reversion to type " which was another puzzling feature of the earlier work on the chemistry of the glutaconic acids (cf. Ingold, Oliver and Thorpe, *ibid.* 1924, **126,** 2128).

H. N. R.

GLUTAMIC ACID, α-Aminoglutaric Acid, $CO_2H\cdot CH(NH_2)\cdot CH_2\cdot CH_2\cdot CO_2H$, was discovered by Ritthausen in 1866 (J. pr. Chem. 1866, [i], 99, 454) among the products of the hydrolysis of wheat gluten by sulphuric acid, and hence called by him *glutaminic* acid. Subsequently, Ritthausen and Kreusler *(ibid.* **1871,** [HI 3. 214), Gorup-Besanez (Ber. 1877, **10, 780), Bennlae** *(Z.* physiol. Chem. 1892, 9, 253) and Wroblewski (Ber. 1898, 31, 3218) showed that it was formed by the hydrolysis of other vegetable proteins; and Hlasiwetz and Habermann (J. pr. Chem. 1873, **[ii]** 7, 397), Panzer (Z. physiol. Chem. 1897, 24, 138), Abderhalden and Fuchs *(ibid.* 190», 57, 339) isolated it from the products of hydrolysis: of animal prctei-s. It has been found in blood (Abderhalden, *ibid.* 1913, 88, 478); in tomato conserve (Monti, Chem. Zentr. 1912, I, 501); in molasses (Stoltzenberg, Ber. 1913, 46, 557); in echinodcrm (Edlbacker, Z physiol. Chem. 1915, 94, 264); in yeast (Mcisenheimer, Chem. Zcntr. 1915, II, 1259); in certain brown seaweeds as an octapeptidc (Haas and Hill, Biochem. J., 1931, 25, 1472); and among the products of hydrolysis of crystalline insulin (Jensen and Wintcrstcincr, J. Biol. Chem. 1932, 97, 93), of certain seaweeds (Schindelmeiscr, B.P. 481898), of beef fibrin (Bodensky, J. Biol. Chem. 193G, 115, 101) and of the protein of silk-worm chrysalis (Pan and Sun, Chem. Ind. China, 1936, 11, No. 2, 1). For theglutamic acid content of various proteins, *see* Jones and Moeller (J. Biol. Chem. 1928, 79, 429), *also* Fiirth (Scientia Pharm. 1934, 5, 21). tf-Glutamic acid is formed from J-histidine by the action of liver histidasc (Abderhalden and Hanson, Fermentforsch. 1937, 15, £74), and probably from proline in kidney (Weil-Malherbe and Krcbs, Biochem. J. 1935, 29, 2077).

Glutamic acid is ordinarily prepared and manufactured by hydrolysis of casein or molasses* and of vegetable proteins such as gluten, psually with hydrochloric acid or sulphuric acid (LfcS.P. 1928840), but alkali (3-7% as sodium hydroxide) has been used (B.P. 385054; U.S.P. 1947563). In the literature there arc many descriptions and numerous patents for the use of hydrochloric acid for this hydrolysis, most of them differing only in details such as the concentration of the acid, the time and temperature of heating, the use or omission of preliminary digestion, etc. The effects of these variable? on the yield from soya-bean protein have been studied systematically by Tseng and Chu (Sci. Quart. Nat. Univ. Peking, 1932, 3, 53; A. 1933, 814) and by Rokusho, Tanaka and Saito (J. Agric. Chem. Soc. Japan, 1937, 13, 916). jlartow describes an autoclave for the hydrolysis of gluten or molasses in which the reaction can be conducted undrr pressure (Chem. Zcntr. 1936, II, 246). The addition of ferric chloride, tin, nickel, lead or copper as catalysts to assist hydrolysis of gluten is recommended by Cheng and Adolph (J. Chinese Chem. Soc. 1934, 2, 221); small amounts of nitric acid or manganese dioxide have also been specified (U.S.P. 1890590). Kumagai suggests the use<of chlorine water containing 1% magnesium chloride in place of hydrochloric acid (U.S.P. 2050491). A preliminary separation of zcin by aqueous-alcoholic extraction of gluten press-cakes, followed by precipitation with water, has been suggested (U.S.P. 1992804). For reviews covering the preparation of glutamic acid by the hydrolysis of gluten, *see* Tseng and Hu (J. Chinese Chem. Soc, 1935, 3, 154) and Sato and Tsuchiya (J. Taihoku Soc. Agric. Forestry, 1936, 1, 79). The product obtained in these preparations is usually freed from the salts of betaine, and the alkali metals (B.IV 265831; U.S.P. 1928840), by adding HCI and concentrating below 50°, the impurities are separated, and the mother liquor heated to 80° when glutamic acid hydrochloride crystallises on cooling. The free acid can be recovered from the hydrochloride by careful neutralisation with alkali (carl^onate or hydroxide), or, if racemisatioR is to be avoided, by an#ine (King, Organic Syntheses Coll., Vol. I. 281) or N-alkylglycines, *e.g.* sarcosine or betaine (U.S,P. 1976997). Kutscher (Z. physiol, Chem. 1899, 28, 123) isolated glutamic acid from the products of hydrolysis of casein by. sulphuric acid, by precipitating the larger part of the organic bawes with phosphotungstic aciù, and removing the excess of sulphuric acid and phosf liotungstic acid from the filtrate by means of barium hydroxide; the leucine and tyrosine crystallised out of the filtrate, and from the mother liquor the asjartic and glutamic acids were separated ihrough their copper salts, that of glutamic acid being more soluble. Glutamic acid may be prepared* from its hydrochloride by passing ammonia through the solution and evaporating to dryness; the greater part of the acid may be separated by fractional crystallisation and the remainder precipitated bj alcohol (Abderhalden, Z. physiol. Chem. 1912, 77, 75). A«drlfk (Z. Zuckerind. Bohm. 1915, 39, 387) obtained the acid from aqueous solution by means of tartaric, sulphuric or phosphoric acid. Siegfried and Schutt (Z. physiol. Chem. 1912, 81, 261) prepared the acid by way of the insoluble normal barium salt. For the application of electro-osmosis to the separation of glutamic acid, *see* Ikeda and Suzuki (U.S.P 1015891); Scheermesser (Pharm. Ztg. 1915, 6a 487); Corti (J.S.C.I. 1917, 36, 979; B.P. 106081); U.S.P. 1986920 and G.P. 652765.

The identification of glutamic acid is possible by the preparation of the 3:5-dinrtrobenzoyl derivative (Saunders, Biochem. J. 1934, 28, 580) or by oxidative deamiration with surviving guinea-pig kidney sections into a-ketoglutaric acid, which is isolated and identified as the 2:4-dinitrophenylhydrazone (Edlbacher and Neber, Z. physiol. Chem. 1934, 224, 261). Glutamic acid and other acyclic amino-acids neutralised with sodium carbonate, give a deep red colour when added to uric acid which has been heated with nitric acid (Arrcguine, Semana méd. Buenos Aires, 1930, 37, 1074; Amcr. Chem. Abstr. 1930, 24, 3488). For its quantitative estimation in the products of protein hydrolysis, *see* Foreman (Biochem. J. 1914, 8, 465), and for the determination by formol titration using litmus paper 86 indicator, *see* Buogo (Annali Chim. Appl. 1934, 24$ 79). Fw the determination by potcntiometric titration, *see* Balson, Earwicker and Lawson (Biochem. J. 1935, 28, 2700). Although the structure given at the head of this article explains the chemical behaviour of glutamic acid, there is evidence that in solution it exists in a Zwittorion form;



$$\begin{array}{c} O{=}C{-}OH^{+} \\ | \\ H{-}C{-}NH'' \\ | \\ C_8H_5O_2 \end{array}$$

for example, the exchange reaction with HDO (Ogawa, Bull. Chem. Soc. Japan, 193o, 11, 367) and the formation and behaviour of complexes with iron (Smythe and Schmidt, J. Biol. Chem. 1930, 88, 241). For the activity coefficients in aqueoup- solution, *see* Hoskins, Randall and Schmidt *(tbid.* 1930, 88, 215; *cf.* Miyamoto and Schmidt, *ibid.* 1931. 90, 165); for the dielectric constant in aqueous solution, *see* Devoto (Gazzetta, 1932, 61, 897); and for the infra-red absorption spectrum, *see* Heintz (Arch. phys. bipl. 1937, 14, 131). Glutymic acid is asymmetric and exists in *d-*$_t$ *I-* and *dU* forms. Lutz and Jirgensons (Ber. 1930, 63^B], 448) describe a, graphical method of assigning optically active a-aminoacids to the *d-* or Z-series. The rotatory power of the optically active forms is a function of the p_E of the solution (Vellinger, Compt. rend. 1932,194, 718).

d-Glutamic°Acid, the naturally occurring compound, crystallises ?from aqueous alcohol in the rhombic system-, a:6:c=0-6868:l:0-8548 (Oebbeke, Ber. 1884,17, 1725); m.p. 208° (213° corr.) decomp. (Fischer, *ibid.* 18p9, 32, 2451); 224-225° (corr.) decomp. (Abderhalden, Z. physiol Ghem. 1-910,64, 540); 211° when heated rapidly (Skola, Z. Zuckerind. Czechoslov. 1920, 44, 347); decomposes at 247-249° (Dunn .and Brophy, J. Biol. Chem. 1932, 99, 221). The crystals exhibit piezo-£lectric phenomena. It is sparingly soluble in water (0-88 g. in 100 g. *al* 25°) but the solubility is raised in the presence of alkali and alkaline earth salts (Pfeiffer, Ber. 1915,48,1938); it is insoluble in methyl or ethyl alcohol (less than 0-007 g. in 100 g. at 25°), ether and acetone and practically insoluble in cold glacial acetic acid (Pertzoff, J. Biol. Chem. 1933, 100, 97). For the solubility in water-alcohol mixtures at various temperatures, *see* Dunn and RosJ *(ibid.* 1938, 125, 309). The heat of combustion is 966 kg.-cal. and the heat of solution in water is*9,600 g.-cal. (Pertzoff, Z.o). For the free energy, AF_{29S} (crystalline) -170,700 g.-cal. and the values of *AH and AS, see* Borsook and Huffmann, *ibid.* 1933, 99, 663; J. Amer. Chem. Soc. 1932, 54, 4297; Huffmann, Ellis and Fox, *ibid.* 1936, 58, 1728. The dissociation constants of glutamic acid are K'_a 5*62 x 10~^{B} and 2-19 x 10-^{10}, K'_b 1-56 x 10-^{12} (£irk and Schmidt, J. Biol. Chem. 1929, 81, 237 ; Harris, *ibid.* 1929, 84, 179); *see* Schmidt, Kirk and Appleman *{ibid.* 1930, 88, 285) for the values at 0°, and *also* Neuberger (Biochem. J. 1936, 80, 2085); Wilson and Cannan (J. Biol. Chem. 1937, 119, 309). In aqueous solution *[a]*^{2}*£* +12-04°, and Mfl +*H"0°; in 10% aqueous hydrochloric acid [a]^{2}p +34-9°. Increasing amounts of strong acid cause a continuous increase in the specific rotation, which tends towards a maximum. The addition of bases first changes the dextro- into laevo-ritation, which attains its highest numerical value with the formation of the acid salt, further quantities of base convert the laevo-rotation again to a dextro-rotation. With lead hydroxide, no change in sign of the rotation takes- place (Andrlik. Z. Ver. Rubenzuck.-Ind. Bōhm, 1903, 948; *see also* Pellet, Chem. Zentr. 1911,1, 1766). When an aqileous solution of *d-* glutamic acid is boiled, an equilibrium is set up between the d-glutamic acid and its dehydration product* Z-pyrrolidone-2-carboxylic acid, the position of equilibrium depending on the p_R. In solutions near neutrality, dehydration is favoured but slow at 100°; in solutions greater 4haa *2M* with respect to hydrochloric acid or 0-5*M* to sodium * hydroxide reconversion to glutamic acid occurs (Skola, Z. Zuckerind. Czechoslov. 1920, 44, 347; Foreman, Biochem. J. 1914, 8, 492; Fischer and Boehner, Ber. 1911, 44, 1332; and for the equilibrium constants at various p_R values, *see* Wilson and Cannan, *I.e.).* Theopticalpropertiesof the equilibrium solutions at various p_u values indicate that the first stage in the dehydration is the formation of an internal salt (Okinaka, A. 1928, 435). Staněk (Z. Zuckerind. Böhm. 1912, 37, 1) on heating the aqueous solution above 200°, obtained cW-pyrrolidone-carboxylic acid, below that temperature the laevo-rotatory form is the chief product.

A solution of d-glutamic acid (1:22,000) gives a characteristic colour reaction with triketohydrindene (Abderhalden and Schmidt, 'Z. physiol. Chem. 1913, 85,143).

When glutamic acid is administered as a food, 96% is aosocbed, a portion being used in protein synthesis and the rest oxidised to urea (Andrlik and Velich, Z. Zuckerind. Böhm. 1908, 32, 313; Butts, Blunden and Dunn, J. Biol. Chem. 1937, 119, 247). Its administration to phloridzinised dogs leads to increased elimination of d-glucose in the urine (Warkalla, Beitr. Phys. 1914, 1, 91) ar4 in normal animals increases the excretion of urea and sulphate (Stekol and Schmidt, Univ. California Pub. Physiol. 1933, 8, 31; A. 1934, 440). Glutamic acid shows little toxicity (Sullivan, Hess and Sebrell, U.S. Publ. Health Repts. 1932, 47, 75) and is used in foods in the form of the sodium salt which has a strong meat-like flavour (see B.P. 269576). *In vitro* it is haemotoxic to the blood corpuscles of warm-blooded animals (Sulmann, Z. Immunitätsforsch. 1932, 74, 45), but its copper, iron, manganese and magnesium salts are effective in preventing anaemia in rats (Brand and Stucky, Proc. Soc. Exp. Biol. Med. 1934, 31, 627, 689, 739). For its effect on haemoglobin production, *see also* Drabkin and Miller (J. Biol. Chem. 1931, 90, 531); and for its hyperglycaemic action, *see* Nord (Acta med. scand. 1926, 65, 1, 61).

For its katabolism in the animal organism, *see* Ringer *et al.* (J. Biol. Chem. 1913, 14, 541) and also the series of papers dealing with the intermolecular transfer of amino-groups between glutamic and pyruvio acids by Braunstein and Kritzmann (Biochimia, 1937, 2, 242, 859; Enzymologia, 1937, 2, Pt. Ill, 129; Nature, 1937. 40, 503) and by Von Euler, Adler, Das *et al.* (Z. physiol. Chem. 1938, 254, 61; Arkiv Kemi, Min., Geol. 1938,12B, No. 40). For the biological dehydrogenation, *see idem.,* Compt. rend. Trav. Lab. Carlsberg, 1938, 22, 15; 1938, A III, 438; and for the oxidation of its phenyl derivatives in the animal body, *see* Von Beznak, Biochem. Z. 1929, 205, 420; Oesterlin, *ibid.* 1929, 215, 203.

Fermentation of glutamic acid by members of the genqs *Clostridium* which are widely distributed in soil, gives rise to n-butyric and acetic acide, carbon dioxide, ammonia and hydrogen (Barker, J. Bact. 1938, 8& 322). Under the influence of strictly anaerobic spore-forming bacteria from soil the fermentation leads tc the formation of acetic and propionic acids *(idem* Enzymologia, 1937, 2, 175, *cf.* Brasch and

Neuberg, Biochem. Z. 1908,13, 299). Alcohol^ fermentation gives methyl alcohol (Leoncini, Boll. ist. super, agrar. Pisa, 1934, 10, 418). Dccarboxylation by certain (legume) bacteria yields y-aminobutyric acid and carbon dioxide (Virtanen, Rintala and Laine, Nature, 1938,142, 674; Ackermann, Z. physiol. Chem. 1910, 69, 273; Abderhalden, *ibid.* 1913, 85, 131). Certain bacilli cause the formation of a polypeptide from glutamic acid (I vino vies, Zentr. Bakt. 1938, I, 142, 62). For the conversion to glutamine by enzymes, *see* Krebs (Biochem. J. 1935, 29,1951). Glutamic acid breaks down under the action of sunlight to propaldehyde, ammonia and carbon dioxide, especially in the presence of sensitisers such as aluminium, titanium and zinc oxides (Ganassini, Giorn. Farm. Chim. 1912, 81, 226; Rao and Dhar, J. Indian Chem. Soc. 1934, 11, 617). Dissociation of the carboxy 1 groups occurs on absorption of ultra-violet light (Anslow, Phys. Rev. 1932, 40, 115). Oxidation„ of glutamic acid with hot sodium dichromate or potassium permanganate in sulphuric acid, or with hydrogen peroxide, yields succinic acid (Dakin, J. Biol. Chem. 1909, 5, 409; Chu and Tseng, J. Chinese Chem. Soc. 1933, 1, 46). The action of sodium hypobromito in alkaline solutions gives gjutarmonoaldehyde; in neutral solution the product is j8-cyanopropionic acid (Friedman and Morgulis, J. Amer. Chem. Soc. 1936, 58, 909). Electrolytic oxidation in dilute sulphuric acid yields succinic and succinamic acids, succinimide and further breakdown products (Takayama, J. Chem. Soc. Japan, 1931, 52, 155; Bull. Chem. Soc. Japan, 1933, 8, 125). The direct oxidation of glutamic acid with oxygen is catalysed by adrenaline, {fyrocatechol -and related compounds with the intermediate formation of glyoxylic acid and finally ammonia, formaldehyde and carbon dioxide (Barrenschecn and Danzer, Z. physiol Chem. 1933, 220, 57).' In the presence of charcoal this oxidation leads to the formation of jirea (Arai, Biochem. Z. 1930, 226, 233). For the oxidation with silver oxide* *sea* Herbst and Clarke (J. Biol. Chem. 1934, 104, 769).

When treated with nitrous acid glutamic acid fields a-hydroxyglutaric acid (glutanic acid, *q.v.)* (Ritthausen, J. pr. Chem. 1868, [i], 103, 239). Natural d-glutamic acid is converted by nitrous acid into /-a-liydroxyglutaric acid, and by nitrosyl chloride or hydrochloric acid and nitrous acid into /-a-chloroglutaric acid, which in turn yields d-a-hydroxyglutaric acid (Fischer and Moreschi, Ber. 1912, 45, 2447).

For electrolytic diazotisation of the acid, *see* Krauss (J. Amer. Chem. Soc.*1917, 39, 1427).

(/-Glutamic acid forms normal and acid salts, the latter being the more common. Of these the *sodium^* $C_5H_8O_4NNa$; *potassium* $C_6H_8O_4NK$; *calcium,* $(C_6H_8O_4N)_2Ca$; *barium,* $(C_6H_8O_4N)_2Ba$; *had,* $(C_5H_8O_4N)_2Pb$ salts, prepared by neutralisation or double decomposition in aqueous solution, are crystalline and* hygroscopic. The g'utamates of general focpiula CsHgO^M'^{1} are readily soluble in water and have a characteristic meat-like flavour. The manufacture and consumption of the sodium salt are general in China and Japan (Ikeda, Orig. Com. 8th Intern. Cong. Appl. ('horn. 1912, 18, 147 ; Tseng and Chu, Acad. Sin. Mem. JjTat. Res. Inst. Chem. 1931, No. 5, 1; .Han,* Ind. Eng. Chem. d929, 21, 984). The disodium salt can be prepared by adding the acid dissolved in liquid ammonia to sodium in liquid ammonia until the blue colour disappears (Voss aj]d Guttmann, Ber. 1930, 63 [B], 1726). For its Raman spectrum, *see* J. Chem. Phys. 1937, 5, 508. The acid ,>sodium salt is converted tc sodium pyrrolidonecarboxylate on heating to 150-163° (Tseng and Chu, Sci. Quart. Pekia, 1932, 3, 1) and the calcium salt cyclises at 180-185° (Abderhalden, Z. physiol. Chem. 1910, 64, 447); it is precipitated quantitatively from aqueous solution." if sufficiently concentrated (For/jman, Biochem.!J. 1914, 8, 479). For solubility data of the $_a$dibasic calcium salt, *see* Takayama (J. Soc. Chem. Ind. Japan, 1930, 33, Suppl. binding, 91). The normal barium salt is almost insoluble in water (Siegfried and Schutt, Z. physiol. Chem. 1912, 81, 2P1). If the hydrochlonde, hydro bromide or hydriodide of .glutamic acid be boiled in aqueous solution with freshly precipitated calcium or barium carbonate, the filtrate on concentration deposit well iornied crystals of a salt of the type

$$(C_5H_8O_4N)_2\ BaBaCl_2,a:H_2O.$$

The corresponding strontium compounds are obtained by crystallising the glutamate with excess halide (Anslow an(l King, Biochem. J. 1927, 21, 1168). For the transference numbers and conductivities of the sodium, calcium and barium salts, *set* Miyamoto and Schmidt (J. Biol. Chem. 1933, 99, 335; *also* Univ. Odlif. Pub. Physiol. 1932, 8, 9). The normal *ammonium* salt, $(NH_4)_2C_5H_7O_4N$, loaes NH_3 at 110-115°, and forms the *acid salt* $(NH_4)C_5H_8O_4N$; $[a]_D$ about -3-6° (Schulze and Trier, Ber. 1912, 45, 257). Evaporation of rf-glutamic acid with aqueous ammonia causes decomposition of the ammonium salt but with ammonium chloride the acid salt is formed (Tseng and Chu, Sci. Rep. Nat. Univ. Peking, 1936, 1, No. 4, 17), which is also obtained by dissolving the acid in liquid ammonia (Voss and Guttmann, *I.e.).*

The blue copper derivative,

$$(C_6H_9O_4N)_5 4CuO,7\pounds H_2O,$$

is crystalline; *zinc* and *cadmium* salts and *cobalt* and *nickel* derivatives have been prepared (Hugouncnq and Flcjrence, l^ull.* Soc. chim. 1920, [iv], 27, 750). Wolff described an amorphous greenish-blue *copper salt* as

$$C_6H_7O_4NCu,IH_2O,$$

which dissolves in 400 parts of foiling water (Annalen, 1890, 260, 79); Pfeiffer and Werner formulate the copper salt

$$[Cu(C_5H_7O_4N)_2]Cu,H_8O$$

since it reacts with sodium hydroxide precipitating copper hydroxide and forming a bluish-violet solution which contains a substance precipitated by alcohol and having the required Cu:N ratio (Z. physiol. Chem. 1937, 246, 212). For an asymmct/ic synthesis of optically active cobalt complexes with the formula $[Co(C_6H_7O_4IM)_3]Na_3$, *see* Lifschitz Proc. Acad. Sci. Amsterdam, 1936, 39, 1192). Two forms of -this complex,. each having *d-* and *I-* forms, have?been*.described; one is red with insoluble silver and lead salts, the othep violet with salts soluble in boiling water. The *silver salts,* *$C_5H_7O_4NAg_2$ and $C_5H_8O_4NAg$, are white insoluble powders; the *ferrous salt* is obtained.when glutamic acid 48 boiled with an excess of iron powder in an oxygen-free atmosphere (Hoffmann, G.P. 26439f>); the *zinc salt* is,-basic $(C_6H_8O_4N)_2Zn\text{-}ZnO$; the *mercuric salt* a heavy crystalline powder decomposing at 208-209° (Habermann, Annalen, 1871, 179, 248; Abderhalden and Kautzsch, Z. physiol. Chem. 1910, 64, 447; 6£ 487; 1912, 78, 333). The *hydrochloric* has m.p. 202°, or heated rapidly, m.p. 213° (Abderhalden, Z. physiol. Chem. 1910, 64, 450); w^en precipitated from hydrochloric acid solution it contains 2 mol. H_2O (Wei and King, Science, Ch^ia, 1936, 19, 354). It has [aft^0 +25° (Abdferhalden, *I.e.);* or 24-5°^ (Fischer and Boehner, Ber. 1911, 44, 1334). For crystallography of the hydrochloride, *see* Kaplanova (Abh. Bohm. AkaU 1015, No. 23, from JahrJ). Min. 1917, 1, 123), and for the Raman spectrum, *.see* Edsall (J. Chem. Physics, 1937, 5, 508). Data are given by Takayama for its identification with the polarising microscope (J. Chem. Soc. Japan, 1931, 52, 245). *d-Glutamic acid picrolonate* has LO]^2^ +85° (Levene and Van Slyke, J. Biol. Chem. 1912, 12, 127). The *strychnine* salt has m.p. 225-230°, [■] -25-5°; the *brucine* salt has m.p. 240°, [affi -23° (Dakin, Biochem. J. 1919, 13, 998). For the *imido-orthophosphoric ester,* $C_7H_{14}O_7NP$, of glutamic acid, *see* Langheld (Ber. 1911, 44,-2076). The *a-ethyl ester* has m.p. 110° (Neuberger, Biochem. J. 1936, 30, 2085); the *y-ethyl ester* forms prisms from 50% alcohol, m.p. l'94° (188° Menozzi and Appiani, Gazzetta, 1894, i, 24, 384), *hydrochloride* m.p. 134°. The *diethyl ester* is an oil with b.p. 139-140°/10 mm., d^{17} 1-0737 and [aft +7-34° (Fischer,j3itzungsber. Akad. W*s. Berlin, 1900, 48, 1062), and is very soluble in water. For the dissociation constants of the ethyl esters, *see* Neuberger *(l.c).*

Glutamic acid forms a soluble *benzene sulphonyl derivative,*

$$PhSO_2NHCH(CO_2H)CH_2CH_2CO_2H,$$

m.p. 129-132°, wi?ich can easily be methylated to N-benzenesulphonylmethylglutamic acid, m.p. 138-139°, or esterified to the di-w-butyl ester, m.p. 58-59° (Hedin, Ber. 1890, 23, 3196; Gurin, J. Amer. Chen}. Soc. 1936, 58, 2140; *see also* Z. physiol. Chem. 1937, 250, 189). The *^-toluenesulphonyl* öbrivativc is an oil but gives a di-n-butyl ester, m.p. 64-65°, and a methylated derivative, m.p. 131-132° (McChesney and Swann, jun. J. Amer. Chem. Soc. 1937,59,111b^1). *Qlutamic-N-sulphonic acid* is obtained by the action of N-pyridinium sulphonic acid; its potassium salt crystallises with acetic acid; $2C_6H_6O_7NSK_3,CH_3CO_2H$ and forms double salts withheld potassium*glutamate,

$$C_5H_6O_7NSK_3,C_5H_8O_4NK,H_2O$$

(Baumgarten, Marggraff and Dammann, Z. pfcysibl. Chem. 1932, 209, 145). *Acetyl-d-glutamic acid,* m.p. 199°, is forme when ketene is passed into an aqueous solution of (/-glutamic acid (Bergmann and Stern, Ber. 1930, 63 [B], 437); or from the sodium salt and acetic anhydride (Nicolet, J. Amer. Chem. Soc. 1930, 52, 1192), but the sodium salt of acetylglutamic acid is readily racemised in aqueous solution; by acetic anhydride (Du Vigneaud and Meyer, J. Biol. Chem. 1932, 98, 295). The acetyl derivative readily gives, with methyl sulphate, *acetyl-methylglutamic acid,* decomp. 203° (Knoop and Oesterlin, Z. physiol. Chem. 1927,170, 186).

Ckloracetyl'd-glutamic acid,

$$CH_2ClCONHCH(CO_2H)CH_2CH_2CO_2H,$$

m.p. 143° (corr.), [afg -13-5° (±0-2°) in aqueous solution; with ammonia it yields *glycyl-d-glutamic acid,*

$$NH_a.CH_2<:ONHCH(CO_2H)CH_a.CH_2CO_2H$$

(Fischer, ·Ber. 1907, 40, 3704; Fischer, Kropp and Stahlschmidt, Annalen, 1909, .365, 181). *Phenylacetylglutamic acid,* $C_{13}H_{15}O_5N$, microscopicneedles,has m.p. 132°,[a]$_D$ -19°in3-10% 'aqueous solution; the brucine salt has [a]$_D$ -1-37° (Thierfelder, Sherwin, Z. physiol. Chem. 1915, % 1; Ber. 1915, 47, 2630). *o-Nitrobenzoylgluiamic acid,* m.p. 151°, is formed from the hydrochloride and o-nitrobenzoyl chloride in the presence of magnesium oxide. The formation of *N-carboxyglutamic* acid in sugar solutions containing glutamic acid and carbon dioxide is suggested by Majer (Listy Cukrovar, 1928,47,123; Amer. Chem. Abstr. 1929,23,728). For the *half anilide* of glutamic acid, m.p. 209° (decomp.), seeVosl and Guttmann (Z. physiol. Chem. 1932, 204, 1); for the synthesis of N-alkyl derivatives, *see* Sugasawa (J. Pharm. Soc. Japan, 1927, No. 550, 1041); and for *y-phenylglutamic acid, see* von Beznák (Biochem. Z. 1929, 205, 414). Numerous di- and poly-pcptides have been synthesised from glutamic acid and the original literature should be consulted for descriptions of these substances.

(//-Glutamic Acid is obtained in 60-65% yield from the (/-acid or its acid sodium salt by heating with solid ammonium chloride at 230-235° for an hour and then refluxing for 5 hours with 6^-hydrochloric acid. Anhydrous *dl-*glutamic acid and the monohydrate were obtained in this way by Dunn and Stoddard (J. Biol. Chem. 1937, 121, 521). A slightly better yield (71%) is obtained by heating the d-acid with barium hydroxide in aqueous solution for 9 hours at 160-170°. Sodium carbonate, bicarbonate and hydroxide and calcium hydroxide do not cause racemisation (Tseng and (Jhu, J. Chinese Chem. Soc. 1933, 1, 188; Schulze and Bosshard, Ber. 1885, 18, 3$8; Schulze, Z. physiol. Chem. 1892, 9, 253). Syntheses of *dU* glutamic acid have been carried out by Wolff (Annalen, 1890, 260, 79), by Knoop and Gesterlin (Z. physiol. Chem. 1927, 170, 186), and ty Dunn, Smart, Rcdqmann and Brown (J. Biol. Chem. 1931, 94, 599). Wolff started with hevulic acid and by boiling dibroraolaevulic acid with water, obtained glyoxylpropionic acid, $OHC{\cdot}CO{\cdot}CH_2CH_2CO_2H$, which reacts with hydroxylamine to form yS-dii'sonitroaovaleric acid, $CH(:NOH)C(:NOH)CH_2CH_2C0_2<H$, from which wonitrosocyanobutyric acid,

$$CN.C(:NOH)\cdot CH_2\cdot CH_2CO_2H$$

is obtained by dehydration with sulphuric acid and subsequent treatment with cold sodium hydroxide. When wonitrosocyanobutyric acid is hydrolysed with boiling alkali, it yields *iso*-nitrosoglutaric acid,

$$CO_2HC(:NOH)CH_2\cdot CH_2CO_2H,$$

and this is reduced to inactive glutamic acid by tin and hydrochloric acid. Knoop and Oesterlin's method consisted in the reduction of a-ketoglutaric acid in the presence of ammonia; c/. Shemin and Herbst, J. Amer. Chem. Soc. 1938, 60, 1954. The third synthesis started from the ?\sonitroso-derivative of malonic ester, ethyl oximinomalonate, $HON:C(CO_2Et)_2$. On reduction with aluminium amalgam, this gives ethyl aminomalonate which was benzoylated and then condensed with /?-bromoproplonic acid to ethyl Vbenzamidopropane-aay-tricarboxylate,

$$C_eH_5CO\cdot NHC(CO_2Et)_2CH_2\cdot CH_2CO_2Et.$$

This ester, on hydrolysis, gives (ZZ-glutarcic acid which forms rhombic plates from water, sm.p. 199° (Dunn, Smart *el al., I.e.,* show photomicrographs of *d-* and *dl-ghit&mic* acids); Dunn and Brophy give the m.p. as 225-227° (J. Biol. Chem. 1932, 99, 221). It is soluble in hot water and sparingly soluble in cold water (1 part in 66*7 parts at 20°), also sparingly in alcohol, ether, light petroleum and carbon disulphide. The flavours of the *sodium^potassium, lithium, calcium, barium, strontium, magnesium, methyl ammonium* (m.p. 75°; hydrochloride, m.p. 168-169°), and *dimethylammonium* (hydrochloride, m.p. 178*5°) salts have been described (Tseng and Chu, *I.e.).* The potassium and methylammonium salts are hygroscopic. The *copper* salt, $C_5H_7O_4NCu,2£H_2O$, forms blue needles, becomes anhydrous at 135° and is not soluble in less than 1,000 parts of boiling water. A number of derivatives have been reported: the *hydrochloride* crystallises in needles, m.p. 193° (Wolff), 200° (Abderhalden and Kautsch, Z. physiol. Chem. 1910,68, 487), and is crystallographically identical with the hydrochloride of the d-acid, a:6:c=0-8873:l:0-3865 (Wolff, *Lc);* the *acid sulphate,* m.p. 164-6°; *picroloyiate,* fine short spindles, decomposing at 184° (Levene and van Slyke, J. Biol. Chem. 1912, 12, 127); the *N-chloracetyl derivative* has m.p. 123°, *formyl,* m.p. 181-7°; *acetyl,* m.p. 187-5°; *propionyl,* m.p. 173-1°; *n-butyryl,* m.p. 179°; and *isovaleryl,* m.p. r%0-6°. The hydrochloride of the ethyl ester has m.p. 113-1° (Tseng and Chu, *I.e.). 61-Be?izoyl-glntafiiic acid* crystallises with 1 H_2O, m.p. 152-153° (155-157° corr.), and is soluble in 124 parts of wa+er at 20° (Fischer, Ber. 1899, 82, 2451).

When cH-glutamic acid is crystallised from water, right- and'left-handed enantiomo?phous crystals are deposit 3d, but the fact cannot conveniently be utilised for resolution and the preparation of the /-isomeride; this was, however, effected by the cultivation *oiPenicillium glaucum* in a solution of the ctf-acid, whereby the rf-acid is destroyed and the Z-acid remains in solution (Menozzi and Appiani, Gaz-etta, « 1894, i, 24, 370). 'Fischer (Ber. 1899, 32, 2451) resolved rfZ-glutamic acid by the fractional crystallisation of the strychnine salt. The optical resolution is best carried out by converting dJ-glutamic acid to eW-pyrrolidonenarboxylic acid by heating to the melting-point and resolving the latter acid by heating *with* an equimolecular portion jf quinine in the presence of water. The quinine salts-are easily separated by successive treatment with alkali, acid and absolute alcohol. The mother liquor, after separation of the d-acid, is concentrated *in v&cuo,* filtered, hydrolysed with normal sodium hydroxide, neutralised and drird *in vacuo.* Exvraction with alcohol and evaporation give the Z-pyrrolidonecarboxylic acid. .Recovery of d-glutainic acid from the Z-pyrrolidonecarboxylic acid and Z-glutamic acid from the d-pyrtolidonecarboxylic acid is readily effected by heating "with 15% hydroch^ric acid (Sugasawa, J. Pharm. Soc. Japan, 1926, No. 537, 964).

l-Glutamic Acid is usually obtained by resolution of ^/-glutamic add *(v. supra)* but it may be obtained by the cultivation of certain bacilli, *e.g. B. mesentericus,* on rf-glutamic acid thereby forming a polypeptide-like substance the difficultly soluble copper salt of which is hydrolysed by hydrochloric acid to Z-glutamic acid (Bruckner and Ivanovics, Z. physiol. Chem. 1937, 247, 281). A theoretical yield of l-glutamic acid is given on hydrolysis with hydrochloric acid of the purified capsular substance of anthrax bacillus *{idem.* Z. Immunitätsforsch. 1938, 9&J 119).

Z-Glutamic acid forms leaflets from water, m.p. 213°, with decomposition (rapid heating). It is tasteless and has [oft? -12-9° in water. The crystal structure has been studied by Bernal (Z. Krist. 1931, 78, 363, in English). *\-Qlutamic acid hydrochloride* has m.p. 200-204° and [o]5 -30-06°. Data are given by Takayama (J. Chem. Soc. Japan, 1931, 52, 245) for its micro-identificeAion with the polarising microscope. *Benzoyl-X-glutamic acid* has m.p. 130-132°, dissolves in less than 2 parts of water at 100°, or 21 parts at 20°, and has $[a]_D$ +13-81° in 5% aqueous solution, and the potassium salt has $[a]_D$ -vl8-7°; it yields J-glutamic acid on hydrolysis and by the Curtius degradation gives Z-benzamido-1:3-diaminopropanc hydrochloride, m.p. 158° (picrate, m.p. 100°), \Tnich is hydrolysed to jS-aminopropaldehyde *(dimedone* derivative, m.p. 208-209°), (Bergmann, Zervas and Schneider, J. Biol. Chem. 1936, 113, 341).

jff-Hydroxyglutamic Acid,

$$CO_2H\cdot CH(NH_2)\cdot CH(OH)\cdot CH_2\cdot CO_2H.$$

The isolation of 0-hydroxyglutamic acid from the product of hydrolysis of caseinogen with 25% sulphuric acid has been described by Dakin (Biochem. J. 1918, 12, 290) and by Gulland and Morris (J.C.S. 1934,1644). According to the later authors, the hydrolysate is neutralised to Congo Red with barium hydroxide and the barium sulphate, which adsorbs all the ^-hydroxyglutamic acid, is eluted with 1% hydrochloric- acid at 25°. The amino-acids so obtained are treated to remove glutamic and aspartic rcids, Meucine and other amino-acids, and the barflim sH.t of 0-hydroxyglutamic acid is separated. This salt on crystallisation decomposes to give the monohydrate,

$$C,H,O_5N,H_2O,$$

similar to Dakin's specimen. > Syntheses of *p*-hydroxyglutamic acid have been described by iTakin (from glutamic acid, Biüchem. J. 1918, 12t 290; 1919, 13, 398) and by Harington and Randall (by catalytic hydrogenation of the a-*isonitToso* derivative of ethyl acetonedicarboxylate, *ibid.* 1931, 25, 4917), but there were marked discrepancies between the products from these.two syntheses.*

The estimation of 0-hydroxyglutamic acid is best made after a preliminary purification by electrodialysis. The anode liquid is then freed from methionine with n-butyl alcohol and oxidised^ with chloramine-T. *The product,

$$CO_aHCH_2COCHO,$$

is not isolated but determined as the *p*-nitrophenylosazone (Gullmd and Morris, *I.e.).* The anhydrous <K-acid has m.p. 195° with decomposition and is soluble in water but insoluble in alcohol. The hydrochlorides of the <ft-acid and of its ethyl ester have m.p. 87° and 168-5° respectively. The *silver, copper* and *acid calcium* salts have been prepared (Harington and Randall, *I.e.).* d-0-Hydroxyglutamic acid crystallises from water in prisms which sinter at 100°; it is soluble in water and acetic acid, sparingly soluble in methanol and insoluble in ethyl alcohol and ether. Its isoelectric point •occurs at p_H 3-28. IJpr the dissociation constants, *see* Kirk .and Schmidt, j. Biol. Chem. 1929, 81, 237. In aqueous solution (4%) it has [afg about +0-8° and in 2% hydrochloric acid solution [a]^{2}j5 +16-3°. On prolonged heating at 100-110° over phosphorus pentoxide it yields hydroxypyrrolidonecarboxylic acid. It yields *silver, copper, mercury, had, cadmium, zinc, calcium* and *barium salts* of which the silver and mercury salts only are insoluble, and it gives a *diethyl ester,* m.p. 62-63°, which is converted, in the presence of light and moisture, into ethyl hydroxypyrrolidonecarboxylate, m.p. 115°, and on boiling with concentrated hydrochloric acid to a-ketoglutaric acid (Abderhalden and Murke, Z. physiol. ChemM937, 24fT, 227). The *benzoyl* derivative has m.p. 175-176° and the derived hydantoin, 191-193° (Knoop *et al., ibid.* 1936, 239, 30). The *brucine salt* has m.p. 200°, with decomposition and [afg -25-0°. The *strychnine salt* has m.p. ^245° and [off -20-3°. When heated with hydriodic acid at 150°, d-j8-hydroxy-glutamic acid is converted to rf-glutamic acid. As a hydroxy-acid, it gives colour reactions with phenols and concentrated sulphuric acid, purple with resorcinol, bright green with thymol and red (flesh) with phloroglucinol.

M. A. W.

GLUTAMINE,

$$CO_2rtCH(NH_2)CH_2CH_aCONH_a,$$

its a half amide of glutamic acid.* It was discovered in 1877 by Schulze and Urich (Ber. 18?7,->10, 85) in tho juice of young pumpkin plants and isolated from beet-root sap by Schulze and Bosshard *(ibid.* 1883, 16, 312), 1 litre yielding 0*7-0«9 g. of glutamine; *see also* Smolenski (Chem. Zentr. 1911, I, 518, from Z. Ver. deut. Zucker-Ind. 1910, 1215), Schulze (Z. physiol. Chem. 1894, 20, 327; 1897, 24, 18; Ber. 1896, 29, 1882; Landw. Versuchs.-Stat. 1898, 49, 442) and Deleano (Z. physiol. Chem. 1912, 80, 79). It appears to replace its homologue, asparagine, in some families, *e.g. Caryophyllaceas, Cruciferss* and *Filices,* where it occurs in the leaves, seedlings, roots and tubers. The amount of glutamine found in seedlings, etc., is only about 3% of the dry weight, which is much less than the amount of asparagine found in leguminous seedlings. The glutamine content does not appear to be constant but, for example, in the beetroot, it increases in the growing plant, reaches a^ maximum and then disappears, apparently being replaced by allantoin (Ravenna and Nucoorini, Annali Chim. Appl. 1928, 18, 509). By the application of ammonium sulphate, the* glutamine content can be raised to 5-4% of the dry weight (Vickery, Pucher and "Clark, Plant Physiol. 1936,11, 413). It appears to be % direct product of the hydrolysis of protein** during germination (Nuccorini, Annali Chim. Appl. 1930,20,239). Glutamine is widely distributed in plants; thus, it occurs with asparagine in the juice of ripening oranges (Scurti and de Plato, Chem. Zentr. 1908, II, 1370); in rhubarb leaves (Vickery, Pucher, Leavenworth and Wakeman, J. Biol. Chem. 1938, 125, 527) and in appreciable amounts in tobacco leaves, accounting for the formation of ammonia when the leaves ar§ boiled with water (Vickery and Pucher, J. Biol. Chem. 1936,113,157). The white exudation which appears on the tip of Chewing's fescue grass, after the application of ammonium sulphate, has been identified as glutamine (Doak, New Zealand .J. Sci. Tech. 1937, 18, 844). For distribution and role in plants, *see also* Stieger (Z. physiol. Chem. 1913, 86, 245) and Schwab (Planta, 1935, 24, <*60; 1936, 25, 579). According to Thierfelder and and Von Cramm, glutamine is a component of protein molecules (Z. physiol. Chem. 1919, 105, 58). For the formation of glutamine by enzymic digestion of gliadin, *see* Damodaran, Jaaback and Chibnall, Biochem. J. 1932, 26, 1704.

The isolation of glutamine from beetroot can be effected by the method of Schulze and Bosshard *(I.e.),* modified in detail by Vickery, Pucher and Clark (J. Biol. Chem. 1935, 109, 39). The roots are ground and pressed out. The residue is cytolysed in ether for 30 minutes and on pressing again the glutamine is expressed. The juice is treated with lead acetate, filtered and precipitated with mercuric nitrate at neutrality. The precipitate is decomposed with 10% sulphuric acid and with hydrogen sulphide and the filtrate is concentrated *in vacuo* at not more than 60°C, refiltered and concentrated to crystallisation, when 2 vol. of ethykulcohol are added. The produot is crystallised fr^m water by adding 2 vol. of alcohol. A similar method of extracting glutamine from expressed beet juice (giving 3-4 g. per litre) has been described by Eisenachimmel (Z. Zuckerind, Czechoslov. 1927, 51, 337). The synthesis of d-glutamine from d-glutamitf acid has been carried out by Nienburg (Ber. 1935, 68 [B], 2232). The y-ethyl ester of glutamic acid was converted to the carbobenzyloxy derivative and treated with liquid ammonia at 15-20° and the amide so formed,

$$PhCH_2OCO.NH(CO_2H)[CH_2]_2CO_2H,$$

was hydrogenated in the presence of palladium catalyst to d-glutamine. The y-esters of glutamic acid have also been converted to the amide (glutamine) by way of the hydrazide and azide (B.P. 437873). For the conversion of *d*-glutamic anhydride to d-glutamine, *see* Berg-raann, Zervas and Salzmann, Ber. 1933, 66 [B], 1288. For the biochemical synthesis of glutamine from ammonium glutamate, *see* Krebs, Biochem. J. 1935, 29, 1951.

Glutamine crystallises in needles from aqueous alcohol, m.p. 184-185°; it dissolves in about 25-7 parts of water at 16° (SchuSze and Godet, Landw. Versuchs-Stat. 1907, 67, 31b) and is sparingly soluble in alcohol. It is unstable in aqueous solution (Damodaran, Jaaback and Chibnall, *I.e.)* and behaves as a very weak acid towards indicators (Sellier, Chem. Zentr. 1904, I, 789). Glutamine is dextrorotatory in aqueous solution; seven specimens from various vegetable sources were found to have $[o]_D$ between +1 -9° and +9*5°, the differences being probably due to the presence of the two stereoisomers in varying proportions (Schulze and Bosshard, Ber. 1885, 18, 390; Sellier, *I.e.*; Schulze, Ber. 1906, **39,** 2932; Landw. Versuchs-Stat. 1906, 65, 237). Schulze and Trier (Ber. 1912, 45, 257) found that a 4% aqueous solution of glutamine, purified through its copper salt, has *[a]*™ +6° to +7°, while for synthetic samples, Bergmann, Zervas and Salzmann *(I.e.)* give $[a]_D$" +8-0° and Nienburg *(I.e.)* $[a]_D$ +8-3°. A 7-8% solution in 5% hydrochloric acid has [a]^ +31° to +32° (Schulze and Trier, *I.e., cf.* Pellet, Chcm. Zentr. 1911,1, 1766, frbm.Z. Zuckerind. Bohm. 191.!, 35, 437). For the refractive index, density and [a] of solutions of glutamine, *see* Eisenschimmel *(I.e.).* The isoelectric point is 8-0 to 10-0 (Errera, Compt. rend. 1931, **193,** 1347). ·In the presence of liver tissue, glutamine is converted into urea (Leuthardt, Z. physiol. Chem. 1938, 252, 238); for the action of asparaginasc on glutamine and also on asparagine, *see* Geddes and Hunter, J. Biol. Chcm. 1928, **77,** 197.

The estimation of glutamine can be effected by Schlōsing's method (Schulze, J. pr. Chem. 1885, [ii], **31,** 233), ammonium salts being removed by distillation with magnesia at a pressure sufficiently reduced to cause the solution to boil at 40°. Under these conditions the amide group is not hydrolyscd (Sellier, Bull. Soc. chim. Sucr. Dist. 1907, 25, 124; Schulze, Landw. Versuchs-Stat. 1906, 65, 237). More recent determinations oi glutamine by hydrolysis were carried out in solutions buffered to p_H 6-5 (Chibnall *el al.,* jtiochem. J. 1935, 29,*.2710; Mendel and Victor., Carnegie Inst. Washington Yearbook, 1935, 3< 298). The van Slyke determination of amino-compounds using nitrous acid gives abnormal results with glutamine but normal with aRpurairim'. ami tfieso differences have been applied by Chibnall and Westall to the determination of glutamieie in the presence of aspiragine. For the determination of glutamine (+asparagine) in citrus juices by formol titration, *see* .Solarino, Ind. ital. conserve, 1938, **13,** 32. Titration constants for d-glutamine and *d-isoglutsunine* are given by Melville and Richardson (Biochem. J. 1935, 29, 187). For methods of separating and determining glutumine, *see also* Tanbŏck and Winterstein, Handb. Pflan&enanalyse, 1933, 4, 190; Chem. Zentr. 1933, II, 3321 and Schwab, Planta, 1936, 25, 579.

Owing to the feebly/acidic character of glutamine, very fewnsalts have been isolated: the *copper* derivative, $-Cu(C_5H_9O_3N_2)_2$, forms bluish-violet crystals* the *cadmium* derivative, $Cd(C_6H_9O_3N_2)_2$, fine prisms. Glutamine forms a *compound* .with tartaric acid, that separates in large transparent crystals (Schulze and Godet, ***l.c.). PhenyUzcetylglutamine* has $[a]_D$ o-18° in** 2-4% aqueous solution; the specific rotation decreases in acid solution (Thierfelder and Sherwin, Z. physiol. Chem. 1915, 94, 1). N-*ehloracetylglutamine* lorms needles from ethyl acetate, m.p. 130-132° and has [a]^ -104° in water. For a description of dipeptides and tripeptides containing glutamine, *see* Thierfelder and von Cramm, *I.e.; also* Abderhalden and Spinner, Z. physiol. Chem. 1919,**107,** 1.

d-isoGlutamine,

$$CONH_2{\cdot}CH(NH_2)CH_2{\cdot}CH_2CO_2H,$$

has been synthesised by Bergmann and Zervas (Ber. 1932, 65 [B], 1192) by converting the IM-carbobenzyloxy derivative of (/-glutamic acid,

$$PhCH_2OCONHCH(bo_2H)[CH_2]_2CO_2H$$

(m.p. 120°, [a]^ -7-1° in acetic acid) into the anhydride (m.p. 94°) and so to the half amide. N-carbobenzyloxy-d-i'soglutamine, m.p. 175°, which on catalytic hydrogenation gives *d-iso*-glutamine, [o]^ +2M° in alcohol. It is soluble in water but Very sparingly so in organic solvents.

By the action of alcoholic ammonia on the ester of *d*- or /-glutamic acid, the amide of the corresponding pyrrolidonecarboxylic acid is formed; these are called *glutimides* by Menozzi and Appiani, and the *d-*, 2- and cM-forms have been described.

$$\text{d-Glutimide,}\ \begin{array}{l}CH_2{-}CH_2{\diagdown}\\ |\qquad\qquad\ \ )CHCONH_2,H_2O,\end{array}$$

crystallises in needles belonging -*x> the nnorthic system, a:6:c=l-403:1:l-421, /3=86°,j58'; it has m.p. 165° and $[a]_D$ +41*29°. \\-*Glutimide* has $[a]_D$ —40° and has the same m.p. and other properties as its dextro-isomcr. *d\\-Glutimide* is formed when l-glutimide is heated with alcoholic ammonia at 140-150°, or alone at 200°; it has m.p. 214° (220-221°), the hydrochloride crystallises in the orthorhombic system,

a:6:c=0-?853:1:0-3860

(Menozzi and Appiani, Atti. U. Accad. Lined., 1892, 7, i, 33* Gazzetta, 1894, i, 24, 370).

M. A. W.

GLUTANIC ACID, *a-hydroxyglutaric acid.*

$CO_2H\cdot CH(OH)CH_2\cdot CH_2\cdot CO_2fl.$

(1), d-a-Hydroxyglutaric acid, m.p. 72° (from ether), [a]$_D$'' +1-76°, occurs In sugar-beet rfiolasses (*see* Lippmann, Ber. 1882, 15, 1156; 1891, 24, 3301), is formed *bj* the hydrolysis of Z-a-chloroglutaric acid (E. Fischer and Moreschi, '*ibid.* 1912, 45, 2447) or in almost quantitative jjield by the dismutation of methylglyjpxalylacetic acid by ketoaldehyde mutase from top-yeast (Neuberg and Collatz, Biochem. Z. 1930, 225, 242), by the enzyme from germinating peas (Mayer, *ibid.* 1031, 233, 361), by animal glyoxalase (S. Fujise, iftid.,1931, 236, 237) or by the action of *B. coli* (S. Veibel, *ibid.* 1931; 232, 435).

(2) J-a-Hydroxyglutaric acid, from tf-glutamic acid by HNO_2 at -7°, has m.p. 72-73° (Fischer, *I.e.).* fcla salt [aft -8-65°.

(3) cM-a-Hydroxyglutaric acid is isolated as Zn salt ($+3H_2O$) from the products of the action of MnO_2 on synthetic glutamic acid (Wolff, Annalen, 1890, 260, 12).

GLUTARIC ACID,

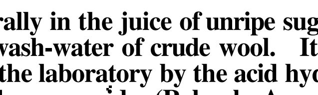
$$\overset{-a}{CO_2HCH_2}\overset{P}{CH_2}\overset{y}{CH_2}CO_2H,$$

a P a'

occurs naturally in the juice of unripe sugar-beet and in the wash-water of crude wool. It is best prepared in the laboratory by the acid hydrolysis of trimethylene cyanide (Reboul, Ann. Chim. Phys. 18$8, [v], 14, 501; Marvel and Tuley, Organic Syntheses, 1925, 5, 69) or of methylenedimalonic ester (Knoevenagel, Ber. 1894, 27, 2346; Drcssel, Annalen, 1890, 256, 176; Otterbacher, Organic Syntheses, 1930, 10, 58) or by the oxidation of c&cZopentanone with dilute nitric acid (Hentzschel and Wislicenus, Annalen, 1893, 275, 315; Bcedtker, J. Pharni. Chim. 1932, [viii], 15, 225).

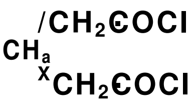
Glutaric acid crystallises in large monoclinic plates, m.p. 97-98°, b.p. 20(J°/20 mm. It is readily soluble in water (100 c.c. dissolve 63*9 g. at 20°; Lamouroux, Cornet, rend. 1899, 128, 999) and in alcohol and ether. For the separation of glutaric acid from succinic, adipic and pimelic acids, *see* Bouvcault, Bulh Soc. chim. 1898, [iii], 19, 562.

When aqueous solutions of glutaric acid are evaporated at 100° and the resulting syrup allowed to crystallise over H_2SO_4, butyrolactone-y-carboxylic acid is formed, m.p. 49-50°

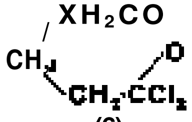


Ethyl butyrolactonccarboxylate is formed by the action of epichlorhydrin on ethyl sodiomalonate. Colourless oil, b.p. 175/25 mm. (Traube and Lehmann, Ber. 1901, 34, 1971).

Dimethyl (b.p. 93-5-94-5°/13 mm.) and *diethyl glutarate* (b.p. 103-104°/7 mm.) are obtained by est.crifyir% the acid witlf the respective alcoholic hydrogen chloride (Meerburg Kcc, trav. chim. 1899,18,373; Reboul, *I.e.,* p. 505). When the acid is hoatcd with acctyl chloride it yields the *Znlfydride* in needles, m.p. 5fr-57 (Mol, Rec. trav. chim. 1907, 26, 381). On heating, ammonium glutarate is converted into *glutarimide,* m.p. 152°. With phosphorus pentachloride or thionyl chloride, glutaric acid yields *glutaryl chloride,* b.p. 107-108°/16 mm. (Reboul, i.e., p. 504; Ruggli, Annalen, 1913, 399, 179) which reacts as a mixture of the straight-chain form (a) and the cyclic form *(b),*



(a).



(6).

(Plant and Tomlinson, J.C.S. 1935, 856). For purposes of identification the following derivatives (in addition to the'' anhydride and imide) may be used: *amide,* m.p. 175°; *anilide%* m.p. 126-127^; *frtoluidide,* m.p. 218°; *y-phenylphenacyl ester,* m.p. 152°; *j)-nitrobenzyl ester,* m.p. 69°.

Halogenoglutaric Acids.—*a-Chloroglutaric acid* is obtained by the action of sodium nitrite on the hydrochloride of a-amirioglutaric (glutamic) acid; it is a solid, m.p. 97-100° (Jochem, Z. ^mysikal/Chem. 1900, 31, 124). *Ethyl a-bromoglutaraie,* b.p. 142°/11 mm., is obtained by directly brominating glutaryl chloride and pouring the product into alcohol (Pcrkin and Tatteraall, J.C.S. 1905, 87, 366; Ingold, *ibid.* 1921, 119, 316). *P-Bromoglutaric acid,* m.p. 139-140°, is obtained by the direct addition of hydrogen bromide to glutaconic acid (Ssemenow, J. Russ. Phys. Chem. Soc. 1912, 31, 389).

Dibromination of glutaric acid (as its chloride) yields a mixture of the two stereoisomcric aa'-*dibromoglularic acids* (Auwers and Bcrnhardi, Ber. 1891, 24, 2230; Ingold, J.C.S. 1921, 119, 316; Ing. and Pcrkin, *ibid.* 1925, 127, 2387); the meso-acid melts at, 170° and forms a solid *dimethyl ester,* m.p. 45°, whereas the dJ-aeid, m.p. 142°, forms a liquid *dimethyl esten>* b.p. 143-145°/10 mm. Only one of the two possible *aP-dibromoglutaric acids* is known; this form, m.p. 157°, is obtained by the direct addition of bromine to glutaconic acid (Verkade and Coops, Rec. trav. chim. 1920, 39, 586).

Alky I Derivatives.—*a-Methyhjlntaric 'acid,* m.p. 79°, is best obtained by the acid hydrolysis of ethyl propane-ayy-tricarboxylate (Auwers, Annalen, 1896, 292,' 210; Mellor,. J.C.S. 1901, 79, 128) and has been resolved, the *d-acid,* m.p. 81°, having [a]^ +20° in water (Berner and L*>onardscn, Klg. Norske Vidcnskab. Selkabs. Forh. 1935, 7, 125). *P-Methylglutaric acid,* m.p. 86°, is obtained by acid hydrolysis of the Michael addition product from ethyl malonatc and ethyl crotonate (Auwers, Ber. 1891, 24, 308; Auwers, Kbbncr and von Meycnburg, *ibid.* 2888).

aoL-Dimethylghdaric acid, m.p. 85°, is best preparei by heating aa-dimethplbutyrolaetone with potassium cyanide in a seajed tube at 270° and hydrolysing the product with alkali (Blanc, Bull. Soc. chim. 1905, [iii], 33, 886). *pp. Dimethylglutaric acid,* m.p. 101°, is obtained by the hydrolysis of the cyano-imide formed by condensation of ethyl cyanoaeetate with acetona, in the presence of alcoholic ammonia (Guareschi, Atti R. Accad. Sci. Torino, 1901, pi], 50, 235; Kon and Thorpe, J.G.S. 1919,115, 694; Vogel, *ibid.* 1934, 1758), this process may be extended to the preparation of the aflS-triali' ylglutaric acids (Kon and Thorpe, *ibid.* 1922,121, 1795) or by the hypobromite oxidation of dimethyldihydroresorcinol (Komppa, Ber. 1899, 32, 1423; Walker and Wood, J.C.S. 1906, 89, 599). ***aB-Dimethylglutaric acid,* m.p. 87°, is obtained** by hydrolysis of the corresponding imide (Thorpe and Young, *ibid.* 1903, 83, 357). *aa'-Dimethylglutaric acid* is obtained (i) by the action of methylene iodide on ethyl sodio-a-cyanopropionate, followed by acid hydrolysis of the resulting cyano-ester (Zelinsky, Ber. 1899, 22, 2823), (ii) by hydrolysis and decarboxylation of ethyl ao'-dimethyl-o-cyanoglutarate (Howies, Thorpe and Udall, J.C.S. 1900, 77, 949) and (iii) by acid hydrolysis of the condensation product from ethyl methylmalonate and ethyl a-methylacrylate or ethyl a-bromoi*obutyrate (Auwers and Jackson/Ber. 1890, 23, 1611; Auwers and Thorpe, Annalen, 1895, **285,** 310; Auwers and Kobner, Ber. 1891, 24, 1936). The *meso-y* m.p. 128°, and *racemic,* m.p. 143°, forms may be separated by treatment of the mixture with acetyl chloride, whereby the latter is converted into the anhydride. *(See also* CABBOXYLIC ACIDS.)

H. N. R.

GLUTEN (v. Vol. II, 84c).

GLUTENIN, GLUTELIN (v. Vol. II, 856c).

" *CLUTOLIN* " (*v.* Vol. **II**, 480a).

GLYCERIC ACID, HO-$CH_2CH(OH)CO_2H$.

dZ-Glyceric Acid is prepared by the action of fuming nitric acid (1 part) on a 50% aqueous solution of glycerol (2 parts). The acid is separated from the products of the reaction in the form of the lead or calcium salt and isolated by treatment of these salts with hydrogen sulphide or oxalic acid respectively (Debus, Annalen, 1858, **106,** 80; Beilstein, *ibid.* 1861, **120,** 229; Moldenhauer, *ibid.* 1864, **131,** 324; Mulder, Ber. 1876, 9, 1902; Bottinger, *ibid,* 1877, **10,** 267; Rosenthal, Annalen, 1886, 233, 16; Meyer, Ber. 1886,19, 3294; Lewkowitsch, *ibid.* 1891, 24, Kef. 653; Wohlk, J. pr. Chem. 1900, [ii], 61,209). Also prepared, together with other products, by the action of air or H_2O_2 on an alkaline solution of glucose (Glattfield, J. Amer. Chem. Soc. 1929, 50, 151; *cf.* Nef, Annalen, 1914, **403,** 217). Glyceric acid forms a thick syrup, soluble in water and alcohol but insoluble in ether.

Methyl ester has b.p. 119-120°/14 mm., *dN* 1-2814. *Ethyl ester* has b.p. 12O-121°/14 mm., *dN* M909 (Frankland and McGregor, J.C.S. 1893, 63, 512).

d-Glyceric Acid? The calcium salt is- obtained from the corresponding Bait of the *dl.* acid by tjie action of *B. ethaceticus* (Frankland, e* *al.* J.C.S. 1891, 59, 97; 1893, 63, 296); of *P. glaucum* (Lewkowitsch, Ber. 1883, 16, 2720; McKenzie and Harden, J.C.S. 1903, 93, **431)**; or by the action of *A. niger* and *A. grteeus* on ett-glyceric acid (Mackenzie ani Harden, *I.e.);* also by lithe fractional crystallisation of the brucine salts formed by the dZ-acid (Frankland and Done, *ibid.* 1905, 87, 622). The aqueous solution of the acid is dextrorotatory, the salts are laevorotatory and more soluble in water than those of the dZ-acid."

The *methyl estw* has b.p. 119-120°/14 mm., *dN* 1-2799, [agjf -4-80°, the *ethyl ester* has *dN* 1-1921/Mjf -9-18° (Frankland and McGregor^ *ibid.* 1893, 63, 511). The *amide* forms plates or prisms, m.p. 99-6-Kto°, dj^{00} 1-3347, [aft^{00} 39-98° (Frankland*, Wharton and Aston, *ibid.** 1901,-79, 269).

Z-Glyceric Acid, prepared by the action of milk of lime on glucuronic acid (Neuberg and Silbermann, B*r. 1904, 37, 339). The salts are dextrorotatory, the *barium* salt having $[a]_D$ + 171°.

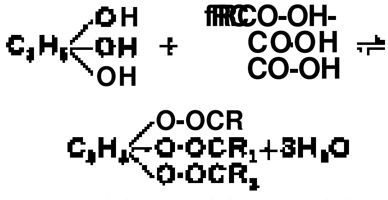
GLYCERIN (Glycerol; afr-trihydroxypropane; l:2:3-propanetriol,

$CH_2(OH)CH(OH)CH_2(OH)$),

a trihydric aliphatic alcohol occurs in combination with fatty acids as esters or " glycerides " in all fatty oils and fats. Glycerin was discovered by Scheelo (CrelTs Chem. J. 1779,4,190; Crell's Chem. Ann. 1784, 1, 99) in the course of studies on the action of litharge on olive oil (preparation of " lead plaster ") and other fatty oils, and termed by him *principium dulce. **oleorum.***

The name *glycerin* (from the Greek *y\vi<cp6s,* sweet), later modified to *glycerol*[1] in conformity with the usual nomenclature for alcohols, was conferred upon it by Chevreul, who recognised it as an essential and characteristic component of the fats, and pointed out the nature of its association with the fatty acids therein.

The composition of glycerol was ascertained by Pelouze (Ann. Chim. Phys. 1836, [ii], 63, 19; Compt. rend. 1845, 21, 718) and its constitution was finally established by the work of Berthelot (Ann. Chim. Phys. 1854, [iii], 41, 216) and of Wurtz (Compt. rend. 1857, 44, 780; Annalen, 1857, 102, 339) and confirmed by its synthesis by Friedel and Silva (Compt. rend. 1872, 74, 805; 1873, 76, 1694) and by Piloty (Ber. 1897, 30, 3161). The fatty oils and fats consist essentially of *glycerides* the esters formed by the combination of fatty acids with glycerol with the elimination of 3 mol. of water, as expressed by the'following equation:



in which **RCO-, R_1CO-v R_2CO-** represent radicals of fatty acids, which may be all alike, or derived from different fatty acids.

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[1] In view of the common usage of the trivial name *glycerin,* It is convenient to retain this to denoto tho ordinary technical or commercial material, and to reserve the term *glycerol* for the pure chemical.

If the three fatty acid radicals are identical, the ester is known as a *simple triglyceride*: if, however, the three hydrogen atoms are replaced by two or three different fatty acid residues, then ***mixed glycerides* are obtained.**

It was formerly assumed that the natural fats consisted of mixtures of simple triglycerides, and (erroneous) references to the presence of simple glycerides such as tristearin, triolein, tripalmitin, etc., are common in the older literature. Modern researches, however, and especially those of Hilditch and his pupils (*cf.* T. P. Hilditch, " The Chemical Constitution of the Natural Fats," London, 1940) have shown that simple triglycerides rarely occur in more than very small amounts in natural fats (particularly so in seed-fats), and that most of these are composed chiefly of " mixed triglycerides," such as oleo-dipalmitin, palmito-oleo-stearin, oleo-distearin, etc. (*cf.* Table X\H1I). The seed fats of lriufel and of nutmeg, which contain some 30% of trilaurin and 40% of trimyristin respectively, are remarkable.

The equation shown above, when read from right to left, symbolises the hydrolysis or saponifi*cation* of fats and expresses the fact that by the addition of the elements of water (which is usually effected with the assistance of suitable catalysts), neutral glycerides may be resolved into 3 mol. of fatty acid and 1 mol. of glycerol.

Glycerol exists solely in the combined state in fresh natural fats and oils, although traces of the free alcohol may be found occasionally in fats which have suffered a certain amount of deterioration from hydrolysis. Free glycerol is to be found in small amounts in the blood and is also a constant product of the alcoholic fermentation of sugar (Pasteur, Compt. rend. 1858, **46,** 857; 47, 224); 100 parts of sugar yield about 3-5 parts of glycerol under the ordinary conditions of fermentation. Until the beginning of the century, such a source of glycerin was of no commercial interest, but later the increasing value of glycerin made it profitable to recover even this small proportion and various processes were devised to treat the *vinasses* from distilleries for this purpose.

For example, in Barbet's process (F.P. 449961 of 1912) the material is concentrated, mixed with calcined plaster and kieselguhr, and the glycerin distilled under reduced pressure, while caramelisation is prevented by the action of scrapers within the retort. In another process (B.P. 27300 of 1912) the *vinasses* are dried, treated with acid, and the glycerin extracted by means of solvents such as alcohol.

A great advance was made as a result of the investigations of C. Neuberg (*cf.* papers in Biochem. Z. 1913-21; Ber. 1919-20; Biochem. Z. 1929, **216,** 233) and of Connstein and Liidecke, who showed that the course of the fermentation of sugar could be modified and the production of glycerin (at the expense of alcohol) be greatly increased by conducting the fermentation in the presence of sodium sulphite in an alkaline medium (v. FERMENTATION, ALCOHOLIC, Vol. V, 23</, 24a6). These researches led to the development by Connstein and Liidecke (Ber. 1919, 52, 1385; J.S.C.1.1919, 287R) of a process for the industrial production of glycerin by the fermentation of beet sugar, which was worked by the Protol Gesellschaft in Germany and Austria during the war of 1914-18, some 1,000 tons per month of glycerin being manufactured by this method (*cf.* Connstein and Liidecke, and/or Vereinigte Chem. Werke, G.P. 298593-6, 343321, 347604, 486699, 514395; B.P. 138099, 138328-9, 138331; U.S.P. 1511754, 1698800). For the theory of the sulphite-modified and alkaline fermentation of sugar, *cf.* references quoted above; Tomoda, J. Chem. Ind. Japan, 1924, etc.; Proc. World's Eng. Congress, Tokyo, 1929; 1931, **31,** 500; FERMENTATION, ALCOHOLIC, *l.c.*

Still higher yields of glycerin, corresponding almost to the theoretical yield to be expected from Neuberg's second equation, are stated to be obtained when fermentation is performed in the presence of a mixture of neutral and acid sodium sulphites in such proportion as to be approximately neutral to litmus (Cocking and Lilly, B.L\ 164034/1919; Lilly and I.C.I., Ltd., B.P. 349192/1930; *cf.* K. and N. Liidecke, B.P. 278086/1926).

In the United States also, the processes of alkaline fermentation attracted attention to the possibility of fermenting blackstrap molasses: thus Eoff, Linder and Beyer (J. Ind. Eng. Chem. 1919, **11,** 842; U.S.P. 1288398/1918; B.P. 133374; F.P. 499824), using pure cultures of ***Saccharomyces ellipsoideus*** **var. Steinberg in an** alkaline mash, obtained a conversion of 20-25% of the sugar into glycerin as well as considerable production of alcohol. Further processes for the production of glycerin by the *alkaline* fermentation of crude sugar have been patented by E. I. Du Pont de Nemours & Co.; *v.* U.S.P. 1678150, 1725363, 1936497, 1990908; B.P. 316567, 316597.

Interest in the fermentation processes for the production of glycerin, which tends to lapse in normal peace-time in consequence of the plentiful supplies of cheap glycerin from fats, may be expected to revive in time of war, when a shortage of glycerin for the manufacture of explosives is experienced; and in fact, such processes have again been brought into use in Germany at the present time.

The manufacture of *synthetic glycerin* from propylene, which can be obtained from the unsaturated gases produced during the cracking of petroleum, may also become of commercial interest in times of shortage. A patent issued to Heinemann (U.S.P. 1180497; B.P. 12366/1913) claimed the conversion of propylene through the stages of dichloropropane and allyl chloride into trichloropropane, which was then hydrolysed to glycerol (*cf.* McElroy (Carbide and Carbon Chemicals Corp.), U.S.P. 1466665; E. C. Williams, Oil and Gas J. 1938, 37, 28). **The** conversion of propylene into glycerol may also be effected by making use of the chlorohydrin derivatives as intermediate steps (*cf.* McElroy (Chemical Development Co.), U.S.P. 1253615; Essex and Ward (Du Pont de Nemours & Co.). U.S.P. 1477113, 1594608).

The various stages in the process recently worked out on the technical scale by the Stall Development Co. have been outlined by E. C. Williams (Chem. Met. Eng., **1940, 47, 834).**

Propylene is chlorinated directly at a temperature of 500°C. (the so-called " hot chlorination process," *cf.* Groll and Hearne, Ind. Eng. Chem. 1939,31,1530) to yield allyl chloride, from which the synthesis of glycerol may proceed by either of two routes. Thus allyl chloride may be treated with caustic soda at a controlled *pH* of 8-11 to convert it into allyl alcohol: this reacts with aqueous hypochlorous acid to form glycerol mono- and di-chlorohydrins, which in turn are hydrolysed by a solution containing 10% of caustic soda and 1% of sodium carbonate to yield glycerin. The alternative method (which appears to be preferable for large scale production) is to chlorohydrinate the allyl chloride directly, by treating it with a solution of hypochlorous acid and sodium chloride (prepared by the action of chlorine on caustic soda solution) so as to obtain glycerol dichlorohydrin (in 90-95% yield), which is then hydrolysed to glycerin by the aid of caustic soda or caustic soda and lime. The crude glycerin synthesised by such methods is concentrated and distilled: by taking appropriate cuts during the distillation, and refining them by extracting coloured impurities with xylene *(v.* Shell Development Co., U.S.P. 2154930) and redistilling, a glycerin meeting all commercial specifications may be recovered in high yield.

Laboratory preparations of glycerol from propylene (itself synthesised from acetylene) *via* tribromopropane or trichloropropane have been described by Berthelot *(l.c.)* and Wurtz *(l.c.).* Allyl alcohol may be oxidised to glycerol by means of potassium permanganate (Wagner, Ber. 1888, 21, 3347, 3351), or by potassium chlorate in the presence of osmium tetroxide as catalyst (Hofmann, Ehrhart and Schneider, *ibid.* 1913, 46, 1657, 1007).

Glycerol may likewise be prepared from propane, which itself may be recovered from petroleum.

Crude glycerin is obtained on the large scale from fats and oils as a by-product of soap-making and of the various saponification processes (fat-hydrolysis) practised in soap and candle works for the manufacture of fatty acids. According to the process by which the fat is hydrolysed, the following five commercial qualities of glycerin have been distinguished hitherto, viz: (1) *Soap-Lye Glycerin,* or *Soap Crude Glycerin;* (2) *Saponification Crude Glycerin ;* (3) *Twitchell Crude Glycerin*; (4) *Crude Distillation Glycerin;* and (5) *Fermentation Crude Glycerin (N.B.* this refers to the glycerin obtained by hydrolysing fats by the help of enzymes or ferments, and not to glycerin obtained from the fermentation of sugars). In view of potential developments discussed above, crude glycerin derived from the fermentation of sugar and, perhaps, also synthetic crude glycerin should be added to complete the list of crude glycerins from all sources. Typical analyses of some crude glycerins are shown in Table I.

In the soap and stearine industries, the by-product glycerin is obtained as a dilute aqueous solution (soap lyes or " sweet waters "), containing various impurities, viz., salts, inorganic and/or organic acids and other organic substances—the nature and quantity of which depend upon the manufacturing processes themselves—and which must be removed as far as possible before the liquors can be concentrated by evaporation to obtain commercial crude glycerin. The method employed depends naturally upon the type of impurity to be eliminated.

The organic contaminants, which although small in quantity may cause considerable difficulties in the processing, may arise from the use of low-grade, impure or deteriorated fats for saponification. The purest raw material results from saponification by means of lime in open vessels; hardly inferior to this is the glycerin obtained by " autoclaving." Less pure is the raw material recovered from the " acid saponification process," " Twitchell's process," and the " ferment process." The crude glycerin obtained from soap lyes, notwithstanding its high proportion of inorganic salts, may, on the one hand, surpass in purity (i.e. as regards the amount of organic impurities) the crude material from the last-named processes; but, on the other hand, it may be very impure if fats and oils of low quality have been saponified by means of black-ash lyes, as was done until some years ago in Lancashire and in Marseilles. Modern processes of refining have, however, overcome a number of difficulties caused by the several impurities, so that to-day a chemically pure glycerol from good soap lyes cannot be distinguished from chemically pure glycerol obtained by lime saponification. Crude glycerins further vary as regards quality in accordance with the care exercised in the manufacture. Crude glycerins obtained from the acid saponification, the Twitchell and the ferment processes, retain tenaciously certain impurities and are therefore rather more difficult to purify.

(1) Soap-Lye Glycerin, Soap Crude Glycerin, Soap Crude.—Since Chevreul established the constitution of fats and oils, it has been known that the spent soap lyes, obtained in the manufacture of soap by boiling oils and fats in an open pan with caustic soda, contain practically all the glycerol which the natural oils and fats are capable of yielding. During the first half of last century, however, no attempt was made to recover the glycerol from those lyes, not only on account of the difficulty attending this operation, but also for the reason that the small demand for glycerin then ruling in the market could be readily satisfied by the candle makers' crude glycerin. When, at the end of the 'seventies of the last century, a great demand for nitroglycerin *(dynamite)* sprang up, attention was drawn to this source of glycerin, and serious endeavours were made to recover the hitherto wasted product. Although as early as 1858, H. Reynolds had patented (B.P. 1322) the main features of a process of recovery, features which essentially reappeared in all subsequent processes, yet serious failure at first attended all attempts at the recovery of glycerin, on account of the considerable amount of impurities in the spent lyes, and most prominently on account of the large amount of dissolved salts. The first process to achieve successful technical production of crude glycerin from soap lyes was

patented in 1879 by Thomas, Fuller and King (B.P. 1282). Modern processes, especially improvements in apparatus on the one hand, and the rapidly growing employment in the soap industry of caustic soda of the highest purity, tended to evolve a process which is now worked with more or less success in all the large soap works, not only of Europe and America, but also of Australia, Africa, India and New Zealand. The earliest successful attempts to recover glycerin from soap lyes were made in English soap works, which were the largest soaperies of the world; this process may be said to have established its success in Great Britain towards the middle of the 'eighties of the last century. Since that time, crude glycerin recovered from soap lyes, " soap crude glycerin," has established its great importance in the world's commerce.

According to the manner in which the soap is processed, the spent lyes contain from 6 to 8% of glycerol, also the common salt used in " cutting " or " graining " (*i.e.* salting-out) the soap, and small amounts of free caustic soda, sodium carbonate, soap and organic impurities. The smaller the amount of free caustic soda, sodium carbonate and organic impurities present, the more readily can the process of recovery and purification be carried out. In cases where impure caustic soda lyes have been used, the spent soap lyes may contain, in addition to the substances enumerated above, thiocyanates, sulphides, thiosulphates, cyanides, and ferro-cyanides. These impurities were present in the crude (black-ash) lyes which were at one time used in the Marseilles district. The difficulties caused thereby in the recovery of crude glycerin, coupled with the establishment of Solvay's soda works in that neighbourhood, led to the almost complete abandonment of black-ash lyes, so that even in Marseilles the vast majority of soaps are now prepared with pure caustic lyes. The exact treatment of the lyes in a soap works depends on the state of purity of these lyes, and has, as its object, the removal or destruction of the soapy, resinous, albuminous and mineral impurities present, so that the final dilute glycerin liquors passing to the evaporators shall contain practically no impurity other than common salt.

This is achieved by first separating any undecomposed fat, then very carefully acidifying with hydrochloric acid to decompose traces of soap, and adding ferric chloride (or less commonly aluminium sulphate) until no further precipitation takes place. (Formerly iron sulphate was much used, *cf.* Van Ruymbeke, U.S.P. 458647; G.P. 86563). The liquor is then filter-pressed, made alkaline to precipitate any excess of iron and again filter-pressed. Other methods (*cf.* Schlenker, Chem. Umschau, 1932, 39, 28) involving the use barium carbonate and other salts have been proposed but are not much used on the large scale.

If " chemically pure" glycerin is subsequently to be prepared from the crude product, attention must be paid to the elimination of arsenic compounds, and arsenic-free reagents should be employed for the purification of the lyes. A. C. Langmuir (Ind. Eng. Chem. 1932, 24, 378) states that simple treatment with crude ferric sulphate and filtration is sufficient to remove arsenic from spent lyes. The removal of arsenic from concentrated glycerin solutions is more troublesome (*v. infra,* " C.P. Glycerin ").

The chief difficulty attending the concentration of the purified soap lyes arises from the high content of common salt; for, unless special arrangements are made, the salt is liable to crystallise out as a deposit on the walls and in the tubes of the evaporator, reducing its working efficiency and necessitating frequent stoppages for cleaning.

In the early days of the industry, the concentration of the purified glycerin liquors was carried out in fire- or steam-heated open pans of conical shape, so that the salt, as it crystallised, could slide down into a vessel fixed to the bottom of the pan, whilst rotating gear kept the heating surface free from incrustation. In the case of large and modern installations, the lyes are evaporated, usually under reduced pressure, with the help of steam in single- or multiple-effect closed evaporators of special design. The *Foster double-effect* evaporator, illustrated in Fig. 1 (*cf.* Foster, B.P. 3118/1895, 23681/1899, 26830/1902), which is most commonly used in England, is a typical example of such apparatus. The glycerin liquors are heated as they circulate from the conical bottom of the evaporator up through a number of narrow tubes located in the calandria or steam-chest into the vapour zone or evaporation space proper, where some of the water volatilises: thence the liquors return for recirculation to the bottom of the vessel through the wide downcomer which is a notable feature of all such evaporators, and facilitates the rapid circulation of the lyes. Various other patented evaporators—such as the *Scott* and the American *Wurster-Sanger, Oarrigue* and *Buflovak* evaporators—differ in details of construction,[1] but embody similar principles, the object of the design being to achieve a rapid, positive circulation of the lyes without churning, so that a high rate of heat transfer and evaporation is attained, and the separating salt crystals are able to grow freely and to settle down on the bottom of the evaporator, whence they are withdrawn continuously or intermittently by suitable salt-extractors or salt-drums, without breaking the vacuum in the evaporator.

In the *Blair, Campbell and McLean* system, the lyes are heated under pressure (so that no salts are deposited in the tubes), and the actual evaporation is produced by " flash " effect in a separate vessel remote from the source of heat.

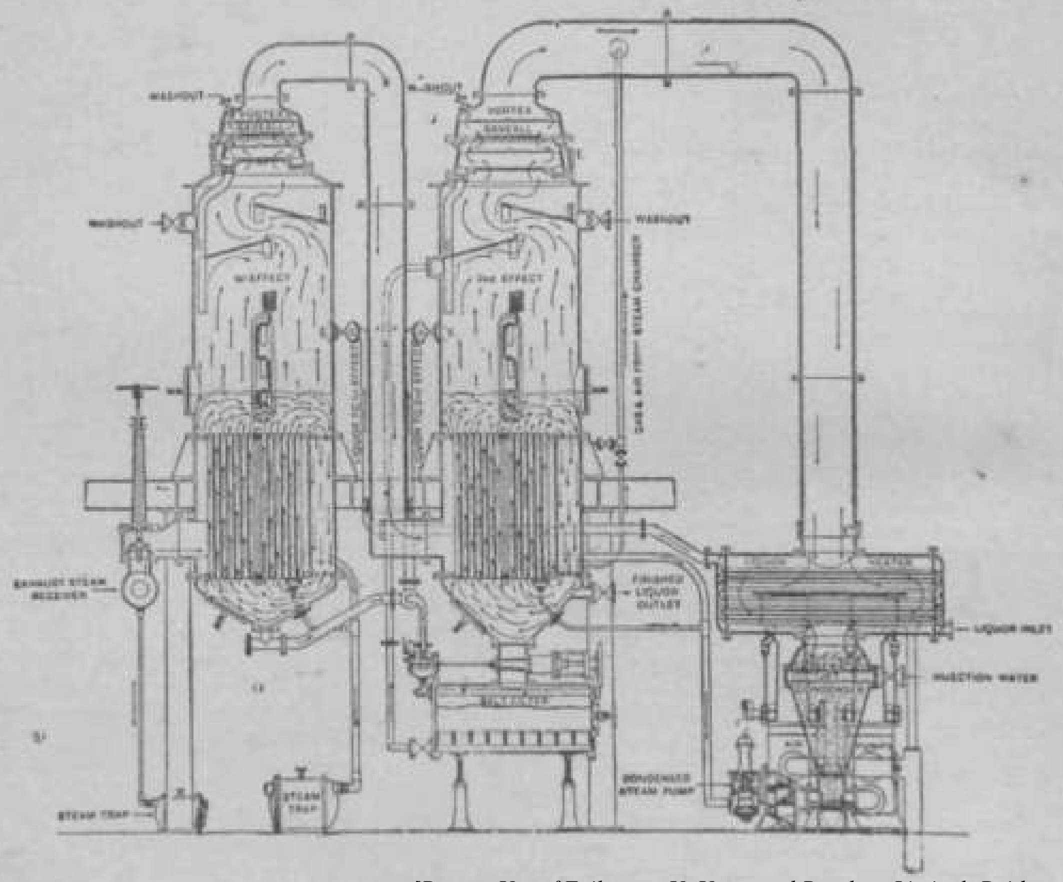
The well-known *Kestner climbing-film* evaporator has also been adapted for concentrating glycerin by the provision of a salt-separating vessel through which the liquors flow after each passage up the tubes of the evaporator (*v.* EVAPORATION, Vol. IV, p. 4106); as a rule, two or four evaporating units are coupled with one salt-separating vessel.

[1] The various English and American evaporators are illustrated, and their operation described in some detail by E. T. Webb, " Soap and Glycerine Manufacture," London, 1927; G. Martin, " Modern Soaps and Detergents Industry," Vol. III, London, 1925; and by J. W. Lawrie, " Glycerol and the Glycols." New York, [illegible].

The collected salt sludge is ultimntely filter-pressed or centrifuged, nnd washed with purified dilute glycerin lyes in order to recover any entrained glycerin. The salt itself is recovered in a sufficient state of purity to be returned to the soapery.

The **glycerin** solutions are concentrated until the crude glycerin has reached a ap-gr. of 1-3. The progress of concentration is controlled by the ep.gr. test, or, equally well, by taking out samples and ascertaining the boiling-point in a porcelain dish, by meant; of a thermometer, **while** the contents of the dish are kept stirred, so that the salt may not cause bumping of the contents or cracking of the dish. The **glycerin** has reached the sp.gr. of 1-3 and the percentage required by commerce, if the boiling,) point is 150°. The crude glycerin than contains 80% of purt glycerol, and about 10% of salts, the remainder consisting of water and a small amount of organic impurities. If the concentration is carried a little further, crujle glycerin, containing as much as 86% of glycerol, can readily be obtained.

The proportion^ of organic impurities in soap lye glycerin varies considerably, depending on the piicess of purification and the care of the operator. Some commercial " soap crude " glycerins contain less than 1% of organic impurities (thus representing a better quality glycerin than " crude distillation glycerin,' crude glyceri'i from, the "Twitchell process," and crude glyccrin from the " fermentation process "). Other specimens of crude glycerin, again, contain large quantities of impurities, consisting of fatty acids, rosin acids, and of albuminoid **Buhrtanoes,** gelatin and hydrocarbons (from bone fat), and also trimcthylenegtyeol in the lyes resulting from bone fat which have been allow*.I **to ferment** Given organic bases, amongst which picoline and lutidine mere identified, have **been** found in the distillates from such impure glycerins (Lewkowhsch. " Oils, Fats ind Waxes," 6th ed., '923, Vol. I1l, 383.



[By eourUtu of Fuilerton, UoUoart and Barclay, Limited, Paitley.

Flo. 1.—Section of Foster's patent Evaporators *

The colour of " soap crude glycerin " is pale-yellow to brown, or almost black, according to its **purity.** The taste of good " soap crude " is* sweet',, modified, of course, by that of the com* won salt contained therein. Impure samples have a most unpleasant garlic-Kkc taste, even if sulphides be ab»ent. This is speci?lly characteristic of the lyes **obtained is** the Marseilles district, owing to the use of " aulphur " olive oil.

Soap-lye glycerin can be rapidly distinguished from the crude glycerins described below by the largo proportion of common salt **which** it" conlams (heavy precipitate with silver nitrate solution) and by itaiugh Bpecifiv gravity.

Crude soap-lyo glycerin, if containing considerable quantities of sulphide*, tbiosuluhutes or sulphites, is almost **nCoelea to the *x&ner*** of crude **glycerin.**

TabJo I illustrates the composition of **recent** soap-lye and saponification crude **glycerina.**

TABLE I.

SOAP-LYE CRUDE GLYCERIN.

	1.	2.	3.	4.	5.
Sp.gr. at 15-5°	1-3016	1-2994	1-2971	1-3002	1-3073
Total acetyl value	83-38	81*66	82-72	84-91	87-24
Acetyl value of residue	—	066	051	2-39	1-01
Net glycerol	—	8100	82-21	82-52	8(l-23
Ash	9-45	9-40	9-25	9-51	8*88
Organic residue	1-66	2-97	1-25	316	1-2U
Water	5-79	5-50	7-01	4-90	324
	100-1S[1]	98-87	99·72	100-09	99-64

SIGNIFICATION CfiODE GLYCERIN.

	1.	2.	3.	4	G.
Sp.gr. at 15-5°	1-2517	1-2447	1-2546	1-2S79	1-2472
Total acetyl value	90-18	88-67	86-06	81-85	00-88
Acetyl value of residue	0-20	—	0-73	0-31	—
Net glycerol	89-98	—	85-33	91-54	—
Ash	0-97	,d-83	2-47	1-39	0-47
Organic residue	1-36	0-48	2-72	113	0-33
Water	7-55	1(MW	9-24	G-S2	8-34
	99·86[1]	99-93	99-78	B9-88	10.) 1)2

[1] When the organic residue of soap crude glycerin is less than 2-5% it is customary in the trade not to determine the acetyl value of the residue. In such cases the sum of total acetyl value, ash, organic residue and water will usually be a little over 100. When the acetyl value of the residue is determined and deducted so as to arrive at net glycerol the sum will usually be a little "ras than 100. In the ca» of saponifloatlou crude glycerin the acetyl value of a residue less than 1 % is not usually determined (*set* p. 826).

(2) Saponification Crude Glycerin.—This product represents the best quality of crude glycerin. It is recovered from the " sweet waters " of the autoclave process (a process in **which** fats are hydrolysed with water at **high** temperatures and pressures in the presence of small quantities of lime, magnesia or zinc oxide as catalyst) or as a by-product from the manufacture of soap by double **decomposition.** (In this method the fats are completely converted **bate** calcium soaps by treatment with excess of lime and water, and subsequently converted into sodium or potassium **soaps** by double decomposition with appropriate alkali salts": the glycerin liquors aro washed out of the lime soaps at the end of the first step in the process.)

Thi proportion of glycerin in the " sweet waters " varies from about 0 to 16%. The refining of these liquors is comparatively simple, and some of the operations necessary for the treatment of soap lyes may be omitted. Preliminary purification may be effected by partial concentration over closed steam coils assisted by skimming. The liquors are then acidified with sulphuric acid, in order to decompose metallic hydroxides and soaps, and after filtering off any separated fatty acids, the solution is neutralised with lime and concentrated in single- or multiple-effect evaporators: since the purified autoclave "sweet waters " contain relatively little dissolved salts, the provision of special salt-extractors, etc., such as are required in dealing with soap crudes, is superfluous.

The evaporation is carried on until the crude glycerin contains abo^t 85-00% of glycerol. Its sp.gr. is then from 1-240 upwards, corresponding with the commercial brand of " P8°Be. saponification crude " or " candle crude glycerin." The colour of this glycerin varies from yellow to dark-brown; its taste is sweet. With **b&no load** acetate, it gives but a slight precipitate. *By* refining this crude glycerin with charcoal, a " refined" glycerin (used for a number of commercial purposes) is obtained. This crude glycerin contains up to 0-3% of **ash,** chiefly calcium (or magnesium or zinc) sulphate, and only small quantities of organic impurities. It is valued on the percentage of pure glycerol, of **ash** and of organic impurities.

Tho " sweet water " obtained in the process of soap making by double decomposition is treated in the same manner es described above, and yields a good " saponification crude," which is equal in quality to a " candle crude glycerin," **provided that** the original fatty matter was of good quality. Since this process is used in mmifi works only, where achierly low-quality greases are worked up, ^the crude glycerin thus obtained may lmvo ,i vi-ry high ash content and ia apt to contain a considerable amount of organic impurities, so that it is liable to ferment when stored. (The experience of Lewkowitsch that such crude glycerins did ferment shows that the organic impurities in low-class grease are not destroyed by treatment with lime.) In the course of the fermentation, trimethyleneglycol is formed.

(3) **Crude Glycerin from the Twitchell and Analogous Processes.**—This kind of crude glycerin is obtained from the acid " sweet waters " resulting from the Twitchell process of fat-splitting, which consists in treating the fat with water containing a little sulphuric acid in the presence of a complex organic sulphonate as catalyst. The acid liquors are treated with baryta or barium carbonate or lime to precipitate as far as possible the dissolved sulphuric acid, after which the purification and concentration proceed as described under " saponification crude glycerin." Any dissolved calcium sulphate may be removed by precipitation with barium hydroxide or carbonate, in order to avoid complications during the evaporation. The purified liquors are concentrated up to a sp.gr. of about 1·24 or more. The quality of this crude glycerin varies considerably with the quality of the fatty material from which it has been obtained. If the raw material is of good quality, the glycerin is fairly good; but even in that case, owing to the high amount of ash it contains, and owing to its unpleasant taste, it is valued at a somewhat lower price than is crude candle glycerin. Since the Twitchell saponification process is best adapted to low-class material (such as greases), the glycerin obtained from such material contains so considerable an amount of organic impurities that it cannot be refined by itself, even for the production of dynamite glycerin. Each special make of such glycerin must therefore be valued on the basis of the impurities it contains.

(4) **Crude Distillation Glycerin.**—This kind of crude glycerin is obtained from the acid water resulting from the so-called acid saponification processes in which fats are hydrolysed with the help of sulphuric acid. It is termed in commerce " crude distillation glycerin " for the reason that the fatty acids obtained by this process must be distilled to yield candle material. The dilute glycerin waters (" sweet waters ") are worked up in much the same manner as described under " Twitchell glycerin." Owing to the large amount of sulphuric acid used in the process, a considerable quantity of salts remain in solution after the mineral acid has been neutralised with lime. As the concentration of the solution proceeds, especially when the thickened liquor approaches the sp.gr. of 1·240, calcium sulphate separates out and is deposited on the heating surface of the evaporating apparatus in the form of a hard crust, thereby rapidly diminishing the evaporative power of the steam. This difficulty is obviated by employing a type of evaporator which permits the heating surface to be continuously scraped.

The finished crude distillation glycerin contains considerable proportions of calcium sulphate, inasmuch as the solubility of calcium sulphate in glycerin (*see below*) is increased by the organic impurities which are also present. The ash of this kind of crude glycerin rises to as much as 2 and even 3·5%. The amount of organic impurities is greater than in crude saponification glycerin, and may rise to even 2%, the colour is usually pale-yellow, the taste sharp and astringent, and when rubbed between the hands it emits an unpleasant odour. On adding basic lead acetate, a voluminous precipitate is obtained; hydrochloric acid produces a turbidity, due to the presence of fatty acids.

The trade term for this kind of glycerin is "crude distillation glycerin, 28°Bé," it has sp.gr. 1·240-1·242, and as a rule contains from 84 to 86% of glycerol.

(5) **Fermentation Crude Glycerin.**—The " sweet water " from the hydrolysis of fats by means of enzymes is rich in proteins and other organic impurities. In addition to the usual treatment described above, it must be filtered over char, which retains the bulk of these impurities. Nevertheless, a certain amount is still retained and the finished crude is not only dark in colour, but has also a very unpleasant odour and taste, even if the glycerin be made from good raw material, such as refined cotton-seed oil or refined linseed oil, and in the infancy of the process this crude glycerin was practically unusable. In consequence of improvements, the amount of impurities has been considerably reduced and a sample examined by J. Lewkowitsch (*op. cit.* III, 379) gave the following somewhat favourable results: sp.gr. 1·2369; ash, 0·49%; organic impurities (proteins, etc.), 1·54%. But the difficulties have not yet been surmounted, and the process is still but little used. This product, like the Twitchell crude glycerin, is difficult to refine by the usual process of distillation and must be mixed in the still with better kinds of crude glycerin.

(6) **Crude Glycerin from the Fermentation of Sugars.**—The purification of the relatively dilute glycerin liquors obtained from the fermentation process presents special problems on account of the quantity and variety of the associated contaminants. After filtering the fermented mash to remove the yeast, the cleared glycerin slop may contain only from 2 to 7% of glycerol together with a wide variety of organic products of the fermentation, alkaline salts, sulphites and other inorganic salts which were originally added as nutrients for the yeast. Alcohol, aldehydes and other volatile impurities may be removed by distillation. According to Verbeek's description of the process used by the Protol Co. in Germany (Seifens.-Ztg. 1921, 47, 591, 633), this distillation was continued until the liquors reached the point of incipient crystallisation of the contained salts; the concentrated solution (containing some 14-18% of glycerol) was settled, filtered and treated with calcium chloride and calcium hydroxide to precipitate the bulk of the salts present. These were removed by filtration, and the iron and calcium salts in the filtrate were precipitated by the addition of sodium carbonate in the presence of a little solid ferrous sulphate (the calcium salts might also be precipitated as insoluble oxalate, cf. Vereinigte Chem. Werke, Altenburg and Menz, (J.l\ 403077), and the filtered solution was acidified with hydrochloric acid prior to the final evaporation to " crude glycerin." Even the best crudes obtained,

however, 'did not contain more than 60% of glycerol, and wen heavily contaminated with sulphites, thiosulphates and trimethylene glycol, etc. Kellner (Z. deut. Oel- u. Fett-Ind., 1920,40, 677) states that it was found impossible to prepare a pharmaceutical quality of glycerin from these crudes.

Improved methods for the purification and recovery of dynamite glycerin "from fermented blackstrap molasses have been patented by Du Pont de Nemours & Co., U.S.P. 162*986, 1627040, 1881718, 1936497; B.P. 316567, 316597, 410782, etc.; Bafbet et Fils & Cie., B.P. 168835, and eroded containing 75% of glycerin have been produced. These are, however, dark in colour and contain a considerable amount of organic impunities which tend to cause excessive foaming and other difficulties in the subsequent distillation.

(Methods for the analysis of sugar fermentation crude glycerins worked out by Cocking and Lilly, Fachini. Lawrie and others are described by J. W. Lawrie, " Glycerol and the Glycols*" London and New York, 1928, pp. 139-151).

Considerable quantities of crude glycerin, especially crude saponification glycerin, are used in the arts for various purposes *{see below).* By far the largest quantities of crude glycerin are, however, purified by distillation, and thereby converted into *distilled glycerin.* In commerce, two kinds of distilled glycerin are differentiated, *i.e.* distilled glycerin for making nitroglycerin (dynamite), *dynamite glycerin,* and *chemically pure (C.P.) glycerin,* sometimes termed *double-distilled glycerin.*

Distilled Glycerins.—The distillation is most commonly carried out in a vacuum. In the early days of the industry, fire-heated stills were employed which remained in use to some extent even after the introduction of steam as a carrier vapour *{cf.* Wilson and Payne, B.P. 1624/1854) and the development of processes for steam-distillation *in vacuo (cf.* O'Farrcll, B.P. 3284/1881; Clark, B.P. 534£/1881). Some manufacturers work off a certain amount (depending on the size of the still) of crude glycerin in one batch. Other manufacturers resort to continuous distillation, the still being fed as the glycerin distils off.

The successful distillation of crude glycerin depend largely on the skill and care of the operator, and although a considerable number of special apparatus have been patented,'and are still being patented, the success depends more on attention to details than on the particular apparatus employed, and the details of the *modus operandi* in conducting the distillation are considered valuable secrets.

In the *Van liuymbele* still (U.S.P. 458647-8, 1891; B.P. 24556/1893; G.P. 86829/1896) the steam is simultaneously expanded and superheated by passing through the coil of a preheater, before injection into the glycerin, which itself has been previously heated by means of a closed steam-coil. The superheating coil is heated by boiler steam. The working of the Van RuynTbcke still, which is employed extensively both in England and on the Continent, and is capable of yielding a very high grade glycerin, is described in detail by Webb " Modern Soap and Glycerine Manufacture," London, 1927. Hot-water or air-cooled jacketed condensers are employed for the first fractions, and water-cooled condensers for the least condensable " sweet waters."

The condensates from the last few air condensers require to be concentrated subsequently by evaporation to bring them to the requisite strength. Similarly, the last condensed " sweet waters " may be concentrated, if they contain sufficient glycerin to justify the treatment.

Similar principles are involved in the *Scott,* and the *Blair, Camj&ell and McLean* processes.

Considerable economy in steam consumption is effected by the so-called " closed systems," favoured in the United States. In the American *Wood* plant the stills are arranged in series; the vapours from the first still are only cooled to such an extent that the strongest glycerin liquors are condensed, whilst the steam passes on through the nest unit, and so on, until, at the end of the series, the vapours are taken through a water-cooled condenser to the sweet-water collector.

The steam obtained from the evaporation of the very dilute glycerin distillates (" sweet waters.") is used as the heating fluid for the evaporator, which in turn supplies the steam to be injected into the glycerin still *(cf. also* the *Wurster-Sanger* and *Garrigue* systems, which are described fully by J. W. Lawrfc, "Glycerol and the Glycols," London and New York, 1928).

The economy of this system is offset by the inherent disadvantage, that volatile impurities present in the sweet-water condensate are returned to the evaporator, and so recirculated throughout the whole system. The quality of the glycerin obtained by this method is no better, and may be lower, than that prepared by the *Van Ruymbeke* process.

One distillation of crude glycerin, especially in the case of soap-lye glycerin, may not give a satisfactory product for nitrating purposes, owing to contamination with sodium chloride and organic impurities (volatile fatty acids and even polyglycerols), and a second distillation becomes imperative.

The yield obtainable from crude glycerin depends, just like the distillation itself, on the care of the operator. The losses incurred by faulty methods are large, and may range from as much as 15 to even 40%. A large proportion of the loss is due to destruction of glycerol with the formation of volatile acids and acrolein on the one hand, and to the formation of polyglycerols on the other. The polyglycerols which are formed in the course of distillation should remain in the still itself, and are found with the still residue *(see below).*

The distilled glycerin liquors collected from the columns are treated with char, if required, to remove some organic impurities, and, at the same time, to clarify the glycerin and improve its colour. The collected and filtered glycerin liquors are finally concentrated in a vacuum evaporator, up to the desired specific gravity.

The commercial " distilled glycerins " vary in colour from yellow to white; they also vary in their content of glycerol according to their specific gravities, which range, as a rule, between

1-220 and 1-260. Glycerin, purified by distillation, should contain only a very small amount of ash and is thereby easily distinguished from crude glycerins.

For the grade known as dynamite glycerin, the specific gravity must be at least 1-261 at 15°. Other commercial qualities of distilled glycerin need only be concentrated to a sp.gr. of 1-250 or 1·240.

The *distilled glycerins* described above contain, as a rule, amounts of impurities, which although small, are yet sufficiently large to prohibit their employment for pharmaceutical and dietetic purposes. The " distilled glycerins " must therefore be subjected to a second distillation. If this distillation be carried out with sufficient care, the distillates give, after concentration and treatment with char, the *chemically pure* (C.P.) *glycerin* of commerce.

At a time when the art of preparing chemically pure glycerin was not so far advanced as it is at present, some chemically pure glycerin was manufactured by allowing glycerin to crystallise, and centrifuging the crystals, whereby the impurities were removed with that portion of glycerin which melted in the centrifugal machine: This process has, however, been abandoned, not only on account of its costliness, but also on account of the inferiority of the product as compared with the best brands of chemically pure glycerin obtained by careful distillation, since it was found that the crystals were apt to occlude impurities.

As stated above, C.P. glycerin for edible purposes must be virtually free from arsenic *(cf. below).* Such glycerin is most convenien prepared by the distillation of arsenic-free crudes. A. C. Langmuir (Ind. Eng. Chem. 1932, 24, 378) states, however, that arsenic compounds may be effectively removed from 20-25% distilled glycerin by agitating the hot glycerin with powdered cast-iron borings by means of an air-jet. In the case of more concentrated distilled glycerin, this may be freed from arsenic by treating it with 0-05-0-1% (calc. on the anhyd. glycerol present) of potassium permanganate which has been previously dissolved in sufficient water[1] to reduce the concentration of the glycerin to 65%; the mixture is heated to 90-5°C, made alkaline with 0-3% caustic soda and filter-pressed. The excess of alkali serves to hold back volatile fatty acids during the subsequent distillation."

Electro-osmotic processes of decolorising and purifying glycerin have been patented (B.P. 144727, 145946, 146865, of 1920).

Chemically pure glycerin is obtainable in commerce in the following " strengths " : sp.gr 1-24, 1-25 and 1-26. That of the highest specific gravity approaches, as nearly as is possible for a product made on a large scale, the chemical substance glycerol.

Glycerol (pure glycerin) is a hygroscopic, odourless, colourless, highly viscid liquid, having a sweet taste. The preparation demanded by the Pharmacopoeias of different countries is the purest commercial article, which consists practically of glycerol containing a very small amount of water. Glycerol is optically inactive, and is neutral to litmus. On exposure to intense cold for a prolonged time it crystallises in rhombic bisphenoid forms *(see* Lang, Poggendorff's Ann. Phys. Chem. 1874, 152, 637; *cf.* Henninger, Bull. Soc. chim. 1875, [ii], 23, 434). By seeding with a few crystals, large quantities of glycerol can easily be solidified at a temperature even above the freezing-point of water. The freezing-points of aqueous glycerol solution are shown in Table XV (p. 64).

The crystals have m.p. *18°C.* (Sampsoen, Compt. rend. 1926, 182, 846; *cf.* Gibson and Giauque, J. Amer. Chem. Soc. 1923, 45, 93; confirmed by Pushin and Glagoleva, J.C.S. 1922, 121, 2818). The latter authors find glycerol to have a cryoscopic constant of approximately 3-1.

Glycerol is oily to the touch, and produces on (specially on the mucous membrane, the sensation of heat, owing to its absorbing moisture from the tissues. The water-absorbing power of glycerol is so great that, on exposure to the atmosphere, it takes up as much as 50% of its weight of water.

The determination of the *specific gravity* of pure glycerol has been attempted by many workers (Kailan, Gerlach, Skalweit, Lenz, Strohmer and others), whose results show considerable disagreement, which is due, no doubt, to the difficulty of removing the last traces of water. The values of 1-26414 at 15°/4° found by Kailan (Z. anal. Chem. 1912, 51, 81) and 1-26533 at 15-5°/15-5° by A. C. Langmuir (Ind. Eng. Chem. 1921, 13, 944), are in good agreement with those recorded by other chemists and with the figures published by Bosart and Snoddy *(ibid,* 1927, 19, 506; 1928, 20, 1377) and reproduced below (Table II).

TABLE II.—SPECIFIC GRAVITY AND DENSITY OF PURE GLYCEROL (Bosart and Snoddy).

Specific gravity at . .	15°/15°.	15-5715-5°.	20°/20°.	26725°.
Apparent sp.gr. (in air) . .	1-26557	1-26532	1-26362	1-26201
True sp.gr. (weighings reduced to vacuum) . . .	1-2652*	1-26501	1·26331	1-26170
Absolute density* . . .	1-26415/15°	1-26381/15-5°	1-2(1108/20°	1-25802/25°

1 *l.e.*-sp.gr. related to water at maximum density, all weighings being reduced to vacuum.

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[1] *Warning:* If concentrated glycerol comes into contact with *dry* potassium permanganate, even in the cold, the mixture ignites spontaneously with the production of an intensely hot flame and red-hot residue (Langmuir, *l.c.; see* p. 66).

Values for the specific gravity of aqueous glycerol solutions at 15°/15° and 20°/20° determined by Bosart and Snoddy are shown in Table III; full tables showing apparent sp.gr. at 15·5°/15·5° and 25°/25°, true specific gravities (*in vacuo*), absolute densities and coefficients of **expansion** of glycerol solutions are given in the original papers.

The figures of Bosart and Snoddy were obtained as the result of a most careful and exhaustive investigation, and must be regarded as the most trustworthy data at present available. They agree closely with results obtained in the Eastern Laboratory of the E. I. Du Pont de Nemours Co. from which Table IV has been constructed.

TABLE III.—SPECIFIC GRAVITY OF GLYCEROL SOLUTIONS (Bosart and Snoddy).

Glycerol % by weight.	Apparent specific gravity[1] (in air).		Glycerol % by weight.	Apparent specific gravity[1] (in air).	
	15°/15°	20°/20°		15°/15°	20°/20°
100	1·26557	1·26302	50	1·12985	1·12840
99	1·26300	1·26105	49	1·12710	1·12570
98	1·26045	1·25845	48	1·12440	1·12300
97	1·25785	1·25585	47	1·12165	1·12030
96	1·25525	1·25330	46	1·11890	1·11760
95	1·25270	1·25075	45	1·11620	1·11490
94	1·25005	1·24810	44	1·11345	1·11220
93	1·24740	1·24545	43	1·11075	1·10950
92	1·24475	1·24280	42	1·10800	1·10680
91	1·24210	1·24020	41	1·10525	1·10410
90	1·23950	1·23755	40	1·10255	1·10135
89	1·23680	1·23490	39	1·09985	1·09870
88	1·23415	1·23220	38	1·09715	1·09605
87	1·23130	1·22003	37	1·09445	1·09335
86	1·22885	1·22690	36	1·09175	1·09070
85	1·22620	1·22420	35	1·08905	1·08805
84	1·22355	1·22155	34	1·08635	1·08535
83	1·22090	1·21890	33	1·08335	1·08270
82	1·21820	1·21620	32	1·08100	1·08005
81	1·21555	1·21355	31	1·07830	1·07735
80	1·41290	1·21090	30	1·07560	1·07470
79	1·21015	1·20816	29	1·07295	1·07210
78	1·20740	1·20540	28	1·07035	1·06950
77	1·20465	1·20270	27	1·06770	1·06690
76	1·20190	1·19995	26	1·06510	1·06435
75	1·19915	1·19720	25	1·06250	1·06175
74	1·19640	1·19450	24	1·05985	1·05915
73	1·19365	1·19175	23	1·05725	1·05655
72	1·19090	1·18900	22	1·05460	1·0540[illegible]
71	1·18815	1·18630	21	1·05200	1·05140
70	1·18540	1·18355	20	1·04935	1·04880
69	1·18260	1·18080	19	1·04685	1·04630
68	1·17985	1·17805	18	1·04435	1·04380
67	1·17705	1·17530	17	1·04180	1·04135
66	1·17430	1·17255	16	1·03930	1·03885
65	1·17155	1·16980	15	1·03675	1·03635
64	1·16875	1·16705	14	1·03425	1·03390
63	1·16600	1·16430	13	1·03175	1·03140
62	1·16320	1·16155	12	1·02920	1·02890
61	1·16045	1·15875	11	1·02670	1·02640
60	1·15770	1·15605	10	1·02415	1·02395
59	1·16490	1·15325	9	1·02175	1·02155
58	1·15210	1·15050	8	1·01935	1·01915
57	1·14935	1·14776	7	1·01690	1·01675
56	1·14655	1·14500	6	1·01450	1·01435
55	1·14375	1·14220	5	1·01210	1·01196
54	1·14100	1·13945	4	1·00965	1·00955
53	1·13820	1·13670	3	1·00725	1·00720
52	1·13540	1·13395	2	1·00485	1·00480
51	1·13265	1·13120	1	1·00240	1·00240

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[1] Accurate to the nearest 5 in the 5th place.

TABLE IV.—W/W PEB CENT. GLYCEBOL CcteKitsroNDijro TO SPECIFIC GRAVITY AT 15·6°/15·6° C.[1]

Sp. gr.	P.	1.	2.	3.	4.	' 5.	6.	7.	8.	0.
1·252	—	—	—	—	95-00	95-03	95-07	96-11	9515	95-19
1-253	95-23	95-27	95-31	95-35	95-39	95-43	95-46	96-60	95-54	95-5*
1-254	95·62	95-65	95-69	95-73	95-77	95-80	95-<*4	96-88	96-92	95-96
1-255	96·00	96-03	9607	9611	96-15	96-19	96-23	96-26	96-30	96-34
1*256	96-38	96-42	96-46	96-50	96-54	96-58	9e-62	96-66	96-70	96-74
1-257	06-78	96-82	96*86	96-90	96-94	96-98	97-02	9705	97-09	97-13
1-258	97-17	97-21	97-24	97-28	97-32	^7-36	97-40	97-44	97-48	97-52
J-259	97-56	97-60	97-64	97-68	97-72	97-76	97-80	97-84	97-88	97-92
1-260	97-96	98-00	9803	98-07	9811	9815	9819	98-23	98-26	98-30
1-261	98-34	98-38	98-41	98-45	98-49	98-53	98-57	^8-60	98-64	98-68
1-262	B8-72	98-76	98-80	98-84	98-88	98-92	9S-96	99-00	" 99-03	'.19-07
1-263	9911	99-16	9919	99-22	99-26	9930	99-34	" 99-37	9941	99-45
1-264	99-49	99-53	9956	99-60	99-64	99-63	99-72	' 99-76	99-80	09-84
1-265	99-88	9£)-92	09-90	100·00	—	—	"	—	™—	'—

[1] *Da* Pont de Neiuours & Co., reptodui^d through J. W. Lawrle, " Glycerol and the Glycots," p. 291.

The specific gravity data of Bosart-and Snoddy supersede those of the earlier investigators, including Geriach, whose tables have gained wide currency in the past; Bosart *{ibid.* 1921, 13, 944; and *I.e.)* has shown that, whilst Gm'ach's sp.gr. at 15^{a}/16° are sufficiently accurate *tC* ho usable.for technical purposes, his table of values at 20720° must be discarded entirely.

Provided a specimen of C.P. glycerol satisfies the qualitative tests for purity described on p. 58c, the proportion of glycerol in it may be deduced from a determination of the specific gravity by the pyenometric method with the help of the tables referred to above.

TABLE V.—RATE OF EXPANSION OF GLYCEBOL SOLUTIONS {Bosart and Snoddy).

Glycerol, conceit* Iratlon %.	Change in specitlc (fravity pcr'C.		
	16-20°.	16-25°.	20-25'.
100	0000015	**0-00061B**	0-000010
«7-5	0-OO0C2II	**0-OI Hi615**	**Din 10005**
06	0-00)1(115	**(!•<« 10015**	0-0001)1 S
90	0-000010	"•000816	0000630
80	0-000020	O-OOU615	0-000610
70	0-000580	0-OOO57O	0-0005o:>
0u	o-oour>4ii	it-iM)i):,45	**i'-in 11)550**
50	0-000485	0-....H •,>;'.	00OO510
40	0-000430	0-000435	**M IK1D445**
SO	O-OOO370	0-000385	Q-O0O400
20	0-00030O	0000315	0·000325
10	0-000230	0-000265	0·000280
0	0'Oooieo	0-000205	0·000S30

The variation in the rate of expansion[1] of solutions of glycerol with temperature {i.e. the change in speeifie gravity with temperature) is shown in Table V (Bosart and Snoddy, *ibid.* 1927T 19, 506; f/. Hchncr, J.S.C.I. 1889, 8, 8; Geriach, 2. anal. Chem. 1885, 24, 111 • Comey and Backus, J. Ind. Eng. Chem. lttIO, *2,* 11); hence it ia necessary, when correcting specific gravities from experimental to stf-ndard temperatures, to use the factor corresponding to the temperature at which the determination is made.

The following formujre have been computed by Bosart and Snoddy for the purpose of calculating the specific gravity of glycerol solutions at 15°/I5° and 25°/25° when the actual determination has been made at another experimental temperature:

(i) For calculating from a higher to a lower temperature—•

$$d=\frac{ab+Bc(T-t)}{c}$$

(ii) For calculating from, a lower to a higher temperature—

$$a=\frac{dc-Bc(T-t)}{b}$$

where a=f>p-gr. of glycerol at T°/T°.

ª H t((It ' /' ·

4=sp.gr. of water at T°.

B^changgin sp.gr. of glycerol per°C.
T=higher temp, ofsp.gr. determination.
Slower „ „ „

Analogous formula? and tables are given by Comcy and.ttackus *(i.r$_{r}$.).* For dynamite glycerins, round figures for the values of the average rates of expansion, viz. 000061, 0-000ulR and 0 000(52 at 20°, *2$* and 30° respec tively, arc convenient to remember and sufficiently accurate for most practical purposes.

In cases when the volume yf the available sample does not permit of ac-tiratu determination of specific gravity, **the** content of glycerol may lie derived **from** the *refractive index* of the specimen. The Abbe* refractometcr is convenient anil rapid in uso anil **only** requires a few drops uf m:itrrial$_{f}$ but the mid ing is of somewhat doubtful nc-funit-y in the fo$_{(}$,rlh pince of decimals so that refractive **indices** determined with this instrument must be regarded as a less accurate indication of the concentration of glycerol solutions than determinations >f specific gravity (Hoyt). More accurate result- **[pet**-mitting the determination of coininlration to within 0-1%) can be nltiaim-il by the DM -I 'the

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[1] Bosart and Snoddj- adopt tlie expression " ntv of expansion " tit denote *ftic* rate of change of the *xptcific graviti/* per degree of temperature In order to avoid eonfuatan with tlu> **true** " coefflcJpnt *at* expansion," which npi>ll?a only to tlie change of *talume* with temperature.

TABLE VI.—REFRACTIVE INDEX OF GLYCEROL SOLUTIONS AT 15°C. (Skalweit) AND 20°±0·5° (Hoyt).

Glycerol by weight. %	Sp. gr. at 15° compared with water at 15° (Skalweit).	Refractive index at 15° (Skalweit).	Refractive index at 20° (Hoyt).	Glycerol by weight. %	Sp. gr. at 15° compared with water at 15° (Skalweit).	Refractive index at 15° (Skalweit).	Refractive index at 20° (Hoyt).
0	1·0000	1·3330	1·33303	51	1·1318	1·4010	1·39958
1	1·0024	1·3342	1·33410	52	1·1346	1·4024	1·40107
2	1·0048	1·3354	1·33530	53	1·1374	1·4039	1·40256
3	1·0072	1·3366	1·33645	54	1·1402	1·4054	1·40405
4	1·0096	1·3378	1·33762	55	1·1430	1·4069	1·40554
5	1·0120	1·3390	1·33880				
6	1·0144	1·3402	1·33999	56	1·1458	1·4084	1·40703
7	1·0168	1·3414	1·34118	57	1·1486	1·4099	1·40852
8	1·0192	1·3426	1·34238	58	1·1514	1·4114	1·41001
9	1·0216	1·3439	1·34359	59	1·1542	1·4129	1·41150
10	1·0240	1·3452	1·34481	60	1·1570	1·4144	1·41299
11	1·0265	1·3464	1·34604	61	1·1599	1·4160	1·41448
12	1·0290	1·3477	1·34729	62	1·1628	1·4175	1·41597
13	1·0315	1·3490	1·34854	63	1·1657	1·4190	1·41746
14	1·0340	1·3503	1·34980	64	1·1686	1·4205	1·41895
15	1·0365	1·3516	1·35100	65	1·1715	1·4220	1·42044
16	1·0390	1·3529	1·35223	66	1·1743	1·4235	1·42193
17	1·0415	1·3542	1·35361	67	1·1771	1·4250	1·42342
18	1·0440	1·3555	1·35490	68	1·1799	1·4265	1·42491
19	1·0465	1·3568	1·35619	69	1·1827	1·4280	1·42640
20	1·0490	1·3581	1·35749	70	1·1855	1·4295	1·42789
21	1·0516	1·3594	1·35879	71	1·1882	1·4309	1·42938
22	1·0542	1·3607	1·36010	72	1·1909	1·4324	1·43087
23	1·0568	1·3620	1·36141	73	1·1936	1·4339	1·43236
24	1·0594	1·3633	1·36272	74	1·1963	1·4354	1·43385
25	1·0620	1·3647	1·36404	75	1·1990	1·4369	1·43534
26	1·0646	1·3660	1·36536	76	1·2017	1·4384	1·43683
27	1·0672	1·3674	1·36669	77	1·2044	1·4399	[illegible]
28	1·0698	1·3687	1·36802	78	1·2071	1·4414	1·43985
29	1·0724	1·3701	1·36936	79	1·2098	1·4429	1·44135
30	1·0750	1·3715	1·37070	80	1·2125	1·4444	1·44290
31	1·0777	1·3729	1·37204	81	1·2152	1·4460	1·44450
32	1·0804	1·3743	1·37338	82	1·2179	1·4475	[illegible]
33	1·0831	1·3757	1·37472	83	1·2206	1·4490	1·44770
34	1·0858	1·3771	1·37606	84	1·2233	1·4505	1·44930
35	1·0885	1·3785	1·37740	85	1·2260	1·4520	1·45085
36	1·0912	1·3799	1·37874	86	1·2287	1·4535	1·45237
37	1·0939	1·3813	1·38008	87	1·2314	1·4550	1·45389
38	1·0966	1·3827	1·38143	88	1·2341	1·4565	1·45539
39	1·0993	1·3840	1·38278	89	1·2368	1·4580	1·45689
40	1·1020	1·3854	1·38413	90	1·2395	1·4595	1·45839
41	1·1047	1·3868	1·38548	91	1·2421	1·4610	1·45989
42	1·1074	1·3882	1·38683	92	1·2447	1·4625	1·46139
43	1·1101	1·3896	1·38818	93	1·2473	1·4640	1·46290
44	1·1128	1·3910	1·38959	94	1·2499	1·4655	1·46443
45	1·1155	1·3924	1·39089	95	1·2525	1·4670	1·46597
46	1·1182	1·3938	1·39227	96	1·2550	1·4684	1·46752
47	1·1209	1·3952	1·39368	97	1·2575	1·4698	1·46909
48	1·1236	1·3966	1·39513	98	1·2600	1·4712	1·47071
49	1·1263	1·3981	1·39660	99	1·2625	1·4728	1·47234
50	1·1290	1·3996	1·39809	100	1·2650	1·4742	1·47399

dipping or immersion, refractometer. The onginfil Zeifls instrument did not allow of testing more concentrated solutions than those containing 26% of glycerol,[1] but improved modern types with interchangeable prisms, such as that used by Hoyt for the determinations reproduced below, enable accurate measurements to be made over the whole range of solutions from 0 to 100% glycerol.

The figures for refractive indices at 20°C. shown in Table VI have been computed by Hoyt (Ind. Eng. Chem. 1934, 26, 329) from the results of the examination, by means of such an immersion refractometer, of 30 samples of diluted glycerin solutions prepared from a highly purified specimen of double-distilled 5.P. glycerin. There have been included in the same table values for the refractive indices and specific gravities of glycerol solutions at 15°C, published by Skalweit {Rep. anal. Chem. 1885, 5, 17); this author used an Abbe refractomet -r, the experimental-observations being made on " numerous diluted samples " prepared from crystallised glycerol. Wagner's table of refractive indices of dilute glycerol solutions •(u>/t>%T) at 17-5°C. determined by means of a Zeiss immersion refractometer is shown in Table VII (from Wagner, " Immersion Refractometer Tables," 1907 , p. 46, Table 70; reproduced through Hoyt, pil and Soap, 1933,10,*43>).*

TABLE VII,—REFRACTIVE INDEX OF DILUTE GLYCEEOL SOLUTIONS *{wjv%)* AT I7-5°C.
(Wagner),

Scale reading, °Zeis§.	KeFractlve index.	*wlv %* glycerol, g. per 100 c.c.	Scale reading, • ZelBS.	Refractive Index.	w/e % gtycerol, g. per 100 c.c.	Scale reading, -ZeiSf.	Refractive index.	**w/tt %** tfveru, K, per 100 c.e.
15	1-33320	0-00	46		10-01	76 •		19-48
16		**0-35**	47		10-33	77		19-79
17		0-66	48		10-65	78		20-10
18		0-99	49		10-96	79		2041
19		1-32	50	1-34660	11-28	80	1-35750	20-72
20	1-33513	1-64	51		11-59	81		2103
21		1-97	52		11-91	82		21-34
22		2-29	53		12-22	83		21-65
23		2-62	54		12-34	84		21-96
24		2-94	55	1-34836	12-86	85	1 35930	22-27
25	1-33705	3-27	**56**		13-17	86		22-58
26		3-59	57		13-49	87		22-89
27		3-92'	**58**		13-81	88		23-20
28		4-24	59		14-12	89		23-50
29		4-56	60	1-35021	14-44	90	1-36109	23-81
30	1-33896	4-88	61		14-75	91		**24-1S**
31		5-21	62		1507	92		24-43
32		5-53	63		15-38	93		24-73
33		, 5-85	64		15-70	94		26-04
34		6-17	65	1-35205	1602	95	1-36287	25-35
35	1-34086	(3-49	66		**16-33**	**06**		25-66
36		6-81	67		16-65	97		25-96
37		7-13	68		16-&6	98		26-26
38		7-45	09		17-28	99		26-57
39		7-77	70	1-35388	17-59	100	1-36464	26-88
40	1-1*275	**8*0fl**	71		17-9$	101		27-18
41		**8-41**	72		18-22	102		27-49
42		8-73	73		18-54	103r.		27-80
43		905	74		1&85	104		28-11
44		9-37	75	135569	19 JG	105	1-36640	28-41
45	1-34463	9-69				106		28-72

Table VIII, due to Hoyt *{I.e.* 1934), shows the refractive index of pure glycerol at various temperatures.

The figures given imply a temperature coefficient for the refractive index of 99-84% glycerol averaging —0000225 per 1°C. over the range 10-20°C. This is somewhat lower than the figures of 0-60028/l°a and 0-0002'0/l°C. over the range 12-5~17*5°C. reported by Wolff (Z. angew. Chem. 1919, 32,1, 148} for glycerol of 86% and 77% concentration respectively *: Van der WiUigen{Fortschr. d. Physik, 1869, 25, 288) gives temperature coefficients of refractive index varying from -0-00021/l°C. for glycerol of approx. 4o% concentration to - 0-00025/1°C. for a 90% (approx.) glycerin. Listing *(ibid.* 1869, 26, 294) reported *a,* change iinirefractive

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[1] It Is not permfssltilo to dilute conccntrfttert glywrin witl) a known amount of water to n IQWJT percentage, and thtn to determine the refractive index, lnasn>urli u contraction takes place on mixing glycerin wltn water *(tee p.* 536).

[1] **The** <uhr.il (rations mentioned hnre ami In tlio **next** fow lines are computed from the Hneeifle cavity <bta **given** by the original authors, with the aid of the Bowirt-noddy tables.

TABLE Till.—RKFBAOTTVE INDEX OF PMIE GLYCESOL {(99·84%) AT VARIOUS TEMPEBATUBES (Hoyfc).

Temp.,	IUftactlve Jndex,
102	1-47592
11-2	147575
12-2	1-47552
12-8	1-47536
13-8	1-47M2
150	1-47485
168	1-47464
17-6	1-47418
180	1-47408
200	147367

Index of -000032 per °C; for glyceroi of about 96% concentration. The temperature coefficient of the refractive index of glyeerol solutions ia obviously a function of concentration and hence would be expected to become numerically smaller as the dilution increases, since {he average temperature coefficient of refractive index of pare water is -*000081 per 1°C. over the range 10-20°C,

Glyceroi boila at 290° (oorr.) under 760 mm. (759-7 mm. corr.} pressure (Mendeieef, Annaleu, I860, 114, 1«7; *cf.* Qerlaoh, Z. anal. Chem. 1885, 24, 110) with only alight decomposition; ft distils unchanged under considerably reduced pressure, and table IX contains the most trustworthy observations of the b.p. of glyceroi under reduced pressures {*cf. also* Richardson, J.C.S. 18*6, 49, 746; Kailan, Z. anal. Chem. 1912, 51, 81):

TABLE IX.

Pressure, mm.	Boiling-point, °C.
385-33	260-4
347'Id	257-3
231-87	250-3
201-23	241 -H
100-81	*220-3
5000	2100
46*61	**2014**
3000	191-8
20-46	183-3
12-50	179*6
1000	167-2
6-P3	161-3
500	165-5 •
0-24	118-5
0056	115-llu-

Glyceroi ia^migcible with water in all proportions. Tfre mixing is accompanied by a contraction of volume and an increase of temperature. The greatest increase of temperature, viz, 5°, is observed when 58 parts of gtycerol (by weight) are mixed with 42 parts of water : the greatest contraction is 1-1% (Gerlach). Glycerin cau be completely freed from water by allowing it to stand *in vacw* over sulphuric acid for a prolonged period.

GlycerVM does not volatilise ;it the ordinary temperature, but from concentrated solutions appreciable quantities volatilise with water vapour at 100*.

TKe vapour pressure of a dilute solution of glyceroi falls aa its normal boiling point increases. Since glyceroi and water are miscible in every proportion, the composition of the escaping vapours cannot be calculated according to Dalton's law, but must be derived from actual observations. Gerlach determined, by a barometric method, thB vapour pressures giveo in Table X.

TABLE X,—VAPOUR PBESSIJBES or GLYCEROL **AND *OB* AQFEOUS SOLUTIONS OF GLYCEBOL** (Gerlaoh).

Glyceroi %.	Water %.	B.p. at 760 mm. preasuro, C.	**Vapour pr«B-**ure at 100°C. mm. of mercury-
100	0	200	64
99	1	239	87
98	*2	208	107
97	3	188	126
»6	4	175	144
95	5	164	**162**
f)4	6	156	180
93	7	150	198
9C	8	145	215
&]	9	141	231
B0	10	138	247
89	11	135	263
88	12	132-5	279
87	13	**130-fi**	295
86	14	129	311
85	15	127-5	326
84	16	126	340
83	17.	124-5	355
82	18	123	370
81	19	122	384
80	20	121	396
79	21	120	408
78	22	119	419
77	23	118-2	430
76	24	117-4	**440**
75	25	116-7	450
74	26	116	4i>‹)
73	27	115-4	470
72	28	114-8	480
71	20	114-2	489
70	30	113-6	496
65	**80**	111-3	553
60	40	109	565
55	45	107-5	593
S0	50	106	618
45	55	105	639
40	ttO	104	657
35	65	103-4	675
30	70	102-8	690
25	76	102-3	704
20	80	101-8	717
10	90	lOO'-B	740
0	100	100	760

Ujf to a concentration ^>f about 50%, no glycerol escapes with the water vapours, even if the dilute solutions bt? kept boiling for a prolonged time. At a concentration of about 70%, traces of glyceroi escape from the boiling solution (Hehner, Analyst, 1887, 12, 65). The

TABLE XL—ABSOLUTE VISCOSITIES \CSNTIPQISES) OF GLYCBSOL SOLUTIONS (Shiely).
(Experimental data: interpolated values for every 10% glycerol shown in bltXS]t typti.)

Per cent. Glycerol.	Viscosity (centlpolscs) at				
	20°C.	22-5°C.	25"C.	27-5°C.	30°O.
00 (water)	1005	—	0893	—	0800
3-85	1109	—	0-981	—	0-877
7-31	1 216	—	1073	—	0-856
100	1-311	—	V153	—	1024
10-58	1-331	—	1-172	—	1-040
14-13	1-478	—	1-295	—	M47
17-40	**1-634**	—	1-428	—	1-259
19-79	1-756	—	1-530	—	1-351
200	1-769	—	1-542	—	**1-860**
23-55	1-995	—	1-731	—	1 -.V_>0
27-98	2-323	—	2007	—	1-751
30 00	2 501	—	2157	—	1-876
30-44	2-545	—	2191	—	1-907
33-11	2-822	—	2-420	—	2-098
36-29	3-207	—	2-741	—	2-364
3902	3-595	—	3054	—	2-625
400	3750	—	3181	—	2-731
4 Mill	4-029	—		—	**2-919**
44-78	4-668	—	3-927	—	3-347
48-20	5-518	—	4-611	—	3-909
500	6050	—	5 041	—	4247
51-33	6-516	—	5-409	—	4-552
54-10	7-600	—	6-266	—	5-236
55-59	8-282	7-494	6-804	6-203	6-679
57-12	9092	8-209	7-447	6-778	6-187
58-74	10-070	9-074	8-184	7-430	6-770
59-74	10-787	9-679	8-756	7-918	7-222
800	10-96	933	8-823	8015	7-312
(51-46	12061	10'793	9-731	8-732	7 986
62-50	—	11-642	10-473	9-433	8-548
64 50	14-99	13-35	11-96	10-79	9-750
64-66	15-13	13-46	12-05	10-84	9-80
66-94	17-89	1.7-86	14-12	12-68	11-40
700	22-94	20 23	1796	1596	1432
7019	***23-26***	20-53	18-21	1623	14-53
72-40	28-57	**24-98**	22-03	19-50	17-11
74fil	35-11	30-57	20-81	**23-64**	20-97
7t>69	38-98	33-80	29-61	2U-06	2302
77-71	47-97	4141	3608	31-58	27-81
79-37	57-79	49-52	42-85	37-49	32-86
80 0	620	52-77	45-86	40 00	3492
80-83	**70-28**	60-08	51-90	—	—
82-80	85-73	72-75	62-53	54-01	46-90
84-27	10317	87-23	74-50	6408	55-29
8607	131-08	110-20	93-52	**73-81**	**88-64**
88-50	140-42	117-87	99-86'	85-20	7312
87-89	172-2	143-4	120-9	102-7	87-65
89-89	231-6	191-5	160-6	**136*]**	114 •'>
900	2346	194-6	163-6	1373	1153
9081	2680	220-5	183-8	154-4	130-4
92-19	337-9	276-5	229-2	191-6	131-0
92-82	375-6	306-8	254-7	212-1	177-9
93-70	442-3	359-9	295-9	245-6	205-9
94-32	481-7	390-7	321-5	266-3	222-3
95-0	5450	**4438**	3660	3018	248-8
95-19	565-6	457-6	374-9	309-7	267-2
95-65	618-5	499-5	408-3	336-6	279-8
96-08	J37I-0	542-1	441-8	363-6	300-6
90 48	724-0	**582-9**	474-8	389-9	322-4
96<88	'/83-5	629-6	512-3	420^7	346-7
38-06	986-0	789.9	636-8	5108	427-2
98-84	1158	9260	747-0	607-3	496-2
99-66	13H5	1102	884-0	**71W**	**083*8**
1000	1499	1186	**MM**	7640	**6240**

boittng-poifcf of such a solution is **113·6°** *{see* table). Above this concentration, noticeable umounts uf glycerol escape, ao that fchB qflantitative determination of glycerol in an aqueous sulution by evaporating it down on the water-**bSth** leads to faulty results. Even if the concentration of glycerol solutions be carried out *in vacua,* considerable proportions of glyeerol escape with the water vapour when the concentration of the solution exceeds 80% (Lewkowltech). ^

On heating glycorol filowly in a, platinum dish to 150-160°, it evaporates gradually without leaving a residue; at 150° it^will bum with a bluish non-luminous 8am» without emitting any odour. If, however, glycerol is heated rapidly in a platinum dish, it buVns with formation of acroleln, and yields a' residue consisting of polyglycerok. •

Vitality of Aqueous Glycero?Solutions.—TDK most accurate figures for the viscosities of aqueous glycerol solutions appear to be those of Sheejy, whose experimental values are reproduced in Table XI (a full table, prepared by interpolation, is given in the original memoir, lad. Eng. Chem. 1032, 24, 1060), The concentrations of the test-solutions were deduced from the observed specific gravities {not quoted) by the help of the Bosart and Snoddy tables. The viscosities found agree fairly closely with the lew experimental values of Arch butt and Deeley (" Lubrication and Lubricants," 5th ed., London, 1927, p. 19tt), but diverge appreciably from figures given by Here and Wegner (Z. deut. Del- u. Pett-fnd. 1925, 46, 401), particularly for the higher concentrations, at which the discrepancy may amount to 5-10%. Although the accuracy of the Herz and Wegner figures is under question, it has been thought advisable to reproduce their table of relative viscosities *(see* Table *XKL)* since this covers a wide range of temperatures? for -which no other ngurea are available. Some supplementary figures, due to Darke and Lewis (Chem. a/id Ind. 1928,6,1078), have been included. Herz and Wegner DAM the less accurate specific-gravity tables compiled by themselves to ascertain the concentration.^ of their test solutions. For purposes of comparison, therefore, Sheely has applied the Bosart and Snoddj tables to recalculate the concentrations in question from the data supplied by the earlier authors; these corrected values have been inserted in Table XII.

TABLE XIL—RELATIVE VISCOSITIES OF AQUEOUS GLYCEROL SOLUTIONS AS COMFAKKD WITH WATBK. (Herz and Wegner, I>arke and Lewis.)

wt. % Glycerol.		Temteratuie'C.									
Herz and Wegner.	**Corrected values.** Sheely.[1]	1°	10°	15°	**20°**	30"	**40°**	50°	**œ0°**	**70°**	80"
10	9-77	1-306	1-344	1331	1-321	1-275	**1-274**	**1-272**	1-216	**1-212**	1-180
20	1 :>•:('>	1 -902	**[•87fl**	1-857	1-834	1-753	J-H30	1-598	1-518	**1*462**	1-445
30	29-6(S	2-643	**2-tKKJ**	2-558	2-503	2-358	2-210	**2-06(1**	1 ·›·.·!	**1-875**	**1-886**
40	39-83	4-320	4-175	**4-088**	3-858	3-516	3-198	2-958	**2-820**	2 4 9 5	2-342
50	50-12	7-] 95	6-775	6-256	5-802	**5*190**	**1-621**	4-1BO	**3-835**	; -) . ; :	3-339
00	59-94	13-150	**12-27**	11-20	**10-28**	8-807	7-5*18	**9-712**	**5-904**	**5-358**	5004
70	69-98	**34-230**	**30-82**	**28-90**	^ J 1 1	**18-42**	**1 1-lit**	12·14	**10-11**	8-7-1 L!	**7-80]**
80	79-85 *	**100-880**	**B8-«**	**74-23**	**fe-Sl**	43-(J7	30-75	24-20	13-41	**15-06**	**11-46**
85	84-81	190·4	**15*4**	144-2	09-05	**se-84**	4797	**XVIill**	**27-60**	21·06	17-52
88	87-62	274-0	230-5	181-3	**145-8**	**09-88**	**98-10**	46-77	**85-50**	**29-41**	21-32
90	89-30	419-4	324-9	254-3	194-3	**123-5**	89' it;	**111 tin**	43-81	**82-08**	25·25
92	91-69	—	473-3	:s7i 1	**£88-0**	180-4	110-4	77·24	56·50	**89-42**	30-64
Water viscosity ln\ centlpolses *)		—	**L-SOU**	1-1400	10046	**0-8019**	**0-0538**	0-5497	0-4701	0-4062	0-3556

[1] **fHyaercJ** concentrations re-calruiatfd Iron) the data of Herz and Wegner by Shecly, using the specific gravity concentration tables of Bosart and Snoddy.

The first column «Ives the concentration **derived** *by* **Ban** and Wegner from tlieir own specific gravity tables.

[1] Darke and Lewla, Chem. and Xnd, 1928, 6, 1078.

* Landolt-BomBtein, 5tli ed., 1st Suppl., 1927, p. 83 (after Blngham wd Jackson, 1017).

Figures for absolute viscosities calculated from the experimental data of Table XII are given in +he original paper by Herz and Wegner,[1] *(ef. also* Cocks, J.S.C.I. 1929, 48, 27&T),

Glycerol is miscible with alcohol in all proportfora, dissolves readily in a mixture of alcohol and ether, but is sparingly soluble in ether alone (1 part of glycerol, ap.gr. 1-23, requiring about 500 parts of ether) it is therefore impossiblo to extract glycerol from its aqueous solution by means of ether. Glyeerol ia soluble in acetone. Nine parts of glycerol dissolve in 100 parts of ethyl acetate. It is itiwltib!! HI chloroform, light petroleum, carbon disulphide or benzene; it is also insoluble in oils and fats (Leivkowitsch).

Glycerol has powerful solvent properties; it combines in this respect the properties of water and of ordinary alcohol; many substances dissolve more readily in it than in either of these two othe? liquids. The foUowiri^ list of solubilities illustrates thisfKlever, Cheyi'. Zentr. 1872,434):

100 parts of glycerol dissolve at 15° 98 parts of sodium carbonate; GO parts of borax; 50-5 parts of potassium argenatc; SO parts of sodium arsenatc; 50 parts of zinc chloride; -t8-S parts

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[1] **The values for the viscosity of wat*r used for calculation by Here and We^nec were taken from trie 5th ed, (1923) of the tulilca of Landott-Bdrnatctn and are not quite Edentlr-til with the revinod values (duo to Binghnm and Jackson) given In the 1st Suppl. (1027) of Lantlolt** Börnstein.

of tannic acid; 40 parts of alum; 40 parts if zinc iodide 40 parts of potassium iodide; 35-2 parts of zinc sulphate; 32 parts of potassium cyanide; 30 parts of copper sulphate; 25 parts of ferrous sulphate; 25 parts of potassium bromide; 20 parts of lead acetate; 20 parts of ammonium carbonate; 20 parts of arsenious oxide; 20 parts of arsenic oxide; 20 parts of ammonium chloride; 15 parts of oxalic acid; 11 parts of boric acid; 10 parts of barium chloride; 10 parts of copper acetate; 10 parts of benzoic acid; 8 parts of sodium bicarbonate; 7-5 parts of mercuric chloride; 6 parts of calcium sulphide; 3-7 parts of potas3ium chloride; 3*5 parts of potassium chlorate; 1-9 parts of iodine; about 1 part of calcium sulphate; 0*1 part of sulphur; 0-25 part of phosphorus.

An aqueous glycerol solution, of sp.gr. 1-114, dissolves 0*957% of calcium sulphate. Metallic soaps (which are insoluble in water) aii to some extent dissolved by aqueous glycerol; thus: 100 parts of glycerol solution, sp.gr. 1-114, dissolve 0-71 part of iron oleate, 0-94 part of magnesium oleate, and 1-18 parts of calcium oleate.

Glycerol is completely oxidised to carbon dioxide and water by potassium dichrom^te in an acid solution, and this reaction forms the basis of one of the standard methods for the quantitative determination of' glycerol *{see* p. 61c). In dilute aqueous solution and in the presence of caustic alkali, potassium permanganate oxidises glycerol quantitatively to oxalic acid, carbon dioxide and water (Wanklyn and Fox, Ghem. News, 1886, 53, 15; Benedikt and Zsigmondy, Chem.-Ztg., 1885. 9, 976).

Dry potassium permanganate reacts violently with concentrated glycerol. If finely powdered potassium permanganate be heaped up to form a small truncated cone and concentrated glycerol be poured into a hole made in the top, fumeB escape; after a very short time the glycerol commences to froth and ignites spontaneously with violent evolution of gases.

Glycerol treated with hydrogen peroxide in presence of a ferrous salt yields glyceraldehyde, **$CH_8(OH)CH(OH)CHO$.**

Of the eleven possible products of moderate oxidation of glycerol, ten have been isolated, viz. glyceraldehyde (glycerose), glyceric acid, dihydroxyacetone, hydroxypyroracemic acid, tartronmonoaldehyde, tartrondialdehyde, tartronic acid, mesoxalmonoaldehyde, mesoxaldialdehyde and mesoxalic acid; hydroxypyroracemaldehyde is unknown. The glyceric acid obtained by gentle oxidation with nitric acid is a racemic compound and has been resolved into optically active enantiomorphous acids by J Lewkowitsch (Ber. 1883, 16, 2720). Further oxidation yields carbon dioxide, formic acid and water.

A strong aqueous solution of glycerol reduces Barreswirs (Fehling's) solution only slightly. If, however, the glycerol be diluted previously with 10 times its Bulk of water, no reduction occurs.

A mixture of glycerol and silver nitrate solution heated at the temperature of boiling water with a few drops of ammonia, gives a precipitate of metallic silver. If ammonia solution be added to glycerol in the cold, and heat be then applied, as a rule no reduction takes place on adding silver nitrate; the addition of. caustic soda or potash, however, causes metallic silver to separate slowly.

Glycerol dissolves caustic alkalis, alkaline earths and lead Ocide, forming chemical compounds (c/. Bullnheimer, Ber. 1898, 31, 1453; 1899,32,2347; 1900,33,817). The compounds so forjned are termed metallic *glyceroxidea* or *glycerates* and are thought to have a cyclic structure resembling that of the saccharates. Lime, strontia and baryta are precipitated nearly completely from such soHtions by carbon dioxide, a small quantity only of the bases escaping precipitation. In the presence of caustic alkalis, glycerol also dissolves ferric oxide, cupric oxide and bismuth oxide, no doubt in consequence of the formation of soluble compounds (metallic glyceroxides), such as are represented by monosodiumcupriglyceroxide **$(NaCuC_3H_5O_3)_2,3H_2O$.** The oxides enumerated above are not reduced to metals, or at most only to their lower oxides. The following oxides: silver oxide, gold oxide, mercury oxide, rhodium oxide, palladium oxide and platinum oxide **(Ag_2O, Au_2O_3, HgO, RhO_2, PdO, PtO_2),** are reduced to metals when heated with alkaline glycerol solution (Bullnheimer).

The groat solubility of zinc sulphate, as also of nickel, cobalt and copper sulphates, in glycerol, is.explained by the fact that these salts combine with 3 mol. of glycerol to form compounds (Griin and Bockisch, *ibid*$_m$ 1908, **41,** 3465) of the general formula:

$$(M\text{-}3C_3H_aO_3)JO_4,H_2O$$

Where M represents an atom of one of the above-mentioned metals. For these compounds, the name *glycerinates* has been proposed by Griin, in order to distinguish them from the metallic glyceroxides described above.

QUALITATIVE TESTS FOR GLYOEROL.

One of the simplest tests for glycerol, which is capable of detecting quite small quantities, is based on the penetrating odour of acrolein, which is formed wlysn glycerol is heated in the presence of acid salts. The same odour is also noticeable when a fatty-oil lamp or tallow candle is blown out. For.the test, a smajl portion of the substance should be heated with potassium bisulphate, and the acrolein detected either by its odour or by the red colour formed when the vapour is passed into Schiff's reagent (a solution of rosanilin which has beeD decolorised by sulphur dioxide). Alternatively, an ammoniacal solution of silver nitrate may be used for the detection of the acrolein which produces in it a precipitate or mirror of metallic silver.

Some other useful tests described by Denigès (Compt. rend. 1909,**148,** 570) are based upon the colour reactions of dihydroxyacetone which is formed when glycerol is heated with bromine water. About 0-1 g. of the glyoerol is heated with 10 ml. of bromine water in a bath of boiling water for about 20 minutes or until the free bromine has disappeared. In four separate test tubes tjjere a*$ placed 0*1 ml. of an alcoholic solution of (1) couein, (2) resorcinol, (3) thymol and (4) 0-naphthol. To each tube is added 0*4 ml. of the brominated sample and 0*1 ml. of a 4% solution of potassium bromide;[1] then 2 ml. of cone, sulphuric acid. The tubes containing codein and 0-naphthol are heated for 2 minutes in a water bath. The codein solution will show a* blue tint; the resorcinol a blood-red colour becoming yellow-red on dilution with acetic ac*id; the thymol a wine-red colour becoming rose-red on dilution; and the 0-naphthol will develop an emerald-gree** fluorescence. A more positive identification may be^ based upon the formation of glyceryl tgibenzoate which has m.p. 72°. For this purpose 0-1 ml. of the speoimen is shaken for 5 mifiutes with 0-4 ml. of benzoyl chloride and 5 ml. of 10% sodium hydroxide solution. After shading, 10 ml. of cold water are added and the precipitated tribenzoate is filtered, washed and crystallised from 35% alcohol.

Provided that a sufficient amount of the sample i* available, it is possibly by distillation under reduced pressure to separate moderately pure-glycerol, even from fairly complex mixtures.

QUANTITATIVE DETERMINATION OF GLYCEROL.

Here only the determination of glycerol in commercial products containing considerable quantities of it can be considered. The determination of glycerol in fermented liquors falls outside th| scope of this article.

A direct method for determining glycerol in oils and fats by isolating it has been worked out by Shukoff and? Schestakoff (Z. angew*. Chem. 1905, 18, 294; *cf.* Fachini and Dorta, Boll. Chim. farm. 1910, 49, 237). It is necessary to operate with a solution containing at least 40% of glycerol. If the solution be more dilute, a quantity corresponding to about 1 g. of glycerol is carefully evaporated on the water-bath, the concentration* not being increased to such a point that volatilisation of glycerol can take place (i.e. a concentration of about 60% must not be exceeded). Before evaporating, the solution is rendered slightly alkaline with potassium carbonate* The concentrated solution is then mixed with 20 g. of ignited and powdered anhydrous sodium sulphate and exhausted m a Soxhlet extractor with anhydrous acetone (previously well dried over anhydruos potassium carbonate). As acetone attacks both cork and indiarubber, all connections must bo, made with ground-glass fittings. The extraction requires several hours, and the results, at uest, are only approximately correct.

As a rule, the determination of glycerol in oils and fats is carried out by one of the following indirect methods.

DichYomate Process.—This method which was first described by Hehner (J.S.C.I. 1889, 8, 5) has displaced the older permanganate method of Wanklyn and Fox (*l.c,* p. 80) and Benedikt and Zsignondy (I.e., p. 80). With due attention to the details as described on p. 61c, it affords a most reliable determination and has been often recommended as the standard method. It depends upon the complete oxidation of the jforined glycerol to carbon dioxide and water, but can be suitably applied only after removal of all organic impurities; see p. 61. The application of this method to various types of glycerin has been critically studied by S. Fachini and S. Somazzi (Chim. et Ind. 1924, Spec. No. (Paris 1923 Congress) 5543).

. Acetin Process.—In case an impure glycerin be under examination (such as the crude glycerins described on p. 42), it is best to determine the proportion of glycerol by the Benedikt-Cantor acetin process, which is based on the quantitative conversion of glycerol into triacetin on heating the solution with acetic anhydride. If the product of this reaction is then dissolved in water, and the free acetic acid carefully neutralised with alkali, the dissolved triacetin can be readily estimated by saponification with a known volume of standard alkali, and titrating back the excess.

Details of tffe method are given in the Report of the International Committee on the Analysis of Glycerin (*see* p. 606).

Copper Process.—A newer method of some promise has been put forward by Bertram and Rutgers (Rec. trav. chim. 1938, 57, 681) and revise I by the Glycerin Analysis Committee of the ^American Oil Chemists' Society (Oil and Soap, 1941, 18, 14) which depends upon the formation of a glycerol-copper complex in an alkaline alcoholic solution.

Although the precision obtainable falls somewhat short of the standard required for commercial transactions, the method has the great advantage that it can be applied to impure preparations and mixtures without preliminary purification, and so affords a rapid and easy means of determining the approximate glycerol content of products grossly contaminated with substances which would interfere with the standard acetin of dichromate procedures, such as sugars, trimethylene glycol, diethylene glycol, glycol ethers (*e.g., "bellosolve," "carbitol")* oxalic acids, or hydroxyacids such as tartaric and citric. None of these shows as much *is* 1% of apparent glycerol when tested *by* the new method: ethylene glycol, propylene glycol and hexahydric alcohols (mannitol, sorbitol) show from 2 to 6% apparent glycerol. Polyglyceryl ethers and alkylolamines interfere with the determination, but small quantities of ammonia do not. According to A.O.C.S. revised procedure, not more than 10 ml. of the glycerin solution, containing not more than 0-8 g. of glycerol, is weighed into a 100-ml. calibrated flask and diluted to 10 ml. with distilled water; 10 ml. of sodium hydroxide solution (30 g. per 100 ml.) are added, followed immediately by 60 ml. of 95 v/v% alcohol, and after mixing there is added (from a burette) an alcoholic solution of cupric chloride (10 g. $\mathrm{CuCI_2,2H_8O}$ per 100 ml.) until a permanent undissolved precipitate of copper hydroxide remains after shaking; an excess of 0*5 ml. of the copper solution is added and the Volume adjusted to 100 ml. with alcohol, and $he solution shaken for at least a minute. (The solution is maintained at 20° throughout these operations.) At least 60 ml. of the well-mixed solution is centrifuged at 1,300 r.p.m. for about 10 min., tempered at 20°, and a 50 ml. aliquot of the clear decanted solution is transferred to a 300 ml. conical flask, diluted with 100 ml. of water, and made just acid with glacial acetic acid; 2 ml. excess of the acetic acid is added, and after cooling the mixture in ice, 10 g. of KI are added and the liberated iodine is immediately titrated with 0-1 N-sodium thiosulphate solution, using a starch indicator: just before the end-point, 2 g. of ammonium thiocyanate are added. The percentage of glycerol in the sample is given, by the relation

$$\frac{(T-B)\,N\,18{\cdot}41}{S}$$

where T and B are the titration figures for the sample and blank tests respectively, *N* is the normality of the thiosulphate solution and S the weight of the sample. If greater accuracy is required, a correction can be applied for the volume of the copper precipitate: in this case, the whole of the solution is centrifuged and the factor 18-41 becomes $9{\cdot}205 \times \frac{\quad}{50}$ where V is the apparent volume of the precipitate after centrifuging.

Chemically Pure Glycerin.—The proportion of glycerol in *chemically pure glycerin is* most conveniently ascertained by determining the specific gravity (*see* tables on pp. 49, 50) or by oxidising the glycerol by means of dichromate, provided organic impurities be absent. This is ascertained in the following manner: A somewhat dilute solution is mixed with a cold ammoniacal silver nitrate solution; the solution should remain colourless even after standing for 24 hours. Any acrolein present in the sample is detected by the test described above. Any polyglycerols, due to faulty distillation, are determined by allowing an accurately weighed quantity of the sample to evaporate gently at 160°. Care should be taken not to heat too rapidly, otherwise even the purest glycerol may become polymerised with the production of the very substances that are to be detected. From the weight of the residue, the weight of ash, subsequently found on incineration, must be deducted. The difference (the " organic residue ") is a fair indication of the care with which the glycerol has been manufactured.

The following Table XIII gives the " organic residue " and ash of a number of typical pure glycerins.

TABLE XIII.—ORGANIC RESIDUE AND ASH in COMMERCIAL GLYCERINS.

Once distilled (dynamite) glycerin.

No.	**Residue at 160°, %.**	**Ash, %.**	Organic residue, %.	**Chloride, NaCl, %.**
1	0018	0-007	0011	0-0013
2	0013	0-006	0008	0-0020
3	0-019	0-007	0-012	0-00ai
4	0-020	0-009	0-0u	00030

Double distilled (C.P.) glycerin.

No.	Residue at 160°, %.	Ash, %.	Organic residue, %.	Chloride, NaCl, %.
5	0011	0-005	0006	00013
6	0-014	0009	0-005	00020
7	0009	0004	0-005	0-0010

Chemically pure glycerin must be free from all but the most minute traces of arsenic; the maximum content permitted by the British and United States Pharmacopoeias is 4 and 10 p.p.m. respectively. This is ascertained by the Gutzeit test (*v.* Vol. I, 4706).

It should be neutral to litmus, leave no ash on ignition, and have sp.gr. of at least 1-260 at 15-5°. It should not emit any odour when heated on the water-bath, or any fruity odour when warmed with alcohol and sulphuric acid. It should not contain sulphates, chlorides, oxalates, metals or sugars, and *when* mixed with an equal volume of water must not reduce Barreswil's (Fehling's) solution. *It* should show at most a yellow coloration in Hager's test, according to which 5 ml. of the sample are mixed with 5 ml. of 26% ammonia solution and 5 drops of silver nitrate solution and left in the dark for 15 minutes at the ordinary temperature.

The British Pharmacopoeia (1932) requires glycerin to have sp.gr.™* 1-260-1-265; to have not more than 0-01% of ash; to be free from reducing substances *and* fatty acids; and to contain not more than about 2 p.p.m. of iron, not more than 1 p.p.m. of lead and not more than 4 p.p.m. of arsenic.

Distilled Glycerin (Dynamite Glycerin).—The proportion of glycerol in these products is best determined by the acetin method. " Dynamite glycerin " is usually sold according to a specification agreed upon between buyer and seller. The following conditions are usually stipulated: sp.gr.j™ not below 1-26J; neutral to litmus, light in colour, free from smell; ash not more than 0-05%; saponification equivalent not more than 0-1% as Na_2O; salt not more than 001%; water not more than 1-5% and glycerol at least 98-5%. A test for reducing substances with silver nitrate is generally included and some well-known specifications include a test for the yield and separation on nitration. The latter test requires great care and is by no means always a reliable guide to the yield on the large scale.

ANALYSIS OF CRUDE GLYCERINS.

The *International Standard Acetin Method* still retains official status, although objections against it have been raised, both on **account** of the tedious procedure and a doubt as to the accuracy of the results. Many of the objections raised from time to time are, however, a result of inattention to the important details set out in the I.S.M. For example the use of well-boiled CO_2-free water is essential to accuracy. The committee of the American Oil Chemists' Society (Oil and Fat Ind. 1931, 8, 297; Oil and Soap, **1033,** 10. 71) report that the figures obtained by the dichromate method agree better with those deduced from the specific gravity (Bosart-Snoddy) than do the results of the acetin method.

International Standard Methods,[1]

" Analysis of Crude Glycerol.—The valuation of crude glycerol has assumed great commercial importance owing to the value of the

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[1] Analyst, 1011, 36, 31V

commodfcy. The want of uniformity in the methods and processes of analysis, together with the irregularity of the results obtainefl, emphasised the desirability for the standardisation of crude glycerol analysis; so with this object in* view committees were formed in America, France, Germany, and Gresft Britain. These committees worked in the first instance independently, but were ultimately brought together, and after a series of conferences the conclusions arrived at by the various committees were summarised, and drawn up in the form in which they are now presented. The methods detailed in- this rgport have the^unanimous support of each of the above* committees, and are strongly recommended by them as International Standards.

" **Sampling.**—The most satisfactory method available for sampling crude glyc#rol liable to contain suspended matter, or wfiich is liable to deposit salt on settling, is to have the glycerol sampled by a mutually approved sampler as soon as possible after it is filled into drums, bftt in any case before any separation of salts has taken place. In such cases he shall sample with a sectional sampler (a suitable sampling apparatus is described in an appendix to the report), brand them with a number for identification, and keep a record of the brand number. The presence of any visible salt or other suspended matter is to be noted by the sampler, and a report of same made in his certificate. Each drum must be sampled. Glycerol which has deposited salt or other matters cannot be accurately sampled from the drums, but an approximate sample can be obtained by means of the sectional sample?, which will allow a complete vertical section of the glycerol to be taken,, including any deposit.

"**Analysis.**—(1) *Determination of Free Caustic Alkali.*—Weigh 20 g. of the sample into a 100 ml. flask, dilute with approximately 50 ml. of freshly-boiled distilled water, add an excess of neutral barium chloride solution, 1 ml. of phenolphthalein solution, make up to the mark, and mix. Allow the precipitate to settle, draw off 50 ml. of the clear liquid, and titrate with N-acid. Calculate to percentage of Na_2Q existing as caustic alkali.

" (2) *Determination of Ash and Total Alka-Unity.*—Weigh 2-5 g. of the sample in a platinum dish, burn off the glytferol over a luminous Argand burner, or other source of heat giving a low flame-temperature, the temperature being kept low to avoid volatilisation, and the formation of sulphides. When the mass is charred to the point that water will not become coloured by soluble Organic matter, lixiviate with hot distilled water, filter, wash and ignite the residue in the platinum dish. Return the filtrate and washings to the dish, evaporate and carefully ignite without fusion. Weigh the ash. Dissolve the ash in distilled 'water, and titrate total alkalinity, using as indicator methyl orange cold, or litmus boiling.

" (3) *Determination of. Alkali present as Carbonate.*—*Take* 10 g. of the sample, dilute with 50 ml. distilled water, add sufficient N-acid to neutralise the total alkali found at (2), boil under a reflux condenser for 15-20 minutes, wash down the condenser tube with distilled water free from carbon dioxide and titrate back with N/l-NaOH, using phenolphthalein as indicator. Calculate the percentage of Na_2O. Deduct the Na_2O found in^l). The difference is the percentage of Na«O existing as carbonate.

" (4) *Alkali combined with Organic Acids.*—The sum of the percentage of Na_2O found at (1) and (3) deducted from the percentage found at (2) is a measure of the Na_2O or other alkali combined with organic acids.

" (5) *Determination of Acidity.*—*Take* 10 g. of the sample, dilute with 50 ml. of distilled water free from carbon dioxide, and titrate with N/l-NaOH and phenolphthalein. Express in terms of Na_2O required to neutralise 100 g.

" (6) *Determination of Total Residue at* 160°.—For this determination the crude glycerol should be slightly alkaline with Na_2CO_3, not exceeding the equivalent of 0-2% Na_2O, in order to prevent loss of organic acids. 'To avoid formation of polyglycerol, this alkalinity must not be exceeded.

" *Preparation of Glycerin.*—10 g. of the sample *are weighed into a 100 ml. flask, diluted with water, and the calculated quantity of N/l-HCI or Na.^COg added to give the required degree of alkalinity. The flask is filled to 100 ml., the contents mixed and 10 ml. measured into a weighed Petri or similar dish 2*5 in. diameter and 0*5 in. deep, which should have a flat bottom (and rounded connection with the sides). In the case of crude glycerins abnormally high in organic residue a less quantity is to be evaporated, so that the weight of organic residue does not materially exceed 30-40 mg.

"*Evaporation of the Glycerol*—*The* dish is placed on a water-bath (the top of the 160° oven acts equally well) until most of the water has evaporated. From this point the evaporation is effected in the oven. Satisfactory results arc obtained in an oven measuring 12 in. cube, having an iron plate f in. thick lying on the bottom to distribute tho heat. Stripy of asbestos millboard are placed on a shelf halfway up the oven. On these strips the dish containing the glycerol is placed. The bulb of the thermometer should also rest upon one of the strips.

" If the temperature of the oven has been adjusted to 160° with the door closed, a temperature of 130-140° can be readily maintained with the door partially open, and the glycerol, or most of it, should be evaporated off at this temperature.[1] When only a slight vapour is seen to come off, the dish is removed and allowed to cool.

" An addition of 0*5-1 ml. of water is made, and by a rotatory motion the,, residue brought wholly or nearly, into solution. The dish is then allowed to remain on a water-bath or top of the oven until the excess water has evaporated and the residue is in such condition that on returning to the oven at 160° it will not spit. The ti\ne taken up to this"*point cannot be definitely given, nor is it of ir^portance. Usually 2-3 hours are required. From this point, however, the schedule of time must be strictly adhered to. The dish is allowed to remain in

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[1] *See* note by Grimwood mentioned on p. 02c.

the oven, the temperature of which is carefully maintained at 160° for 1 hour, when it is removed, cooled, the residue treated with water and the water evaporated as before. The residue is then subjected to a second baking of 1 hour, after which the dish is allowed to cool in a desiccator over sulphuric acid, and weighed. The treatment with water, etc., is repeated until a constant loss of 1-1·5 mg. per hour is obtained.

" *Corrections to be Applied to the Weight of Total Residue,—In* the case of acid glycerol, a correction must be made for the alkali added. One ml. N/l-alkali represents an addition of 0·022 g. In the case of alkaline crudes a correction should be made for the acid added. Deduct the increase in weight due to the conversion of the NaOH and Na_2CO_3 to NaCl. The corrected weight multiplied by 100 gives the percentage of *total residue* at 160°.

" Preserve the total residue for the determination of the non-volatile acetylisable impurities.

" (7) *Organic Residue.—Subtract* the ash from the total residue at 160°. (*Note.*—It should be noted that alkaline salts of organic acids are converted to carbonates on ignition, and that the CO_3 radicle thus derived is not included in the organic residue.)

"(8) *Moisture.*—This test is based on the fact that glycerol can be completely freed from water by allowing it to stand *in vacuo* over sulphuric acid or phosphoric anhydride. 2-3 g. of very bulky asbestos freed from acid-soluble material, which has previously been dried in a water-oven, are placed in a small stoppered weighing-bottle of about 15 c.c. capacity. The weighing-bottle is kept in a vacuum desiccator furnished with a supply of concentrated sulphuric acid, under a pressure equivalent to 1-2 mm. of mercury, until constant in weight. From 1 to 1·5 g. of the sample is then carefully dropped on to the asbestos in such a way that it will be all absorbed. The weight is again taken, and the bottle replaced in the desiccator under 1-2 mm. pressure until constant in weight. At 15° the weight is constant in about 48 hours. At lower temperatures the test is prolonged. (*Note.*—A blank similarly prepared from glycerol free from glycols and dried until anhydrous *in vacuo* over sulphuric acid is kept with the test sample and any loss in weight of the anhydrous blank may be deducted from the amount lost by the sample. If glycols are present in the crude glycerins under test the blank may slightly increase in weight.)

" The sulphuric acid in the desiccator must be frequently renewed.

" Acetin Process for Glycerol Determination.—This process is the one agreed upon at a Conference of Delegates from the American, British, French and German Committees, and has been confirmed by each of the above Committees as giving results nearer to the truth on crudes in general, and is the process to be used (if applicable) whenever only one method is employed. On pure glycerols the results are identical with those of the dichromate process. For the application of this process the crude glycerol should not contain over 50% water.

" The following reagents are required:

" (A) *Best Acetic Anhydride.—This* should be carefully selected. A good sample must not require more than 0·1 ml. normal NaOH for saponification of the impurities when a blank is run on 7·5 ml. Only a slight colour should develop during digestion of the blank.

" (B) *Pure Fused Sodium Acetate.—The pur*chased salt is again completely fused in a platinum, silica or nickel dish, avoiding charring, powdered quickly and kept in a stoppered bottle or a desiccator. It is most important that the sodium acetate be anhydrous.

" (C) *A Solution of Caustic Soda for Neutralising, of about N/1-Strength, free from Carbonate.*—This can be readily made by dissolving pure sodium hydroxide in its own weight of water (preferably water free from carbon dioxide), and allowing to settle until clear, or filtering through asbestos (in the absence of carbon dioxide). The clear solution is diluted with water free from carbon dioxide to the strength required.

"(D) N/1 *Caustic Soda, free from Carbonate.*—Prepared as above, and carefully standardised.

" Some caustic soda solutions show a marked diminution in strength after being boiled; such solutions should be rejected.

" (E) N/l *Acid.*—Carefully standardised.

" (F) *Phenolphthalein Solution.*—0·5% phenolphthalein in alcohol and neutralise.

" THE METHOD.—Into a narrow-mouthed flask (preferably round-bottomed), capacity about 120 ml., which has been thoroughly cleaned and dried, weigh accurately and as rapidly as possible 1·25-1·5 g. of the glycerol. Add first about 3 g. of the anhydrous sodium acetate, then 7·5 ml. of the acetic anhydride, and connect the flask with an upright Liebig condenser. For convenience the inner tube of this condenser should not be over 50 cm. long and 9-10 mm. diameter.

" The flask is connected to the condenser by either a ground glass joint (preferably) or a rubber stopper. If a rubber stopper is used, it should have had a preliminary treatment with hot acetic anhydride vapour.

"Heat the contents and keep just boiling for 1 hour, taking precautions to prevent the salts drying on the sides of the flask. Allow the flask to cool somewhat, and through the condenser tube add 50 ml. of the carbon-dioxide-free distilled water, heated to about 80°, taking care that the flask is not loosened from the condenser. The object of cooling is to avoid any sudden rush of vapours from the flask on adding water, and to avoid breaking the flask. Time is saved by adding the water before the contents of the flask solidify, but the contents may be allowed to solidify, and the test proceeded with the next day without detriment. The contents of the flask may be warmed to, but must not exceed, 80°, until the solution is complete, except a few dark flocks representing organic impurities in the crude. By giving the flask a rotatory motion solution is more quickly effected. Cool the flask and contents without loosening from condenser. When quite cold wash down the inside of the condenser tube, detach the flask, wash off stopper or ground glass connection into the 'flask and filter contends oflask through -an acid-washed filter into a Jena glass flask of about «L litre capacity: the filtrate should amount to about 200 ml. Wash thoroughly with cold distilled wf-ter free from carbon dioxide. Add 2 ml. of phenolphthalein solution ($), then run in a ca^tic soda solution (C) or (D) until a faint pinkish-yellow colour appears "throughout the solution. This neutralisation must be done most carefully. The alkali should *b&* run down the sides of the flask, the contents of which are kept rapicjly swirling, with occasional agitation or change of motion, until the solution is nearly neutralised, "as indicated by the slower disappearance of the colour developed locally by the alkali running into the mixture. When this point is reached the sides of the flask are washed down with carbon-dioxide-free water, and the alkali subsequently addett drop by drop, mixing 3fter each drop until the desired tint is obtained.

4"Now run in from a burette 50 ml. or a calculated excess of N/l-N aO H (D) and note carefully the exact amount. Boil gently for 15 minutes, the flask being fitted with a glass tube acting as a partial condenser. Cool as quickly as possible and titrate excess of NaOH with N/1-acid (E) until the pinkish-yellow or chosen end-point colour just remains. A further addition of the indicator at this point will cause a return of the pinkish colour; this must be neglected, and the first end-point taken.

"From the N/l-NaOH consumed calculate the percentage of glycerol after making the correction for the blank test described below.

" 1 ml. of N/l-IMaOH=0'03069 g. of glycerob The coefficient of expansion for normal solutions is approximately 0*00033 per ml. for each degree C. A correction should be made on this account if necessary.

" ***Blank Test.—AB*** the acetic anhydride and sodium acetate may contain impurities which affect the result, it is necessary *£o* make a blank test, using the same quantities of acetic anhydride and sodium acetate as in the analysis. After neutralising the acetic acid it is not necessary to add more than 5 ml. of the N/l -alkali (D), as that represents the excess of alkali usually left after saponifica&on of the triacetin in the glycerol determination.

" *Determinatior of the Glycerol Value of the Acetylisable Impurities.*—The total residue at 160° is dissolved in 1 or 2 ml. of water, washed into a clean acetylising flask, 120 ml. capacity, and the water evaporated. Now add anhydrous sodium acetate and proceed as in the glycerol determinations before described. Calculate the result to glycerol.

" *Analysis of the Acetic Anhydride.*—Into a weighed stoppered vessel, containing 10-20 ml. of water, run about 2 ml. of the anhydride, replace stopper and weigh; allow to stand, with occasional shaking for several hours, until all anhydride is hydrolysed; then dilute to about 200 ml., add phenolphthalein and titrate with N/l-NaOH. This gives the total acidity due to free acetic acid and acid formed from anhydride.

" Into a stoppered weighing-bottle containing aoknbwn weight of recently distilled aniline (from 10-20 ml.) measure about 2- ml. of the sample, stopper, mix, allow to cool and weigh. Wash contents into about 200 ml. of cold water and titrate acidity as before. This yields the acidity due to the original, preformed, acetic acid, plus one half the acid due to anhydride (the other half having formed acetanilide); subtract the second result from the first (both calculated for 100 g.) and double result, obtaining ml, N/l - N aO H per 100 g. sample. One ml. NaOH equals 0-0510 g. of acetic anhydride.

" Bichromate Process for Glycerol Determination.—*Reagents Required: (a) Pure Potassium* ***Bichromate*** powdered and dried in air free from dust or organic vapours at 110-120°. This is taken as the standard.

" *(b) Dilute Bichromate Solution.*—-7-4564 g. of the above bichromate (a) are dissolved in distilled i^ater and the solution made up to a litre at 15*5°.

" (c) *Ferrous Ammonium Sulphate.*—Dissolve 3*7282 g. of potassium dichromate (a) in 50 ml. of water. Add 50 ml. of 60% (by volume) sulphuric acid and to the cold undiluted solution 'add from 'a weighing-bottle a moderate excess of the.ferrous ammonium sulphate, and titrate bad*with the dilute dichromate (6). Calculate the .value of the ferrous salt in terms of dichromate.

(d) Silver Carbonate.—This is prepared as required for each test from 140 ml. of 0-6% silver sulphate solution by precipitation with about 4*9 ml. N-sodium carbonate solution (a little less than the calculated quantity of N-sodium carbonate should be used; any excess of alkali carbonate prevents rapid settling), settle, decant and wash once by decantation.

11 (e) ***Lead Subacetate.***—Boil a pure 10% lead acetate solution with an excess of litharge for 1 hour, keeping the volume constant, and filter while hot. Disregard any precipitate which subsequently forms. Preserve out of contact with carbon dioxide.

" (/) *Potassium Ferrkyanide.—A* very dilute solution containing about 0-1%.

" THE METHOD.—Weigh 20 g. of the glycerol, dilute to 250 ml. and take 25 ml. Add the silver carbonate, allow to stand, with occasional agitation, for about 10 minutes, and then add a slight excess (about 5 ml. in most cases) of the basic lead acetate (e), allow to stand a few minutes, dilute with distilled water to 100 ml. and then add 0*15 ml. to compensate for the volume of the precipitate, mix thoroughly, filter through an air-dry filter into a suitable narrow-mouthed vessel, rejecting the first 10 ml. and return filtrate if not clear and bright. Test a portion of the filtrate with a little basic lead acetate, which should produce no further precipitate. (In the great majority of cases 5 ml. is ample. Occasionally a crude glycerol will be found requiring more, and in this case another aliquot of 25 ml. of the dilute glycerol should be taketfand purified with 6 ml. if the basic acetate. Care must be taken to avoida marked excess of basic acetate.) Measure oft 25 ml. of the clear filtrate into a glass flask or beaker (previously cleaned with potassium bichromate and sulphuric acid). Add 12 drops of sulphuric acid

(1:4) to precipitate the small excess of lead M sulphate. Add 3-7282 g. of the powdered bichromate *(a).* Rinse down the bichromate with 25 ml. of water and stand, with occasional shaking, until all the bichromate is dissolved (no reduction will take place).

"Now add 50 ml. ot 50% sulphuric acid (by volume), and immerse the vessel in boiling water for 2 hours, and keep protected from dust and organic vapours, such as alcohol, until the titration is completed. Add from a weighing-bottle a slight excess of the ferrous ammonium sulphate (c), making spot tests on a porcelain plate with the potassium ferricyanide (/). Titrate back with the dilute bichromate. From the amount of bichromate reduced calculate the percentage of glycerol.

" 1 *S*- glycerol equals 7-4564 g. bichromate.

" 1 g. bichromate equals 0*13411 g. glycerol.

" *Notes.*—(1) It is important thaj the concentration of acid in the oxidation mixture and the time of oxidation should be strictly adhered to.

" (2) Before the bichromate is added to the glycerol solution it is essential that the slight excess of lead be precipitated with sulphuric acid as stipulated in the process.

" (3) For • crudes ' practically free /rom chlorides the quantity of silver carbonate may be reduced to one-fifth and the basic lead acetate to 0-5 ml.

" (4) It is sometimes advisable to add a little potassium sulphate to ensure a clear filtrate.

" *Instructions for Calculating Actual Glycerol Content.—(I)* Determine the apparent amount of glycerol in the sample by the acetin process as described. The result will include acetylisable impurities if any be. present.

" (2) Determine the total residue at 160°.

" (3) Determine the acetin value of the residue at (2) in terms of glycerol.

^{14} (4) Deduct the result found at (3) from the percentage obtained rt (1), and report this corrected figure as glycerol. If volatile acetylisable impurities are present, these are included in this figure.

^{11} *Notes and Hecommendations.*—Experience has shown that in crude glycerol of good commercial quality the sum of water, total residue at 160° and corrected acetin result, comes to within 0-5 of 100. Further, in such * crudes ' the bichromate result agrees with the uncorrected result to within 1%.

" In the event of greater differences being found, impurities such as polyglycerols or trimethylene glycol are present.

. . . . .

" In valuing crude glycerol for certain purposes it is necessary to ascertain the approximate proportion of arsenic, sulphides, sulphites and thiosulphates. The methods for detecting and determining these impurities have not formed < he subject of this investigation.

" *Recommendations by Executive Committee.*—If the non-volatile organic residue at 160° in the case of a soapflye * crude' be over 2-5% —*i.e.* when not corrected for carbon dioxide in the ash—then the residue shall be examined by the acetin method and any excess of glycerol found over 0-5% shall be deducted from the acetin figure." . (*Cf.* footnote to Table I, p. 45.)

^{14} In, the case of saponification, distillation and similar glycerol the limit of organic residue which should not be passed without further examination shall be fixed at 1%. In the evont of the sample containing more than 1%, the organic residue must be acetylatcd, anw&ny glycerol found (after making the deduction of 0-5%) shall be deducted from the percentage,of .glyce*ol found by the acetin test."

With reference to this Report, Grimwood (J.S.C.I. 1913, 32, 10,39) has shown that the overt recommended therein does not enable a steady temperature to be maintained. In the case of one oven he found a maximum variation of 45° between the temperatures of two shelves. In place of the standard oven he has devised an electrically heated oven cased with uralite. He also describes an accelerated method of evaporating the glycerin, in which the -vapours are removed by means of an electric fan.

^Standard Specifications for Soap Lye and Saponification Crude Glycerins.—The following standard specifications were drawn up by the British Executive Committee on Crude Glycerin Analysis, and approved at a meeting of glycerin makers, buyers and brokers held in Lonjon on October 3, 1912:

Soap Lye Crude Glycerin.—Analysis to be made in accordance with the International Standard Methods. *Glycerol*—The Standard shall be 60% of glycerol. Any crude glycerin tendered which tests 81% of glycerol or over, shall be paid for at a *]ro rata* increase*, calculated as from the standard of 80%. Any crude glycerin which tests un ler 80% of glycerol, but is 78% or over shall be subject to a reduction of *H* times the shortage,-calculated at the *pro rata* price as from 80%. If the test falls below 78% the buyer shall have the right of rejection. *Ash.*—The standard shall be 10%. In the event of the percentage of ash exceeding 10%, but not fix (.-ceding 10*5%, a percentage reduction shall be made for the excess calculated as from 10% at *pro rata* price, and if the percentage of ash exceeds 10-5%, but docs not exceed 11%, an additional percentage reduction shall be made equal to double the amount in excess of 10-5%. If the amount exceeds 11% the buyer shall have the right to reject the parcel.

Organic Residue.—The standard shall be 3%. A percentage deduction shall be made of 3 times the amount in excess of the standard of 3%, calculated at *pro rata* price. The buyer shall have the right to reject anj parcel which tests over 3-75%.

Saponification Crude Glycerin.—Analysis to be made in accordance with the International Standard Methods. *Glycerol.*—The standard shall be 88%. Any crude glycerin which testa 89% or over shall be paid for at a *pro rata* increase calculated as from the standard of *ll/o-* Any crude glycerin which tests under 88%, but is 8C% or over, shall ho subject to a reduction of 1} times the shortage, calculated at *pro rata* price as from 88%. If the test faUs below 8(i<>/or the buyer shall have the right of rejection. *Ash.*—The standard shall be *0-5%.* In the event of the percentage of aeh exfieedir'.^ 0*5%, but_ not exceeding 2-0%, a percentage reduction shall be. made equal to double the amount in excess of 0-5%. If the amount of ash exceeds 2-0,% the buyer shall have the right to reject the parcel.

Organic Residue.—The standard shall be 1%. A pfpeentage deduction shall *be* made of twice tjie amount in excess of the standard of 1%, calculated at *pro rata* price. The buyer shall **hfve** the right to reject any parcel which tests over 2%.

Glycols in Glycerin.—Rayner (J.S.C.I. 1926, 45, 26OT) has shown that *trimethyUne glycol,* HOCHJ^CH^CHJOH, b.p, 210-211% sp.gr. $20^D/20°$ 1-0554 (Coflw and 8arw»y, ***ibid.*** 1922, 41, I7T) may be»formed by bacterial fermentation {<•/. " *CUrobacUr* «/'.," Werknian and Gilleii, J. Bact. 1032, 23, 167) when dilute crude glycerin lyes are stored firlong perinds. Rayner>#tatcs that small amounts of the glycol are not objectionable in glycerin intended for nitration, but if the crude contains considerable quantities *{e.g.* 2-3%) it is difficult to manufacture a dynamite glycerin of the requisite density.

DETEIOH NATION OF GI.YCOLS.

Since the standard methods for glycerin analysis were agreed upon in 1911, and later accepted as Internationa) Standard Methods, it has been found possible to devise means for the estimation of the glycols present in crude glycerin, in addition to *irimetliyleneglycol* (1:3-dihydroxy propane), crude glycerin is known to contain 1:2-dihydroxjjpropane, and other glycola are probably also present. An accurate method for tbe quantitative differentiation between the 1:3- and the)*;* 2-diLydroxypropanes is not available, but the method described below, which is substantially that of Cocks and Kahvay (J.LSX'.I. Id22,41, 1 IT) represents a substantially accurate means of determining the total amount of the glycols present in crude glycerin?

100 g. of the original sample are weighed into a 400 nil. distillation flask, to which is attached an air condenser (3 ft. long) connected to a 100 ml, receiving vessel. The distillation flask is also fitted with the usual glass tube^lrawn to a fine capillary and tbe distillation is carried out at approximately 30 mm. -pressure. If troublesome frotliing occurs it can bo checkal by the addition of hydrochloric acid to faint acidity. The heating should be so regulated that distillation proceeds at the rate of 1 drop per second. Approximately 30% is distilled, **the** receiving fla^k having been previously roughly calibrated, but the exact weight of the distillate is ascertained at the end of the **distillation.**

If any printing has occurred during distillation, the distillate must be completely r«-diwtiUed. The specific gravity of the distillate at $2O^J/2O^a$ is determined, and the percentage of acctylisable compounds calculated as glyccrol is ascertained by tin- .-u-t'tin test.

Method of Calculation.-2-T\\Q sp.gr. at 2O°/2O° of a glycerin I'orreK ponding to the acetin **Talus** of the distillate as found above is ascertained from specific gravity tables *{cf.* Tables III and *IK,* £p. 49, 50). From this is deducted **the** specific gravity of the distillate actually found by experiment, and the result is divided by a variable factor obtained from Table XIV. The quotient returns the percentage of glycolfl calculated as trimethylene glycol in the distillate, from which the percentage in the original sample may be computed. For example:

100 g. of the crude glycerin gave 35 g. of distillate having a sp.gr. of 1-1865 at 20*720°. The acetin value of the distillate corresponded to an apparent glveerol content of 77-4%, and the appropriate factor *(see* Table XIV) is 000161.

The sp.gr. at $20^D/20°$ of a glycerol of 77-4% concentration is 1-2038 (»ee Table III): hence the percentage of trimethylene glycol in tbe diytillate

$$\frac{1\text{-}2038\text{-WS}65}{000161}\cdot 10\text{-}7\%,$$

and the perc&itage of trimethylene glycol in tbe original crude glycerin

$$\frac{10\text{-}7\times 35}{100}=3'75\%.$$

TMSI.K XIV.—FACTOBS FOB USE IN THE CALCULATION OF GLYCOL CONTENT,

Acetin value, %.	Factor.
50	000134
55	0-00139
60	0-00144
C5	000149
70	000154
7fi	000159
80	000164
86	**000169.**
90	**0-00174**
95	000179

An alternative method for the determiiujtion °f glycolfl is afforded by'Faebini and Somazzi's process (Ind, Olii e. Gnussi, 192:J, Nos. 2, 6, 10; c/. Chem. Trade J. 1923, 78. 127, 702; Chim. et Ind., 1924, Spec. No., p. 118D). These authors determine the apparent glycerol content by the dichromate titration method which is suitably modified so that the carbon dioxide evolved by the oxidation may be collected and weighed. From a consideration of the two relations:

(1) $C_3H_5(OH)3+7O=3COs,+4HjO$, and
(2) $C_3H_6(OH)_{ii}+80\text{^}3C0_2+4H_{;i}O$

it is evident that the glycol content can be readily calculated from the dichromate figure and the amount of carbon dioxide produced. The value of this method foi; the analysis of crude **glycerins** is confirmed by Berth (Seiferui.-Ztg. 1929, 56, 2G9, 279).

USES OF GLYCERIN.

Besides the well-established UKC of glycerin for dynamite manufacture and In the preparation of tobacco and in pharmacy, a few of the recent applications of glycerin in the arts may be briefly mentioned {see also Darke and **Lewih**

Chem. [illegible]; J. W. Lawrie, "Glycerol and the Glycols," New York, 1928).

Alkyd ("Glyptal") Resins.—Glycerin may be condensed (esterified) by heating with phthalic acid (or anhydride) (*cf.* Van Bemmelen, 1856; Callahan, U.S.P. 1108329/1914) to yield fluid products which polymerise and resinify as the heating is continued. These form moderately soluble "heat-convertible" ("green") resins, which can be transformed into hard insoluble and infusible resins by baking. If part of the phthalic acid is replaced, *e.g.* by succinic acid, more soluble flexible resins are obtained. If drying oil fatty acids are incorporated, a class of "oxygen-convertible" or "oil-modified glyptal resins" can be prepared; these are soluble in drying oils and solvent naphtha, forming varnishes which dry to hard resistant films on exposure to [illegible] (*cf.* Kienle, Ind. Eng. Chem. 1929, 21, 349). These glyptal resins are extensively used in lacquers, air-drying or baking varnishes, insulating and petrol-proof varnishes, adhesives, etc., [illegible] small moulded articles.

Glycerin is used as a moistening and pre[illegible] agent in many food products and in the manufacture of printer's roller compositions and various inks. [illegible] applied successfully as a drying agent for town-gas (*cf.* Knecht and Muller, J.S.C.I. 1924, 43, 177T), and for a time it was used in France [illegible] alcohol (Marillier and [illegible] Chim. [illegible] Ind. Spec. No. [illegible] 08; Chim. et Ind. [illegible] 19, 296 (84T); Marillier and Granger, [illegible] P. 27171 and [illegible] solutions have been suggested for steel-quenching (*v.* [illegible] Trans. Amer. Soc. Steel Treating, [illegible]).

Gly[illegible] widely used to provide circulating non-freezing solutions, *e.g.* for motor-car radiators; such solutions may with advantage [illegible]ntain small amounts of anti-oxid[illegible] even when supercooled freeze wi[illegible] [illegible]ing dangerous pressures by expansion.

The figures in the follo[illegible] the freezing points of gly[illegible] from Lane (Ind. [illegible]).

TABLE XV.—FREEZING POINT OF GLYCEROL SOLUTIONS (Lane).

% Glycerol (by weight).	F.p. °C.	% Glycerol (by weight).	F.p. °C.	% Glycerol (by weight).	F.p. °C.
11·5	− 2·0	64·0	−41·5	70·9	−37·5
22·6	− 6·0	64·7	−42·5	75·0	−29·8
25·0	− 7·0	65·6	−44·5	75·4	−28·5
33·3	−11·0	66·0	−44·7	79·0	−22·0
44·5	−18·5	66·7	−46·5	84·8	−10·5
50·0	−23·0	67·1	−45·5	90·3	− 1·0
53·0	−26·0	67·3	−44·5	95·3	+ 7·5
60·4	−35·0	68·0	−44·0	98·2	+13·5

[illegible] solutions [illegible]ercooled without crystallisation taking place; seeding is usually [illegible] but as stated [illegible] quantities of glycerin will solidify when left undisturbed for long periods at low temperatures.

A paste made by moistening litharge with glycerol sets rapidly without contraction to a hard cement-like mass. By selecting suitable proportions, and diluting with other oxides, fuller's earth, etc., the setting-time can be varied, and a series of useful cements and luting-compounds prepared (*cf.* Stäger, Z. angew. Chem. 1929, 42, 370; Gleason, Paper Trade J. 1932, 95, T.A.P.P.I. Sect. 169; Neville, J. Physical Chem. [illegible]).

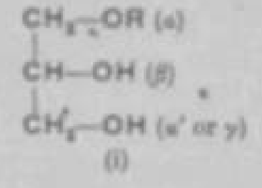
For many of these [illegible]s, including nitration, ethylene [illegible] glycerol, and [illegible] increase the glycol may prove a serious rival (*v.* DYNAMITE, Vol. IV, 245d).

DERIVATIVES OF GLYCEROL.

For compounds of glycerol with metal oxides, *see* p. 56c.

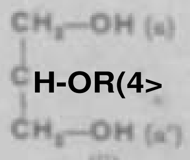
Esters of Glycerol.—As a trihydric alcohol, glycerol is capable of forming esters with organic or inorganic acids, or esters containing both inorganic and organic acid residues.

Organic Esters of Glycerol.—*Glycerides.*—The most important esters of glycerol with organic acids are the tri-esters—*triglycerides*—resulting from the combination of the three hydroxyl groups of the glycerol molecule with [illegible] of a higher monobasic fatty acid, which [illegible]haracteristic and principal components of the natural oils and fats of animal or vegetable [illegible] esterification [illegible] or two of the three hydroxyl groups, glycerol forms mono- and di-acid esters respectively, [illegible] of the fatty acid esters, are usually [illegible] as *monoglycerides* and *diglycerides*. As wo[illegible] expected from [illegible] constitution of gly[illegible] structurally isomeric monoglycerides may exist, according to the position which the acid radical [illegible] indicated in [illegible] represents the aci[illegible]. Monoglycerides corresponding to these formulæ are termed α- and β-monoglycerides respectively.



$$\begin{array}{l}CH_2\text{—}OR\ (\alpha)\\ |\\ CH\text{—}OH\ (\beta)\\ |\\ CH_2\text{—}OH\ (\alpha'\text{ or }\gamma)\end{array}$$

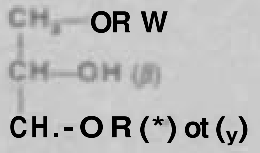
(i)



$$\begin{array}{l}CH_2\text{—}OH\ (\alpha)\\ |\\ CH\text{—}OR\ (\beta)\\ |\\ CH_2\text{—}OH\ (\alpha')\end{array}$$

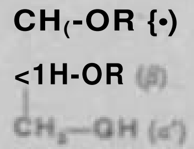
(ii)

When a second [illegible] the molecule, diglycer[illegible] both acid radicals are alike, two isomers are possible, viz. the symmetrical α[illegible]ii) and the αβ (iv) diglyceride:



$$\begin{array}{l}CH_2\text{—}OR\ (\alpha)\\ |\\ CH\text{—}OH\ (\beta)\\ |\\ CH_2\text{—}OR\ (\alpha'\text{ or }\gamma)\end{array}$$

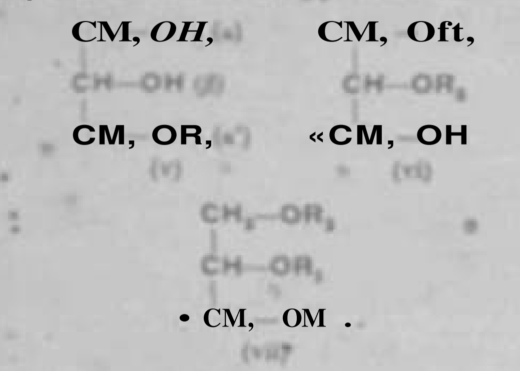
(iii)



$$\begin{array}{l}CH_2\text{—}OR\ (\alpha)\\ |\\ CH\text{—}OR\ (\beta)\\ |\\ CH_2\text{—}OH\ (\alpha')\end{array}$$

(iv)

[illegible] acid radicals are different, three isomers (v), (vi) and (vii) are possible, which m[illegible] "mixed diglycerides":



The α-monoglycerides (i), the αβ-diglycerides (iv) and the three mixed diglycerides contain an asymmetric carbon atom, so that, theoretically, two optical isomers are possible in each of these cases, and the ordinary synthetically prepared inactive compounds presumably represent racemic forms.

Grün and Limpächer (Ber. 1927, 60 [B], 255; cf. ibid. 266) have succeeded in resolving the sulphuric ester of αβ-distearin into two fractions by means of the brucine or strychnine salts; the potassium salt of the recovered distearin sulphate exhibited optical activity in cold solution, although the distearin prepared from it was entirely inactive.

Abderhalden (Ber. 1915, 48, 1847) and Bergmann et al. (Z. physiol. Chem. 1924, 137, 27, 47) have synthesised amino-αβ-diglycerides (diacylaminopropanes) which could be resolved into optical antipodes, from which [illegible] slightly optically active αβ-diglycerides were obtained. Optically active mono- and triglycerides have also been synthesised from d-(+)-acetone-glycerol by H. O. L. Fischer and Baer (Naturwiss. 1937, 25, 588; Baer and H. O. L. Fischer, J. Biol. Chem. 1939, 128, 479).

If one or more of the fatty acids concerned is (are) optically active—ricinoleic, chaulmoogric or hydnocarpic acids, for example—they confer [illegible] glycerides, apart [illegible] any [illegible] configuration of the acyl [illegible] within the glyceride molecule.

Mono- and di-glycerides [illegible] fresh fat, [illegible] formed in the course of slow hydrolysis of the natural tri[illegible]cerides; hence [illegible] by a natural process on exposure [illegible] air, light and moisture.

Diacetin, the diglyceride of acetic [illegible] finds some use as a solvent is discussed [illegible] the article ACETIN.

All the tri-esters of glycerol (the *triglycerides or fats*) may exhibit stereo-isomerism; the following varieties exi[illegible] of simple [illegible] $C_3H_5(OR)_3$, [illegible] all the acid radi[illegible] alike; two types of isomeric [illegible]ixed triglycer[illegible]ich two of the three acid radicals are identical (e.g. α-oleodistearin and β-oleodistearin); and three isomeric mixed trigly[illegible] radicals [illegible]re different.

Although theoretically any triglycerides containing an asymmetric carbon atom may exist in optically active isomeric forms, such active glycerides have never been found in the natural fats as recovered from animal or vegetable tissues; in [illegible] the known cases of optically active oils, e.g. [illegible] (q.v.), chaulmoo[illegible]ra oil (q.v.), [illegible] glycerides. B. S[illegible] Proc. Imp. Acad. Tok[illegible] that in the [illegible] optically active, [illegible] in very rapidly [illegible] the tissues and extraction of the fat.

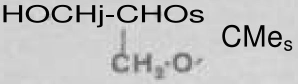
[illegible] GLYCERIDES.

α-Monoglycerides and αα′-diglycerides may be prepared by treating the corresponding α-monochlorohydrin and αα′-dichlorohydrin respectively (or [illegible] iodo-hydrins) with the sodium, pot[illegible] of the [illegible] fatty acids (G[illegible] 78; Kr[illegible]xed diglyc[illegible]cyl-c[illegible] mixed [illegible] 1909, 42[illegible]. By treating digly[illegible] an acyl chloride, a third fatty acid [illegible] be introduced into the molecule. Simple triglycerides are also formed (together with some di- and mono-glyceride) by heating glycerol [illegible] excess of the fatty acid (Berthelot, Ann. Chim. Phys. 1854, [iii], [illegible] 216, 240; cf. Scheij, Rec. trav. chim. 18[illegible] [illegible]ating the sodium or silve[illegible] fatty acid [illegible] tribromohydri[illegible]; cf. Partheil and Von Velsen, Arch. Pharm. [illegible]900, [illegible] 261, 267) or by heating mono- or diglycerides [illegible] further quantity of the fatty acid [illegible]

The w[illegible] to produce β-monoglyc[illegible]glycerides by meth[illegible], e.g. starting from β-chlorohydrin, or by introd[illegible] fatty acid radic[illegible] fatty acid chloride) [illegible]yl-α′-chlorohydrin and then hydrolysing [illegible] α′-chlorine atom.

It has been proved, [illegible]. Fischer that, in reactions invol[illegible] di-glycerides, [illegible] acyl (or [illegible] general [illegible]de; further, migration [illegible] group to an [illegible] readily, [illegible] and his successors [illegible] of α- and β-monoglycerides w[illegible] the earlier workers from syntheses designed to produce β-glycerides: [illegible] the "αβ-diglycerides" rec[illegible] early literature [illegible] αβ-dichlorohydr[illegible] been [illegible] the [illegible]mann [illegible]actions, [illegible] by which [illegible] des, [illegible] 1927, 170, 31; 1928, 175, 311): Bergmann and Carter (*ibid.* 1930,191,211).

The starting-point of many of these syntheses is " acetone-glycerol " (aj9- *hop* ropy lidene ether of glycerol)



$$\begin{matrix}HOCH_2\text{-}CH\cdot O \\ \mid \\ CH_2\cdot O\end{matrix} \!\!> CMe_2$$

or a/J- or ay-benzylidene glycerol. Fatty acid radicals are introduced by interaction of the free hydroxyl group with the appropriate acyl chloride in the presence of quinoline or pyridine (see E. Fischer, M. Bergniann and Bar«iml, Ber. 1920, 68 [BJ, 1589, 1606, 1621; Bergmann *et al, ibid.* 1921, 54 [B], 936; *Z.* physiol. Chem. 1924, 137, 27, 47; Fairbourne, J.C.S, 1926, 3148 ; Fairbourne **el** *al., ibid.* 1926-32 ; Hibbert *et al.,* J. Amer. Chem. Soc. 1928 onwards; C. G. King *«t al., ibid.* 1932 onwa^is).*

These methods have been extended by Helferich and by P. E. Verkade and his collaborators, who have achieved syntheses of authentic a- and j8-monoglycerides, *aa'-* and a^-diglycerides and of mixed triglycerides of known configuration by employing the " trityl" (triphenylmethyl) derivatives of glycerol as intermediate stages (*cf.* Verkade and Van der Lee and collaborators, Proc. K. Acad. Wetensch. Amsterdam, 1934, 37, 812; 1937, 40, 580; Rec. trav." chim. 1035, 54, 716; 1936, 65, 267; 1937, 56. 365, 613). (The work of Verkade, Helferich and others is reviewed in *extenso* (with 42 references) and discussed by Verkadi in Fette u. Seifen, 1938, 45, 457; *cf. hlso* F. A. Norris, Oil at?d Soap, 1940,17, 257.)

The application of methods of deacylation and detritylation of mixer! acyl - trityl-g I yee rides to the determination of the configuration of mono- and di-gly^eridea is discussed in the same paper *(cf, also* **Verkade** and Van der Lee, Rec-trav. chim. I93&, 57, 4)7 *et smj.).*

Another method for the synthesis of unsymuetrieal simple diglyceridea is described by Daubert and King (J. Amer. Chem. Soe. 1939, 61, 3328): o-monoaodium glyceroxide is treated with benzyl chloroform[1] ate, and the free hydroxyl groups in the resultant a-carhofoen7,yloxyglyce*xd are acylated with an acyl hatide in the presence of quinoline, and the ater BO obtained is reduced catalytically to the «j9-diglyceride.

Pure triglycerides commonly exhibit the phenomenon &f a so-called " double melting-point " which was originally noted by Chevreut: if a glyceride is examined shortly after having bjen melted and fairly rapidly cooled, it will be found to melt (wholly or partially) at a certain temperature, then to solidify again at a **higher** temperature, only to roiuclt on further hen ting. On the other hand, the *crystalline* **glyceride** obtained, for example, by crystallisation from solution, or a solidified specimen which has been allowed to stand for & considerable time after solidification, shows a single melting-point corre**Bponding** to the higher figure registered in the previous case (c/. Table XVI). This behaviour was ascribed by Puffy (J.C.S. 1853, 6, 197} and Heintz (J. pr. Ch<-m. 1841), [i], 48, 382; *l$?>4,* [i], -63, 108; Poggendortf's Ann. Phys. Chem. 1854, 93, 4H • *cf. also* Grun and Htrhacht, Ber. 1907, 40, 1778; 1912, 45, 3691; Bonier, *Z,* I liters. Nahr. Gcnussm, 1&07, 14, 90, 97 ; 1909, 17, 353, 363} to the existence of two physical modifications of each **individual** glyceride: viz. an unstable (labile) low-melting modification nntl . stable, hi^li-int'lting form. (Bomer also refers to the melting-point of the labile form as the " transit! on-point," but tiiis nomenclature must be rejected, since the change from the labile to the stable form may take place even in the solid state, albeit less rapidly than in the molten condition.)

Crystallisation of the stable modification is a slow process (Le Chatolier and Cavaignac, Compt. rend. 1913, 156, 589), und when **Ehe melted gtyceride** is rapidly chilled, it first solidifies in the labile form, which gradually changes into the stable modification if it is allowed to stand for a **prolonged period** in the solid state, or is warmed for some time a few degrees **abova** the lower ni tit ing .point (c/. the m.p. of cocoa

TABLE XVL—MELT^IO-POIMTS OF PUBK GLYCERIDES (Böiner and Limprich).

Glyceride.	Melting-point.[2]	" Trail Bition-point."[1]	Solidifying-point.	Began to solidify.	Melting-point or glyceride heated above its "transition-poirtt,"
	°C.	°C.	°C.	°C.	°C.
Tristearin {from mutton tallow)	732	55-5	53-5	68	73·6
a-Palmitodistearin[8] (from tallow)	61-5	521	49-7	55	63-4
^-Palmitodiatcarin[8] (from lard)	681	62-J	60-0	55	68-5
Stearodipalmitin (from rout-ton tallow) . . . . .* .	58-1	(48)	45-9	52	685
Stearodipalmitin {from i«ni).	58-3	48-2	45·9	53	**58-8**

[1] Determined by Polenske'a method.

[2] *I.e.* lower melting-point.

[8] The reverse configurations assigned by Burner to the palmitodliUiaririB from tallow and lard respectively have been corrected In the light or Inter information.

butter (VoJ. J11 **£364)).** Further evidence for the above view **eras** given by the later experiments of Bomer and Ltmprich (Z. Unter*. Nahr. Genussm. 1913, 25, 307, 373) and by the work of Kcinders, Doppler and Oberg (Rec. trav. chim. 1932, 51, 917) on the existence of two crystalline modifications of cacao buttery and the existence not only of two, but of three polymorphic modifications of glycoridtsa (c/. Du£y, I.c.; Othmer, Z. anorg Chem. 1915, 91, 237; Nieolet, J.Ind. Eng.Chem. 1920,12,741 ; and Loskit, Z. p^iysiol. Chem. 1928, A, **134,** 135) has been established by the X-ray investigations of Clarkson and Malkin (J.C.S. 1934, 6o(i). The highest-melting to-called j9-modification is 3ho stable form referred to above, in which the gjyeeride erystal-Uses from solution: th<?intermediate a-form, obtained by fairly rapid cooling from a melt is crystalline, but the lowest-malting modification, obtained by very rapid cooling, is described"[1] by Mulkin as not truly crystalline but as possessing rather the properties of a glass. The melting-points **determined** by Malkin *£or* various simple triglycerides axe shown in Table XVII (c/. Othmer,^oskit, i.e.).

TABLE XVII.—MELTING-POINTS (°C.) OP TRittLYCERiDES (Clarkson and Malkin).

	£-form.	**a-form.**	Gloss.[1]
Trlatearin **[Octadi'cylin)** .	**7ir>**	**650**	54-5
XjamarEadn **(Hcjjtadcoylin)**	**03'5**	**81-0**	**50'0**
Tri]VLlmitii# (Hexadccylin) .	B6S	f-.tWl	•1 ;V(i
Tripentadecylln	**510**	51-5	**WO**
Trliiiyristin fTt!tra<kuylln)	**57-0**	**46-5**	**330**
Tntddroylui .	**440**	**41 0**	**250**
Trllaiirln {Dodecylin)	**46-4**	**85-0**	15-0
XHundecylin .	**30-5**	**K6-G**	**1-0**
Trfcaprin (Decylln) . .	**31-5**	**180**	**-15-0**
Tricaprylin (Oetylln) . .	**9-8-10-1***		

[1] These temperatures arc not triw **mefttag-potnta,** hut **an** tML* means of *a.* small **mettlos-range** : they usually vary by ±*V* (Clarkson and Mu]kin>.

[1] Hcrachberger, J. Amer. Clicm. Soc. 11)39, **ftl,** 3587-

In the case of other invcatigatofs who have only recorded two melting-points for each glvceride (as is general in *the older literature), these correspond as a rule with th<3 melting-points of the stable form and of Malkin's **lowest-**melting labile modification.

The property of " triple melting " was ibund to be general for all the simple triglycerides examined from tricaprin to triafcearm. In I In-case of the labile modifications, smooth curves are obtained on plotting the melting-points against the number of carbon atoms in the *f-M* i v acid concerned: the melting-points of the stable form, however, show an alternating or **eig-zag** progression (c/. Table XVII); or rather, the **melting-points** full on to two curves—the one for glycerides of acids with an even number of carbon atoms and the other representing the odd scries.

The existence of aimilnr triple polymorphism waa abo established in the case of the a-monoglycerides (T. Malkin *et* oi., J.C.S. 1936, 1628; f/.'Fiseher, Bergmann and Barwind, Ber. 1920, 53.[B], 1591; Rewadikar and Watson, J. Indian Inat. Sci. 1930, ISA, 128) and among the simple act'-diglyceridcs up to aa'-dipentadecoin : in the case of dipalmitin and higher glycerides, only two modifications of each glyceride could be found (Malkin *el al.,* J.C.S. 1937, 1409). The transitions between the various forms of the diglycerides is more rapid, however, than in the case of the triglycerides.

Since the natural fats are composed of mixtures of several individual glycerides, the phenomenon of the double- or triple-melting-point is liable to be obscured : in some cases, however, such as that of cacao butter, which consists of a relatively small number of component glycerides, the behaviour on melting and solidifying resembles that of a single •glyceride. I{i all cases, however, if it is desired to ascertain the ^melting-point of a fat which has recently been fused, it is necessary to allow the sample to stand for at least 24 hours (and preferably longer) before making the test.

The chemical formulie and melting-points of a number of synthetic simple triglycerides, of mixed triglycerides which occur commonly in natural fats and of some triglycerides which have been isolated from hydrogenated oi)B are shown in Table XVUI (figures drawn from the data of many authors collated by Hilditch in Hi I'ter-Schonfeld, " Chemie u. Technologic **der** Fette u. Fettprodukte," 1936, Vol. I, p. **lfW,** where the original references are quoted: melting-point data, details of preparation, etc., of many monoglyccridcs, diglyeeridea and synthetic mixed tri|lyceride« together with the original references are given in this work, also in Lcwkowitsch's " Chemistry and Technology of Oils, Fats and Waxpw," ami in similar *•xt-books).

Triacelin is used extensively as a solvent and plasticiscr *(v.* ACETTN).

Glycerol Esters of Inorganic Acids.—*GJyctryl Chlorohydrhts.*—The glyreryl r*ilorohydrlns or chloridVs of glycerol art- **chiefly** of interest as intermediate products in the synthesis of glycerol from propylene or ally! alcohol (r/. p. 42), and as the starting point for the older syntheses of glycerides.

n- *MunocMorohydrin,* an oily liquid, b.p. 2277760 mm. (Berthelot), 1597100 mm., 139718-mni. (Ihuiriot), 121-6-122-5715 mm. (Niviere); d", 1-338 (Hnnriot),rf" l-3215(Smith. Z. physikal. Chem. 1918, 92, 717), is miscible in nil proportions with water, alcohol or ether: it is formed, together with minor amounts of the 0-isomer, when glycerol is heated at 100°C. with moderate amounts of hydrogen chloride (Berthelot, Ann. Chim. Phyi. 18.')4, [in], 41, 296; Niviere, Bulk **Boo. ohim.** 1913, [iv], 13, 893; Compt. rend. 1913, 156. 1628; Hanriut, Ann. Chim. Phys. 1879, fv% 17, 62, 67; C0na.1t and Quayle, Organic Syntheses, 1932, **CoD,** Vol. J, p. 288).

With excess of hydrogen chloride—for example, by treating glyc^ol with hydrogen chloride in the presence of glacial acetic acid—*arx'-dkhlorohyririn,* b.p. 70-7371* mm. ia obtained (Conant and Quayle, *op. cit.,* p. 281)).

TABLE XVIII.

Glyceride.[1]	Formula.[2]	M.p. °C.	Isolated from [3]
Simple triglycerides.			
Tri-laurin	$C_3H_5(O·OC_{12}H_{23})_3$	45·6	Laurel oil.
Tri-myristin	$C_3H_5(O·OC_{14}H_{27})_3$	56·2	Nutmeg butter.
Tri-palmitin	$C_3H_5(O·OC_{16}H_{31})_3$	61·5	Palm oil.
Tri-stearin	$C_3H_5(O·OC_{18}H_{35})_3$	70, 72	Beef-fat; Borneo tallow (traces), cacao butter (traces).
Tri-olein	$C_3H_5(O·OC_{18}H_{33})_3$	liquid	Goose-fat.
Mixed triglycerides.			
Di-palmito-stearin	$C_3H_5(O·OC_{16}H_{31})_2(O·OC_{18}H_{35})$	55	Coconut oil (traces).
Di-palmito-α-stearin	" " " " "	57·5	Goose-fat, mutton-fat.
Di-palmito-β-stearin	" " " " "	63	" "
α-Palmito-di-stearin	$C_3H_5(O·OC_{16}H_{31})(O·OC_{18}H_{35})_2$	63·3	" "
β-Palmito-di-stearin	" " " " "	68	Lard, cacao butter.
Palmito-di-olein	$C_3H_5(O·OC_{16}H_{31})(O·OC_{18}H_{33})_2$	liquid	Lard, goose-fat.
Oleo-di-palmitin	$C_3H_5(O·OC_{18}H_{33})(O·OC_{16}H_{31})_2$	38·5	Goose-fat.
" "	" " " " "	38	Cacao butter.
Oleo-di-stearin	$C_3H_5(O·OC_{18}H_{33})(O·OC_{18}H_{35})_2$	42	Lard.
" "	" " " " "	44·5	Cacao butter.
β-oleo-di-stearin	" " " " "	45–46	Seed-fat of *Allanblackia Stuhlmannii.*
Stearo-di-olein	$C_3H_5(O·OC_{18}H_{35})(O·OC_{18}H_{33})_2$	liquid	Goose-fat.
Oleo-palmito-stearin	$C_3H_5(O·OC_{18}H_{33})(O·OC_{16}H_{31})(O·OC_{18}H_{35})$	31·4	Cacao butter.
" "	" " " " "	41	Lard.
Oleo-palmito-linolin	$C_3H_5(O·OC_{18}H_{33})(O·OC_{16}H_{31})(O·OC_{18}H_{31})$	—	Linseed oil.
Glycerides from hydrogenated oils.			
Myristo-palmito-arachin	$C_3H_5(O·OC_{14}H_{27})(O·OC_{16}H_{31})(O·OC_{20}H_{39})$	49·5	Hydrogenated whale oil.
Palmito-stearo-arachin	$C_3H_5(O·OC_{16}H_{31})(O·OC_{18}H_{35})(O·OC_{20}H_{39})$	57·3	" " "
Di-stearo-arachin	$C_3H_5(O·OC_{18}H_{35})_2(O·OC_{20}H_{39})$	62·3	" "
Stearo-di-behenin	$C_3H_5(O·OC_{18}H_{35})(O·OC_{22}H_{43})$	?	Hydrogenated rape oil.
Dihydrochaulmoogro-di-dihydrohydnocarpin	$C_3H_5(O·OC_{18}H_{33})(O·OC_{16}H_{29})_2$	30·7	Hydrogenated chaulmoogra oil.
Dihydrohydnocarpo-di-dihydrochaulmoogrin	$C_3H_5(O·OC_{16}H_{29})(O·OC_{18}H_{33})_2$	42·2	" " "

[1] Hyphens have been inserted in the names of the glycerides to facilitate reading, although they are commonly omitted in the literature.

[2] The order in which the acid radicals are formulated merely follows the order used in naming the glycerides: it is not intended to give any indication of their configuration in the glyceride molecule.

[3] Most of the glycerides occur in many different fats: the source mentioned is merely one such, from which the glyceride has been isolated and studied by the investigator.

P-Monochlorohitfrin, b.p. 146°/18 mm., d° 1-328 (Hanriot, *1%.,* p. 68) can be prepared by the action *of* hypochlorous acid upon allyl alcohol, whilst *ap-dichlorohydrin,* b.p. 182°, is obtained by treating allyl alcohol with chlorine.

Trichlorohydrin (glyceryl trichloride, propenyl trichloride), b.p. 158°, is produced by the action of phosphorus pentachloride upon dichlorohyclrin.

The bromo-* and *iodo-hydrins* may be prepared** by analogous methods, using the appropriate halogen or halogen acid (for the synthesis of glyceryl-aa'-dibromohyditfn, b.p. 110-112°/20 mm., *cf.* G. Braun, Organic Syntheses, 1934,14, ***41).

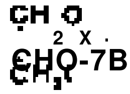
Data concerning a number of derivatives of the chlorohydrins containing" fatty acid radicals, such as chlorodilaurin and chlorodistearin, which have been prepared by Griin and^othcrs in the course of their work on the synthesis of glycerides,^ire collated by J. Lcwkowitsch in " Oils, Fats and Waxes," 6th ed. Vol. I, ch. 3.

The *sulphuric acid esters* of glycerol are obtained by dissolving glycerol in concentrated sulphuric acid. On heading with steam, the esters are easily dissociated into glycerol and sulphuric acid. All three possible glycerol sulphuric acids, glyccroltrisulphuric acid, glyceroldisulphuric acid and glyccrolmonosulphuric acid are known.

Nitric acid esters of glycerol—Nitroglycerin (v. EXPLOSIVES, Vol. IV, 491).

Glyceryl arsenite is formed by dissolving arsenious oxide in glycerol and heating to 250°. Above **25<P** it decomposes. It is volatile with the vapours of glycerol, hence, when distilling the arsenite in a current of superheated steam it is either volatilised unchanged, or is hydrolysed by the steam so that the distillate contains arsenious acid. Glyceryl arsenite is used in calico printing.

Olyceryl borate.—When glycerol is heated to 160° with boric anhydride a yellow hygroscopic mass of glyceryl borate



is obtained; this ester is unstable aild is decomposed by water but is somewhat soluble in alcohol (W. R. Dunstan, Fkarm. J. 1884,14, 41).

***Glycerylphosphoric esters* are obtained by heating** phosphoric acid with glycerol. The most important ester, commercially, is *monoglycerylphosphoric acid,* $C_3H_5(OH)_2O\text{-}PO(OH)_2$, which forms a scries of suits (sodium, lithium, calcium, strontium, *ron, etc.), largely used in pharmaceutical practice (especially in France).

It has been found by Umney and Bennett (Proc. Brit. Pharm. Conf. 1914, 22) that the composition of commercial calcium glycerophosphate varies. It should contain at least 15% of calcium, and may contain added citric acid to increase the solubility. The magnesium salt should contain not less than 10% of magnesium, and the ferric salt at least 15% of iron, and be soluble in 2 parts of water. Sodium glycerophosphatc crystallises with 5 mol. of water.

"The synthetic glycerylphosphoric acid is optically inactive and consists of a mixture of glyceryl-a-monophosphoric acid with some glyceryl-j8-monophosphoric acid: it is not, however, identical with fully racemised "natural glycerylphosphoric acid" which may be recovered from phosphatides of animal or vegetable origin. It has been shown by King and Pyman (J.C.S. 1914, **105,** 1238) that the commercial crystallised sodium salt- introduced by Poulenc Frères *(cf.* F.P. 373112) consisted of sodium glyceryl-j8-monophosphate. Natural glycerylphosphoric acid consists of a mixture of about 3 parts of the 0-acid with 1 part of the a-isomer, and displays a certain degree of optical activity *{cf.* Karrer *el al.,* Helv. Chim. Acta. 1926, 9,3).

Both glyceryl-monophosphoric acids havo been prepared by Karrer *et al. (I.e.)* from natural lecithin. ^The 0-acid can be precipitated as a crystalline insoluble double salt with barium nitrate. The a-acid forms only a simple barium salt, which is precipitated from solution on boiling.

Both glyceryl-a-monophosphoric acid and glyceryl-)8- monophosphoric acid have been synthesised by King and Pyman *(I.e.*; *cf.* Hill and Pyiran, J.C.S. 1929, 2236); the respective quinine salts melted at 153-154°C. *(cf.* m.p. 155° recorded by Karrer and Benz, Helv. Chiro. Acta, 1926, 9, 23) and 178-180°C Glyceryl-a-monophosphoric acid has also been synthesised by Karrer and resolved into its optical isomera through the strychnine salt (Karrer and Benz, ***I.e.,* and *ibid.* 598).**

Optically active^glycerylphosphoric acid may be synthesised by adding phosphoryl chloride to a solution of rf-a-bromohydrin in dry pyridine at below —10°. The bromine is removed by lithium hydroxide and the product is isolated as nearly pure lithium cl-glyceryl-a-phosphate

$$HOCH_2CH(OH)CH_2OPO(OLi)_2,$$

[a]Jf=+3-51° in aqueous solution. Lithjjpn *l*-glycerylphosphate has $[a]\}>^8$=-3-02^0 (Abderhalden and Eichwald, Bcr. 1918, **51,** 1308).

l-(—)-glyceryl-a-monophosphoric acid synthesised from d(+)-acetone-glyccrol by H. O. L. Fischer and Baer (Naturwiss. 1937, **25,** 589; Baer and H. O. L. Fischer, J. Biol. Chem. 1939, **128,** 491) is stated to be identical with the natural product obtained from lecithin.

Phosphatides.—Very great physiological interest, as well as some commercial utility, attaches to a group of mixed triglycorides which contain both fatty acid and phosphoric acid residues, and are known as *phosphatides* (Thudi**chum), *phospholijrins* (Leathcs) or *phosphoainino lipids.***

Although their precise rôle is not yet fully understood, it is clear that the phosphatides play an extremely important part in the fat-metabolism of the living organism.

In these compounds, two lwig-chain fatty acid radicals (which may be saturated or unsaturatcd, *e.g.* stearyl or oleyl residucs)"and one phosphoric acid residue arc combined with glycerol: further, one of the two remaining free hydroxyl groups of the phosphoric acid nucleus is combined with an organic base—choline in the case of the *lecithin* group of phosphatides, and colamine (fl-aminoethanol, jB-hydroxyethylamine) in the case of the *kephalins.* The phosphatides, which are described more fully elsewhere *(cf.* H. and I. S. MacLean, " Lecithin and Allied Substances: —The Lipins," London, 1927; Thierfelder and Klenk, " Chemie der Cerebroside u. Phosphatide," Berlin, 1930; Leathes and Raper, " The Fats," London, 1925), are found widely distributed in small quantities in animal and vegetable tissues (frequently in association with fats), and especially in the physiologically active organs and secretions such as the brain, liver, blood, egg-yolk, milk, etc. They occur in smaller quantities in plant tissues, notably in the seeds of the soya bean.

For the separation of a- and ^-lecithins and -kephalins from soya bean and brain phosphatides, *cf.* B. Suzuki and collaborators (Y. Yokoyama *etal),* Proc. Imp. Acad Totyo, 1930, 6, 341; 1931, 7,12, 226; 1932, 8,183, 358, 361, 424, 428, 490).

Bodies of the lecithin and kephalin type containing saturated fatty acids have been synthesised by Grim and Limpacher (Ber. 1926, 59 [B], 1350; 1927, 60 [B], 147; *cf.* Hundeshagen, J. pr. Chem. 1883, [ii], 28, 219): > the configuration of these products is discussed by Verkade and Van der Lee (Proc. K. Akad. Wetensch. Amsterdam, 1937, 40, 858; Fette u. Seifen, 1938, 45, 457) and by Kabashima and Suzuki (Proc. Imp. Acad. Tokyo, 1932, 8, 492; Kabashima, Ber. 1938, 71 [B], 76, 1071). Phosphatides containing oleic and other unsaturated acids have been synthesised by Griin and Memmen (unpublished; *v.* ~Hefter-Schonfeld, " Chem. u. Technologie d. Fette u. Fettprodukte," 1936, Vol. I, 483; method patented by Hoffmann-La Roche & Co., A.-G., G.P. 608074). For the synthesis of chaulmoogryl and hydnocarpyl glycerophosphatides, *set* Wagner-Jauregg and Arnold, Ber. 1937^70 [B], 1459; Arnold, *ibid.* 1938, 71 [B], 1505.

The new methods of Verkade and his collaborators for the synthesis of glycerides *(see above)* may also be adapted for the synthesis of glycerophosphoric acids and phosphatides of known configuration.

The phosphatides are soluble in fats but differ from these in being soluble in alcohol and insoluble in acetone: they emulsify readily with water, and hence find extensive commercial use as emulsifiers in the manufacture of margarine and other technical emulsions, as additions to soap and as a viscosity-modifying agent in the manufacture of chocolate *(v.* Vol. Ill, 87c). Lecithin recovered from soya beans now largely replaces lecithin prepared from animal sources (egg-yolk, brains) for commercial purposes.

Glyceryl Ethers.—Mono- and di-alkyl (or aryl) ethers may be prepared by treating the corresponding chlorohydrins with the appropriate alcohol and caustic soda. The tri-ethers are made from the di-alky) derivative) by reaction with sodium and an alkyl sulphate.

These ethers are stable, inodorous compounds, possessing excellent solvent properties for organic substances, such as nitrocellulose, resins, oils, etc. The following belong to the class of "high boiling" or "medium boiling" solvents: monomethyl ether, b.p. 196°; dimethyl·ether, b.p. 169°: trimethyl ether, b.p. 148°; monoethyl ether, b.p. 230°; diethyl ether, b.p. 191°; triethyl ether, b.p. 230°; di-wopropyl ether, b.p. 112°; di-i«oamyl ether, b.p. 270°. The iroperties of a number of glyceryl ethers (and also of some glyceryl acetals and ketalbj are listed by Du Puis, Lentk and Segor in Oil and Soap, 1941,18, 31.

Somo, *e.g.* the *diethyl ether,* are used as lacquer solvents, and others, *e.g.* the mixed *diiolyl ethers* (b.p. 200-210°/20 mm. »n steam), as plasticisers (cf. Fairbourne, Chem. and Ind. 1930, 49,1021). The lower members of this series are water-soluble. For the configuration of the isomeric glyceryl ethers, *see* Fairbourne (J.C.S. 1930 *et seq.);* Hibbert (J. Amer. Chem. Soc. 1928 *et seq.).*

The *ap-\8Op,opylidene ether* **of glycerol** ("*acetone-glyerol*") **and the** *aft-* **arri** *aa'-* benzylidene ethers are of interest in connection with the synthesis of artificial glycerides {*see* p. 66a).

Polyglycerols; Diglycerin. — *Diglycerin* (Diglyceryl ether, diglyceryl alcohol, bisdihydroxypropyloxide (Ncf, Annalen, 1904, 335, 239)), $(HO)_2C_3H_6$—O—$C_3H_5(OH)_2$, is the lowest member of a series of condensation products—ethers—of glycerol which are formed when glycerol is heated. It is present in, and may be separated from, the *glycerin foots* or still residues obtained in the distillation of glycerin. In ordinary circumstances, however, it is more convenient to manufacture diglycerin and polyglycerols by the condensation of pure glycerin *(cf.* Claessen, GrP. 181754, 198768; Nobel Explosives Co. *et al.,* B.P. 24608/1910; Lever Bros. Ltd., B.P. 442950; U.S.P. 2071459; Henkel & Cie, G.P. 494430; I.G. Farbenind. A.-G., G.P. 575911, 623482). The condensation of glycerin by heating it in the presence of magnesia or silica is claimed to furnish a product consisting large'y of diglycerin. Iodine has been used as catalyst for the condensation by Hibbert (U.S.P. 1126467) and Lewis (J.S.C.I. 1922, 41, 97T), but this method is adversely criticised by Rayner *(ibid.* 1922, 41, 224T).

Lourenco^Ann. Chim. Phys. 1863, [iii], 67, 299) prepared both diglycerin and triglvcerin, ($C_9H_{20}O_7$), b.p. 275-285°/10 mm., by heating glycerol with monocKiorohydrin.

Diglycerin is an extremely viscous, hygroscopic liquid, b.p. 257-260°C./30 mm. (Lewis), 261-262°C./27 mm. (Ncf, *l.c);* 235-240°C./6 mm. (Niviere, Compt. rend. 1913, **156,** 1776), rfj° 1-3215; djjj 1.3183 (Lewis).

Polyglycerols.—-As the temperature of the condensation of glycerin is increased, "polyglycerols" of higher molecular weight are formed. Thus Rangier (Chim. et. Ind. 1929, Spec. No. 8e. (Strasbourg and Luxembourg, Congr. de Chim. ind., (1928), p. 535C) has isolated tri- *(cf.* Lourenco, I.e.), tetra-, penta- and hepta-polyglyccrols together with other unidentified solid condensation derivatives, from the products of the polymerisation of glycerol at 245-265°C. in the presence of sodium acetate. Rangier *(I.e.)* suggests that condensation products of the glycide type {I4. in which water has been eliminated between adjacent hydroxyl groups of the same glycerol nucleus) may be formedias well as the ether-type of condensation derivative.

Apart from the older use of glycerin foots in the manufacture of shoe-blackings, hectograph mass, etc., applications of pofyglycerols or their esters (including esters of fatty acids and of rosin acids) as lathering and detergent agents, or as assistants in the drawing of threads of cellulose derivatives have been proposed in various patents.

For methods of analysis of mixtures of diglycerol and glycerin, *cf.* Rayner (i.e.), Lewis (i c), Lawrie *[op?ciL,* p. 303). »

E. L. and H. E. C.

GLYCIDIC ACID,

$CH_aCHCO_aH.$

d\-Glycidic acid is prepared by the action of alcoholic KOH on the mixture of d-chlflr-hydracrylic acid and 0-chjprlactic acid obtained by treating acrylic acid with hypochlorous acid (Melikow, Ber. 1880, 13, 458; *cf.* Freudenberg, *ibid.* 1914, 47,2034). It is a liquid miscible in all proportions with water, alcohol and ether. The free acid and its salts readily pass into glyceric acid on warming with water. The ammonium, sodium, potassium and silver salts are crystalline, the calcium and zinc salts are amorphous.

The *ethyl ester* is insoluble in water and has b.p. 161-163°, *df** 10933 (Melikow and Zelinsky, *ibid.* 1888, 31, 2052).

d-Glycidic acid: the potassium salt is prepared by the action of alcoholic KOH on J-j3-bromolactic acid and has [a]" +30-2°. *1-Qlycidic acid* is similarly prepared from ci-jS-bromolactic acid and has [a]Jf -11-7° (Abderhalden and Eichwald,t'6icZ. 1915,48, 116).

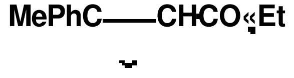
Substituted glycidic acids ard obtained from a/9-unsaturated aldehydes by treatment with alkali and either alkali hypobromite or hydrogen peroxide, *e.g. phenylglycidic acid* from cinnamaldehyde, and *methylglycidic acid* from crotonaldehyde (Kaufmann, B.P. 335391).*

GLYCIDIC ESTERS. Of recent years somewhat mysterious bo$es appeared on the synthetic-perfume market under the names "C$_{16}$ aldehyde (strawberry aldehyde)" and " C$_{.0}$ aldehyde (raspberry aldehyde)."

These so-called aldehydes are in fact glycidic esters, either pure or mixed.

The manufacture of these bodies, which are of considerable importance in the flavouring and perfume trades, is described in detail in B.P. 372013/1931, and is effected by condensing, by means of an alkaline condensing agent, a halogen-acetic acid ester with a cyclic aldehyde, or with an open chain ketone or a saturated cyclic ketone.

The typical strawberry compound, ethyl β-phenyl-0-inethylglycidate,



$MePhC——CHCO_2Et$

is*pre'pared by dissolving acetophenone and ethyl chloracetate in benzene or xylene and condensing with sodamide. It is a colourless liquid, b.p. 132-134°/5 mm., and has an agreeable odour resembling that of strawberries.

The three following esters have a raspberry odour: ethyl 4-ethylphenylglycidate, b.p. 155-160°/3 mm.; ethyl 4-methylphenylglycidate, b.p. 145-147°/3-4mm.; and ethyl 2:4-dimethylphenylglycidate, b.p. 150-155°/3 ram.

The ethyl esters of the di-wopropylphenylglycidic acids have musk or ambergris odours, and many others of the series are used for modifying flavours and odours. For example, ethyl 2:4-di-f*opropylphenylglycidate is a liquid, b.p. 175-185°/3 mm., having an ambergris odour.

Jg. J F.

GLYCIDOL *(glycide, epihydrin alcohol),'*

$CH_a\text{-}CH\text{-}CH_a\text{-}OH.$

dl'Glycidol.—A yield of 90% is obtained by the action of metallic sodium on glycerol monochlorhydrin dissolved in anhydrous ether. It is a liquid, b.p. 65-66°/2-2-5 mm, 41°/1 mm., *d*** M143, *r%* 1-4302.

Characteristic derivatives are the *pkenyl-* and *a-naphthyl-urethanea* which form colourless needles from high-boiling petroleum and melt at 60° and 102° respectively (Rider and Hill, J. Amer. Chem. Soc. 1930, 52,1521).

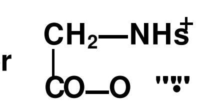
Ethers.—Methyl, b.p. 115-118°; *ethyl,* b.p. 124-126°, *d*° 0-9646; *inoamyl,* b.p. 188°, <*» 0-90; *phenyl,* b.p. 243-2&^{0}, 133°/23 mm.

l-Olycidol has d^{18} 1-1050 and [ojj,^{8} -8-55°.

d-0fycirfoZhas<n-lO54and[a]$_D$ +7-69° (Abderhalden and Eichwald, Ber. 1915,48,1855-1864).

GLYCINE. *Glycocoll, Aminoacetic acid,*

NH_2CH_aCOOH or



$\begin{array}{l} CH_2—NH_3^+ \\ | \\ CO—O^- \end{array}$

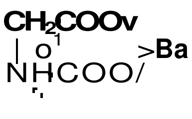
(Sakurai, Chem. Soc. Proc. 1894, 90; 1896, 38; Walker, *ibid.* 1894, 94), was discovered in 1820 by Braconnot (Ann. Chim. PhyB. 1820, [ii], 13, 114) among the products obtained by decomposing glue with sulphuric acid. It is obtained similarly from various proteins (Spiro, Z. physiol. Chem. 1874, 28, 187), and is present as the chief amino-acid in the sugar cane (Shorey, J. Amer. Chem. Soc. 1897, 19, 881; 1898, 20, 137).

PREPARATION.—(I) From *chloracetic acid.* Chloracetic acid (1 mol.) is dissolved in 4 litres of NH_4OH (sp.gr. 0-90) and allowed to stand for 24 hours at 30° or 2 days at 20° and the excess NH_3 recovered by distillation. The glycine solution is evaporated to 500 c.c. and 1 mol. of pure silver oxide stirred in until the reaction is over. The filtrate from AgCI is concentrated to 2Qp c.c, boiled to decompose any silver-ammonia complex, and again filtered. The glycine solution is treated *v,\h* " *norit*" (1-2 g.) filtered and treated with an equal volume of 95% EtOH and after 1 hour at 0° filtered; the separated glycine is washed with 95% EtOH and the crystals dried in a desiccator. Yiela, 43 g. (63% containing 0-1 mol. % of NH_4CI). To purify—dissolve the product .in 200 cc, water and shake with 10 g. granular *"permutite"* (after Folin), filter and precipitate the glycine with 250 cc. 95% EtOH. Wash and dry as above. Yield, 37-5 *e.,* 50% on whole process. It is free from NH_3lAd Cl' (Robertson, *ibid.* 1927, 49, 2889; *see also* Boutwell and Kuick, *ibid.* 1930,52, 4166; (Men and Hill, *ibid.* 1931, 53, 2797; Krause, Chem.-Ztg. 1931, 55, 666; Kulikov *et* of., J. Gen. Chem. U.S.S.R., 1932, 2, 730, 777; Contardi and Ravazzoni, Rend. 1st. Lomb. Sci. Lett. 1933, [ii], 66, 786; G.P. 616412).

(II) From *Aminoacetanitrile.*—Aminoacetonitrile hydrogen sulphate is hydrolysed with 40% H_2SO_4 for 3 hours at 125°. The yield may be >92%. The purification suggested is: heat the glycine solution by superheated steam with enough pure $BaCO_3$ to neutralise alLacids and expel all NH_3. Precipitate th3 barium as $BaSO_4$. Treat the filtrate with pure $PbCO_3$ until neutral, and if Cl' is present, cool to 0° for about 12 hours. Filter and decompose with H_8S. Concentrate the glycine solution and wash the product in MeOH (Cocker and Lapworth, J.C.S. 1931, 1391; *see also* Anslow and King, *ibid.* 1929, 2465).

Glycine can also be obtained by passing cyanogen into boiling hydriodic acid (sp.gr. 1-96) (Emmerling, Ber. 1873, 6, 1351); by heating potassium phthalimide with ethyl chloracetate (Gabriel and Kroseberg, *ibid.* 1889, 22, 427); by treating nitrosomalonic ester with zinc and acetic acid (Conrad and Schulze, *ibid.* 1909, 42, 729); by boiling hippuric acid with strong sulphuric acid (Curtius' J. pr. Chem. 1882, [ii], 26, 145; Dessaignes, Annalen, 1846, 58, 322); by treating glyoxylic acid with ammonium carbonate and subsequently heating to 120° with hydrochloric acid (Erlenmeyer, junr. and Kunlin, Ber. 1902, 35, 2438); by the action of hexamethybnetetramine on potassium monochloracetate (Bourcet, Bull. Soc. chim. -1898, [iii], 19, 1005; Auger, *ibid.* 1899, [iii], 21, 5).

In order to obtain the pure acid, the solution containing the acid, prepared by any of the above methods, is {reed from ammonia (if present) and freshly precipitated copper hydroxide is added. The copper salt of the acid which crystallises out is filtered off and decomposed with sulphuretted hydrogen. Another method consists in separating the acid from the impurities present by extraction with glycerol (Farbw. vorm. Meister, Lucius and Briining, G.P. 141976; Z. angew. Chem. 1903, 16, 527). Siegfried (G.P. 188005; Chem. Zentr. 1905, I, 1140; 1906, I, 451; 1907, II, 1466) adds barium (or strontium) hydroxide to the ice-cold solution, passes in carbon dioxide, precipitates the barium carbaminoacetate,



$$\begin{array}{l} CH_2COOv \\ |\ O^1 \quad >Ba \\ NHCOO/ \end{array}$$

by alcohol and decomposes it into glycine and barium carbonate, by heating with water (v. Vol. I, 120).

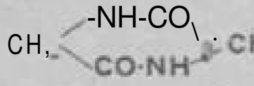
PROPERTIES.—Glycine crystallises from water in plates and from dilute alcohol in needles {*see* E.^ischer, Ber. 1905, 38, 2916; King and Palmer, Biochem. J. 1920, 14, 582). After drying at 100° the plate form begins to decompose at 212°, whilst the needle form remains unchanged until at r228° it turns brown and at 232-236° melts, turning purple and evolving gas; sp.gr. 1-1607 (Curtius, *I.e.).* It is soluble in 4-3 parts of cold water and in 930 parts of ethyl alcohol (sp.gr. 0-828) but is insoluble in absolute alcohol. Hydriodic - acid reduces glycine to ammonia and acetic acid (Kwisda, Monatsh. 1891, 12, 419), whilst sodium amalgam yields aminoacetaldehyde (Neuberg, Ber. 1908, 41, 956; E. Fischer, *ibid.* p. 1019). Electrolysis of the acid or the copper salt yields ethylenediamine (Lilienfeld, G.P. 147943; Chem. Zentr. 1904, I, 133- Kuhling, Ber. 1905, 38, 1638; 1907, 40, 757).? Hydrogen peroxide oxidises glycine to glyoxylic acid and formaldehyde (Dakin, J. Biol. Chem. 1905, 1, 171); treatment with nitrosyl chloride results in the formation of chloracetic acid (Tilden and Forster, J.C.S. 1895, 491). Glycine and its derivatives arc used in photography as developers in place of pyr6gallol, etc. (Farbw. vorm. Meister, Lucius and Briining, G.P. 142489; U.S.P. 767815; B.P. 20377/02; J.S.C.I. 1903, 22, 380). For the biochemistry of glycine, *see* Nord, Acta. mcd. Scand. 1926, 65, 1; Lundin, Biochem. Z. 1929, 207, 91; Edlbacher and Kraus, Z. physiol. Chem. 1928, 178, 239; Blix, Skand. Arch. Physiol. 1929, 56, 131; Christman and Mosier J. Biol. Chem. 1929, 83, 11; Re, 'Rev. Soc. argentina biol. 1929, 5,498; Reuter, Z. ges. exp. lied. 1935,95,217.

DERIVATIVES.—Aromatic Glycines are prepared from aromatic amines and monohalogenated acetic acids or dihalogcnatcd vinyl ethers (Imbert and Consortium fur Elektrochemische Industrie, G.P. 199624). *Glycocollamide* is produced when glycocoll and alcoholic ammonia are heated together at 1 G0°. *Glycocollanilide* is prepared from chlor- or bromacetanilide and ammonia (Majcrt, B.P. 5269, 1891; G.P. 59121; J.S.C.I. 1892,11, 369).

Esters.—The *ethyl ester* is prepared by the action of ammonia on chloracetic acid, and subsequent'treatment of the crude dry product with absolute alcohol and dry hydrogen chloride (Hantzsch and Mctcalf, Ber. 1896, 29, 1684; Hantzsch and Silberrad, *ibid.* 1900, 32, 70) or by the interaction of hcxamethylenetetramine and chloracetic acid and subsequent treatment as above (Auger, Bull. Soc. chim. 1899, [iii], 21, 5). It boils at 51-5-52-5°/10 mm. and has d_4 10358 (Schmidt, Ber. 1905, 3C, 200; *see also* Organic Syntheses, 1934,14, 46).

The following esters and their hydrochlorides are described by Abderhalden and Suzuki (Z. physiol. Chem. 1928, 176, 101): *Propyl,* b.p. 50-53°/16-18 mm., hydrochloride m.p. 73-75°; *isopropyl,* b.p. 52-55°/12-15 mm., hydrochloride m.p. 84-86°; *butyl,* b.p. 55-58°/8-ll mm., hydrochloride m.p. 64-00°; *^obntyl,* b.p. 00-63°/8-ll mm., hydrochloride m.p. 70-72°; *n-amyl,* b.p. 7J-76°/8-ll nim.Jiydrochloride m.p. 118-120°; *imamyl,* b.p. 7K-80°/8-10mm.; and *hrnzyl* b.p. 193-95/8-11 mm., hydrochloride m.p. 126-128°., Glycocollamkiocarboxylic Acid Esters (u. Einhorn, Chem. Zcntr. 1901, I, 1115; G.P. 108027).

Glycine anhydride, diketopiperazine,



discovered by Curtius and Goebel (J. pr, Chem. 1888, [ii], 37, 173). Ifc separates fro^o an aqueous solution of glycine ester on long standins.', but is bent prepared by treating the hydrochloride of the ester witC caustic soda (Fischer, Ber. 1906, 39, 2993). It is a *grhita* crystalline solid which, on heating, becomes browa at 245° and melts at 275°. ,

It forma the compound

$$C_4H_0O_2N_2CuCl_{i!J}2H_sp$$

v. ith CwC)$_2$, light blue rhombic needles. *CuBr.,* forms the corresponding bromide, bright green monoclinic prism a {Asahina and D6no, Bull. Chem. fcoc. Japan, 1328, 8.151).

Two luuleculct; each of glycinc anhydride and silver nitrate combine to form scaly lustrous crystals, in 80% yield (Asahina, Z. physiol. Chcm. 1028, 179,83; *see also* Dono Mid Amhino, *ibid.* 1929, 186, 133; and for FeCI$_3$ Dubsky, Vitu and Lunger, Metal) boree, 1932, 22, 1533).

Acetaminoacetic acid, ibnns colourless, compact, rhombic pri.ims, m.p. 200—2 '7^{11}, dutjomp. (Chattaway, J.C.S. **1931, 2495).**

Heptanolmercuric glycocollate, forms crystals, m.p» 210°, decomposed by **HCI.** It is very toxic and has no diuretic effect (Levy, Kayser and Sfiraa, %11. Sci. pharmacol. 1931 38, 573).

Ethyl aminoacetateglucoside, melts at 112° and is soluble in but decomposed by water. It has a bitter taste (H. von Euler and Zeile, Annalen, 1931,487, 103).

a-Monog)ycylglyceride, m.p. l(i7-17O°, decomposing at 250° (Weizmann and Haskelberg, Compt. rend. 1920, **189,** 104). ^{a}

The following therapeutic compounds are described by Chemische Fabriken J. Wiernik & Co.. A.-G.:

(i) Benzyl diethylaminoacotate hydrochloride. The ester has b.p. 149-150712 mm., and is a Btrongly basic oily liquid. The crystalline hydrocltloride ia very soluble in water and begins to melt at 89° (G.P. 637450). »

(ii) Benzyl dime thy laminoaeetate hydroehtoride, the ester boils at 138°/18 mm.; the hydroehtoridfl melts at **118"** (G.P. 037461).

(iii) Boozy] triinethylaminoacetatc hydrochloride, ha^ m.p. 6()-67° and is very soluble in water (G. I*. 5-13550).

(iv) Benzyl triet hat to laminoaeetate hydrochloride,

$$(CH_2(OH)CH_2)_3NCl\cdot CH_2\cdot COOCH_2Ph,$$

m.p. 165° (G.P. 54355C).

(v) Benzyl trimttthylaminoaeetate hydriodide.

$$Me_aNICH_aCOOCH_2Ph,$$

is made by the action of **CH$_3$I** on benzyl dime thy laminoaeetate, and has m.p. 13&-138^6 (G.P. 556883).

«Glycine reacts with phenols forming dyes, giving a blue dyestuff with phenol, A dye is also formed if glycine is treated with 40 c.c. of 25% thymol and 20 c.c. of 5% NH$_4$CI solution and bromine added until a red colour appears, followed by NaOH until the red colour is just discharged (Furth and Gotzl, Biochem. Z. 1936, 283, 358).

Tents for Glycine are described by Denig&s, Bull. Soc. pharm. Bordeaux, 1935, 73, 101, 108; Sandiest, Semana Mcd. (Buenos Airfcs), 1930, 37, 1287; Pfeiffer and collaborators, J. pr. Chem. 1930, [ii], 126, 97.

"*GLYCO&ROM.*" Glyceryl dibromhydrocinnamate.

GLYCOCHOLIC ACID (*v.* Vol. I, 689c).

GLYCOCYAM1NE. Guanidoacetic acid, $NH:C(NH_a)NHCH_2CO_2H$.

GLYCOGEN (*v.* Vol II, 302d).

GLYCQGENASE (». **Vol.** V, 14c).

GLYCOLLJC ACID, hydroxyacetic add, CH^(OH)CO$_2$H, ia present in sugar cane juice (75-78% of the total acidity), in unripo grapes and in wool wash-water. It is formed by the action of alkali on glyoxal, of potassium cyanide on formaldehyde, or by the oxidation of alcohol, glucose or other sugars, etc. On the small scale it jri best prepared from chloracetic acid by treatment with lime or other alkali *(cf.* U.S.P. 2028004), but technically electrolytic reduction of oxalic acid (CJ.P. 194038, 204787 ; *cf.* Tnja and Ceva, Giorn. Chim. Ind. Appl., 1926, 8, *:i)* appears to bo advantageous. A process of oxidising acetylene with intermediate formation of glyoxal forms another subject of patent claims (U.S.P. 1741394).

Glyeullic acid forms needles (from water), m.p. 78-79°, although an unstable modification, m.p. 63*, has been described (Miiller, Z. physikal. Chem. 1914, 86, 219; Schaum, Schaeling and Klausing, Annalen, 1916, 411, 193). On dehydration it yields the normal acid anhydride, as well as the ether anhydride, diglycollic acid, COJHCHJO-CHJCOJH, and polyoJtymethyleue. Esters of glycollic acid may be or/;-*ined not only by normal methods but also by the interaction of anhydrous alcohols with sodium chloracetate {B.P. 337609):

$$CH_2Cl\cdot CO_2Na+R\cdot OH \rightarrow CH_2(OH)CO_aR+NaCl$$

Glycollic esters of lung-chain aliphatic alcohols are of value in that they combine with sodium thiosulphate to give soap-like compounds.

GLYCOLYSIS. DEKISITION.—The term " glycolysia " was originally applied to the process by which sugar contained in blood gradually disappears when blood is allowed to stand under sterile conditions outside the body. This phenomenon was first noted by Claude Bernard and the. term " glycolysis " was introduced by Lepine. The disappearance of glucose was ascribed by Stosse, and by Em Men and Kraun (Biochem. Z. 1912, 4V, 1) to an enzymje fission of a molecule of the carbohydrate into 2 mo), of lactic acid.

Nowadays the term " glycolysis " is understood to cover a wider field than that involved in the breakdown of glucose in blood. Many investigations since Lèpine's work have shown that the breakdown of carbohydrate into lactic acid is a common characteristic of living cells. The classical investigations of Fletcher and Hopkins in 1907 on lactic acid formation in muscle pointed to the great physiological importance of the processes involved in the formation of lactic acid from carbohydrate. To-day it is recognised that many, and probably all, of these processes are linked together in the normal metabolic events of the living cell. Each has its part to play in the cell equilibria even if the conditions are such that lactic acid *per se* makes no actual appearance.

It is usual now to define the term " glycolysis " as the sequence of processes involved in the biological formation of lactic acid from carbohydrate.

There has been a tendency in certain schools of biochemistry to restrict the term "gjjycolysis" to the processes involved in the, formation of lactic acid from polysaccharides, glycogen in particular. " Glucolysis " has been the name given to the phenomenon of glucose breakdown to lactic acid, and " fructolysis" has been applied when the sugar in question has been fructose. The majority of workers at present, however, use the term " glycolysis " in its vider meaning—the biological production of lactic acid from all forms of carbohydrates. Accordingly it will be discussed in this sense in this article.

RELATION TO FERMENTATION.—Our present knowledge of glycolytic processes has grown with our knowledge of the processes involved in the alcoholic fermentation of glucose by yeasts. The two phenomena are intimately related, the facts concerning one bearing"in great detail on those concerning the other. The reader is referred to the articles on FERMENTATION for a full description of many of the substances and reactions which are important both in glycolysis 'and fermentation.

BLOOD GLYCOLYSIS.—This process, the first example of the biological breakdown of glucose into 1-ctic acid to be investigated, varies in speed in the blood of animals of different species. It is relatively rapid in the blood of dog and slow in that of rabbit. Engelhardt and Ljubimowa (Biochem. Z. 1930,**227,** 6) give the following order of glycolytic activities of the bloods of different animals: ox > goat> dog > horse>guinca-pig> man>rabbit (*see,* however, Bürger (Arch. Exp. Pharm. Path. 1930,**150,** 298) who considers the glycolytic activities of the bloods of puinea-pig, man, rabbit and rat to be about the same). The velocity of glycolysis in blood is approximately constant at 37° for the first 2 or 3 hours, about 20 mg. per cent, glucose per hour disappearing in the case of human blood. The velocity of glycolysis falls off more and more sharply after the initial constant period, this being largely due to the development of acid conditions caused by lactic acid liberation. According to Roche and Roche (Compt. rend. Soc. Biol. 1927, 96* 361) a decrease in blcvd p_n of 0-5 diminishes the rate of glycolysis by 30-40%; it ceases at p'_A 5-5 and is optimal at p_H 8-2. Three hours' glycolysis causes a drop in p_H of 0'2-0-3. The temperature coefficient of the process is 2-1.

According to Irving (Biochqm. J. 1926, **20,** 613) blood glycolysis takes place in red blood cells, lysis of which results in a disappearance of the glycolytic process. Apparently, therefore, integrity of the cells is important for the accomplishment of the breakdown of glucose. Glycolysis does not occur in »;erum or plasma. Red blood cells which have been washed with saline solution (0*9% **NaCI)** wiii bring about glycolysis in «\ glucose-saline solution. Meyerhof (Biochem. Z. 1932, **246,** 249) has shown that it is possible to separate a glycolytic system from the red blood cell.

Both leucocytes and erythrqeytes contribute to the glycolysis of blood, the former being much more reactive per cell than the latter. Ratios of 100:1 and 1,000:1 haw been recorded (Maclean and Weir, Biochem. J. 1925, 9, 412). It has been calculated that 6-35% of the glycolysis of normal blood is due to the leucocytes.

The rate of blood glycolysis, in contrast to that of intact tissues which will be discussed latter, is the same whether the reaction takes place in oxygen or nitrogen (Katayama, J. Lab. Clin. Med. 1926,· **12,** 239). This is to be correlated with the fact that the respiration of red blood cells is practically nil. The rate of aerobic glycolysis of leucocytes which are capable of respiration, is a little less than that of anaerobic glycolysis, but this has been disputed (Bakker, Klin. Woch. 1927, 6, 252). Levene and Meyer (J. Biol. Chem. 1912,11, 301; **12,** 265) found that leucocytes form lactic acid from glucose, mannose and galactose.

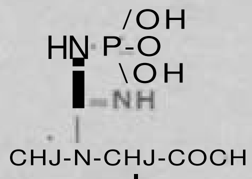
The rate of glycolysis in blood is independent of the concentration of glucose when this lies M'ithin the limits found in human blood. There is no difference between the rates of glycolysis of the blood of normal and diabetic individuals. Addition or absence of insulin lias no influence on the process.

Little is known with certainty of the mechanism of the glycolytic processes in blood. There is evidence to suggest that a phosphorylation takes place (Meycrhof, Biochem. Z. 1932, **246,** 249) and the indications are that the processes are similar to those taking place in other tissues.

GLYCOLYSIS IN MUSCLE.—According to von Fiirth (tout. 1915, 69, 199) there are between 350 and 550 mg. lactic acid in 100 g. fresh muscle of man, horse, dog and ox. The lactic acid arises chiefly from breakdown of muscle glycogen. Fletcher and Hopkins (J. Physiol. 1907, 85, 247) showed that lactic acid is formed when frog's muscle contracts in the absence of oxygen but that under aerobic conditions the lactic acid docs not accumulate. It was concluded as a result of investigations of Hill and Meyerhof that during the contraction of muscle, glycogen breaks down to lactic acid, the energy liberated being used for the contraction. After relaxation of the muscle, lactic acid is resynthesised into glycogen, the energy for resynthesis lieing supplied by the complete oxiclntion of a fraction (J) of the glycogen.

It is known, however, that during the contraction of muscle phosphates make their appearance aB well as lactic acid. Addition of phosphates in excess to muscle kept under anaerobic conditions leads to an increased yield of lactic acid. Hexosedi phosphate formed during the fermentation of glucose by yeast, yields lactic acid and free phosphate in the presence of muscle juice, and the addition of this ester to a contracting muscle has much the same effect on the yield of lactic acid as the addition of phosphate and glycogen. These observations led Embden and his colleagues to suggest that the precursor of lactic acid in muscle was a carbohydrate-phosphate complex to which they gave the name *lactacidogen.* They isolated such a substance from the fresh pulp of striated muscle and showed that it yielded an osazone on treatment with phenylhydrazine,* identical with that formed from hexosediphosphate prepared by yeast fermentation of glucose. Embden and Zimmermann (Z. physiol. Chem. 1924, 141, 225) prepared the brucine salt of lactacidogen (1-5 g. of the recrystallised salt from the muscles of one rabbit) and proved it to be the salt of hexosediphosphoric acid. Its physical properties (solubility, optical rotation and melting-point) were identical with the same salt of hexosediphosphoric acid obtained from yeast. It is to be concluded that the same phosphoric acid ester is involved in muscular contraction as in yeast fermentation ; that in the former case it is a precursor of lactic acid and in the latter case of alcohol.

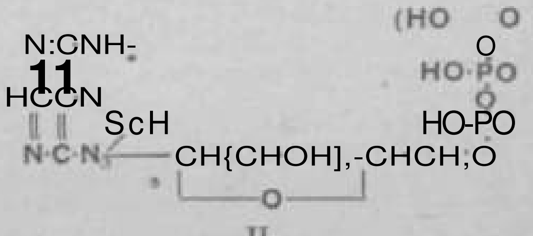
A further phosphoric acid ester important in the sequence of metabolic events in contracting muscle was then discovered (Eggleton and Eggleton, Biochem. J. 1927, 21, 190). This ester is hydrolysed during muscular contraction and is re-synthesized after relaxation; it was proved by Fiske and Subbarrow (Science, 1926, 65, 403) to be phosphocreatine (I).



I.

This ester assumed considerable importance when Lundsgaard (Biochem. Z. 1930, **227,** 51) discovered that muscle poisoned with iodoacetic acid contracted without lactic acid formation, but with the hydrolysis of phosphocreatine into creatine and free phosphoric acid. It appeared from this discovery that lactic acid as such plays no important part in the contraction of muscle and that its formation depends on subsequent chemical events. Its production, in fact, occurs mainly after relaxation and coincides with the anaerobic re-synthesis of phosphocreatine. Lundsgaard has shown that with muscle poisoned with iodoacetic acid contraction in nitrogen is followed by phosphocreatine breakdown and has put forward the view that the energy of glycolysis (glycogen to lactic acid) is used for the re-synthesis of creatine phosphoric acid at a subsequent stage,

ADENYL-PYROPHOSPHATE.—The classical discovery by Harden and Young of a filterable and thermostable co-enzyme essential for the fermentation of glucose by yeast was followed by investigations* as to whether muscle glycolysis was equally in need of a co-enzyme. Meyerhof (Z. physiol. Chem. 1918, 101, 185; 102, 1, 185) showed that a co-enzyme was required for lactic acid formation in muscle and he came to the conclusion it was related to the cozymase of Harden and Young. Work by Euler and Myrbäck proved that the co-enzyme contained adenine and phosphoric acid and indicated it to be adenylic acid or a derivative of this substance. Lohmann in 1929 isolated from muscle adenylpyrophosphate (II)



II.

and this ester has now assumed the greatest importance in the sequence of events in the cell leading to the formation of lactic acid from carbohydrate.

Meyerhof, Lohmann and Meyer (Biochem. Z. 1931, **237,** 437) and Lohmann (*ibid.* 1931, 237, 145) showed that the glycolytic activity of a muscle extract gradually disappears on lengthy standing at 37° or 20° due to autolytic changes and that the activity is restored by the addition to the autolysed extract of minute quantities of adenylpyrophosphate. Autolysis results in the disappearance of this ester which must be restored to regain glycolytic activity. If the extract is dialysed, the loss in activity is not restored by the addition of adenylpyrophosphate alone but the further addition of magnesium ions is essential. The total co-enzyme system consists of adenylpyrophosphate and magnesium ions together also with phosphate ions.

Lohmann (*ibid.* 1931, 241, 50) further showed that whereas adenylpyrophosphate acted as a co-enzyme for lactic acid formation from glycogen in a dialysed muscle extract, cozymase had no such effect.

It is now recognised that adenylpyrophosphate owes its catalytic influence to its power of transferring phosphate to other molecules in the presence of appropriate enzymes. The adenylic acid system is a **phosphorylating-dephosphorylating** system for which magnesium ions appear to be indispensable. It is not known whether magnesium ions are required for all phosphorylating processes.

The recognition that adenylpyrophosphate acts as a phosphate donator, adenylic acid being formed with the loss of 2 mol. of phosphoric acid, arose from the discovery that phosphocreatine breakdown in muscle occurs only in the presence of the adenylic acid system (Lohmann, Naturwiss. 1934, 22, 409). Meyerhof and **Lohmann** (Biochem. Z. 1932, 253, 431) had shown earlier that synthesis of phosphocreatine in muscle takes place at the expense of adenylpyrophosphate. The following equilibrium b established:

Adenylic acid+2 Phosphocreatine
^Adenylpyrophosphate+2 Creatine.

In the presence of a dephosphorylating enzyme in the muscle extract, breaking down adenylpyrophosphate to adenylic acid and free phosphoric acid, the equilibrium above is shifted far to the right.

PRODUCTS OF CARBOHYDRATE BREAKDOWN IN PRESENCE OF MUSCLE TISSUE.—It was shown by Lohmann (Biochem. Z. 1930, 222, 324) and by Lipmann and Lohmann *{ibid.* 389) that muscle tissue in the presence of glycogen and of fluoride gives rise to other phosphoric acid esters besides the true Harden-Young hexosediphosphate to which reference has already been made. A fraction of the esters has the same elementary composition as hexosediphosphate but it is more resistant to acid hydrolysis. These resistant " unhydrolysable " esters are also formed when the monophosphoric acid esters of hexose described by Robison, Neuberg and Embden are added to muscle extracts containing fluoride and phosphate ions.

Embden, Deuticke and Kraft (Klin. Woch. 1933, 12, 313) showed that a constituent oC the " unhydrolysable " ester was phosphoglyceric acid (glyceric acid-monophosphoric acid) which had already been isolated in 1930 by Nilsson in his studies of yeast fermentation of carbohydrate. Another constituent of the " unhydrolysable " ester proved to be Z-a-glycerophosphoric acid and the acid-resistant ester was found to consist of equimolecular proportions *jpi* phosphoglyceric acid and glycerophosphoric acid, *i.e.*

$$HO_2CCH(OH)CH_2OPO(OH)_2$$

and

$$HOCH_aCH(OH)CH_2OPO(OH)_2$$

Embden and his colleagues found that phosphoglyceric acid is transformed into pyruvic acid i» presence of minced muscle. They showed, moreover, that although the addition of pyruvic add alone, phosphoglyceric alone, or of a-glycerophosphoric acid alone to muscle extract free from carbohydrate led to no formation of lactic acid, the addition of a mixture of phosphoglyceric acid and of a-glycerophosphoric acid resulted in the production of lactic acid. Further, the addition of a mixture of pyruvic acid and a-glycerophosphoric acid to muscle tissue led to lactic acid formation according to the following equation:

$$CH_3CO\cdot COOH\text{-f-}$$
$$HOCH_2CH(OH)CH_2OPO(OH)_2+H_2O$$
$$-2CH_3CH(OH)COOH+H_3PO_4$$

The addition of glyccraldchydephosphoric acid (synthesised by Fischer and Baer (Bcr. 1932, 65 [B], 337)) to muscle tissue leads to the formation of lactic acid (Embden); and Meycrhof and Kicssling (B'ochem. Z. 1933, **264-** 40) showed that in muscle extracts one half of the glyceraldchydeQhosphoric arid (one optical component) is changed into a mixture of phosphoglyceric acid and glycerophosphoric acid. These facts led Embden to the following scheme for the course of lactic acid-formation in a muscle extract:

Hexosediphosphoric acid ->
2 TriosephosphoriQ acid.
2 Trioscphosphoric acid ->
Phosphoglyceric ac^d+ a-Glycerophosphoric acid.
Phosphoglyceric acid ->
Jfyruvic acid+Phosphoric acid.
a-Glycerophosphoric acid+Pyruvic acid ->
Triosephosphoric acid-f Lactic acii.

Meyerhof and McEachern (Biochem. Z. 1933, **260,** 417) found that in-a muscle extract pyruvic acid was formed from hexosediphosphate or glycogen. On addition of sulphite the yield of pyruvic acid was increased and that of lactic acid decreased. They concluded that pyruvic acid is a normal intermediate in the formation of lactic acid, *pa* required by Embden's scheme. It was recognfted independently -by Embden and by Meyerhof that the formation of ^pyruvic acid in muscle must be accompanied by a simultaneous reductive process; this was the formation of a-glycerophosphoric acid.

The details of Em&den's scheme have been confirmed in Meyerhof's laboratory, where independent work on the same lines was in progress. Meyerhof has developed the scheme to apply to the formation of alcohol from glucose by yeast.

Meyerhof considered at first that the triosephosphate, produced as the initial stage in the breakdown of hexosediphosphate, was glyceraldehydephosphoric acid. He and Lohmann (Naturwiss. 1934, **22,** 134) found thai[1] the triose-ester formed by the action of dialyscd muscle *en* hexosediphosphate wa* composed largely of dihydroxyacetonephosphate, and it was shown (Biochem. Z. 1934, **271,** 89; 273, 413) that in dialysed muscle extracts an equilibrium mixture of hexosediphosphate and dihydroxyacetonephosphate is rapidly formed from each other. This reaction is controlled by an enzyme *zymohexaae* which is not inhibited by fluoride or iodoacetatc. The equilibrium obeys the equation

$$\frac{[\text{Dihydroxyacetonephosphate}]^2}{[\text{Hexosediphosphate}]} = K.$$

the breakdown of hexosediphosphate being an endothermic reaction. Dihydroxyacetonephosphate has been synthesised by Kiessling (Ber. 1934, **67** CB], 8G9). lc is decomposed quickly by N-NaOH at room temperature yielding lactic and phosphoric acids. With N-HCI at 100° methylglyoxal and phosphoric acid arc formed. Meyerhof and Kiessling (Biochem. Z. 1935, **279,** 40) have shown that in dialysed[1] muscle phosphoglyceraldehyde is transformed ir.to dihydro-oxyacetonephosphate; possibly an equilibrium is established between the two trioses.

According to Meyerhof, Lohmann and Schuster *(ibid.* 1936,**286,** 301,319) there exists in dialyHcd muscle extracts an enzyme *{aldolasc)* bringing about aldol condensation of dihydroxyaectonephosphate M'ith various aldehydes. They suggest that the following.equilibrium occurs:

Hexosediphosphate^
Dihy d roxy acctoncphosphatc+
Glyceraldchydcphosphntr.

The glycer^aldebvdephosphate changes subsequently into dihydroxyacetonephosphate.

Two further phosphoric esters, forded as intermediate substances, have been isolated, viz. phospho(enol)pyruvic acid by Lohmann and Meyerhof *(ibid.* 1934, **273,** 60) and 2-phosphoglyceric acid by Meyerhof a&d Kiessling *(ibid.* 1935, **276,** 239). In a dialysed extract of muscle fr-phosphoglyceric acid is converted into 2-p)iosphoglyceric acid through the agency of an **enzyme named *phosphoglyceromutase,* whilst 2-**phosphoglyceric acid is converted by an enzyme *(enolase)* into phospho(~wol)pyruvic acid. All these esters *forgo,* equilibrium mixtures *{ibid.* **200,**99,100). (For the syntheses of these esters, *see* Kiessling, Ber. 1935, 68 [B], 243, 597.) Sodium fluoride inhibits'the breakdown of 2-phosphoglyceric acid.

The decomposition of phosnhapyruvic acid into pyruvic acid, which is the immediate precursor of lactic acid, requires the co-operation of a catalyst, viz. adenylpyrophosphate. The participation of this molecule in phosphorylations«of carbohydrate and its breakdown products will now be considered.

CATALYTIC INFLUENCE OF THE ADENYLIC ACID SYSTEM IN GLYCOLYSIS.—Meyerhof and Lohmann (Naturwiss. 1931, 19, 575) were the first to suggest that the rôle of adenylpyrophosphate as a coenzyme in muscle glycolysis consists in the phosphorylation of carbohydrate, the pyrophosphate breaking down and being resynthesised at a later period.

Embden and Parnas demonstrated that ammonia is formed during muscular contraction, the ammonia arising from the breakdown of adenylic acid by a dfominase yielding also iifl osinic acid. Muscle deaminase does not attack adenylpyrophosphate, so that evidently the appearance of ammonia is an indication of the appearance of adenylic acid. In presence of a high phosphate concentration ammonia is not formed and this was ascribed to the conversion of adenylic acid into the pyrophpsphate (Parnas. Ostern and Mann, Biochem. Z. 1934, 272. 64; 1935, 275, 74, 164). It was found by Parnas and his colleagues that the breakdown of glycogen in the presence of phosphates was mainly responsible for the prevention of the^appearance of ammonia and for preserving the^ntegrity of the adenylpyrophosphate. If glycogen breakdown was inhibited by iodoacetate or fluoride, ammonia made its appearance. It was shown that the re-synthesis of adenylpyrophosphate was accomplished by breakdown products of glycogen, viz. phosphopyruvic and phosphoglyceric acids. *(See also* Needham and van Heyningen/Biochem. J. 1935, 29, 2040.)

Since adenylpyrophosphate, in muscle pulp poisoned with iodoacetic acid, is not synthesiser! from adenylic acid and free phosphate ions, and since phosphopyruvic acid or phosphoglyceric acid is essential as a source of phosphate for the synthesis, it follows that phosphate transfer takes place from these acids to adenylic acid. The phenomenon is similar to that already mentioned, which occurs in a muscle extract, between adenylic acid and phosphocreatine. The enzymes responsible for the phosphate trans**fers from phosphorylated. molecules to adenylio** s&id have been termed *phosphorylasea* (Quastel, Ann. Rev. Biochem. 1936, 5, 45).

Lohmann and Mcycrhof demonstrated that breakdown of phosphopyruvic acid in a muscle extract only occurs in presence of the adenylic acid system (Biochem. Z. 1934, 273, 60).

Phosphorylases appear to be necessary for the phosphorylation of carbohydrate as the first stage in glycolysis, but this is not yet certain. Probably the following reactions take place:

2 Hexose+Adenylpyrophosphate=2 Hexosemonophosphate+Adenylic acid.

2 Hexosemonophosphate + Adenylpyrophosphate = 2 Hexosediphosphate+Adenylic acid.

Runnström and colleagues *(ibid.* 1934, **271,** 15; J. Gen. Physiol. 1935, **18,** 717) and Dische (Biorhcm. Z. 1934,**274,**51; 1935, **280,** 248) have reported experiments showing that esterification of inorganic phosphate in lysed red blood cells is coupled with the degradation of hexosephosphate. Degradation of glucose or its phosphate is preceded by phosphorylation, the phosphate being derived from adenylpyrophosphate (Dische, *ibid.* 1935, **280,** 248). Evidence exists that phosphoric acid can be transferred from hexosepho^phates to adenylic acid as well as in the reverse direction (Neuberg, *ibid.* 1935, **280,** 1$3; Lutwak-Mann and Mann, *ibid.* 1935, **281,** 140; Ohlmeyer, *ibid.* 1935, **283,** 114).

Parnas (Ergeb. Enzymforsch. 1937, 6, 57), however, considers that a phosphorylation of glycogen to hexosemonophosphate may occur in the absence of the adenylic acid system. Recent evidence indicates that from glycogen in a muscle extract, glucose-1-phosphoric acid is first formed (Cori and Cori, Proc. Soc. Exp. Biol. Med. 1936, 34, 702; 1937, 36, 119). This is known as the *Cori ester.* This ester is rapidly converted into the 6-ester by an enzyme termed *phosphoglucomutase* (Cori, Colowick and Cori, J. Biol. Chem. 1938, **124,** 543). Oori and his colleagues state that the synthesis of the Cori ester from glycogen in muscle extracts is greatly accelerated by adenylic acid (Cori, Colowick and Cori, *ibid.* 1938, **123,** 375, 381). Kendal and Stickland (Biochem. J. 1938, 32, 572) find that adenylic acid is essential for the conversion of glycogen into the Cori ester, the reaction being strongly stimulated by magnesium ions.

The conversion of the Cori ester into the 6-ester is also stimulated by magnesium ions. This transformation is followed by the phosphorylation of the 6-ester, via the adenylic acid system, into hexosediphosphate (Harden-Young ester).

The enzyme, *hexokinase,* discovered by Meyerhof in 1927, catalyses, in the presence of Mg ions, the transfer of phosphate from adenylpyrophosphate to glucose or fructose. The reactions involved are:

Adenylpyrophosphate -f Hexose ->-Adenosinedipho8phate+ Hexose-6-phosphate.

Adenosinediphosphate + ^exose -> Adcnvlic acid + Hexose-6-phosphate.

The second reaction requires in addition to hexokinase a protein catalyst present in muscle, but not in liver or kidney extracts *[see* Kalckkr, Chem. Rev. 1941, 28, 71).

The following equations express the series of reactions in glycolysis and indicate the important position'taken by adenylpyrophosphate:

Glycogen + »iPhosphate -*• nHoxose-1 -phosphate.
Hexose-1-phosphate-* Hexose-6-phosphate.
2 Hexoae-6.pho»phate+Adenylpyrophosphate -* 2 Hexosediphosphate+Adenylic acid.
Hexosediphosphate -*• 2 Triosephosphate.
2 Trioaephosphate -> Phosphoglyccric acid + a-Glyceropboaphoric acid,
Phosphoglyceric acid -* Phosphopyruvic acid.
2 Phosphopyruvic acid + Adenylic acid -»• AdenylpyrophoBphate-f-2 Pyruvic acid.
Triosephoaphate + Pyruvie acid -*• Phosphoglycerate+Lactic acid.

{see also Vol. V, p. 31).

It has lately been shown by Warburg and Christian (Biochom. Z. 1939, **303,** 40) that a separation of enzymes involved in glycolytic changes is possible and this has resulted in the demonstration, and isolation, by Negeleiu and Bromel, of another important intermediate, viz. l:3-diphosphoglyceric acid. The sequence of enzyme-catalysed reactions are apparently as follows:

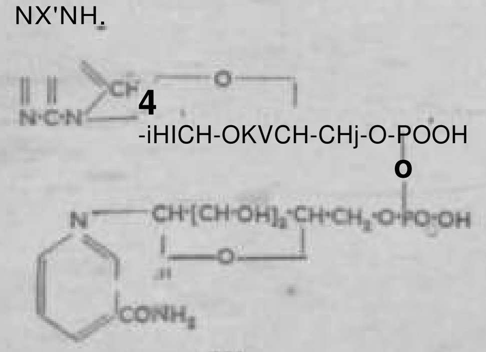
Triosephosphate + phosphate ^ 1:3-I>iphosphotriose.
1:3-Diphosphotriose + " pyrtdine nucleotide" ^i I-3-Diphoaphoglyceric acid + reduced " pyridino ^nucleotide ".
1-3-Diphosphoglyceric acid + Adenosinediphosphate ^ 3-Phoephogly eerie acid + Adenylpyrophosphate.

The reaction between adenylpyrophosphate and creatine is important, so far as glycolysiB ia concerned, in providing a store of phosphate donator in the form of phosphocreatine. It proceeda in two atagya: -

A4enylpyrophosphate+Creatine = Adenosinediphosphate+Creatinephosphate.
a Adenoaincdiphoaphate + Creatine = Adenylic Mid+Crcati nephosphate.

{Lehmann, *ibid.* 1936, 286, 336).

According to Meyerhof, Ohlmeyer and Mohle *(ibid.* 1938, 297, 90, 113) phosphorylation of adenylic acid may be coupled with oxidativc changes and Needham (Euzymologia, 1938, 5, 158) has arrived at a similar conclusion (c/. Parnas, *ibid.* 1938, 5, 106 for a recent review of the subject of phosphorylation).



III.

Part Played by Cozymasr in Qtycolysis.—Cozymase plays an important part in muscle glycolysis since it ia a necessary carrier in the reduction of pyruviu acid to lactic acid. This molecule is an adenine-nieotinamidedinueleotide III *(v.* Vol. V, p. 15). It acts as a hydrogen carrier, the nicotinic acid amide moiety of the molecule undergoing reduction and oxidation under appropriate conditions. Cozymase is necessary for the activity of lactic acid dchyd.rogenase and it ia this enzyme which activates pyruvic acid as a hydrogen acceptor. Lactic acid is formed accordf ig to the equation : i

Pyruvic acidH- Reduced cozymase = Lactic acid+Cofcytnase.

Cozymase is reduced by triosephosphate or by a-glycerophospliorio acid in presence of their respective aek-drogenases, thus:

Triosephosphate + Cozymase = Phosphoglyceric acid-{-Reduced cozymase.
* a-Glycerophosphoric acid + Cozymaso = Triosephoapha^e-H Reduced cozymase.

Thus the presence of appropriate dehydrogenasea in muscle extracts together with that of cozymase enables the necessary hydrogen transfer to take place between triosephosphatc and pyruvie acid with lactic acid production. The existence of these dehydrogenases in muscle extract ha been established by Adler, Euler and Hughes (Z. physiol. Chem. 1933, 252, 1) and Quastel and Wheatley (Biochem. J. 1938. 32, 930). It was already known from the work of Euler and his colleagues (Z. phyaiol. Chem. 1937, 246, 217) that cozymaae is required for the interaction of triosephosphate and pyruvic acid in a tissue extract.

According to Meyerhof, Schulz and Schuater (Biochem. Z. 1937, 293, 309) the reaction between triosephosphate and cozymase only takes place if at the same time there is & transfer of phosphate through adenylpyrophoaphate to a suitable phosphate acceptor. *{See also* Needham and Pillai, Biochem. J. 1937, 31, 1837.) The question of coupling between oxido-reductions and phoBphorylation processes, particularly that of adenylic acid, is at present under investigation.

How far cozymaso is involved in any of **the** other steps of the glj'coly tic process is not known with certainty. *{Cf.* Runnstrom and Michaelis, J. Gen. Physiol. 1935, 18, 717.)

GLYOXALASS.—Dakin and Dudley {J. Biol. Chem. 1913,14, 155, 423; 15, 127) and Neuberg (Biochem. Z. 1913, 49, 502; 51.-484) **discovered** that mcthylglyoxal is transformer! in tissues into lactic acid, the enzyme responsible being termed by Dakin *glyoxalaat.* The rapidity of this transformation gave rise to the view that mcthylglyoxal might occupy an important position in glycolysis, particularly when considered in relation to Neuberg'a conceptions of the course of alcoholic fermentation (<•/. Neuberg andOppenheimer, *ibid,* 11^5.166,450; Nouberg and Gorr. *ibid.* 482). Mcthylglyoxal was **held** to arise by loss of wattr from glyceraldehyda, tho latter molecule being formed by fission of the heioNc molecule. Neubvrg and bii colleagues

(1929) isolated methylglyoxal as the 2:4-dinitrophenylhydrazone in almost theoretical yield from specially prepared yeast extracts incubated with hexosediphosphate; the yield was 20-30% of theory with mammalian tissues. *Case* and Cook (Biochem. J. 1931, 25, 1319) were able to detect both methylglyoxal and pyru'^c acid among the products of metabolism. It is, however, uncertain whether the methylglyoxal is a normal product in the course of breakdown of carbohydrate.

The transformation of methylglyoxal into lactic acid by glyoxalaes requires the participation of a co-enzyme, which Lohmann found to be glutathion^(Biochem. 2.1)932, 254, 332). Jowett and Quastel (Biocfferu. J. 1933, 27, 48ii) showed that methylglyexal combines with glutathione and that it is this compound which breaks down in presence of glyoxajaso to form lactic acid and glutathione :

$$CH_3COCHO + GSH \rightarrow CH_3COCH(OH)SG \xrightarrow{H_2O} CH_3{\cdot}CH(OH){\cdot}COOH + GSH$$

The formulation of the Embden-Meyerhof scheme of glycolysia includes no participation of methylglyoxal. Support for the conclusion that methylglyoxal is not a necessary intermediate in the formation of lactic acid from glycogen comes from Lohmann'a observation (Biochem. Z. 1933, 262, 152) that a muaclo extract free from glutathione converts glycogen into lactic acid. Moreover, the addition of glutathione brings about no additional glycolysis.

This fact, however, does not necessarily mean that a second route of lactic acid formation from carbohydrate does not take place in the living cell. Support for this dual route of glycolysis *via* methylglyoxal has been found. Investigating lactic acid fermentation, by yeast, Auhagen and Auhagen *(ibid.* 1934, 268, 247) tiinl that methylglyoxal is formed and that it is a primary product of reaction and not an artefact. KobelandCoUatz(t"4«Z. 1934,266,202) conclude that methylglyoxal is **formed** from sugars. Tissue treated so as to inhibit glyoxalase activity produces methyglyoxal from hexonediphosphato (Neuberg and Simon, Ergen. Enzymforsch. 1033, 2, 118) and from glyceraidehydcphospiiate (Barrenscheen and Beneschovuky, Biochum. Z. 1933. 265, 169). Jowett and Qaa3tel (Biochem. J. 1934, 28. 162) show that glyoxalaao activity of intact tissues in presence of low concentrations of methylglyoxal is sufficiently rapid to account for the rate of tissue glycolysis.

It is reasonable to assume that a separate mechanism of glycolysis in addition to that embraced by the Embden-Meyerhof scheme may occur in the intact cell *(see also* Ashford, *ibid,* 1933. 27, 903).

GLYCOLYSIS IN BRAIN.—Warburg, Posener and Ncgelciii (Biochem. Z. 1924, **152,** 309) showed that brain tissue in presence of glucose produces lactic acid with great rapidity *in vitro.* McGiuty and Genel! (Anier. J. I'hy.sji.il. 1925-26, 75, 70) have carried out experiments showing that lactic **acid formation** in brain takes **place at 37" immediately** after **removal** of the brain **from** the **body.** The lactic **acid** was formed at the rate of 20 mg. per 100 g. tissue per minute. Carbon monoxide anoxaemia results in an increase in the amount of lactic acid found in brain after death. Avery, Kerr and Ghantua (J. Biol. Chem. 1935, **110,** 637) find that if brain, taken immediately after death of the animal, is frozen in liquid air, the lactic acid content of the brain is initially smaller than was originally supposed. An average value of lactic acid was found to 15-3 mg. per 100 g. cat's brain and 22-3 mg. per 100 g. dog's brain. No significant difference between the lactic acid contents of cerebrum and cerebellum was observed.

Both glycogen and glucose are known to be precursors of brain lactic acid. Kerr *(ibid. VMS,* 123,443) has isolated 36 mg. glycogen from 100 g. brain tissue, the carbohydrate being identical with liver glycogen. Glucose, however, appears to be the main precursor of brain lactic **acid.** Holmes and Sharif (Biochem. J. 1032, 26. 381} found that the amount of lactic acid formed on anaerobic incubation of brain **depends on** the level of blood sugar at the time of death. During insulin hypoglycaimia cerebral lactic acid may amount to only small *{e.g.* less than half the 'normal) values. Hyperglycssmia increases brain lactic acid formation. The amount of lactic acid formed is equivalent to the fall in carbohydrate in the brain.

Whereas brain tissue anaerobically *in vitro* (either in the form of thin slices or in a **minced** condition) breaks down glucose rapidly to lactic acid, it has practically no glycolytic effect on added glycogen. In muscle, on the other hand, the reverse is the case, glycogen **breakdown** being far more rapid than glucose breakdown to lactic acid (Gciger.'t&td. 1935, 29, 811; Caddie and Stewart, *ibid.* 1935, 29, 2101). Probably glyoxalaso activity is very much greater in brain than in muscle. Glutathione, the co-enzyme of glyoxalase, has little or no effect on glycogen breakdown in brain or muscle but increases lactic acid production from glucose in brain (Geiger, *I.e.; see,* however, Baker, Biochem. ,1. 1937,31,980).

Ashford and Holmes *[ibid.* 1929,23,748; 1930, 24, 1119) consider that brain may produce lactic acid in two ways; one, involving glycogen, **proceeds** through a stage of phosphorylation and another, involving glucose, does not include a phosphorylation stage. The former is quantitatively the less important.

The **question,** however, as to whether glucose undergoes preliminary phosphorylation in intact brain before further metabolism occurs is still unsettled. Adler and his colleagues (Naturwjss. 1937, 24, 232) have shown that a cell-free product prepared by acetone precipitation of a brain extract is capable of causing glycolysis of glucose so long as adenylic acid, cozymase and a trace of hexosediph'jjphate are present. This would indicate that phosphorylation of glucose is necessary prior to glycolysis in a brain extract. Geigcr (Nature, 193S, **141,** 373) states that cytolyiia of brain releases^ an inhibitor of glycolysis. By the addition to a brain extract of a factor in muscj*.- **extract and of glutathione,** creatine phosphate and cozymase a glycolytic breakdown of glucose is obtained the activity of which may be twice that of intact brain.

Such a system also breaks down glycogen, a. a smaller rate than glucose, to lactic acid. Phosphate is esterified in brain during glycolysis *{*s&e also* Geiger, Biochem. J. 1940. 34, 4<5;5). 'According to Cori, Colo wick and Cori (J. Biol. Chem. 1938, 123, 375} glucose-1-phoaphate is formed from glycogen and inorganic phosphate in dialysed extracts of rabbit brain. The amount is increased by tho addition of adenylic acid. The conversion of glucose-1-phosphate into glucose-6-phosphate takes place more slowly than in muscle.

Macfarlane and Weil-Malherbe {Biochem. J. 1941. 36, 1) conclude that brain glycolysis is maintained by a cycle of phosphorus transferences involving 0-1-0-2 mg. P per g. dry brain tissue. They find that during anaerobic glycolysis by rabbit-brain slices the inorganic phosphate is maintained at its initial level whilst the content of pyrophoaphate falls to about one-third of tho original. Anaerobic «icubation without glucose leads to a rapid disappearance of pyrophosphate with a simultaneous loss of glycolytic power, HexosetJiphosphate is present in small quantities in glyeolysing brain.

ANAEBOBIC GLYC0LY3IS OF TISSUES *tX VlTRO.*—Warburg and his colleagues have measured the rates of lactic acid formation of thin actions of animal tissues examined in a glucose-Ringer medium under anaerobic conditions. Typical results are recorded in Table I (Biochem. Z. 1927, **184,** 434).

TABLE I.

	$Q^{N_2}_{M}$*
Kidney (rat). . . ! . . .	3
Liver	.3
Intestinal mucose (rat). . ' . .	4
Spleen (rat).	.8
Testia (rat).	.g
Pancreas (rabbit).	.3
Thymus (rat).	.8
Brain cortex (rat).	.19
Embryo (rat).	.23
Placenta (rat).	.15
Papilloma of bladder (man) . .	26
Carcinoma of bladder (man) . .	36
Rat sarcoma (Flexnerjobling) .	31
Hat sarcoma (Jensen)	34
Fowl sarcoma (Rous)	30
Retina	.88

• Q^*=taotle add (eu. rhra.) formed In N_t per mg dry weight of tissue per hour. 22.-100 cu. mm. lactic acid =-90 mg. lactic acid.

It will bo observed that very high rates of glycolysis are secured by brain cortex, retina, embryo and tumours.

The glycolytic activity of tumours is obviously of **great** significance; it is 120 times greater than that of blood.

Normal adult tissues usually show high rates of oxygen consumption (respiration) ail little glycolysis. Embryonic tissues show both high respiration and# high anaerobic glycolysis. Neoplastic tissues have high rates of anaerobic glyrolyflin and smfiU respiratory rates. Retina, **and to a lew** extent brain cortex, are exceptional in showing high rates of anaernbioglytolysisand relatively high rates of respiration.

It 'i a commonly accepted conclusion that glycolyma provides the cell with an alternative supply of energy to that provided by respiration. Presumably the tumour cell equipped with a highly active glycolytic system ia not so dependent on a supply of oxygen for its normal existence as an adult tissue cell, and this ti'so applies to newly developing tissues aueh a3 tho embryo.

The question as to whether glycolysis in embryo and tumour **p* of the phosphorylating or non-phosphorylating type is still unsettled.

Needham and Lehmann (i>iochom. J. 19-}7, 31, 1210) come to the conclusion that in the chick embryo there ire two separate routes of carbohydrate breakdown, (1) a non-phosphorylating glyenlyaia depending greatly on the integrity of tbs cell structure, (2) a phosphory> lating glycolyais similar to that of mjscle but of much lower activity. Dialysis of minced embryo leads to inactivation of glycolysis which is partially restored by the addition of ghitathione. They concltfje also that mcthylglyoxal is not an intermediate in embryo glycolysia.

AEROBIC GLYCOLYSIS AND TUB PASTFUR EFFECT.—Pasteur recognised that, in the absence of oxygen, yeast colls will ferment carbohydrate, but that admission of oxygen retards the rate of fermentation. Glycolysis in **intact** tissue cells (not in extracts) is similarly inhibited by the presence of oxygen and the phenomenon haa been termed the," Pasteur Effect " by Warburg. (For a discussion of the Pn4eur Effect, *see Dixon, ibid.* 1935, 29, 973; *1936,* 30, 1479.)

Results (by Warburg) showing the relative rates of glycolysis of tissues in nitrogen (Q^*i and in oxygen (Q^{O}_{M}') ire shown in **Table** Ii. The respiratory ratL'B (Qo_3- nu.mm. O_2 absorbed per mg. dry Weight of tissue per minute) arc also given.

• TABLK H.

Tissue	$Q^{O_2}_{M}$	$Q^{N_2}_{M}$	Q_{O_2}
Liver (rat* . , . .	0-6	**3-3**	11-6
Kidney (rat)	0	**3-2**	**2-1-0**
Testis (rat)	7-2	**8-fi**	**12-3**
Brain cortex (rat) . .	2-5	191	**10-7**
Retina (rat)	430	**8SO**	**80-7**
Embryo (chicken) . .	1-1	20-6	100
Carcinoma (Flexner) . .	250	**310**	7-2
Sarcoma (man) . . .	**15-6**	**894**	4-9

A noteworthy feature is the high aerobic **gly-**coly-isof tumour cells indicating the possibility that such cells may gain their energy for grow th mainly from glycolysis even under aerobic conditions.

According to Crabtrre *(ibid.* 1928, **22,** 1289) a bigh aerobic **glyoalysu m»y** take place **undo!** pathological **conditions** in tissues. Warburg agrees (Biochem. Z. 1929, **204,** 482) that it i» not specific for tumours.

There is no doubt, however, that, *a»* a **general** rule, respiration rjn a cell greatly represses its glyeolysis. The mechanism by which this phenomenon takes place is not yet clear. *

The view has been advanced that oxygen re-places" pyruvic acid as a hydrogen acceptor in the Embden-Meyerhof sequence of reactions leading to glyeolysis. Thus Lytic acid formation would be inhibited or eliminated, water being formed instead. Szent-Gyorgyi (" Perspectives in^ Biochemistry," Cambridge, 1937, p. 172) hazards the view that in aerobic glycOlyais, oxalacetic acid replaces pyruvic acid as a hydrogen acceptor in the EmWen-Meyerhof scheme. Reduction of oxalacetic acid leads eventually to succinic acid which is oxidised l>y oxygen in the respiratory system of the cell back to oxalacetic acid. This hypothesis has as yet no experimental support.

The addition of a variety of substances to intact tissues may greatly incre&e the rate of aerobic glyeolysis, up to that of anaerobic glyeolysis, without appreciably affecting the respiratory rate. This phenomenon, known as tjic inhibition of the Pasteur effect, was first described in relation to i'eftnentation. Warburg (Biochem. Z. 1920, 172, 432) showed that carbylaminc intensifies aerobic fermentation without any marked action on the respiration. Quastcl and Whcatley (Biochem. J. 1932, 26, 2109) showed that gluUithionc has a precisely similar action. Weil-Malkcrbe *(ibid.* 1938, 32, 2257) finds that glutathione as well as glutamatc increases aerobic glyeolysis of brain. It is claimed that certain dyestuffs inhibit the Pasteur reaction (BMiott and Baker, *ibid.* 1935, 29, 2396; Dickens, *ibid.* 1930, 30, 001, 1004, 1233), and phenosafraninc in particular has a powerful effect. Dickens *(ibid.* 1939, 33, 2017) has recently shown that guanidinc (M/1000) completely and rcversibly inhibits the Pasteur effect in brain cortex slices. Curtain substituted guanidines and amidincs are even more powerful in their inhibitory influence on the Pasteur reaction, viz. l:ll-un<lecanctliamidine and decamethylcnediguanidino (" *Sijnthalin")* which are fully active at M/1,000,000. Excess of potassium ions (Ashford and Dixon, *ibid.* 1935, 29, 157), lack of both potassium and calcium ions (Dickens and Grcville, *ibid.* 1935, 29 141)8) or the presence of ammonium ions (Weil-Malherbc, *ibid.* 1938, 32, 2257) all effect the Pasteur reaction—conccittibly through permeability changes in the cell membrane (Dixon and Holmes, Nature, 1935,135, 995).

Increase of temperature from 37° to 45° brings about a breakdown of the Pasteur effect and aerobic glycol>^is increases to a high rate in spite of an increased respiratory rate (Dixon, Biochem. J. 1936, 30, 1483).

Activators and Inhibitors of Glyeolysis.

PYRUVIC ACID.—Mendel, Bauch and Strelitz (Klin. Woch. 1931,10, 118) found that traces of pyruvic acidgreatly increase anaerobic glyeolysis, in tissues where glucose, and not glycogen, breakdown is responsible for lactic acid formation. Pyruvic acid appears to maintain glyeolysis (of glucose) at a maximum level.

POTASSIUM AND CALCIUM IONS.—Ashford and Dixon (Biochem. J. 1935, 29,157) found that the presence of M/10 KC1 greatly increases aerobio glyeolysis of brain but decreases anaerobic glyeolysis. Dickens and Greville *(ibid.* 1935, 29, 1468) reached a similar conclusion and showed the antagonistic effects of potassium and calcium ions on respiration. Quastel and Wheatley (J. Biol. Ghem. 1937, 119, SOP) found that calcium ions at low concentrations markedly increase anaerobic glyeolysis and that strontium and magnesium have similar but smaller effects.

DEPRIVATION OF OXYGEN AND OF GLUCOSE.—Deprivation of brain tissue of both oxygen and of glucose for short periods *(e.g. 5* minutes) very greatly decreases the rate of anaerobic glyeolysis when glucose is subsequently added to the tissue (Dickens and Greville, Biochem. J. 1933, 27, 1138). It had been concluded that ,anaerobiosis in the absence of glucose brings about irreparable damage to the brain. It was shown later, however (Quastel and Wheatley, *I.e.),* that if brain tissue which has been kept anaerobically in the absence of glucose is subsequently exposed to oxygen- its power of bringing about anaerobic glyeolysis is regained.

This fact, coupled with the facts that pyrophosphate breaks down rapidly in brain in absence of glucose and that aerobic rcsynthesis of (Wenylpyrophosphate takes place in brain (Engcl and Gerard, J. Biol. Chem. 1936, 112, 379) lend support to the view that anaerobic glyeolysis in brain takes place through the intermediate formation of phosphoric esters.

IODOACETIC ACID.—Iodoacetic acid at low concentrations suppresses glyeolysis whether glucose or glycogen be the carbohydrate which is broken down. In muscle extracts iodoacetic acid inhibits the interaction of trioscphosphate and pyruvic acid. Triosephosphate dehydrogenase is highly sensitive to iodoacetic acid (Kapkine, Biochem. J. 1938, 32,1729). Possibly the sensitivity of this enzyme to iodoacetic acid explains the latter'a powerful inhibiting effects on glyeolysis in muscle extracts.

Iodoacetic acid reacts rapidly with glutathicne, a thioether being formed (Quastel and Wh^tley, *ibid.* 1932, 26, 2169; Dickens, *ibid.* 1933, 27, 1141), and the problem has arisen as to whether this reaction accounts partly, or wholly, for the cessation of glyeolysis in presence of iodoacetic acid. Tho reaction would obviously explain the highly inhibitory effect of iodoacetic acid on glyoxalaso .activity (Dudley). With our present limited knowledge of the influence of thiol compounds in glyeolysis it is difficult to assess the importance of the reaction between iodoacetic acid and glutathione on the inhibition of glyeolysis.

SODIUM FLUORIDE.—This substance at low concentration (M/200) suppresses glyeolysis whether from glucose or from glycogen. Its inhibitory effect is presumably linked with the fact that it prevents the breakdown of phosphoglyeerie acid into phosphopyruvic acid (Lohmann and Meyerhof, Biochem. Z. 1934,273, 60).

DickChs and Šimer (Biocher>. J. 1929, 23, 936) have shown that fluoride sensitivity of glyeolysis varies in differentgorgans.

PIILORIDZIN.—This substance inhibits yeast fermentation (Dann and Quastel, *ibid.* 1928, 22, 245) and glyeolysis in muscle extracts. Lundsgaard (Biochem. Z. 1931, 233, 322) showed that phJoridzin (M/100) inhibits phosphorylation of glycogen. According to Kalckar (Nature, 1935, **136,** 872) phloridzin prevents the formation of phosphoglyeeric acid from triosephosphate.

GLYCEKALDEHYDB.—Mendel (Klin. Woch. 1929, 8, 169) found that <U-glyceraldehyde inhibits anaerobic glycolysis of glucose by tumours and that this inhibition can be reversed by the addition of pyruvic acid. Ashford confirmed this phenomenon forbrain glycolysis, but Holmes (Ann. Rev. Biachem. 1934, 3, 395) could find no inhibition of glyeolysis of glycogen by glyceraldehyde in muscle extracts. Needham and colleagues (Bioehem. *J.* 1937, 31, 1165, 1210) find an inhibition of embryonic glycolysis by glyceraldehyde and conclude that this aldehyde specifically inhibits non-phosphorylating glycolysis *{see,* however, Adler and colleagues, Naturwias. 1937, 25, 282; Z. phyriol. Chem. 1937, 249, 40).

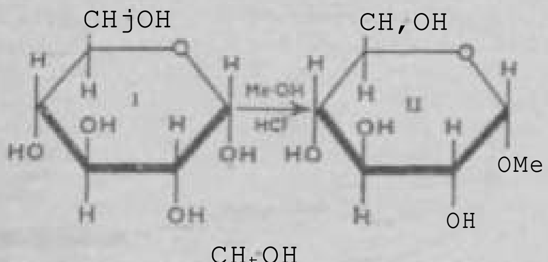
OTHER INHIBITORS.—The following substances also inhibit glycolysis (of glucose): hydroxyniaionato (Jowett and Quastel, Biochem. J. 1937, **31,** 275); glutaniate and £-$_r$ hydroxygltitamato (Weil-Malherbe, *ibid.* 1938, 32, 2257); maleic acid (Morgan and Friedmann, *ibid.* 1938, 32,862).

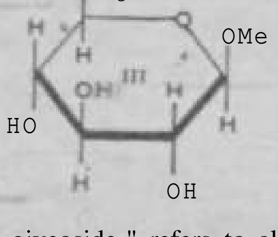
GLYCOLYSIS OF VAKIOUS SUGARS.—Mannose usually undergoes glycolysis under conditions where glucose is broken down to lactic acid. Fructose is broken down less rapidly than glucose by tumour slices and is also broken down by liver. It is, however, in common with galactose, but feebly attacked, with lactic acid liberation, by tumours, brain or chick embryo.

J. H. Q.

" *GLYCOSAL"* Trade name for a preparation of glycerol and salicylic acid.

GLYCOSIDES. Glycosidea are formed by the condensation of one or more carbohydrate molecules with a non-carbohydrate, with elimination of one or more molecules of water. The junction involves a hydroxyl group of the non-carbohydrate, and the reducing or glycoaidie hydroxyl of the sugar. Thus the simplest glyeoside is formed from glucose and methyl alcohol by the catalytic action of hydrogen chloride:





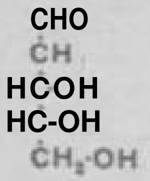
The term " giyeoside " refers to all compounds of this type, irrespective of the nature of the sugar (hexose, pentoae, etc.) which *in* present. Strictly, the name " glucosidf " is reserved for elycosides in which the sugar is glucose; the term fa still, however, frequently applied to other glycosides. Galactosides, mannosides, Btc., are glycosides in which the sugar is known to be galactose, mannose, etc.

Methylglycosid*s have not yet been found in nature, but glycosides of a more complex type are very abundant, occurring especially in the fruit, bark and roots of plants. Glycosides are in general readily bydrolysed by dilute arid, giving the free sugar or sugars and the non-carbohydrate portion iof the molecule, which is conveniently referred to as the " aglycone." Hydrolysis of glycosides may also be effected -by enzymes, which are usually present in the Bame plant tissue as the giyeoside. If the cell tissue is destroyed, the enzyme comes into contact with the glyconi^e, and under suitable conditions *{e.g.* p$_B$) hydrolysis will occur.

Corresponding with the two isomcric forms of glucose (o-glueoee, I), there are two series of g'ycoaides, of which *a-* *ajid /J-methylghieosides (II and III) may be regarded as the prototype. The enzyme emulsin iiydrolyses many glycosides containing the j3-h'nkage, but few, if any, with *a** linkages; conversely, thn enzyme mnltase hydrolysu the a-bond in maltose, but not the /9-linkage in the corresponding disaocharido cello iiiosc. **Boob** reactions frequently aflbrii evidence of the nature of the bond in glycosidea. Other possibilities of isomerism exist in the sugar series, especially in the nature of the heterocyclio ring, which may, for **EnBtasoe,** be pyranose (6-atom) or furanose (fi-atotn) (t>. CARBOHYDHATES), Investigation of the sugar portion of a giyeoside enquires evidence upon all such points.

THE CABHOHYDRATES OP NATUKAL GLYCOSIDES.

Whilst glucose *in* by far the moat common sugar found in natural gly cos idea, galactoso also frequently occurs. The pentoses arabinose and xylose, and the methylpentose rhumnose (v. Vol. II, 287c), occur widely, whilst the sugars of the cardiac glycosides have been shown recently to be of the 2;6-deoxyhexose type, digitoxose (p. Vol. II, 381c), and cymarose (». Vol. I1l, fi38A), which have not yet been found elsewhere in nature. The brached chain pentosc, apiose *{v.* Vol. I, 4o0c) is one of the constituents of apiin. It is interesting to note that 2-dcoxy-d-ribose,



$$\begin{array}{c}\mathrm{CHO}\\ \mathrm{CH_2}\\ \mathrm{HCOH}\\ \mathrm{HC\text{-}OH}\\ \mathrm{CH_2\text{-}OH}\end{array}$$

occurs in nucleic acid.

Uronie arids, although common in polyoaceharidea, ratvh **oocar** in glvcoaides. **Ettxanthio** acid, a glucuroi, ide, is c. **product of uhnal** metabolism and is lint **otbnrwiM** found in nature. Baicaloin is a flavonc giyeoside containing (jlucunmic **add**

Wher* 2 inol. of carbohydrate are fouii'l **io** a glyeoside, *they*[1], may be present as a disaccbaride (bioise). Common disaceharides of this ty*pe are given in the table below, togeth with some glycosides in which they occur.

Disaecharide,	*Sir tint u re.*	*Occurrence,*
GentiobioBo	6- (|9-<i-gl u cos i d o) -tf-g li i coso	Amygdalin, crocin.
Vicianose	b'-(£-J-arabinoaido)-(/.glucose	Vicianin, violutoside, gem.
Primeverose	6-(|3Xxylasido)-d-glucoae	Monotropitin, primeverin, primulavcrin.
Rutinose	ti-(J9-?-rhamnosido) -rf-glucose	liuiiii, datmcin.

Itlis interesting to note the prevalence of *-6-|9-Iinkages in these bioses. Some trisaceharides are found in glycosides, b^it their constitution is, in most eases, not **eetablifihecL** Robinose, **obtained** from tH> glycosidc robin in, appears to *hi:* of the **rhamnoee-galftctflae-thainnose** type.

The ring **itmctum** of tire sugars in the natural glycosides are **chiefly** pyranose, but the n bose and 2-deoxyribose in nucleosidea have & iuranoso **configuration** (Leverp and Tipton, J. BioL fthem. 1**932,** B4,809). Furanose pentoses are now being found frequently in nature in the plant gums. The majority of polyaaccharides have linkages of the glycoaridic type and therefore are glycosides from that js>int of view,

In general, one form *(d-* or *1-)* of the possible optical isowers of a sugar predominates in nature. Thus (/-glucose, *d~* man nose and *I-*rhamnose are the only naturally occurring **fonns** of these sugars which have been, so far, identified, **but** karabinose is the chief constituent of the plant gums whilst rf-arabinose occurs in the glycosides barlmloin and **fcobaxbaioin.**

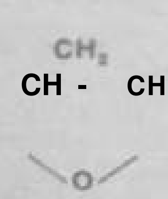
Most natural glycosides arc of the **$>type,** they are hydrolysed by the enzyme **emulsin** and are therefore Isevu-rotatory (c/. j S y-gl l d).

THE MAIN TYPES OF GLYCOSIDES FOTTHD IN XATUBE.

The types of glycoaidea found in nature vary **Widely,** I>nt nt.ty lie roughly grouped ns follows, according to their no n- carbohydrate constituent a (aglyeones):

(«) Phenolic Glycosides.-o-The aglyeones **include** ***o-hydroxybentgl*** *aleafad* (in salicin), *quinol* {in **orbutin),** *conifwyl alcohol* (in coni-Lerin). The sugar molecule is attached **to the nhenob'c** hydroxyl group. Nearly related arc the ***hydroxyanlhraquinone*** **nucleus,** whicji occurs **in roberythric acid, rubiadin** and purpurin, etc, and the ***hydwzyeoumarin*** nucleus, present in **nscolin, daphnin, etc.**

(b) y-Pyran Derivatives.—This group inchides ninny of the must **important pycoikke.** The uuijorit v *nf* red and blue **plant-** and berry **pigments,** anthoeyanins *(q,v.)* arc derivatives of y-pyran.



y-1'yraii.

Closely related axe ttio flavone, lluvono) and xanthone **pigmenta, which oonstftate** a large proportion of tho yellow dye« of flowers, roots and woods. Chryain, qucrcitrin **and** euxanthono respectively are typical examples of these three classes, which may occur without any combined sugars. Qucrcitin-3-rhamnoside is the glycoside quercitrin.

(c) Steroid Glycosides.—The aglycones of the important digitalis glycosidea and of some of tho aaponins are related to the sterols. The powerful physiological properties of these glycosides, and their structural similarity to the hormones, the hi!.' ;i.-i<ls and **vitamin** f>, are of great inteiest (j>. CARDIAC GLYCOSIDES).

Sapouins have similar physiological properties to the cardiac glycosides. They produce a stable foam on agitating an aqueous solution even at great dilution, have a bitter taste, irritate tho mucous membrane and hoemolyse red blood corpuscles in very low concentration (1:108,000 for (ligitonin). Administered intravenously they are therefore very poisonous.

(d) Purine and Pyrimidine Glycosides.—The nucleic acids, which in combination with protein material appear to constitute tho main portion of the nuclei of plant and animal **cells,** yield on hydrolysis nucleosidea, which are glycosides formed by the combination of purine or pyriihidine bases with a sugar. The latter is frequently (/-riboite or **2-d^oxy-d-riboae,** with a furanose ring structure. Typical nglycones are adenine, guanine ami eytomne.

(c) Nitriles frequently occur combined with **•agaiB, forming the cyaaogeastioor** cyanojihoric glycuiiides *{</•>'.),* The well-known glycoside amygdalin *('l.v.j* is of this type.

(/) Sulphur Compounds.—A mimlwr of plants yield glycosides which contain sulphur and which on hydrolysis give mustard oils of the jillyl **Mothioflyanatfl** type, and a sugar. **Sinigrin (p. 96a}** and **enulbin** (p. *UHd)* arc typical examples of sueh glycosides, **occurring** in the needs of tho **black and** white **mwtard** respectively. These glycosides are in general hydrolysed by a specif ic enzyme occurring in the same plant, *eg* my rosin asc.

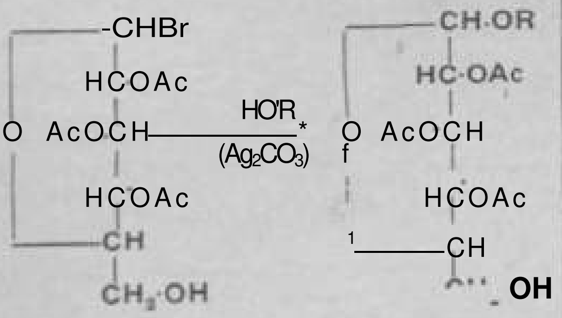
Cert • tin important **gljeoridea** ***{e.g.*** **dboflavin,** viliiinin *li₃)* and inditan (3-^-glu<:o.HJdo-oxyin-**dole)** are not readily <l;Lwsih'ed, whilst others have so far been insufficiently investigated.

.SYNTHESIS OF GLYCOSIDES.

(«) The simple glycosides tire most readily prepared by the direct interaction of **the** alcohol (CH_3-OH, CjH^-OH, etc.) with the sugar, **in** the presence of hydrogen cldoride (c. 1%) as **a** catalyst (Fischer, Ber. I8»3, **26,** 241HJ). In **thia** way # mixture of the *a-* ajid (3-forms of the glycoside is **obtained,** which may usually be separated partially by fraefmat crystallisation.

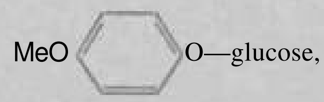
(b) A more selective method uses a sugar derivative of the aetobromoglucose type, which condenses with a hydroxyl group of t In-

aglyeone, the HBr being removed by silver carbonate.



Tho acety) groups are usually removed by alcoholic ammonia at 0°, giving the desired glycoside. It should be noted that a Walden inversion occurs in this reaction, and if a-acetobromoghit'ose is used, then the /9-glucoside is obtained, and *viu versa.* The formal method of preparation of acetobromo-sugars (by the action of hydrogen bromide in glacial acetic acid upon the penta-acetate of the sugar) yields the a-isomcride as the chief product, even if the j3-penta-aeetate is used, and this procedure there-' fore results in the formation of j9-glycoaides only. *IS,* however, quinoline is used in place of/silver carbonate in the condensation, a mixture of a- and jSglycosides is formed (Fischer and Von Mechcl, Ber. 191(3,49,2813). Further, 0-methyl-glucoae tetra-acetate may be transformed nearly quantitatively into a-metbylglucosido tetra.-acctate by heating with titanium tetrachloride in chloroform solution (Paesu, *ibid.* 1928, 61 [BJ, 137, 1513).

The corresponding chlorc-compound, aceto-ehloroglneose, may also be used in this reaction. In this way Michael *[ibid.* 1881, 14, 2097) obtained inethylarbutin,



the hrst naturally occurring glycoside to bo synthesised. Acetobromoglucose has been used extensively by Robinson in his extensive syntheses of anthocyanins *{e.g.* of malvin, J.C.S. 1932,2209).

The synthesis of glycnsides by means of enzymes falls into a somewhat different category, but may be mentioned here. Bourijuelot (scries of papers, Compt, rend. 1912-15) found that enzymic hydrolysis of gly resides is reversible, and sugars may be made to combine with alcohols by the me of enzymes (e.y. emufcin) under appropriate conditions. Thus Herissey *{ibi,l.* 1921, 172, 1530; 173, 1406) obtained a-mcthvlmannosirfe by the action of an enzyme, scmiiiasc (present; in germinated lnceme sceda), upon a solution of mannosc in 10% methyl alcohul. Other methods for the synthesis of glycoaides are given in Tollens-Elener," Kurzes Handbuch der Koblenhyd/ate," 4tb ed., Leipzig, 1!M5, p. 45.

GENERAL PBOFMRTIES OF QLYCOSITH:*.

The dimple glyeosidca *(e.g.* methytgluoosidcs) are colourless, crystalline solids, readily soluble in water and alcohol, and nearly insoluble in ether. They are optically active, hydrolysed by acids with varying ease, but comparatively stable to tho action even of concentrated alkali. They are non-reducing to Folding's solution and to alkaline iodine (as regards their sugar portions). *v*

The size and active groups of the aglycone obviously influence the properties of the glycoside, although the hydroxyl groups in the carbohydrate continue to make the compound soluble in water, even if the aglycone is of the sterol type *(e.g.* the spponins). In general, the properties of the glycoside may be regarded as the sura of the properties of the two components. Some glycosides *{e.g.* saponins) are amorphous and difficult toobtahvin astute of purity.

The relationship between the rate of hydrolysis of glyeosides, the critical increment and their constitution has been investigated byMoelwyn-Hughes (Trans. Faraday Soc. 1928, 24, 300; 1929, 25, 81, 503).

HYDROLYSIS OF GIYCOSIDES BY ENZYMES.

Owing to the extreme difficulty of characterising preparations of enzymes it is not surprising that a mass of conflicting evidence has been accumulated upon this subject, but certain well-established facts may be mentioned. The chief enzyme preparations in this field, are emulate, maltase and invertase. Emu Jain, extracted from bitter almonds, is a mixture of enzymes, of which the outstanding function is the hydrolysis of jS-glu cos ides, *e.g.* tamygdalin, gentiobiose, /3-methyl-^-glucosidc. The presence tif an a-glueosidase anda-siannosidase in emulsiu haa been reported (Helferich and co-workers, Z. physiol. Ohem. 1932, 214, 139; 215,'277; 218, 123), Maltase is present in yeast and effects the hydrolysis of a-glucosides in general, *e.g.* maltose, a-metbylglucoside. Invertase *is* also present in yeast and hydrolyses /J-fructosides such an suorose. Tho action- of cmulsin and maltase appears to bo of a general nature, i.e. nearly all J3- or a-glucosides, respectively, are attacked. Myrosinase similarly hydrolyses llio " —S— glucose " linkage in the mustard-oil glucosides. Other enzymes appear to bo more sjjecific in liature and hydrdyse special carbohydrate configurations only, *e.g.* indimolsm hydrolyses indican, vfcian&se hydrolyses viciaiiin ((/•mandelonitrile-vicianoside) and neither seems to attack any general group of glycosides, Wddenhagen has proposed a theory concerning the Rjicrilirity of curbohydruses, in which tho action of mi enzyme is cli-ti-nnhi.il by the ring structure, canngiir.itiim and C[Bteanoisomeriam of the substrate, but not by tln> non-sugar portion (Weidenhegenj *ibid,* 1033, 21£ 2S5; Angew. Chem, 1934, 47, 451). Tfcett is substantial experimental evidence against this view (see, for example, Hestrin, Biochem. J. 1940. 34, 213, where further references are given).

The effect of various changes in the constitution of glycoside3 upon the rate of hy.lrolysis by Buyout bM been Investigated by Helferich (Z. phyrioLChem. *VXil,* 248,85; Annalen, 1937, 531. *IW;* 534t27t;i

THE BIOLOGICAL SIGNIFICANCE OF GLYCOSIDES.

Various proposals have been made as "to the function of glycosides in plants. They may be waste materials, being the form in which toxic compounds such as phenols and sterols are made soluble and removed. «Bunge has made the interesting suggestion that their rdle is bactericidal; when the tissue is damaged the enzyme hydrolyses the glycoside, liberating the aglycone, which is frequently antiseptic *(e.g.* phenols), and prevents the harmful action of micro-organisms. The subject is discussed by E. F. and K. F. Armstrong, " fhe Glycosides," Longmans, 1931. *

The occurrence of a .glycoside in several different plant types is of interest, and in the list of natural glycosides which follows, mention is made of such distributions. In iBome cases, glycosides of very different types are found in the same source; thus horse-chestnuts (from *JEsculus hippocastanum)* contain aescin (a steroid of the saponin type) and sesculin (a coumarin glycoside). The presence* of crocin (a carotenoid) in some species of crocus and of picrocrocin (a terpene glycoside) in other species is noteworthy because carotenoids and terpenes are generally regarded as being formed from isoprene units.

' *Bibliography.*—An excellent account of the cardiac glycosides is given in Fieser's " The Chemistry of Natural Products Related to Phenanthrene," 2nd ed., Reinhold Publ. Corp., New Yorkj 1937. Developments in the field of anthocyanins have been reviewed by Robinson in a series of papers, including Nature, 1935, 135,732, 1936, 137,* 94; 1938,142,356. £ general review of the subject is given by E. F. and K. F. Armstrong *(op. cit.).*

An alphabetical list of glycosides found in nature now follows, in which the literature has been reviewed up to and including 1938. The structures of glycosides belonging to the important group of the anthocynnins are given with reference to a " type formula" to be found in the survey of the various types of glycosides, earlier in this introduction. Glycosidic links (from the reducing hydroxyl group of the sugar) are to be assumed unless it is otherwise stated, and if a glycoside is hydrolysed by emulsin it is normally |b /?-glycoside. The specific rotation quoted is measured in, aqueous solution unless the solvent is stated. The activity of some cardiac glycosides has been given, expressed in frog-doses per mg. (F.D./mg.). .

Acaciin *(v.* Vol. I, 12).

Acacipefhlin, $C_nH_{17}O_6N$, m.p. '176-7°, HD — 36-6°, is a cyanogenetic glucoside from *Acacia* species. Complete hydrolysis (alkali and then acid) yields ò*-glucose and wobutyrylformic acid (Rimington, 1937, A., II, 136). It appears to be dimethlyketen cyanohydrin j8-glucoside.

^ o ecrta,,nln, $C_{2o}H_{20}0_{13}$, m.p. 165°, $[a]_D$ +21° (acetone), occurs in *Acer ginnale.* It is probably the digalloyl derivative of an anhydro- ?h?l to Li Fi8cher and Freudenberg, Annalen, IS^J?* 238; Perkinand Uyeda, J.C.S. 1922, 121, 66).

*9-Adenine-thiomethylpentoside has been found in yeast extracts (Mandel and Dunham, J. Biol. Chem. 1912, 11, 85; Suzuki *et al,* Biochem. Z. 1924, 154, 278; Levene, J. Biol. Chem. 1924, 59, 465; *ibid.* 1925, 65, 551; Sobotka, *ibid.* 1926, 69, 267). Falconer and Gulland (J.C.S. 1937, 1912) have shown that the sugar is attached to position 9 in the adenine molecule. The constitution of the sugar is not yet known.

Adenosine, C^H^O^^UHjjCWp -60°, 9-adenine-o*-ribofuranoside, has been isolated from heart-muscle and from yeast, and is a component' of their nucleic acids. Acid or enzymic hydrolysis gives d-ribose and adenine (Levene and Jacobs, Ber. 1909, 42, 2703). Monophosphoric esters of adenosine occur as muscle-adenylic acid and yeast-adenylic acid; the latter has the phosphoric acid residue in position 3 of the ribose. Adenosinetriphosphate occurs in muscle extract (Lohmann, Naturwiss. 1928, 16, 298; 1929, 17, 624) and plays an important part in sugar metabolism in animals and plants and in alcoholic fermentation (the position of the ribose side-chain is discussed by Gulland and Holiday, J.C.S. 1936,765) *(v.* Vol. V, 186).

Acttnidoside, Adonivernoside, are cardiac glycosides isolated from *Adonis vernalis* (Mercier and Mercier, Rev. Pharmacol. 1927,1,1). Their physiological activities are 600 and 300 F.D./mg. respectively *(v.* Vol. II, 3876).

/Escin, $C_{53}Hg_8O_{27}$, (decomp. 220-230°), is a saponin occurring in horse-chestnut seeds *(JEsculus hippocastanum).* Hydrolysis is reported to give glucose, <glucuronic acid and aescigenin (v. Vol. I, 160c), which appears to be a triterpenoid of 'the hederagenin type *(see* Hederin, p. *S9d),* since on dehydrogenation it yields sapotalin. Its constitution is not yet known (Chem. Zentr. 1929, II, 2780). *(See also* Winterstein, Z. physiol. Chem. 1931, 199, 25; Burës and Babor, Chem. Zentr. 1935, I, 3936; 1937, II, 403.)

>Esculin *(v.* Vol. I, 160).

Aloin *(v.* Vol. I, 262a)

Althsein, $C_{22}H_{23}O_{12}CI$ (chloride), is an anthocyanin occurring in black mallow *(Althaea rosea).* Hydrolysis yields glucose (1 mol.) and myrtillidin chloride, which is the 7-methyl ether of delphinidin chloride *(v.* Vol. Ill, 554(2) (Willstätter and Martin, Annalen, 1915, 408, 110; Chem. Zentr. 1930,1, .3193). *(Cf.* Karrer and Weber, Helv. Chim. Acta, 1936, 19, 1025, who find althsein to be a mixture of various anthocyanins) *(v.* Vol. I, 264a).

A mo I on in is a crystalline saponin present in the Californian soap plant, *Chlorogalum pomeridianum* (Jure and Noller, J. Amer. Chem. Soc. 1936, 58, 1251). A-molonin has the probable molecular formula $C_{63}H_{104}O_{31}$. Hydrolysis gives d-glucose (3 mol.), d-galactose (1 mol.), Z-rhamnose (2 mol.) and a sterol, tigogenin, identical with the aglycone ofyigonin (p. 97a).

Ampelopsin *(q.v.).*

Amygdalin *(q.v.).*

Iso-Amygdalin is o7-mandelonitrile 0-gentiobioside.

Androsin *(q.v.).* For synthesis, *see* Mauthner,

J. pr. Chem. 1918, [ii], 97, 217; 1925, [ii], 116, 123).

a-Antiarin, 0-Antiarin *(v.* Vol. II, 387c), a- Antiarin on hydrolysis gives a sugar, antiarose, of unknown structure (isomeric with rhamnose); /J-antiarin gives rhamnose (Tschcsche, Ber. *1036,* 69 [B], 1377).

Apiin *(q.v.).*

Aral'm is a saponin of the hederin type (p. 89c) found in varieties of *Aralia* (Winterstein and Stein, Z. physiol. Chem. 1932, 211, 5).

Arbutin *{v.* **Vol.** I, 457c). (Purification of arbutin to m.p. 199-5-200^0, $[a]_D$ -64-3°, has been reported by Reichert and Turkewitsch, Arch. Pharm, 1938, 276, 397.) The rate of hydrolysis and its activation energy have been measured by Moelwyn-Hughes (Trans. Faraday Soc. 1929, 25, 603).

The blackening of the leaves of certain varieties of Pyrtis is due to hydrolysis ojf arbutin by enzymes present; the liberated hydroquinone is readily oxidised to give a black product. Leaves containing much methylarbutin turn yellow and then black, owing to the different oxidation reactions of methyl hydroquinone.

Asperulin *(q.v.).*

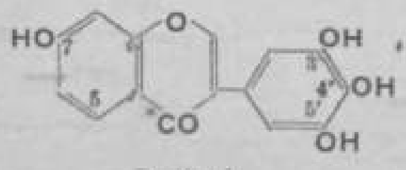
Atractylic Acid, C^H^OjgSjKj (potassium salt), m.p. 173°, *$[a]_D$* —64°, appears to be of the mustard-oil glucoside **type.** It is the poisonous principle of tho roots of *A tract if Us gutnmiftra (Carlina gummifera)* (Chem. Zentr. 1020, II, 614) and is of unknown constitution. Acid hydrolysis gives glucose, valerianic acid (2 mol.), potassium hydrogen sulphate (2 mol.) and an unidentified agluconc, $C_{14}H_{22}O_t$ (Wunschendorff and Braudel, *ibid.* 1932, II, 70; *see aha* Ajello, *ibid.* 1933, II_f 2399; Wun-Bchendorffand Valier, *ibid.* 1934,1, 3752, 3861)

Aucubin *{q.v.).*

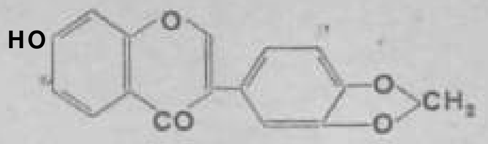
Avenein (glucovaniLlin),$C_HH_{lg}0_8$, m.p. 192°, $[o]_D$ —88-6, is found in *Aveiut saliva* and *Triticum repetis.* It appears to be a glucoside of vanillin *(see* Fischer and Raske, Ber. 1909, 42, 1405). It is an oxidation product of the glucoside coniferin *(q.v.).* Vanillin ^-glucoside has been synthesised (Thorpe and Williams, J.C.S., 1937, 494).

Baicalin *(q.v.).* An enzyme, prepared from *Primus arnieniaca* var. *ansu* consists of biacalinase and j3-glueo3idase **(Him,** Amer. Chem. Abstr. 1930, 8272; Shibata and Hattori, Acta. Phytochim. 1030, 5, 117; Miwa, *ibid.* 1932,6, 155; 1935,8,231; 1936,9, 89).

Baptisin, $C_{I7}H_{31}O$,s, m.p. 240°, *$[a]_B$* -61°, occurs with ^-baptism in the roots of *BaptUia tinctoria.* Hydrolysis with acid gives Z-rhamnose (2 mol.) and baptigenin. 0-Baptisin on hydrolysis gives (Z-gturase, *I*-rhamnose and <*ji*-baptigenin (Spath and Schmidt, Monatsh. 1929, **58/54,** 454).



Baptigenin.



ψ-Baptigenin.

The position of t^e sugar residues in baptisin is not settled. •

Barbaloin *(v.* Vol. I, **262s).**

Bu'Trin, C«$H_MO_{1(}$,2H,$O_($ $[«]_D$ -81-7° fin pyridino), has been isolated from *Butea frondosa* flower (Lai, J.C.S. 1937* 1562; J. Indian Chem. Soc. 1935, 12, 262). Hydrolysis gives glucose (2 mol.) and 7;;if':4'-*rihydr<).\ynavanone. Ti augars are present as a bioside.

Callistephin *(q.v.f.*

Camellia-Saponin, $C_{1T}H_{?4}O_{30}$,6H_aO, m.p. 208° (anhydrous), *[a\\$_n$* +37°, is a saponin of the hederin type *(v.* p. 89) found in *Camellia japonica.* Hydrolysis gives giucoso (3 mol.), arabinose (2 raol.) and camellia-sapogenin, $C_{2(}H,,_4O_{fl}$, decomp. 194-197° (Aoyaraa, Chem. Zentr, 1929,1, 248), of unknown structure. On dehydrogenation the sapogenm yields aapotalin (1:2:7-fcrimethyki&phthalene), suggesting that it ia similar in structure to hederagenin (p. *$9d).*

Cerberin *(v.* Vol. *11,* 481). A cardiac gtycoside (Vol. II, 387c).

Cetyl 4-Glucoside, $C_{Z!}H_{14}O_e$, m.p. 150°, $[al_D$ —2'2°,occurs itithe*Sarsuparillaroot.* Ithas been aynthesised from cetyl alcohol and aceto bromoglucose (Fischer and Holferich, Annalen-1911, 383, 79 j Salway, J.C.S. 1913_{HJ}03, 1022)

Chebuiinic Acid, $C_{41}H_{?4}O$j,, [aJ^H 1."> iMeOH — HjO), occurs iij.th*'fruit of *TtrminaXia ckabula.* Hydrolysis by dilute alkali or by tannaae gives d-glucose, gallic acid (3 mol.) and a dibasic acid of unknown structure (Freudenberg, Ber. 1919, 52 [B], 1238; 1920, 53, [B], 1728). One carboxyl group of this acid appears to be condensed with the glucosidic hvdroxyl group and at least two of the gallic acid molecules are attacKed to the glucoBe (FreudDnberg and Frank, Annalen, 1927, **452,** 303).

Cheiranthin *(q.v,).*

Chellol-Glucoside, $C_{1v}H_{20}O_{.0}$,2H,O, m.p. 175°, occurs in Arabian " chell&h," *Amni visnaga.* Acid hydrolysis gives rf-glucose and a substance of the coumarin type of unknown constitution (Fantl and*, Salem, Biochem. Z. 1930 226, 106)1

Chrysanthemin *(q.v.).*

Cichoriin *(q.v.).*

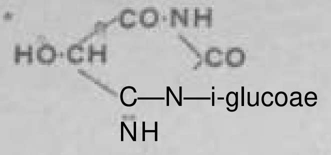
Citronin, CjgH^O!,, m.p. 235°, occurs in various species of *Citrus (cf.* Naringin). Hydrolysis gives rf-glucose, /.rhamnose an*i citronetin, $C_{18}H_UO_B$, m.p. 225°, which is 5:7-dihydroxy-2'-methoxyflavanone (Shinoda and Sato, Chem. Zentr. 1931, II, 2326; Vamamoto and Oshima, Amer. Chom. Abstr. 1932, **26,** **1 lr.1;)],**

Oavicepsin *(q.v.).*

Coniferin *(q,v.).* '

Convallatoxin (». Vol. ri, 3876).

Convicine, $C_{10}H_{15}N_3O_8,H_2O$, is a pyrimiame glucoside occurring with vicine *(v,* p. 97d) in vetch seeds (Ritthansen), It appears to have the formula given at the top of the next page.



(*See* Johnson, J. Amor. Chem.^oc. 1914,36,357; Fisher and Johnson, *ibid.* 193? 54, 2038.)

'Convolvulin *(q.v.). See also* Maiuiicfa and S humana, A., 1938, II, 238.

Coronillin *(q.v.).*

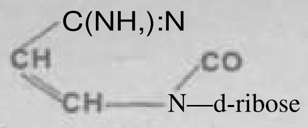
Crocin *(q.v.).*

Cyanin *(q.v.).*

Cyclamln. $Cs\hat{}H_{Bfl}O_{rt}$, decomp. 2/54°, a napunin of the hederin typo *ip.* 89) found in alpine violets *(Cyclamen europteum)* {Plzik, Ber. 1903, 36, 17fil; *cf.* Chem. Zentr. 1927, I, 2331; 1929,1,2655). Hydrolysis gives glucose (3 mol.), arabinose (2 mol.) and cyclamirgtfo, $C_{,8}H_{19}O_4$ (Dafert$_a$e(*al.$_r$* Chem. Zeatr. 1926, Ii; 2437; 1930, I, 1798; 1934, II, 1785 {revision of molecular formula:)). The last compound gives sapotalin on dehydrogenation. Its structure is not yet known.

Cymarin *{q.v.),*

Cytldine ia a pyrimidine nucleosido *(cf.* Uridine, p. 976) formed on hydrolysis of yeaet-nucleic acid. It is 3-cvtoaine d-ribofuranoside.



In the nucleic acid, the hydroxyl group in position 3 of the rlboqe is esterified with pbos$_e$phoric acid (Levene and London, J, Biol. Chem. 1929, 83, 793).

Daldzin, C^HJOOB, m.p. 235°, [«3$_D$ -37°, is an isoflavone glucoside from *Soja hivpida (cf.* Genistin, p. 88c). Hydrolysis givea d-glucose and daidzcin *(v.* Vol. V, 259c).

Daphnin *(q.v.).*

Datiscin *(v.* Vol. n i, 549c).

Delphin *{q.v.).*

Deiphinin *(q.v.).*

^Deoxyadenosine, deoxycytidlne, deoxyguanosine, xjeoxyuridine.—These purine nucleosides are hydrolysis products of nucleic acids, and are similar in structure to adenosine, cytidine, guanosine and uridine respectively, having deoxy-d-ribofuranose in place of *d*-riboturanose. They are obtained by enzymatic cleavage, as deoxyribose is very sensitive to chemical reagents (Levene and London, J. Biol. Chem. 1929, 81, 711; 1020,83,793). Gulland and Story *(J.C.S.* 1938, 259) have shown that in deosyadenosine the sugar is attached to position 9.

Dhurrin *(q.v.),*

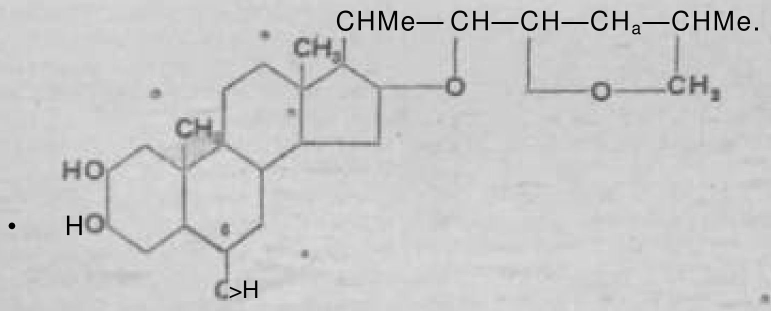
Dibenzoylglucoxylose, $C_2«H_{!e}O_{1s}$, m.p. 148°, *$[d]_D$* -107*, occurs in the branches of *Daviesia Utiifolia* (Power and Salway, J.C.S. 1911,105, 767, 1002; Tutin, *ibid..,* 1915,107, 7). Alkaline hydrolysis gives benzoic ncid and glucoxylose, a disaccharido, $[o]_D$ —36-5°, non-reducing to Fehiiog s Bo^ution and giving no osazono. It appears to be rf-xylosido-d-glucoside, the two glycosidic hydroxyl groups forming the linkage between the sugars,

Dlgilanldes (A, B and C) *{v.* Vol. II, 385).

Diginin («. Vol.,II, 3844).

Digitalin *(v.* Vol. 11,3844).

Diftitonin is a saponin, occurring with several cardiac gly cos ides of somewhat similar constitution *(e.g.* digitoxin) in the leaves of *Digitalis purpurea.* It is one of the few well-characterised Baponins. Its isolation in a pure state is nevertheless difficult. Cardiac glycosides are removed from the crude extract by chloroform or ether. Digitonin is then separated from other saponins (gitontn, tigonin, etc.) by fractional precipitation with "aniyl alcohol (Kiliani, Ber. 1910, 43, 3562; 1916, 49, 701) or as an adduct with ether (Windaus, Z. physiol. Chem. 1925, 150, 205). Repetition of these methods gives pure digitonin. It has the probable molecular formula $C_{se}H_{S2}O_{1fl}$, m.p. 235°. Hydrolysis gives glucose (2 mol.), galactose (2 mol.), xylose (1 mol.) and the steroid *digifageniji,* $C_{n}jH_{14}O_5$, m.p. 253°, which appears to have the following structure *{see* Tschesche and Hagedora, Ber. 1936, 69 [B], 797) i



Digltoxin („. Vol. II, 3846).

Digoxin (». Vol. II, 3856).

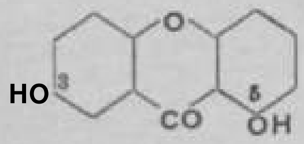
Di roamin), $C_{34}H_{44}O_{21}$, m.p. 280°

Dryophantin, $C_{ra}H^{TM}O_{i(}$, m.p. 220°, occurs in galls produced by *Ihyophania,* on *Qwtrcua* species. Hydrolysis gives glucose (2 mol.) and purpurogallin, m.p. 275° (Nierenstein, J.C.S. 191y, 115, 1328).

Emicymarln, C^H^O,, is a glycoside isolated from the seeds of *Stropfianlhits emini* by Lamb and Smith *(ibid.* 1936, 442) by partial enzymatic hydrolysis. Acid hydrolysis gives digita?ose *(q.v.)* and a sterotd trianhydroperiplogenin *(see* Periplocymarin, p. 93«).

Erysolfn *(see* Glucocheirolin, p. 88rf).

Euxanthlc Acid *(q.v.),* $C_HH_{1(}O_{10t}3H_tO$, m.p. 162°, is the glycoside present in Indian yellow {Kostanecki, Ber. 1886, 19, 2918?. Hydrolysis gives rf-glucuronie^cid and cuxanthone, 3:5-dihydroxyxanthone, m.p. 237° (Graebe, Bcr. 1899, 22,1405).



Euxanthooe.

The uronic acid is attached to position 3 and has a pyranose structure (Robertson and Waters. J.C.S. 1931, 1709).

Floridoside, $C_eH_{ls}O_B$, m.p. 87°, $[a]_D$ +151", occurs in *Rkodymenia palmata.* Hydrolysis by acid or yeast gives galactose (1 mol.) and glycerol. It is not hydrolysed by emulsin, and it is therefore probably an . a-galactoside (Colin and Augier, Chem. Zentr. 1933, I, 3953). It is probably 8-(a-d-gakctosido)-glycerol (Colin, BuU. Soc. chim. 1937, [v], 4, 277).

Folinarin lias been shown to be identical with oleandrin (p. 92c) {Neumann, Ber. 1937, 70 [B], **15*7;** Tschesrhc, *ibid.* 1554).

Frangutin {Franguloside) is a glycoside ef the anthraquinone type, giving rhamnose and 4:5:7-trihydroxy-2-mcthv].mtliraquinone on hydrolysis. It occurs in *Hhamnus fravguta* (Bridel and Charaux, Compt. rend. 1930, **191,** Ufil).

Fraxin, $C_{je}H_{18}O_{10}$, m.p. 205°, is a coumarin glucoside found in the ash *(Fraxitws excelsior)* and species of *JSsculws.* Hydrolysis by emulsin or acids gives (f-glucose and fraxetin, 6-methoxy-7:8-dihydroxycoumarin, m.p, *221-22%*.,* The glucose is attached to position 8 {Weasely and Demmer, Ber. 1928, 61 [B], 1279; 1929, 62 [B], 120; Weasely and Lechner, Monatsh. 1932, 60, 169}.

Fustin, $C_{3B}H5j_6O_4$, m.p. **330°,** has been described as a flnvonol glycoside occurring in the stemi[1] and branches of young fustic *(Ekus cotinvs)* and in *Quebracho Colorado.* Hydrolysis was said to give rhamnose {1 mol.) and fisctin (2 mol.), $C_{15}H_{10}O_6$, m.p. 219°. Fisetin is 3:7:3':4'-tetrahydroxyfiavone (A. G. Perkin, J.C.S. 1897, 71, 1194; Allan and Robinson, *ibid.* 1926, 2334).

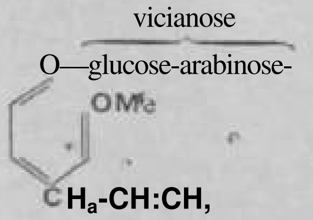
Recently, however, it has been claimed that fustin is dihydrofisetin, and gives no sugars on hydrolysis (Oyatnada, J. Chem. Soc. Japan, 1934, 65, 755; 66,980).

Galuteolin, $C_{21}H_{ao}O_n$, m.p. 280°, is a flavone glycoside isolated from the seeds of *Galega ojficivalis.* Hydrolysis gives glucose and luteolm *(v.* Vol. IV, 189a), the dye of *Reseda lufeola* which wb'-n dried is known as " dyer's weed " (ttnrger and White Biochem. J. **1923j** 17, SUli; Chem. Zentr. 1931, II, 2464).

Gaultherioside, $C_{13}H_{21}O_{10}$, m.p. 185°, $[a]_D$ —58°, is present in fresh *Gaultheria procumbent.* It is noujreduring. Hydrolysis, **yields** glucose, xylose and ethyl alcohol (RabatS and Rabate\ Chem. Zr«tr. 1931, II, 1711). The sugars are present as the biose primeverose *{cf.* Primevcrin, p, 94<i); it is therefore ethyl 0-primeveroside. It is not thought to be formed from primeverose during extraction *(see* Rabat£, BuU. Soc. Chim. biol. 1938, 20, **449).**

Gau Jtherin *(/tee* Monotropitin, p. 92n).

Gein (geoside), $C_{21}H_{30}O_{11},H_2O$, m.p. 146*, $[o]_D$ —54°, occurs in *O'evm urbanum.* Hydrolysis by the enzyme gease gives vicinnose (6-/5-/-arabinosid*o-d*-glucose; c/. Vicianin, p. 97c) and engenol (Vol.. IV, 394rf).



Gcin.

{H^rissey, Ch%th. Zentr. 1926,1,2358; IT, 2436; 1927, I, 1025).

Genistin, $C_{21}H_{20}O|_0$, m.p. 254-256°, $[a]_p$ —28°, is an isoHnvone glurosiiie occiiiring with daiclzin *{v. supra)* in *Soja hiepida.* Acid hydrolysis gives rf-glucose ilnd genistein, $C_{15}H_{10}O_5$, m.p. 297-298°, which is 5:7:4'-trihydroxyiso. flavone. The sugar in genistin is attached to position 7 **(Wak,** Annalen. **1931, 489,** 118). Genistein occurs also in dyer's broom, *Genista tinctar'ia* (Baker and Robinaon, J.C.S. 1925, 127,1981; 1926,2713; 1928, 31ir>).

Gentianin *(q.v.).*

Geranyl-Glucoside, $C_{lfl}H_{2ft}O_{fl}$, m.p. 58°, $[o]_D$ —37", occurs in *Pelargonium odoratum.* It is a ^-glucoside, which has been ?ynthcsised from the terpene gernniol *(<j.t\)* and acctobromoglucose {Fischer and Helferich, Annalcn, 1911, 383, 77), It lms also been obtained by enzyme synthesis, from geraniol and rf-glucoac in the presence of emulsin (Bourquclot and Bridel, Compt. rend. 1913,157, 72; Chem. Zentr, 1913, II, 1309).

Gesnerin *(q.v.).*

Gitalin *{v.* Vol. II, 384r).

Gitonin is orfe of several saponins occurring (with cardiac glyeosidcs) in tho leaves *of Digitalis •purpvTca,* it is separated from digitonin by fractional precipitation with **ether (Windaw** Z. physioi. Chem. 1925, **150,** 205), and also by fractional 'crystallisation from alcohol-water mixtures; it was first isolated by WindauB and Schneckenburger (Be.r. 1913, 46, **2628)** from impure digitonin preparations. It has the probable molecular formula $C_MH_gjO_{33}$, m.p. 272°. Hydrolysis gives golacrose (3 mol.), an u». identified pentose(1 mo].)nnd a steroid gitogenin, $C_{s;7}H_{44}O_4$, m.p, 272°. The last compound ha« been assigned a structure closely sicMlar to that of digitogeniii (p. 87rf) but having no hydro.wl group in position C *(see* Tscheache, Ber. **1930** 68 [B], 1090; Tsehcache and Hagedorn, ***ibid.*** 1936, 69 [B], 797).

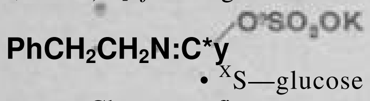
Gitoxin, A cardiac glycoside *(v.* Vol. II, 384/J).

Glucocheirolin, $C_{11}H_{2t)}O_nS_1NKH_!O$, m.p. IbO , $[a]_c$ -21'5°, is a mustard-oil glucoside found in the seede of"wallflowers *{Chtiranthn* ehein).* **It** is **hydrolysed bj the ennaw myroii<** to chcimlin {Vol. II, *R'Ut). d'rfueaae* **and** potassium hydrogen sulphate (Schneider and

Lohmann, *ibid.* 1912, 45, 2954; 46, 2034; *see also* Annalen, 1912, 386, 346) (*cf.* Sinigrin, p. 96a).

A homologue of cheirolin, erysolin, $CH_3SO_2[CH_2]_4NCS$, occurs as a glucoside in the seeds of the orange wallflower, *Erysimum perofskianum*.

Gluconasturtiin, $C_{15}H_{20}O_9S_2NK$, is a mustard-oil glucoside from the seeds of *Nasturtium officinale*. Hydrolysis by myrosinase gives *d*-glucose, phenylethyl isothiocyanate and potassium hydrogen sulphate (Gadamer, Ber. 1899, 32, 2335) [*cf.* Sinigrin and Glucotropaeolin).



$$PhCH_2CH_2N{:}C\begin{matrix}\diagup O{\cdot}SO_2OK\\ \diagdown S{-}glucose\end{matrix}$$

Gluconasturtiin.

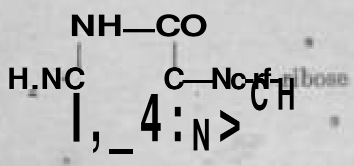
β-Glucosido-Gallic Acid (Glucogallin), $C_{13}H_{16}O_{10}$, m.p. 193°, $[\alpha]_D$ -21°, is found in Chinese rhubarb (Fischer and Strauss, *ibid.* 1912, 45, 3773; 1918, 51, 1804) (*cf.* Tetrarin, p. 97a).

Glucotropaeolin, $C_{14}H_{18}O_8S_2NK$, is a mustard-oil glucoside found in *Tropaeolum majus* and *Lepidium sativum*. Hydrolysis by the enzyme myrosinase gives *d*-glucose, benzyl *iso*-**thiocyanate** ($PhCH_2NCS$), and potassium **hydrogen** sulphate (Gadamer, *l.c.*). It is therefore analogous to sinigrin and gluconasturtiin.

Glycyphyllin, C^t-LjO^SHjO, m.p. 175-180°, occurs in the leaves of *Smilax glycyphylla*; it appears to be a rhamnoside of phloretin (*see* Phloridzin, p. 936) (Wright and Rennie, J.C.S. 1881, 39, 237; Rennie, *ibid.*, 1886, 49, 857).

Gossypitrin (*v.* Vol. III, 406ft; *also* Neelakantam and Seshadri, 1937, A., II, 445; 1939, A., II, 245).

Guanosine (Vernine) was the first nucleoside to be discovered in nature (Schulze and Bosshard, Z. physiol. Chem. 1885, 9, 448; 1886, **10**, 80). It occurs in various plant tissues (*Vicia, Lupinus,* etc.) and is a hydrolysis product of yeast-nucleic acid (*also* thymus- and pancreas-nucleic acids). It is 9-guanine-d-ribofuranoside, guanine being 2-amino-6-oxypurine (*see also*

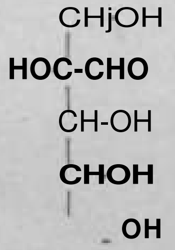


Levene and Jacobs, Ber. 1909, 42, 2474; 1910, 43, 3163; Gulland and Holiday, J.C.S. 1934, 1839; 1938, 692). Guanylic acid has a phosphoric acid residue in position 3' of the ribose, and it is in this form that guanosine occurs combined in the nucleic acids.

Gynocardin, $C_{13}H_{19}O_9N$, m.p. 163°, $[\alpha]_D$ +72·5°, is a cyanophoric glucoside found in the oleaginous seeds of *Gynocardia odorata*. It is accompanied by an enzyme, gynocardase, which hydrolyses it to *d*-glucose, hydrocyanic acid and a diketone of unknown structure (Power and Lees, J.C.S. 1905, 87, 349; Brill, Chem. Zentr. 1923, I, 104; Floriani, 1929, I, 761).

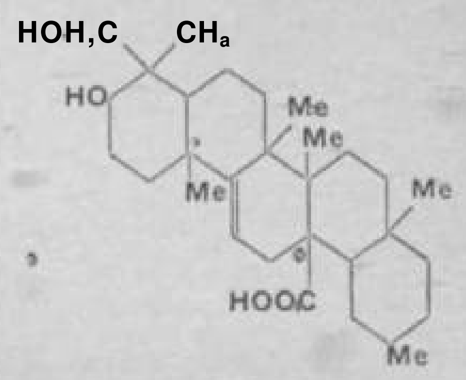
Gypsophila-Saponin ... is a saponin belonging to the hederin group (*cf. infra*). It occurs in *Gypsophila arrostii* and *paniculata* (Kofler and Dafert, *ibid.* 1924, I, 922). Hydrolysis gives arabinose, rhamnose, glucose, galactose and gypsogenin, $C_{30}H_{44}O_4$, which on dehydrogenation yields, among other products, sapotalin (1:2:7-trimethylnaphthalene) (Ruzicka *et al.*, Helv. Chim. Acta, 1932, 15, 1490).

Hamamelitannin, $C_{20}H_{20}O_{14}$, m.p. 11T. occurs in *Hamamelis virginiana* (Freudenberg and Blümmel, Annalen, 1924, **440**, 45). Hydrolysis by the enzyme tannase or by acids gives gallic acid (2 mol.) and a hexose, hamamelose (1 mol.), for which the following constitution has been proposed (Schmidt, *ibid.* 1929, 476, 257).



Reduction of the corresponding aldonic acid with hydriodic acid gives methyl propyl acetic acid; hamamelose gives no osazone and has a slight laevo rotation. Identification is rendered difficult by the fact that the sugar has not yet been obtained crystalline. Freudenberg (*l.c.*) suggests that the gallic acid molecules are attached through their carboxyl groups to the primary alcoholic groups of the hexose.

Hederin belongs to a small group of triterpenoid saponins the aglycones of which are not of the sterol type (as in the case of digitalis saponins; *see* Digitonin, p. 87c) but appear to be triterpenoid in character. Their constitution is still under investigation. Escin, camellia-saponin, caryocarsaponin, cyclamin, gypsophila-saponin, quillaia-saponin, etc., are of this class. Hederin (α-hederin) is one of several saponins found in ivy (*Hedera helix*); others present have not yet been characterised as chemical individuals. It is crystalline, having the molecular formula $C_{41}H_{64}O_{11}$. Hydrolysis yields rhamnose, arabinose and hederagenin, $C_{30}H_{48}O_4$, m.p. 331°, $[\alpha]_D$ +70°. In common with the aglycones of other members of this group, hederagenin on dehydrogenation yields sapotalin (1:2:7-trimethylnaphthalene). A suggested structure for hederagenin is given below:



Hederagenin (provisional).

{Rnzicka *et al.,* Helv. Chim. Acta, 1937, 20, 298, 325; 1938, *21,* 1371 ; *Z.* Kitsato, Acta *Phyto*-chim. 1936-37, 9, 43, Gl, 75; 1937-38, 10, 199). *(See oho* Spring, Cheni. and Ind. 1936, 55, 964, 1050.)

Heficin {.Spirain), $C_{13}H_{,B}O_7$, m.p. 174-175°, *[a]$_a$* —60°, is salicylaldehyde-jS-glucoaide. It occurs in *Spir#a* species and is formed when salicin is oxidised with nitric acid (Schiff, Aiin&len, 1870,164,15). It haa been synthesised from sailcylaidehyde and acetochloroglucose (Michael, J. Amer. Chem. Soo. 1879, 1, 305 ; Ber. 1879, 12, 2260). Emulsin hydrolyaes helicin and also its hydrazone and oxime.

Hellebrin ia a crystalline cardiac glyeoside *(v.* Vol. II, 387cj.

Hesperidinj C^r^O^, m.p. 251°, is a flavannne glycoside found in the peel of several *Citnt3* fruits (not *Citrus deeumana)* (Tieraann and WiU, Eer. 1881, 14, 948). Hydrolysis gives d-glueose, i-rhamnose and hesperitin, $C_{ie}H_{14}O_s$, m.p. 228% which is 5;7;3'-trihydroxy-4'-methoxyflavanone (sj'nthesis: Slunodaand Kawagoye, Chem. Zentr. 1929, I, 244). The sugars appear to bo presunt as a bioae (King and Robertson, J.OS. 1931, 1704).

Hiptagin, $C_{1B}H_HO,N_I,iH_fO$, m.p. 110°, *[a]$_D$* +3'5^C (in acetone), is a cyanophoricgluoosidc found in the root bark of *Uiptage medablota.* Dilute acid gives d-glucose and various degradation products; dilute alkali yields ammonia and hydrogen cyanide even in the cold. It is considered to bo the glucoside of an isoxazole derivative *(see* Gorter, Amcr. Chem. Abstr. 1921, 15, 1299).

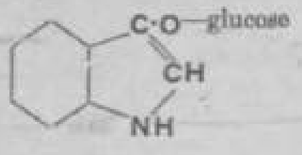
Hlrsutln *{q.v.).*

Hlviscin, $C_{B0}H\hat{}O_{Ig}CI,3ri_2O$ (chloride),is an aiithoeyanin obtained from *Hibiscus aabdarijfa,* m.p. 178°. Hydrolysis gives glucose, a pentose and dolphinidin chloride (see Delphinin) (Yamatnoto and Osinwi, Chem. Zentr. 1933,1, 71; 1937, A., II, 71).

Idaeln, *(q.v.).*

Incarnatrin is a flavonol glycoside, from *Trifalium incarnatum* (crimson clover). It ia hydrolysed by emulsin to glucose and quercetin *(see* Quercitrin, p. 94c) (Rogerson, J.C.S. 1910, 97, 1004).

Indican, $C_uH_{17}O_9N,3HjO$, m.p. 58° (anhyd, 178°), *[a]$_D$* —77-6°, occurs in various species of *Indigo/era* and *Iaalis tinctoria,* etc. It is j9-indoxyl glucoside, being the form in which indigo occurs in the plant. Hydrolysis by the enzyme indeiuulsin (with which it ie found) or by acids gives (/-glucose and indoxy], which is readily oxidised *{e.g.* by air) to indigotin.

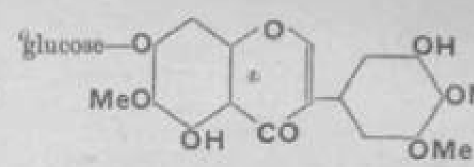


Iudlcan.

Indican U hydrolysed slowly by emulsin. For the synthesis of inlican, *see* Robertson, J.C.S. 1927, 1937; *ibid.* **1933,** 30. **Indole** derivatives are eliminated **from the** body **in** the **form of** indican.

!nosinic Acid is a purine nudeotidc, and was first discovered in meat extract *by* Liebig in 1847. r.Careful hydrolysis gives phosphoric acid and inosine, S-hypoxanthine-ci-ribpfuranoside. In inoBinic acid the phosphoric acid residue ia on position 6 of the sugar (Levene and Jacobs, Ber. 1908, 41, 2703; 1909, 42, 33S; 1911, 44, 746; Levene andTipson, J. Biol. Chem. 1935, 111, 313). In fresh tissues inosine is largelv replaced by its precursor adenine-5-phosphoribofuranOside; the latter is transformed into inosinic acid by a specific enzyme. The position of the ribose side-chainjis discussed by Gotland and Holiday (J.C.S. 1936, 765).

Iridln, $C_{a<}Hg_aO_{13},H_aO$. ^*.p.* 208° (anhydrous 217°), is an I'aoflavone glucoside found in the rhizomes of iris *'^iriafiorerUina, germanica,* etc.). Acid hydrolysis yields rf-glucose and irigenin, $C_{18}H_{,a}O_8$, m.p. 186°, 5:7:3'-trihydroxy-6:4':5'-trimethoxyMoflavone (Baker, *ibid.* 1928, 1022). *(Of.* Tectoridin, p. 96d.)

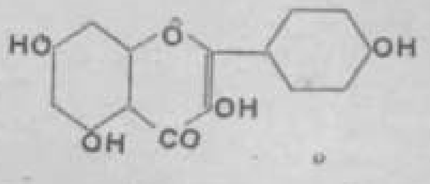


For the synthesis of iridin, see Baker and Robinson, J.C.S. 1929, 152.

Jalapin (ecammonin, orizabin), $C_3|H_{4i!}Ojs$, m.p. 208°, is found in *Stipitea jalapm, Convulvulux orizahnnsis* and *Sctimmonia.* Hydrolysis gives d-glueose, I-rhamnose, </-fucoae (rhodeosc, Vol. V, 330c) and jalaponio add, $C_{,,}H_{3i(}O$, {1 [-hydroxyliexadecanoic acid), m.p, 68° (Davies and Adams, J. Amer, Chcni. Soc. 1928,50,1749; VotoCek and Valentin, Amer. Chem Abstr 1928, 22, 1361) *(v.* Convolvulin).

Jalapin has a hoemolytic effect similar to that of the eaponins; it paralyses the motor paraeympathetic nerves (Heinrich, Biochem. Z. 1918, 88, 13; Hollander, Amer. Chem. Abstr. 1936. 30, 5305).

Ksempferin, $C_{i7}H_{30}O_{1(1}$, m.p. 195°, ia a flavonol glycoside found fti senna leaves. Hydrolysis gives glucose (2 mol.) and kampferol (campherol), 5:7:4'-trihydroxyflavonol, m.p. 277° (Tufcin, J.aS. 1913,103, 2006).



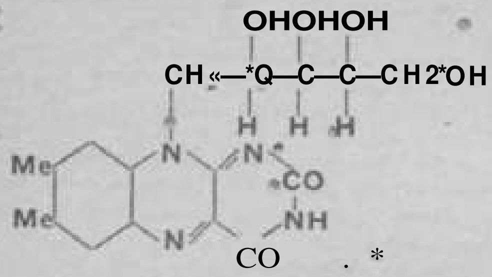
Kfflmpferol is the aglycone of several other glycoHides (kampfcritrin, robiain, etc.).

Kffimpferitrin, $C_wH_MO_{1(}$. m.p. 203°, ia a flavonol glycoside, found iii Java indigo *(Indigofera arrecta).* HydrolyeiB gives rhamnoBe (2 mol.) and kaunpferol *(v, supra)* (Tasaki, 1827, A., 918). The rhamnose appears to be attached, as a disaccharide, to the hydroxyl eroup ia ositiou 3. » •

Keracyanin (I'runicyanin), *v.* Vol. I, p. 449a.

K Vi?20"HO m.p. 180 7. r^ —11 CHCl$_3$, is a galac(olipin occurring in the brain [*see* Klenk and Härle, Z. physiol Chem. 1930, **189,** 243; Chibnall, Piper and Williams, Biochem. J. 1936, 30, 100).

Lactoflavin (now riboflavin, vitamin B_2) 6:7-dimethyl-9-d-ribitylisoalloxazine, is necessary for the growth of rats (György, Kuhn and Wagner-Jauregg, Naturwiss. 1933, 21, 560). For synthesis, *see* Karrer, Helv. Chim. Acta, 1935, 18, 426, 522, 1435.



Lactoflavin.

It is interesting to note that the ribose may be eliminated by irradiation in neutral solution.

Linamarin (phaseolunatin),

$$C_{10}H_{17}O_6N,H_2O,$$

m.p. 142°, $[\alpha]_D$ —29°, is a cyanophoric glucoside found in young flax (*Linum usitatissimum*) and in *Phaseolus lunatus* (Jorissen and Hairs, Bull. Acad. roy. Belg. 1891, 21, 529). It occurs also in the rubber tree, *Hevea brasiliensis.* It is hydrolysed by aqueous alkali to ammonia and phaseolunatinic acid, $C_{10}H_{18}O_8$, which with dilute acid gives d-glucose and a-hydroxyisobutyric acid, $Me_2C(OH)COOH$. The structure of linamarin is

$$Me_2C(CN)\text{-}O\text{—glucose},$$

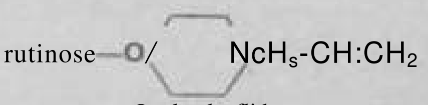
(β-glucosidic link). For synthesis, *see* Fischer and Anger, Ber. 1919, 52, 854; Sitzungsber. K. Akad. Wiss. Berlin, 1918, 203. The action of enzymes upon linamarin has been the subject of contradictory reports. In general, it appears to be accompanied by a specific enzyme, *linase,* by which it is hydrolysed to d-glucose and acetone cyanhydrin. Emulsin yields *d*-glucose, acetone and hydrogen cyanide.

Linarin, $C_MH_MO_U$, is a flavone glycoside found in toad flax (*Linaria vulgaris*). Hydrolysis gives glucose, rhamnose and 6:4'-dimethylscutellarein, C^H^O,,, m.p. 218° (*see* p. 95rf). (Schmid and Rumpel, Monatsh. 1932, 60, 8; Mere and Wu, Amer. Chem. Abstr. 1936, 4166.)

Liquiritin, C^H^O,, m.p. 212° (monohydrate) is a flavanone glycoside found in *Glycyrrhiza glabra* (*Radix liquiritiae*). Hydrolysis gives d-glucose and liquiritigenin, 7:4'-dihydroxyflavanone, m.p. 207°. The glucose is attached at «•* iR??**'011 *•* (Shinoda and Ueda, Ber. 1934, "I 434).

Lotusin, $C_{28}H_{31}O_{16}N$, m.p. >300°, is a cyanophoric glycoside isolated from *Lotus arabicus* by Dunstan and Henry (Proc. Roy. Soc. 1900, 67, 224; 1901, 68, 374). Its structure is still uncertain. Hydrolysis gives d-glucose (2 mol.), hydrogen cyanide and lotoflavin, $C_{15}H_{10}O_6$, m.p. >200°, probably 6:7:2':4'-tetrahydroxyflavone (*see* Robinson and Venkataraman, J.C.S. 1929, 61; Cullinane, Algar and Ryan, Proc. Roy. Dub. Soc. 1628, 19, 77). The cyanogen radical appears to be attached to the sugar groups (*see,* however, T. A. Henry, J.S.C.I. 1938, 67, 248, where Dunstan and Henry's investigations are not supported).

Lusitanicoside, $C_{21}H_{30}O_{10}$, m.p. 188°, $[\alpha]_D$ —74°, is found in Portuguese cherry laurel leaves (*Cerasus lusitanica*). Hydrolysis gives p-allylphenol (chavicol), d-glucose and l-rhamnose (Hérissey and Laforest, Chem. Zentr. 1932, II, 232; 1934, I, 2137). The sugars are present as the biose rutinose (β-l-rhamnosido-6-d-glucose) and lusitanicoside is therefore chavicol-



Lusitanicoside.

β-rutinoside (synthesis: Zemplén and Gerecs, Ber, 1937, 70 [B], 1098).

Luteic Acid is a synthetic glycoside formed by the action of *Penicillium luteum* on d-glucose (Raistrick and Rintoul, Chem. Zentr. 1932, I, 1107). Hydrolysis yields d-glucose (2 mol.) and malonic acid (1 mol.). [*See also* Birkinshaw and Raistrick, Biochem. J. 1933, 27, 370; Vol. V, 58a).

Lycoperdin, $C_{13}H_{14}O_5N_2$, is an amino-sugar glycoside found in lycoperdon. Hydrolysis gives glucosamine (2 mol.) and formic acid (1 mol.); it reduces Fehling's solution and gives the biuret reaction (Kotake and Sera, Z. physiol. Chem. 1913, 88, 56).

(For the constitution of glucosamine, *see* Haworth, Lake and Pent, J.C.S. 1039, 271.)

Malvin, $C_{!S}H_{35}O_nCl$ (**chloride**), is an anthocyanin present in the wild mallow, *Malva sylvestris* and in *Primula viscosa.* Hydrolysis gives glucose (2 **mol.**) and malvidin chloride, $C_{1T}H_{IS}O_7Cl$. The latter is sometimes called syringidin chloride, as degradation yields syringic acid (3:5-dimethoxygallic acid). Malvidin chloride is the 3':5'-dimethyl ether of delphinidin chloride (*q.v.*, Vol. III, 554d). The glucose molecules are attached in positions 3 and 5 (Kondo, Chem. Zentr. 1930, I, 3193; Robinson and Robinson, Nature, 1931, **128,** 413). Malvin has been synthesized by Robinson *et al.* (J.C.S. 1932, 2299). Malvidin (*also* pelargonidin **and** peonidin) do not give colour reactions with ferric chloride and sodium acetate in amyl alcohol solution.

Mecocyanin, $C_{J7}H_{31}O_{16}Cl$ (chloride), is an anthocyanin present in the red poppy (*Papaver rhoeas*) (Willstätter and Weil, Annalen, 1917, **412,** 237; Robinson and Robinson, Nature, 1931, 128, 413). It is cyanidin-3-gentiobioside (Grove, Inubuse and Robinson, J.C.S. 1934, 1608) and yields on hydrolysis glucose (2 mol.) and cyanidin chloride (*see* CYANIN).

Melilotin (melilotoside), $C_{1(}H_{1B}O_8,H_2O$, m.p. 240-241°, $[\alpha]_D$ +68°, is found in the flowers of *Melilotus altissima* and *arvensis* (Charaux, Bull. Soc. Chim. biol. 1926, 7, 1056). It is hydrolysed by emulsin (and acids) to glucose and o-coumaric acid.

Methoxyapiin is a flavone glycoside found with apiin (*q.v.*) in parsley. Hydrolysis gives flmose (2 mol.) and methoxyapigenin (diosmetin), tho 4'-methyl ether of lutcolin *(see* Galuteolin, p. 88) (Von Gerichten, Ber. 1900,33, 2334; Annalen, 1901,318, 121).

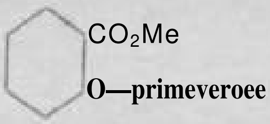
Methylarbutin, *see* Arbutin, p. 36.

Methylcichqriin, *see* CIOHOBUN.

Monardaein (Salvianin), $C_{a8}H_{M}O,_{7}Cl$ (cbloride), is an antliocyanin present in ***Monarda*** *didyma* (Karrer and Widmer, Helv. Chim. Acta, 1927, 10, 67, 729). Hydrolysis gives glucose (2 mol.), 2-hydroxyeirmanuc acid, malonic acid and pelargonidin cldoride *(set* Pelargonin,p. 93). It appears *tu* be similar to salvianin {from *Salvia splendens)* (Karrer and Widmer, *ibid.* 1929, 12, 202).

Monotropitin (Gaultherin, Monotropitoside), $^{c}i.^{H}2e^{\circ}i!-^{H}s^{o}-{}^{m}$-P- $^{92\circ}$ (179-5° anbydrous), $[a]_{D}$ —57°, is found in various species of *Gaitltheria* and *Spirsea.* It is hydrolysed by tbe enzyme gaultherase (primevemsu) *to* primeverose (6-0-xylosidoglueoae) *(v.* Vol. II, 3006); and methyl salieyJate, Acid hydrolysis gives glucose, xylose and salicylic acid:

1



(cf. Salicin, Fopulin and Violutin).

Monotropitin has **been ByttthfisiBed** {Robertson and Waters, J.C.S. 1931, 1881). Both glycosidic linkages are of the 0-type.

Morindin, ra.p. 245°, is an anthraquinone glycoside found in species of *Morindn,* Hydrolysis gives glucose (2 mol.) and morindone, **1:5:6-**trihydroxy-2-methylanthraquiiiono (Simonsen, J.C.S. 1918,113, 760).

Myricitrin, $C_{s1}H_{£a}O_{1£}$, m.p. 200°, found in the leaves of the *Jih'us* species ami in the bark of various *Myrica* epeciea, is a liavonol rhumnoside. Hydrolysis gives rhamnose and myri**eetin,** $C_{,r,}H_{10}O_{g}$, m.p. 360°, which is 5:7:3':-4 :5'-pontafjydroxyflavonol (N ie re n stein, Ber. 1928, 61 *[ti],* 301 ; Hattori and Hayashi, Chem. Zentr., 1932,1, 2043).

Myrttcolorin is identical with rutin (p. *'J'})* (A. G. IV]kin, J.C.S. 1910, 97, 1770).

Myrtiliin, C^jH^O^Cl (chloride), is an anthocyanm oecurriuji; **in wlutttlfibernea** ()'«c*cinium myrttlus, see* Ideein). Hydrolysis yields galactose (I mol.) and myrtillidin chloride, $C_{]B}H,_{3}O_{7}Ct$, the 7-methyl ether of delphinidin chloride *(v.* Vol. I1l, 554dt) (Willstatter and ZoU linger, Annalen, 1915, **408,** 103; 412, 204; Karrer and Widmer, Htlv. Chim, Acta, 1927, 10. 5).

Naringin, $C_{?T}H_{3}2O_{14}$, m.p. 171°, $f_{o}]_{B}$ -M", is a rliivariotie gl>\uside found in the Sowers *and* fruit of *Citrus dtcumanu* f.Vi]!, Ber. 1885, 18, 1311). Hydrolysis gives rf-glucose, I-rhanmose and naringenin, CisHjjOg, m.p, 248°, 5:7:4'-trihydroxyflavanone (synthesis: K, W. and M. Rosenmund, ^er. 1928, 61 [BJ, "608). Naringin is liydrolyaed by an enzyme in celery »eed to give naringenin and a disaccharido {Hall, Chem. and Ind. 1938, 473). It is the bitter principle of grapefruit *(see also* Roller, Cliom. Zentr. 1918, II, 635; Asahina and Inubuse, Ber. 1928,61 [B], 1514; Amtr. Chem Abstr. 1929, 23, 3475).

Nervon, $\mathbf{C_{J1(}H_{Bl}O_{8}N}$**,** m.p. 180°, *[<x]$_D$* -4-3° **(pyridine)** and hydroxynervon, $C_{4S}H_{B1}O_{9}N$, occur in brain *(see* Kienk and Harle, Z. physiol. Chem. 1920, **189,** 243; ChihnaU, Piper and **Williams,** Biocheai. J., 193ti, 30, 100).

Nodakenirt, C-^H_{M}Oj,,$H_{2}O$, m.p. 210°, $[a]_{0}$ +57°, occurs in. *Peucedanum decursivum.* Hydrolysis gives d-glucose and nodakenetin, $^{c}n^{H}U^{\circ}4'\ {}^{m}$-P- $^{185\circ}$. WD -22°. which ia *a,* coumarin derivative of unlmown constitution (Arima, Chem. Zentr. o;929, I, 1698; *ibid. II,* 753; Spath and Kainrath, Ber. 1936, 69 *[H],* 2002).

Nucleic Acids, which are found combined with proteins in the nucleus of plant and animal cells, have been found to contain sugars (especially tf-nbose). Hydrolysis yields various fissiun products^ including purine or pyrimtdine glycosides *(e.g.* adenosine, cytidine, etc.). These are described under their own headings.

CEnin, $C_{a3}H_{a5}O_{12}Cl$ **(chloride),** is an anthocj'anin colouring matter of wine, occurring in ***Vitig*** *vini/era.* HydrVilysis yields glucose (1 mol.) *ami* malvidJii chloride, $C_{ir}H_{1s}O_{7}CI$, (somctinies called oenidin or syringiditi cbloride) which ia also obtained on hydrolysis of malvin (p. 91), The glucose is attached to the hydroxyl group in position 3 of malvidin chloride (Kondo, Chem. Zentr. 1930,1,3193). (Enin has been synthesised by Robinson {J.C.S. 1931, 2701).

Oleandrin (Folinarin). A cardiac glycoside **(«.VoLII,38e6,c).**

Ononin, $C_{?}fiHs,_{t}O_{B}$, m.p. 210°, is an *ieo*flavone glucoeide found i~ the roots of *Otionts* ***qpiitom*** (Hcnimelmayr, Monatsh, 1902. 23, 144 ; 1904, 25, 555). It is the 4/-methyl ether of the glucoside d&idzin (p. 87) {Wessely et *al., ibid.* **[flSl,** 57, 395 ; Ber. 1933, 66 [B], 685; Monatsh, 1933,63, 201).

Orobancbin occurs *in Orobanche rapmn.* **Hydrolysis** gives d-glucose, f-rhamnose and eafleic acid (Bridel and Charaux, Chem. Zentr. 1924, II, 850).

Oroboside.m.p.220^{0}, [«],, -61° (pyridine), is a ilavone glycoside present in *Orobus tuberoeus.* It is hydrolysed by emulsin and is therefore ajS-glycoside, tue products being glucose and *orobol,* a [illegible] ridel and Charaux, Co[illegible]).

Osyritrin is identical with rutin (p. 95) (A. G. Perkin, J.C.S. 1910, 97, 1776).

Ouabain. A cardiac glycoside (v. Vol. II, 386a).

Oxycoccicyanin, $C_{22}H_{!3}O_{1t}Cl$ (chloride), is an anthocyamn present in the fruit cf *Ozycoctus macrocarpu** (American cranberries). Hydrolysis yteld* glucose (1 $_{mo}$i.) $_{ftnd}$ p^dii/chlorUe (Wtfe *uifra).* Ihc glucose is attached to the tiyaroxyl group in position 3 {Grove and Robinson, Uiem. Zentr. 1930, **u** 3252 • Lew Poatemack and Robinson, J.C.s! 1931, 271B).

Paeonin, $Cj_{8}H_{3B}O_{H}CI$ {chloride), in.p. 165°, is an aiithocyanin **which** occur* in the red peony *(Pwoma off.).* Hydrolysis gives glucose (2 mol.) and pajonidin chlcrifle, **C^H^O.CI,** the 3.methyl ether of cyanidin (in the tV lormula, hydroxyl groups in positions 3, 6, 7, 4'

—OCHg in position 3'). The glucose molecules are **attached** to the hydroxyl groups in positions 3 And 5 (Nolan, Pratt and Robinson, *ibi&,* 1920, 1968; Robinson and Robinson, Nature, J931, **128,** '413; Robinson and Todd, J.C.S. 1032, 2488; purification, Karrer and Strong, Holv. Chim. **Acts,** 1936,19, 25).

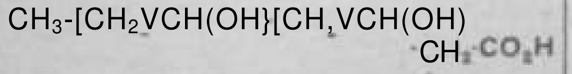
Pelargonin, $C_{,7}H_{31}Oj_5Cl$. (chloride), m.p. 1?5-I80°, is an anthoeyanin pigment present in the scarlet pelargonium, orange dahlia ami red ccrnflower. Hydrolysis gives glucose (U'mol.) and pclargonidin chloride, $C_{15}H_nO_{ft}Cl$. The latter has hydroxyl **groftpa** in positions 3, 5, 7 and 4' in the type formula; the glucose mole-ei-les have been **shown** .by Synthesis to be attached to the **hydroxyls** in positions 3 and 5 (Robinson, Nature, 1 MO,* 137, 94; Ber. IB34, **67** [A], 85). **Pelargonfn** is therefore the \V.r>-dtglueoside of pclargonidin. **Pelarponidin** i* **the** aglycone of other anthocyanins *(e.g.* **caUutephin),**

Peripiocin is a cardiae glyeosicle *(v.* Vol. It, 38(ic).

Periplocymarin is a cardiac glycosidc 4u. Vol. II, 38«a, *d).*

Petunln, $C_{a8}H_{36}O_{17}Ct$ **(chloride),** is an anthocyan in oeeitrriiig in *Petunia hybrida,* **m.p.** 178°. **Hydrolysis** give* glucose (2 raoi.) and **petunidin** chloride, $C_{16}H_{13}O_7CI$, the 3'-methyl ether of dclphinidin chloride. The sugars are probably attached to positions 3 and 5 {liell and Robinson, J.C.S. 1934, HS04). **likedclphinidin,** petunidin is rapidly destroyed by shaking with 10% afjiicnus **Caustic** noda in the presence of air; most other **anthocy&nidina** arc stable. These two ftnthocyanidins arc also distingnished from others of the group by remaining in tin-acid layer when partitioned between *1%* aqueous hydrochloric acid and a mixture of cyc/ohexanol (I vol.) and toluene (5 vol.) (Robinson ***et*** *al., ibid.* 1930, 793; Biocheni. J. 1931,25, 1687).

Pharbitlnic Acid, $C_{ie}H_wO_{13}$, occurs in the seeds ***ofPharbUit nil,*** m.p. 15(M(>2°, $[a]_D$ —47°. Acid hydrolysis gives glucosc^rhamnoso and ipurolic acid, $C_{14}H_{2g}O_4$, 2:I(J-dihydimymyristic acid,

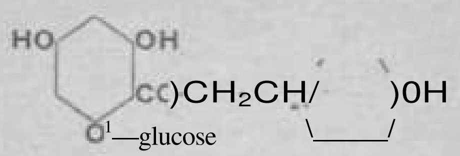


$$CH_3\text{-}[CH_2VCH(OH\}[CH,VCH(OH)\cdot CH_2\cdot CO_2H$$

(Asahina *et al., 3.* Pharm. Soe. Japan, 1919, 452, 821; 1922, 479, 1; 192o, 520, **516).**

It is interesting to note that in the blossoms of *Plutrbitis nil* the glycosides present are anthnt'yamnsfpelanionin, paonin) (Kataoka. A.T »:«!. U07).

Phloridzin. **$C_{2)}H_{,1}O_{1()}$-2H.,0. m.p. HW** (an)**iydrona,** 1fl°), *[a]b* -50°, oct-ure in **the bark** and **root back** ***at*** **man;** fruit **trees** *(n*\^\ pear, I>i"in, fherry, and also in *ltosacea.* and ***EricactA*** t«ndcl and Kramer, Cliem. **Zentr.** 1M2, I, 39(i) ^o1", 1,10 Ieavcs "f *KaUvia lalifolia (idr.m., ibid.* »"•«. IF, 3289). There has been much contradictory evidence concerning the **action** of -?U™2 uP°n p lWidin **(Modwyn-HughoB, J.** Gen. Physiol. 1930, 13, 807; IIiHfII IIIW S oc. Chim. b water 1o;•. ™™> 12, **Ml),** the low solubility In **ttrfaj T u k T 1l11,ilHl,,,, <Jiffi<;uIfc to detect with** and phloretin (*cf.* Glycyphy . 248°, a derivative of phloroglucinol (critinil increment for the hydrolysia, 22,920 g.-cal.; *see* Moelwyn-Hughes, Trans. Faraday Soc. 1929, 25, 503).



Phlorldzin.

POT synthesis, *aee* Fischer and Nouri, Ber-1917, SO, till. The position and pyranose **structnre of** the sugar have been proved by methylation and hydrolysis (Miiller and Robertson. Chem. Zentr. 1933, II, 3288). Injected internally in animals. pHoridzin causes glycosuria; synthetic phloroglucinol-^-glucoside **is** similar in itsaetiuu.

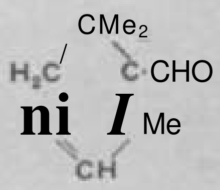
Phrenosin (eorebron), m.p. 212°, $[a]_D$ +8° (CHCIj), \ galactoh'pm occurring in brain and nerve material?

Phyllanthin is a cyanophoric glucoside found in the leaves of *I'hijlhtUhas gusslroemi.* It is the l^hiL-fjsiile of p.bydroxynmndelonitrito *(cf.* Zierin, p. 98). It is hydrolysed by emulsin (J'inncuioro, Rejchard and Large, 1937, A., II, 136).

Pf?ytostero)in (Gloriosol), $C_{3S}H_{Ba}O_8$, m.p. 285-290°, is a **gluooaida** of I'hytoaterol, a mixture of fiterols. It occurs in the wheat germ and in other sources (Nakarauraand Icliiba, Chem. Zontar. 1931, I, 3015) *{cf.* Sitosterolin, p. 9(ii), and Spinastcrolin, p, 96c).

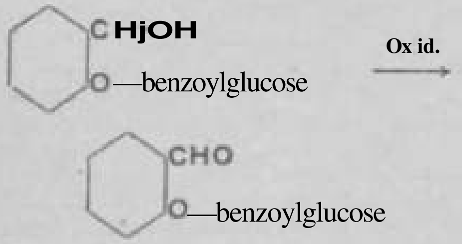
Picein, Piceoside (Salinigrin, Ameliaroside, SaHcinedn), CjjHjgO,, m.p. 194C, $[ol_D$ —89°, a glueoside in the-bark of *Picea exceUa,* and *Salix discolor.* It is **hydrolyaed, by** emulsin **and** liy acids, to glucose and j>-hydroxyaceto* phenoiie, m.p. 109° (Habatc, ***ibid.*** 1930, II, 240; **Jowett,** J.C.S. 1932, 721). For synthesis, *aee* **iCaathner, J.** \>*r.* **Cbem.** 1913, [ii], 88, 7«4.

Picrocrocin, $C_{]f1}H_{26}O_7$, m.p. 1.r)(J°, $[o]_D$ -58°, is a lerpcne glucoside found in the *Crocus* species. **Hydrolysis** gives *d*-glucose and safronal (dehydro-β-cyclocitran *t** M **n**



(Kyr r, Ecr. 1884,17, 2228; Wmterstein, Htlv. rliim. **icta, 1822.** 5, **876j** I-utx, Biochem. Z. HI30, **226,** 97). The true aglucone appears to **be** *],\<\n>sy-P-cyc]otiiTi*\\, and during **hydrolysii** a nioltfuln of water is **eliminated** (Kulm and **WiDtcwtein,** Bcr. 1934, 67 •[»], 344). Tho **dacoeidk** link *i»* p?obably of the ^-typc and accounts for the low rotation. Its relation to the carok-noid plant pigments is interesting **(c/.VoLIII,42»).**

Populin.CanH^O,. beMO?lsaliOT, m.p. 180. rai -s;r, is present in tho bark **of** various ipedefl **of poplar** ***[m*** **Balicln,** P- »'"«)• Hydro-**lysiBgives glucoeo, beraoic** acidntut Naliginin *{a-*liydroxybcjizyl alrohol). Oxidntion gives ben-**soylhclit** in **;** tin- **beoxoyl** group inust therefore be attached to the sugar and not to the —CH_a*OH group of salidn *(ef.* Monotropitin, p. 92a, and Violutin, p. 98a).



The benzoyl group appears to be attached to C_9 on the glucose molecule (Itichtmeyer and Yeakel, J. Amer. Chem. Soc. 1934, 56, 2495).

Populin is not hydrolysed by emulsin, presumably owing to the presence of the benzoyl group. It has been reported that an en ay me from *Papultti moniliftra* hydrolyaes iff to salidn and benzoie acid (Wcevers, Proe. K. Akad- Wetunsch. Amsterdam, 1909.12, 193} and talc a -diastase to BaEgeom *and* a benzoylgfricoM (Kitsato, Biodiem. 2. 1927, 190, 109), It is hydrolysed completely by the bacteria in cheese.

Populnfn occurs in the petals of Uie Indian tulip, *Thespesia populnea* (Neelakantanl and Seshadri, 1938, A., 11, 394).

Primulaverin and Primeverin, $C_{2U}H.j_eO_{13}$, are Homeric glycosides found in the roots of *Primula officinalts* (Goris and Miiscre, Compt. rend. 19lti, 149, 947; Goris and Vischniae, *I.e.* 1919, 169, 871). Primulaverin has m.p. 160°, $[a]_D$ —67°, and hydrolysis by the enzyme primeverase gives primevyuse (see Monotropitin, p. 92a) and methyl 5-methoxysalieylate. Primeverin has ni.p. 203°, $[a]_D$ —7l-6*^{1} and ^ives on hydrolysis primeverose and methyl 4-methuxysalicvlutc {Jones and Robertson, J.C.S. 1933, 1018).

Proscillaridin A, a cardiac glycoside *(v.* Vol. II, 387«).

Prulaurasin, rf/-mandelonitrilc-/}-glueoside, m.pA2a 1 W, $\backslash a\}_v$ -53°, is isolated from *Prunru hmrocerasus* (Cahlwell and Courteuld, J.C.S. 1907, 81, 671) and is also formed by partial hydrolysis of rmemic amygdalin (uoamygdalin) *(q.v.)* by the enzyme prunase present in yeast *(cf,* Prunasin and Sambunigrin; *see also* Fischer and Jiergrnann, Ber. 1917,50, 1047).

Prunasrn, /-manddonitnle-)9-gluco8idc, oi.p. 148°, $[n]_n$ —27°, occurs in *Prvnvs* species, in *Photinia strrutala* and *Eremophila truutliaba* (Power and Moore, J.C.S. 1910, 97, 1099; Fimieniore and Cox, (^heni. Zentr. 1933,1, 1793). It is also formed by partial hydrolysis of amygdalin *{q.v.)* by the enzyme prunase, present in yeast and in cmulsin (from bitter almonds). (See Fischer andTlergmann, *I.e.)*

Punicin, obtained fro* *Punica granatum,* appearu to be idcnticul with pekrgonin {p. 93a) (K^ 7 and Widmer- Helv- Chi mA cta r i 927, 10

Purpurea Gl^oside A, $C_{47}H_{74}O$ • is an Hmphuuj .ardiacglycofiidfl obtafad Bom the leaves ot *DigtatU purpuna.* Enzymie hydrolyws gives digitoxiu and glucose, while acid hydrolyafa *J,)VCH* glucose (1 mol.), digitoxose (" mol.) and the steroid diKitoxigeobj', $C_{23}H_{34}O_4$, m.p. 250° {Stoll and Kreis, Kelv. Chim. Acta, 1935,18, 120; *v.* Vol. II, 385).

Purvurea Glycoside B, $C_{47}H_{74}O,_9$, is a second amorphous cardiac glycoside obtained by Stoll and Kreis *{I.e.)* from the leaves of *Digitalis purpttreu.* Enzymie hydrolysis gives gitoxin and gluiose. Acid hydrolysis gives glucose (1 mol.),i digitoxose (3 mol.) and the steroid gitoxigenin, $C_{23}H_{34}O_6$, m.p. 235° ((/. PurpJirea Glycoside A, *above).*

Quercimeritrin, $C_{21}H_{s0}O_{ia}$, m.p. 245°, is *a.* flavonol glycoside obtained from the flowers of Indian cotton *{Gossyfiium herbaceum).* Hydrolysis gives glucose and qr-jreetin (w. *infra)* (A. G. Perkin, J.C.S. ' 909, 95, 2181). The su^ar is attached to position 7 (Attree and Perkin, *ibid.* 1927, 234).

iso-Quercimeritrin is a flavonol glycoside which accompanies quercimeritrin in Indian, cotton flowers. It is the 3-£-glueoside of quercctin (Attree and Perkin, *I.e.),*

Quercitrin, C»,$H_{ao}O_n$. m.p. 176°, is a fkvonol glycoside found in oak bark *{Quercus lincloria),* which is still used, after drying and grinding, as a dye for silk and wool. It occurs also in the horse-chestnut and in tea. Hydrolysis " gives rhamnose and quercetin, $C_{16}H_{10}O_7$, 5:7:3':4'-tetrahydroxyflavonoI, m.p. 314° (Asahina, Nakagame and Inubuse, Ber. 1929, 62 [B], 3010; J. pr. Chem. 1923, [iij, 106, I). Complete methyl at ion of quercitrin by diazom ethane, followed ᐅy hydrolysis of the sugar group, gives fi:7:3':4'-tetramethylflavcnol; the sugar is therefore attached in position 3 (Attree and Perkin, *l.c.).*

Quillaia-Saponin, $C_{35}H_{58}O$,,,, m.p. 207°, found in *Qvillaia saponaria,* is of thehetferin type (JJ. *6M)* (Kuzicka *et al.,* Helv. Chim. Acta, 1932, 15, 431). Hydrolysis yields glucuronic acid and quillivia sapogenin, $C_{ifl}H_{46}O_s$, m.p. 294° (Windaus, Chem. Zentr. 1926, I_f 1815; Z. physiol. Chem. 192C, 160, 301).

Rhamnazin, $C_{23}H_{22}O$,j, IB a flavanol glycodde occurring with xunthorliamnin (p. 9Sa) in berries of the *Rkanmua* type. Hydrolysis gives glucose and rhanma/.ctin. $Ci_7H,_4O_7$, 7:3'-dimcthyli]uereetin, m.p. 215° *{see* Quercitrin) (Perkin and Martin, Chem. Zentr. 1897, *11,* 313 ; Perkin and Allison, *ibid.* 1900, II, 1243).

Rhamntcoside occurs in *ithmnmts mihurlici.* It *in a,* primeveroaide *{see* Primulaverin) of pentahydroxy-2-methylanthraquinone (Bridel and Charanx, Compt. read, 1026, 180, 1047, 1219; Ann. Chim. 1925, [xj, 4, 79).

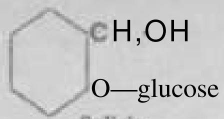
Robinin (robinoside), $C_{?3}H_{4(}$,O_{1B}, m.p. 197°, is a flavonol glycoside from the flowers of *Robinia pseud-acacia,* in which acaciin *{q.v.)* also occurs,"and in *Viaca minor.* Hydrolysis yields galactose (1 mol.), rhamnoso (2 mol.) and ka^mpferol (p. *90d),* The sugars are present us a trisaccharirle, robinose (Charaux, Bull. Soc. Chim. bioL 1926, 8, 915; Chem. Zentr. 1932, I, 1908). Hydrolysis of robinin by enzymes gives ksempferoi aisd robinose. Other workers have isolated kmupferol t-rbaianorid< nitd a disacirharide, robinobiosc, .which i« t-rhiunnO«ido-d-KalaotoM (Zemplcn and Gereca, Ber. 1935, 68, [B1 2054).

Ruberythrlc Acid, $C_{(S}H_{3B}O_{1S}$, m.p. 258-260°, the aiithraquinone gtycoside, is 2-/3-prime verosido-alizarin ^Jones and Robertson, J.C.S. 193$, 1167; **Richier,** *ibid.* 1936, 1701). It occurs in *Ritbia (inntoram,* •

Rutin (Sophorih, Osyritrin, Viola-quercitrin) is a fl'avonol gtycoside found in *Jiuta grareolms* and other plants; on hydrolysis it yields glucose, rharanose and quercetin (p. J94c). The sugars are combined in the form of-a biosc, rutinose (obtained by enzymic hydrolysis), attached to the 3-hydraxyl group in quercetin. Rutinose is jS4-rhamnosido-6-rf-glucose (Zemplcn and Gereee, Ber. **1936,** 68 [B], 1318). *(See also* **Attree** and Perkin, **J.C.S* 1927,** 234.)

Sakuranin, $C_{a2}H;>,O_{10}$, m.p. 212°, *[a]^* — 106°, is a flavanont.* gl^coside found in **the** bark of the Japanese cherry *{1'nttiua* ***ysdcensit).*** *Its* constitution **ia** not **yet\nown**; the **aglycone** is sakuranetin, 7-methylnaringcnin (p. 926) (Shinoda and Sato, Amer. Cheui. .Abstr. 1928, 22, 2947; 1929,23,2956).

Salicrh, $C_{!:!}H_{18}O_{.}$, m.p. 201°, $[_a]_D$ -<i2-5°, is found in willow bark *(Snliz helix)* and other species of *milix.* Hydrolysis yields glucose awl saligenin, *o*-hydroxybenzyl alcohol, m.p. 8(i^a; salicin is o.hydroxybcniSVi-^-glucoaide (Piria, Ann. Chim. Pharm. 1845/56, 35). Its benzoyl derivative, popufin, occurs naturally *(cf. also* Monotropitiu **and** Violulin). It is hydrolysed by emulsin and also by a specific enzyme, , ealicaao, found in the leaves and twigs of willows



Salicin.

{Sigmund, Monatsh. »09, 30, 77). Salicin ha* long been used medicinally for fever and for rheumatism. The enzymic fission of saliciu iu heavy water has been studied by Stcacic (Z. physikal. Chem. 193'|>, B, 28, 230). The rate of hydrolysis by acid has been measured by Moelwyn-Hughes (Trans, Faraday Soc. 1929, 25, 503).

Salicinerin, see Picein **(p.98o),**

Salinigrin, *see* Picein (p. 93d).

Salireposide, C^H^O,,, m.p. anhyd. 200°, t«]p —30'78", occurs in salix species. Hydrolysis gives d-glucose, benzoic acid and salircpol, $C_TH_8O_3$, probably 2:5-dihvdroxyber?zyl alcuho! **(Watties,** Bull. Sou. Chim.* biol. 1931, 13, 658; *cf.* Rabate, ***ibid,,*** 1935,**17, 314).**

Saivianin, **we Moaarohain.**

Sambucin *in* an anthoeyjuiin occurring in elderberries *(Sambucus* ***nigra)*** ami is apparent]) identical with chrysanthemin *{q.v.)* (Nolan anil Casey, Amer. (fliem. Abstr. 1932, 26, 497).

Sambuni^rin, J-mandelonitrilu - 0 - gtacoaide, occurs in the leaves of *Samhucus nigra* (common elder) and *Acacia glaucestnx* (Bourquelot and Danjou, Compt. rend. 1905, **141,** 598; Finnemore and Cox, Chem. Zentr. l<>30, I, 1806). The,. related compound, I-mandclonitrile-j3 g™^sido *{cf.* Amygdalin), **has** not been found in nat"ure (c/. Prunasin and Prulaurasin) by Fischer a«1 Bcrgnmnn, Bcr. 1917,50, 1047.

SapinJus.Saponin is found in *Sapindu** *mukorossi,* e"• **(Wkttenteda** and Meyer, Chem Zentr. 1931, II. 1582; Kitsato and Sone, *ibid.* 193J-, U, 1787). It is of the hedurin typo *(q.v.).*

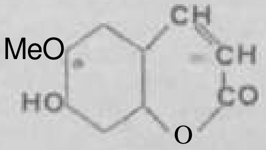
*Saponarin, $Cj5iH_MO_{12},2H_aO$, m.p. 236°, is a flavonol glycoside occurring in the soap plant ***(Sapcmana off.).*** Hydrolysis gives glucose and *vitcxin,* $C_{15}H_HOn$, m.p. 260°, 6:7:4'-trihydroxy 2:3:6:7-tetrahydro'flavonol (Barger, Ber. 1902, 35, 1290; J.C.S. 1900,89,1210),

Sarmentocymarin. A cardiac glycoside *(v.* ***V6L*** II, *ZStib). {Sec also* Tsche3i-he and Bohle, B«. 11)36, 69 {El, 2497.)

Sarsaponin (PariUin) is a saponin isolated from thy Mexican saraaparilla root. *Radix sarsajparillse.* (Jacobs and Simpson, J. Biol. Chem. 1934,105, 601). The probable molecular formula of sarsaponin ia $C_{46}H_{,4}Oi_7$. Hydrolysis gives glucose (2 mol.), rhamnose (1 mol.) and a sterol, *Sarsapagenin* (parigenin), $C_2jH_{<4}O_3$, m.p. 199°. The laat appears to differ from tigogenin («ee Tigonin) only in **the** iis-trans relationship of the ring systems, but the structure is not yet definitely proved *(see* Simpson «nd Jacobs, J. Biol. Chem. 1935, 109, ^73; 1935,110,565; Askew, Farmer and Kon, J.C.S. 1936, 1399; Farmer and K.on, ***ibid.*** 1937, 414).

Scillaren A and B. Cardiac glycosidefl («. Vol. II, 387«).

Scopolin, CooH^On, m.p. 218°, occurs, with metUjl oichoriin, in *Scopolia japoniui.* Hydrolysis gives glucose (1 mol.) and *Scopoleltn* ti-methoxy-7-hydroxy-coumarin (Seka and Kallir, Ber. 1931, 64, 909; Head and Robertson, Chem. Zentr. 1931, II, 851). The glucose is attached to position 7 (Merz, 1933. A.-, 72).



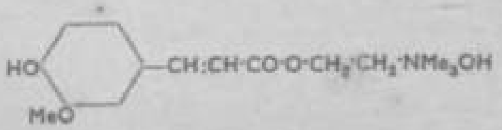
Scopolettn.

Scutellarin, $C_{?1}H_{1S}O_{1£}$, m.p. above 310*, is a flavone glycoside occurring in the leaves of *Scutdtaria batcahnsts* and in the flowers of *ticulrilaria uUisxima.* Hydrolysis gives glucuronie acid and *Scutellarein,* 4'-hydroxy$aiealein. This is of interest in that haicalein occurs in the roots of *Sculelluria baieakn&is,* joined to glucuronic acid *(me* Baiculin) (Robinson and Schwarzenbach, J.C.S. 1930, 822). Scutellarin is hydrolysed by baiealinase (Miwa, Amer. Chem. Abstr. 1932, 26, 4349).

Serotrin, ***$C_{nl}H_{ao}O_u$,3H_zO,*** has been described bv l'i>\vi-r and Moore (J.C.S. 1910, 97, 1090) as a flavonol glycoaidc present in *Prumts eerotina* (wild black cherry). Hydrolysis yields glucose and quercetin.

Stnalbin, $C_{!)D}H_{<1}2OisS_EN_1,5H_2O$, m.p. 84° (anhyd. 140°), *[a]$_n$* -8°, is a mustard-oil glucoside occurring iu white mustard seed *(Sinapit alia; cf.* **Sinjgrin** from *Sinapii nigra).* Hydrolysis by the enzyme "in yroainase gives rf*glueose, sinalbin mustard-oil (j>-bydroxybenxyl t«o-thiocyanate) and *sinapin* hydrogen sulphate. Sinapin is an ester of choline and *sinapic acid.*

• I



(Gadamer, Ber. 1897, 30, 2327). Sinalbin and einigrin appear to be 0-glucosides {Schneider, Fischer and Specht, Ber. 1930, 63 |Bj, 2787).

Sinigrin, CJUH^OOSJNK.HJO, m-p. 127° (anhyd. 132°), $[a]_D$ -18°, is a mustard-oil glucoside found in black mustard seed *(Sinapis nigra)* and in *Cochlearia armoracia.* It is hydrolysed by baryta or by an accompanying enzyme, myrosinase (and by no other kiiowi enzyme) to d-glucose, allyl isothiocyanato and potassium hydrogen sulphate (Ilerissey and Boivin, Bull. Soc. Chem. biol. 1927, 9, 947).

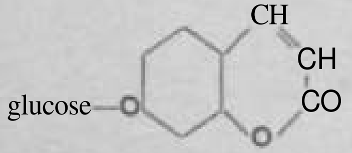
$$CH_2{:}CH{\cdot}CH_2{\cdot}C{<}^{M.\text{^}S—glucose}_{N{\cdot}O{\cdot}SO_2K} \bullet +$$

CH_2:CH-CH,5-NCS+KHSCVHglucose

The sulphur appears to have replaccd,the oxygen in the glucosidic hydroxyl group, as thioglucosc is obtained by treatment with potassium metttaride (Schneider and Clibben, Ber. 1914,47, 2218, 2225). The glucosidic linkage is probably of the jS-type *{see* Schneider *et al.,* Natunviss, 1930, 18, 133; Ber. 1930, 63 [BJ, 2787). Most mustard oils cause local inflammation of the skin and irritation of the mucoua membrane. Internally, the effect is to stimulate the secretions and in larger doses to excite and finally paralyse the central nervous system.

Sitosterolin (Ipuranol), $C_{a6}H_{BB}O_s$, BL.p. 300-305° found in various plant sources, notably in olive bark, in *Ipomosa purpurea,* etc. It is a glucosidc of sitosterol, an ill-defined mixture of sterolu *(see* Anderson and Shrincr, J. Amer. Chem. Soc. 1920, 48, 2970, 2987). (C/. *also* PhytostcroKn and Spiuasterolin; *see alto* Bernstein and Wallis, J. Org. Chem. 1937, 2, 341).

Skimmin, $C_{ia}H_{16}O_B$,H_aO, m.p. 210°, is a coumarin giycoside from *Stimmia japotiica.* Hydrolyaia yields tf-glucose and *Skinimetin* (umbeliiferone), $C_SH_6O_3$, 7-hydroxy-coumarin, m.p.*224° (Eijkmau, Rec. trav. chim. 1884, 3, **204).**



Skimmin.

Umbelliferone occurs widely in species of the *VmMliferx.*

Solanine ia the name given to a group of glycosidea derived from plant* of the *Solatium* genus. They are interesting in that they contain nitrogen and form a link **between** the nlkaluids and the **ftaponinn.** The best characterisedis*xohnmv-t.* $C_{i(}H_nO_{I4}N$, from the sprouts *QfSeianum tuSerotum* (potato); the aglvcone •wlanidinc is also present (Oddo and Caronna, Ber. **19M,** 67 *[M],* **448).** Hydrolysiy gives 1 (i n_W|.), **^aUctoae {1 moLL** ***ziuJaam*** LVand **solaiudin^** $C_{!7}H$«ON. The **but** ppears to have » structure **differing** in the side chain from dioleaterol. **PiwttoSk]** ***tormvim*** have been suggested (Soltys and WaUenfcU., ***ibid.*** 193C, 69 [B], 811; Clemo, ILirgan and Raper, J.C.S. 1936, 1299).

SoL.nocapsine occurs in the leaves of *Solarium pseudocapsicum* (Banger and Fraenkel-Conrat, J.C.S. 1930, 1537). It is of the Bolaoiiu type *(q.v,).*

Sophonn has been shown to be identical with rutin (p. a'ja} (Jlculen, **Rec.** trav. chim. 1923, 42, 380).

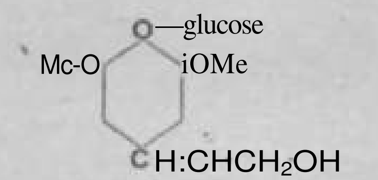
a-Sorinin, $C_{24}H_{2s}O_M$, m.p. 150', is found in the bark of *Ithamnun japouica* (Nikuui, 1938, A., II, 173). Hydrolysis yields primeverose (see Primulaverin) and a-swigenin, C,3$H_{10}O_6$, m.p. 227-229°.

Spinasterolhi, (^H_{5S}O^**nt,p.** 280°, is a glucoside of Bpinasterol, a stcrol of unknown structure (Heyl and i^arscit, Chem. Zentr. 11)34, II, 447; Simpson, J.C.S. 1937, 730).

£-Stroph£nthin-£. A cardiac glycosiiie *(v.* Vol. U_F 3S5?J). "

Syringaic-Acid Glucoside, $C_{ia}H_{i0}O_{1u}$, m.ji. 225°, $[a]_D$ -18°, occurs in *liobima pnaud-acacia.* E\vringaic acid is 3:5-diinethy)gallic ncid *(gee* Syringin) (Fischer and Bergmann, Ber. 1918, 61, 1804).

Syringin, $C_{17}H_MCyH_aO$, m.p. 191-192°, $[a]_D$ —17°, is found in the bark of *Syiutya vulgaris, Ligitslrum vuigare* and in **jasmin.** Hydrolysis by emulsin gives glucose and svringcuin, methoxy coniferin («. \'ol. *Ill,* 324).



Syringin.

Oxidation gives ayringaic acid *{see abt>-*), Syringin has been syutliesiscd (l'auly and Strassbei-ger, Ber. 1929, 62 [B], 2277). The acid corresponding 'to syringcuiu occurs in sinalbin *(v. supra).*

Tagetes patula (African marigold) contains a glucosidc which on hydrolysis yields glucose and quercetagetin (5:G:8:3':4'-pentahydioxyflavauol *(cf.* gossypctin from gossypitrin, Vol. I11, 406c) (A. G. Perkin, J.C.S. 1913, 103, 209).

Tannin, Chine:-e, is obtained from *lihua scmialatd.* It is probably not homogeneous. Hydrolysis gives gallic acid (9-10 mol.) and i-glnooae (1 mol.). No cllagic acid haa **been** found (c/. Tunnin, Turkish).

Tannin, Turkish, $[o]_n$ c. +5°, gives on lydrolvsis gallic ***tdd*** *{?>* moL) o;id 3-glucose (1 mol.). It is prububly not homogeneous. A small atiioiiut of ellagic acid is also obtained on hydrolysis (see Fischer and KreudenIK^IU, Jor. 19U, 47, 2485 ; Karnr, Widmur and Staub, \utialcn. liL'2, 433, **288).** Kllagie acid also occurs, joined to (/-glucose, in Knoppmi-tannin.

Tectoridin (Shckuniu), $C_{i;}H_{21!}O_n$. m.p. 258°, [Q],, —29°, ia an **unSavane** glueoside found in the **rnisonuM** of *Iris factor am* and *Bttamcamla chinenais.* Hydrolysis gives ^ -ulii- ".«• and teetori-^iiiin, C^H'uO,! m.p. 227°, 5:7:4'-trihydroxy-U-methoxytstitlavont; {'/. I rid in) (Asuliina, Shibata and Ogawa, J. Pharm. Soc. Japan, 1928, 48, 1087; Mannich and Schumann, A. 1937, II, 276.

Tetrarin, $C_{ai}H_{3s}O_{12}$, m.p. 205°, occurs in Chinese rhubarb («. /J-Gliwoaido-Gallic Acid). Hydrolysis gives d-gtucose, cinnamie acid, gallic acid and rheosmin, $C_{10}HyO_{Jr}$ m.p. 79-5°, of unknown constitution {Guwn, Chem. Zentr. 1903, 1, 722).

Thevetin, $C_{43}H_{eB}O_{18t}$ is a cardiac glycoside found in the seeds of *Thevitta neriifoli&* (" be-still nuts"). Hydrolysis appears to give glucose (2 moL) and cigjtdose (1 mol.), and a eterol, *thevetigetun,* CjgH^O^, known only as the anhydro-compound. m?p. 218-220° *(see* Tschesdie, Ber. 1936, *M[B],* 2368).

Thymidine is a pyrtmidine nueleoside, obtained by hydrolysis of nucleic acids. It is 3-thymine deoxy-5-ribofuranoside^ (thymine is 2:4-dihydroxy-5-uiethylpyrimiaine). Other deoxyriBbse nucleosidea are known (see Deoxyade* nosine) {Levene and Tipson, Science, 1935, 81,98).

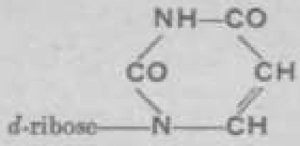
Tigonin is one of the several saponins wBidi occur with cardiac glyftisides in the leaves of *Digitalis purpurea.* The aglycone was isolated from this source by Jacobs and Fleck (J. Biol. Chem. 1930, 88, 545). The separation of the giycoside itself from the saponins with which it occurs (digitonin, gitonin, etc.) is very difficult; it is therefore fortunate that the only saponin in the leaves of *D. ianata* is tigonin, and purification is effected by means of its cholesterol addition product (Tscheache, Ber. 1936, 69 [BJ, 1605). TKgonin has probably the molecular formula $C_{5e}H_{M}O_{S7}$, m.p. 260°. Hydrolysis yields glucose • (2 etuol.), gakctoae (2 *tad.),* xylose (I inol.Jandasterol,*Ugogenin,* $C;,H_{44}O_3$, m.p. 204°. The last compound has been assigned a structure closely similar to that of digitonin (p. 87), but having no hydroxyl group.-* in positions 2 and 0 (sec Taehesehe, *I.e.).* It may be noted that one hydroxyl group {on C_3) only is present and the position Qf attachment of the sugar residues is therefore established.

Toringin, $C_{sl}H_{10}O_9$, is a flavone giycoside, m.p. 240°, isolated from *Pyrud toringo.* Hydrolysis gives glucose (1 mol.) and ehrysin, $C,_{B}H_{10}O_4$, G:7-dinydroxyflavonc, m.p. 275°, which occurs in the buds of several varieties of popUr (Piecard, Ber. 1873, 6, 884; Emilewicz, Kostanecki and Tambor, *ibid.+fim,* 32, 2448; Kostanecki and Lampe, *ibid.* 1904, 37. 31117).

Typha-Glucostde, C^H^O^, is a flavonol glticfwide found in *Tyjrfui angiwtala* and in the Indian dye Asbarg (?.«.). Hydrolysis gives glucose and feorhamnetin, $C_{ie}H_{lit}O_7$, 3'-methylquercotin^ m.p. 307° (Fukuda, CIMMH. Zentr. 1828, I, 2100).

Urechitin, Urechitoxin. CrirstJilliiif-cardiac glycosides («. Vol. II, 3fi7c).

UrwJIne is a pyrimidine glycoside {c/. <'vtidine) formed by hydrolysis of yeast-nucleic acid. It is 3-uraeil.d.ribofurauoside. In the midcic acid, phoKphoric acid is esterified in position 3 of Mi- -ii-$_{i(}$r. Pyrimidina glycosides are in general much more resistant to hydrolysis than purine glyi-osides *(e.g.* adenoeina) and it is frequently necessary to hydrogenate before liyliolyais to obtain the sugar unchanged (Levene and Tipson, J. Biol. Chem. 1934, 104, 385; 105, 419).



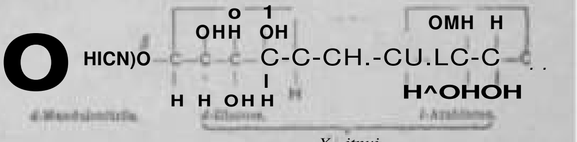
UriUlne.

Uzarin. A cardiac glycoside *tv.* Vol. II, S8&2).

Vaccinln, $C_{13}H_{18}O_7$, [a^ +48°, is obtained as a syrup from whortleberries { *Vatcinium tnlia-idesa).* It is probably 6-benzoylglucoae (Brigl and Zerrweck, Z. physio). Chem. 1934, 229, 117); the bcnzoyl gronp is not in position 1, as vaccinin is reducing and forms a phenylhydrazone, but no osazone. Thus vaceinin is strictly not a glucoside, but an ester of glucose.

Verbenaloside(verbenalin),$C_{1T}H_{si}0_{1()}$, m.p. 180°, *[a]$_0$* -181°, was first isolated from the flowers of *Verbena off.* (Bonrdier, A. 1908, i, 197). Hydrolysis by emulsin or by dilute acid yields glucose and verbenalol, CyH^Os, m.p. H0-5°, *[a]a* —29°, the structure of which is not yet known (ace Cheymol, Bull. Soc. ohim. 1938, [v15$_($ 633).

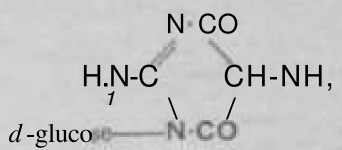
Vlcianin, $C_{10}H_{a6}O_{10}N$, m.p. 147-148°, [ofo —21°, is a cyanophoric glj'co«ide found in the seeds of wild vetch (*Vicia angustifolia).* It is accompanied by an enzyme, vicianase, by which it is hydrolysed to vicianose (a disaccharide), bensaldehyde and hydrogen cyanide. Vicianose is hydrolysed by acids and by emulsin to d-glucoae and f-ara bino.se, and has been shown to be fi-(^4-arabinc6ido)-rf-gtu«o8e (HeU'erich and Brederick, Annalen, 1928, 465, 16ti). Vicianin is therefore analogous to amygdalin *{q.v.)$_t$* one molecule of cl-glucose being replaced by *I-*arabinose.



Vlrinnln

Viciwnose occurs also in the glyco.sides Violutoside and Gein *(q.g.v.).*

Vicine, $C_{10}H_{1g}N_4O_T$, is 2:5-diarajno-4:6-dioxyjiyrimidine glucoside, isolated from vetch seeds (together with convicine, p. 86**) by Ritthausen (J. JT. Chem. 1870, fii]. 2, 333). The structure below has been assigned by



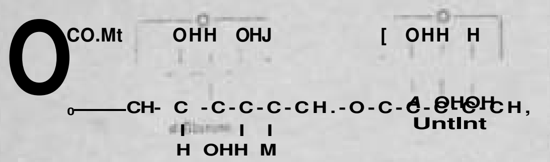
Vicine.

Levene (J. Biol. Chem. 19?4, 18$_f$ 305. *Set aho ibid.* 1916, 25, H07; Heri&soy and Chcymol, Compt. rend. 1930, 191, 387; Bull. Soc. Chim. biol. 1931,13,20; Fisher and Johnson, J. Amer. Chem.Soc. 1932,54.2038).

Violanin. $C_{3e}H_{3T}O_{1a}CI$ (chloride), is aif anthocvanin present in *Viola tricolor.* Hydrolysis yields glucose (I mol.), rhamnose (I mol.), 2>-hydroxycinnaraic acid and delphinidin chloride (see'Delphinin). The sugars appear to t» present as glucosido-rhamnose, attached to position 3 in delphinidin (WiUstatter and Weil, Annalen, 1916, 412, 178; Karrer and Bunz, Helv. Chim. Acta, 1933,16. 287).

Violacjiiercitrin is identical with rntin (p. 95a)'(A. G. Perkin. J.C.S. 19.10,97, 1776).

Violutin {Violutoside), m.p. 169°. *[a]ₚ* -35°, is found in *Viola eornula.* Hydrolysis gives glucose, arabinose and methyl silieylate (Ficaxd, Conipt rend. 1926, 182, I UiT). The arabinose anil glucose are present as the disacrharide vicianoose* r>-(j3-/-arabinosido)-rf-glucose, which i< found also in vicianin mid gein (Robertson and Waters, J.C.S. 1032, 2770). The structure is therefore:



(r/. Monotropitin, Populin and Salicin). Violutin has been Bynthesised from methyl salicylate '?:3: 4-triacetyl-^-glueoside and triacetyl-arabinosy) bromide (Robertson and Waters, *I.e.).* Both dyooaidic linkages appear to be of the /9-typc. J• is hydrolysed by cmulsin.

Xanthorhamriin, $C_{34}H_4,O_{31}$, is found in berries of the *Rhamnua* type, which are used for dyeing as " yellow berries " or " Avignon berries." It is a Uavonol gtycoside, giving on hydrolysis by the *enzyme* rhSmninnse (present in the plant), rhamninpBe (a trinccharиae) and rhnmnetin. Rhanminosc is hydrolysed by acids to galactose (] baol.)andrnamno8e(2 mol.) (c/. robinose from robinin). Rhamnetin is 7-mcthylcjucreetin *{ws* Quercitrin) and the sugar residue is attached to position 3 in the glycosule (Tanret, Bull. Soc. chim. 1899, [iii], 21, 1073; Kobim*>n and Robinson, Bioehem. J. 1933, 27, **206):**

Xanthosine is a purinc nndeoside, probably xantfaine-9-ribofnranoeide (we (iuliand. Holiday and .Macrae. .I.C.fS. 1934, 1639), Xamhinc is 2: 6-dioxypurine.

Zierin. *m.p.* 166°, $[a]_D$ -29-5⁰, is a cyanophone glueoside, found in the flowering' tops of *Zieria Isemgata.* It appears to be the glticoside (if ift-hydioxynumdelonitrile. It is hydrolysed by einiilaiu to glucoee, hydrogen cynnide'and w-hydrosybonzaldehyde (Finnemore and Cooner A., 1937, II, 136) (c/. PhyUanthin).

G. T y.

GLYCYMERtN. AcrystaUine iipochrome, !»•])• W ited from the foot of the, caoUaso *Pmtuntudue gtycytveris.* Its formula has not been determined but it has been tdenti*fied as a carotonokl I>y i ption Bpeotnun, and colour teaetiona with solphanc add (Lederer, **i'pt.** rend , 1 . 1M3,**118,**1015; I ;mr| Lederer, BuD tint, b k i 1934,16,105)

1. IL H. and P.

GLYCYRRHETIN, glyeyrrhetio and, $C_3jH_{4S}O._t$ the aj;Iucone of ghvyrrlluin. Tli.- latter consists ufthe potassium and calcium salts of glycyrrhizic acid, C^Hj^O^. present to the extent of about fi-7% in liquorice root, Aeeor'l Ing to Vosa, Klein and Saner (Ber. 1937, 70 [K], 122) the glycuronic acid obtained by hydrolysing glycyrrbizic acid with boiling dilute sulphuric acid is of a novel type. For the extraction of liquorice and its uses, *see* Houseman and Laccy (Ind. Eng. Chem..J929, 21, 9Iii) and for determination of glycyrrhizic acid, Eder and Sad: (Pharm. Acta Helv. 19211,4, 23).

GL»OXAL, OHCCHO, prepared by the oxidation with nitric acid of alcohol (Debus, Annalen, 1856, 100, 5; H857, 102, 20), of acetaldehyde and of paraldehyde (Ljubavin, J. Rnss. Phys. Chem. Soc. 1876, 7, 249; 1881, 13. 49Bj Ber. 1877, 10, 1366; de Forcrand, Bull. Soc. (•him. 1884, [ii], 41, *24~2f.* It is prepared ctimmerdally by the oxidation of acetylene witii ozone (Wohl ami Brjiunig, G.P. 324202; B.P. 1573*25)).

Prepared by any of these methods the glyoxal is present in solution in a polymerised form, *paraglyoxal* $(CJH_£O_2)J$; a *Irimeride* $(C_2H_2O_2)_3$, is nlso known.

The monomeric glyoxal, CJH_2OJ, is obtained by distilling the paragiyoxal either alone or in tho presence of phosphorus pentoxide (Tcmme, Ber. 1007, 40, lii'l). If ("nils yellow prisms or crystalline spangles which become colourless on cooling and melt at 15° to a yellow liquid having b.p, 517770 mm., d*° **1-14,** and u^ 1-382K. It undergoes the Cannizzaro reaction with alkalis forming glycollie acid.

The *phenylosazotte,* $C_aH,(N_2HPh).,$, m.p. 175°, is crystalline (Fischer, *ibid.* 1884.17, 575; Ciamician and Silber, *ibid.* 1013.46, I06I).

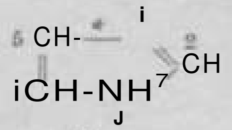
Glyoximi, HON:CH-CH:NOH, crystallises with iHjO and has nip, 178° (Hantzsch and Wild, Annalen, 1896, 289, 293).

Olyoxaline, iminazoh {vide infra).

Quhioxaline

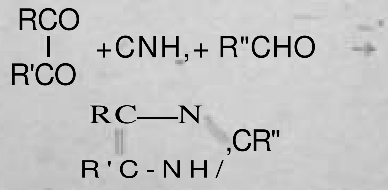
is formed by the condensation of glyoxal •with o-phenyltnediamtne.

GLYOXALINES. Glyosaline.theBiraplest member of this scries was obtained as long «K° as 1856 by Ibe action of ammonia on glyoxal.



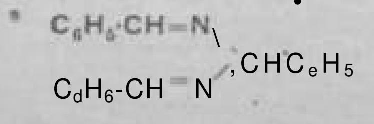
Gly•xnllnc.

The rea,etion was -orrectly interpreted by Kadziflzewski in 188:. and to-day the action of ammonia on a-diketoneB and aldehydes is tho standard method of preparing glyoxalines:

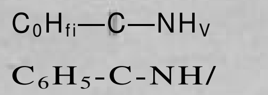


The reaction is usually carried out in hot nlcoholic, or preferably arctic aeul, solution (•

1)avidson, Weiss'" and Jelling, J. Org. Chem. J;i:i7. 2, 819). Under the latter conditions the yields are frequently theoretical. The reaction is quite general as the dikctone may bo aliphatic, or aromatic *(t.<j.* di&cetyi, phenantiuac|uinonc) and a variety of aliphatic and aromatic aldchydea have boen used. In some instances one or the other component maybe omitted, the action of atumonia on the component used producing intermediates of equivalent value. Thus, in the production of the simplest glyoxaline, part of the glyox al 13 converted into formic acid and formaldehyde, the latter providing C_a of the imidazole ring. Again in the production of lophine (2:4:5-triphenyI/jJyoxaline) ammonia may bo allowed to react with benzaldehyde, benzoin, beiml or any Iwo of these. With Ixjiixaldehyde, hydrobenzamide and the isomeric amarine arc intermediates:

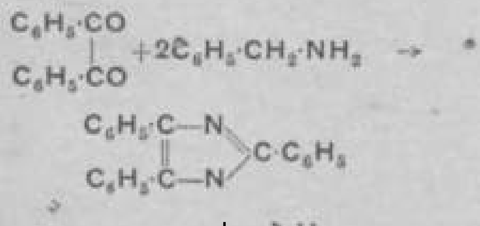


Hydm1icngiiiiulc,



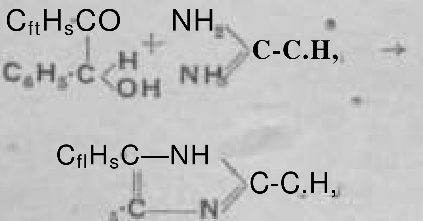
Amarinc.

Finally, in the general reaction even the am nionia. may be replaced by a primary a mine when one carbon atom of the online enters the glyoxaliafi ring:

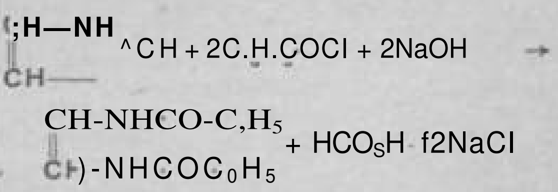


<!«,« C_6H_5

Glyoxalines are obtained by the interaction of anmlincs and a-halogenoketoiies or tbeir equivalents :



Glyoxalines arc weak bases which font quaternary salts from which N-alkylglyoxaline may be obtained. like analogous pyrrolea and pyridin.es those iminazolos which contain a free hydrogen atom in the 2-position will snffe rearrangement on heating, tlie alkyl group ing migrating to the adjacent carbon atom. (it the other hand glyoxsdities containing a free imino-grmip form metal, particularly silver aaltfl. Free imino orronpa can with care b acylated, but the aoyj groups an removed wit easo; occasionally attempted aoylatioa reauli in fission of the ring with production of diaeyi diamines:



The glyoxaline ring is abnormally stable to oxidation and reduction; dihydrogiyoxalines are usually readily oxidised to glyoxalines, and in many cases where aryl groups are present tiiia oxidation, effected with alkaline hypochlorite or hydrogen peroxide, is cheinilumines<<nt.

A number of alkoxyiminazoles, particularly aromatic representatives, have been proposed for use as local anesthetics (c/. U.S.P. 2005538) whilst other glyoxalines with long-chain aliphatic groups in the ^-position are of value as wetting-out agents in detergents, etc. (B.P. 43921>], 479491).

The glyoxab'no ring ia represented in nature ay histidine, and the *Pilocarpue* (jaborandi) alkaloids, etc.

GLYOXYLIC ACID, CHOCOOH, discovtsed by Debus (Ann. Chim, Phys, 1857, [iii], **49,** 216); its constitution was discussed by Debus, Perkin and Odling (Ben 1871, 4, G9; 1875, 8,188) and by Otto and Troger *[ibid.* 1892, 25, 34*25; «ee *also* Debus, J.C.S. 1904, 85, 1383; Annalen, 1905, 338, 332); *occurs* in unripe fruit such as grapes, apples, gooseberries, currants, etc. (Brunncr and Ciiuard, Ber. 1880, 19, 595), in young beet-roots (Lippraann, *ibid.* L891, 24,3305) ano?in the animal body, especially in the urine (Hofbauer, Z. physiol. Chem. 1907, 52, 425; Granstrom, Beitr. Chem. Physiol. Path. 1908, **11,** 138; L. Pineussen in Oppenhcimer's Handbook, " The Biochemistry of Man and Animals," 2nd ed.. Vol. V, 1925, p. 579).

The acid is *formed* by slow oxidation of ethyl alcohol and poly hydros v alcohols with HNO_3 (Debus, Annalen, 1856, 100, 2; 1857, 1(1(3, 28; 1S59, **110,** 319; Bottinger, Arch. Pbarra. 1894, 232, 65); by oxidation of AcOH with HjC^or air (Hopkins and Cole, Proc. Roy. Soc, 1001, 68, 21; Giacomello and Mascaiello, Gazzetta, 1934, 64, 908); by the reaction of H^Oj+FeSO^ with glycocoil, creatinc, crcatiiime, glycollic acid, sarcosine and hippuric acid {Dak'iri. J. Biol. Chem. 190fi, 1, 271); by heating ethyl dichloroacetatc with water at 120° (Fischer and Geuther, Jahresber. 1864, 17, 272); by boiling silver diehloro- or dibromn-ai-tKate with water (Perkin, J.C.S. 1877,32, 90; Debus, J.OS. 1866, **19,** 18; Beckurts and Otto, Ber. 1881,**14,** 581); by many hours' boiling of potassium diacetoxy-acetate with much water (Woebner, AnnUen, 1900, **311,** 130); by reduction of oxalic acid with potassium/sodium amalgam or Zn |- H_aSO_4 fChurch, J.C.S. 1863, 16, 30); Hoyal Baking Powder Co. Frdl. fxiij, 007) j by tho electrolytic reduction of oxalic aoid, tta^estan or its amiit't in sulpliuric acid (Tiifel and Friedrichs, Ber. 1904, 37. 31W ; Woh] and Lange, *ibid.* 1908, **41,** 3614 j Mobiwdaak, Z. Klektrocliem. 1926, **32,** 434; Hatcher and rlolden, Trans. Roy. Soc. Canada, 1925, [iii], 19, III, 11); by degradation of purines (iSchevin and Brunei, Compt. renil. 1937, 205, 294; Mourot, ***ibid.*** 1938, 207, 407); as an intermediate product in the deamination of glycine (H. Barrenscheen and Danzer, Z. physiol. Chem. 1933, 220, 57 ; A bderhulden. and Baertich, Fermentforseh, 1937, 15, 342); by the activation of oxalic acid (ychrtier, Ber. 1936, 69 [BJ, 2037; Weber and ReSek, Ber. 1937, 70 [B], 407); and by the action of moulds on $<(AcO)_a$Ca and AcONa (Bernhauer and Scheuer, Biochem. *Z.* 1932, 258, 11).

Glyoxylie acid may be *prepared* by heating 1 part dibromoucetic acid with 8-10 parts water for 24 hours at 140° (Grimaux, Compt, rend. 1876,78,63; Cramer, Ber. 1892, 36, 714). For preparation of the anhydrous acid, see Talvitie, Amer. Chem. Abstr. 1936, 30, 434.

The acid is *manujaclured* from sodium chloroacetate (Mugdan and Wiminer, G.P. 672481);

Physical Properties.—Glyoxylie acid is a viscid syfup with a suffocating smell; it. crystallises by long standing above H_2SO_4 forming rhombic priams of composition

C j H ^ or **$(HO)_a$HCCOOH**

(Perkin, Ber. 1875, 8, 188; Debus, J.C.S. 1904, 85, 1390; Bottinger, Areh. Pharm. 1894, 232, 88), extremely hygroscopic and easily sciuble in water (Debus, Annalen, 1856, **100,** 11), Electrolytic dissociation const. *k₃ᵢᵢ=0'l'l£X* 10~* (Ostwald, Z. physikal. Chem. 1889, 3, 188). For quantitative electrolytic oxidation of glyoxylie acid, *see* A. Talvitie, Ann. Acad. StiL **Pennies,** l'J3o", A, 4S, No. 6, 32.

Ckzmieal Properties.—Decomposes on heating above its melting-point tirat into giycollie acid, oxalic acid and water vapour (Debus, J.C.S. 1904, 85, 1391). It is a tautomeric substance; it exhibits aldehydic pro [jetties in condensing with hydroxylannne, phenylhydra/.inc, and aemicarbazide (Elbers, Annalen, 1885, 227, 353; Fischer, Ber. 1884, 17, **576***;* .Simon and Chavanne, Compt. rend. 1906, 143, 904), but most of its salt) are of the type

(HO)jCHCOOM,

whilst dialkyl ethers of the type

$(RO)_2CHCOOH$

have been prepared. It is oxidised to oxalic acid by HNO_3 (Adler, Arch. exp. Path. Pharm. 1907, &6, 210}; by aqueous bromine solution (Debug, Annalen, 18ti3, 126, 152); by silver oxide (Debua, ***ibid.*** 1S5«, 100, 6); and, together with glycoUic acid, by **KOH** (Bottinger, Ber. 1880 13, **1932).** KMnO< oxidises glyoxyhc acid in alkaline solution to oxalic acid and CO;, (Evans and Adkins, J. Amer. Chem *Hoc.* 1919, 41, 1407). Oxidised by H,O. **in** alkaline solution **to** CO_3 and **H-COOH** (Heimrod and Levene, Bicchera. Z. 1910, 29. 46). Reduction with zinc in aqueous aolutkm yields giycollie acid; in acetic solution, tartario acid (Genvresse, Compt. rend. 1892, **114,** 5551 In the presence of AgO,H,S yields thiogl-fcollic acid with other products (Biittiii^-r, Annalen. 1879, 196, 213). With HCN it forms a cyan! hydrin which, on hyilmlysis, yields **tartronic** acid; $NaHSO_3$ **viekh** *a* rrjstnlline compound (Debus, ***ibid.*** 1856, **100,** 5). It condenses with urea to form allantoin and with guanidine to form in the cold glyoxylie puanidide and on warmiiig to 100° iminoallantoin (Doebner nrul Gartner, *ibid.* 1901, 315, I; 1901, 317, 157; Simon and Chavanne, Compt. rend. 1906, **148,** 61; Kaess and Gruszkiewicz, Ber. 1902, 35, 3(J04). For other condensation products, aec . Bottinger, Arch...Phann. 1894, 232, 549, 704; 1895, 233, 100, 199; Bougaiilt, Compt. rend. 1909, **148,** 1270; Griesheim, Frdl. II, 647; Wochster, Frdl. X, 588.

Detection.—Glyoxylie acid may be identified even in dilute solution by precipitation of dixanthy Ihydrazone-glyoxylie acid,

$$[O(C_6H_4)_2CH]_2N\cdot N:CH\cdot CO_2H,H_2O,$$

with xanthydrol anl hydrazine hydrate in acetic acid (Fosse and Hieulie, Compt, rend. 1925, 181, 286). The acid also yields an intense magenta red colour with Scbryver's reagent **(Foflae** nnd Hieulie, *ibid.* 1924, 179, GJ'3>. For • I- ^riptions of the substituted phenyl hydra zones, *see* Chattaway and Bennett, *J.C.S.* 1927, 2850; Cluittaway and Dalby, ***ibid.*** 1928, 2756. Civoxylic acid may be titrated with alkali, or **with** permanganate in the presence of H₃SOj (Hatcher and Holden, Trans. Roy. Soe. Canada **L926,** [iii], 19, III, II). For colour reaction with indole derivatives, *sec* Granstrfim, Beitr. Chem. Physiol. Path. 1908,11, 132).

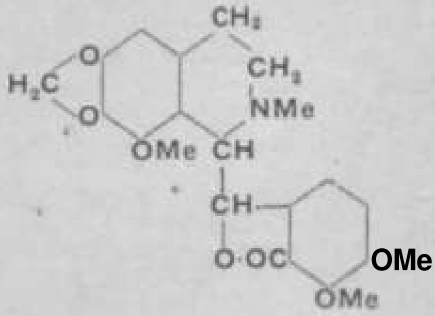
Mirroehemical Di'tcction,—Behrens (Chem.-Ztg. 1902,26, 1128).

GLYPHENARSINE *(v.* Vol. **I,** 487fr).

" *GLYPTALS " {v.* Vol. **11,** 472./).

GMELINOL, $C_{12}H_uO_v$ The wVite deposit in the cells of *Gmalina leickkardtii* **(Colonial** Beec ii}. Omelinol contain,* two methox yl groups present as in veratric acid, and yields a mono-**acetyj** derivative (.Smith, J. Roy. Sci. N.S, Wales, 1913, 46, 187). It melts at 122° and on cooling solidifies to a transparent resin-like solid which melts at G2-C3°, but when powdered has nit'li **ins-point** 12(1-121°.

GNOSCOP1NE, dJ-narcotine,



occurs in opium and is formed by racemising narootine. It forms colourless needles, m.p-220"; *picrate,* m.p. 188-189°; *methiodide <lihydnO$,* prisms, in .p. 210-212°. For synthesis and resolution, *set* Perkin and Robinsor, J.C.S. 1911,99, 775.

GOA POWDER (p. Vol. I, 4f>76).

GOETHITE (named flfter the poet Goethe). H vinited fvrric oxide,

Fe_2Oj.HjO or FeO(OH),

crystiillised in the orthorhombic system and IsomorphouB with the corresponding aluminium and manganese minerals diaspore and manganite. It is included with limonite under the term "*brown iron-ore,*" and when fibrous and massive the two are not readily distinguished, especially as they have the same colour and streak. Goethite, however, contains more iron (Fe_2O_3 89-9, Fe 62-9%) and less water (10-1%) than limonite ($2Fe_aO_3$-$3H_2O$). Although limonite is»sometimes fibrous and crystalline, it is never found as distinct crystals; crystals of goethite, however, are not uncommon. They are prismatic, acicular, platy or scaly in habit, and have a perfect cleavage in one direction (parallel to the. brachy-pinacoid). Reniform and stalactitic masses wit£ a Radiating fibrous structure also occur. Sp.gr. 4-0-4-4, of crystals 4-37; hardness 5-5£. Tire colour is yellowish-brown to brownish-black, with usually a brilliant lustre on crystal-faces. Thin crystals and splinters are blood-red by transmitted light. The coltfUr of the streak or powder is yellowish-brown. Analyses often show the presence of small amounts of manganese oxide and silica. Several varieties are distinguished. The acicular forms, usually with a radial grouping, are known as *needle iron-ore.* The needles may be very fine and closely packed together, giving the appearance of plush, as in *sammetblende* or *sammeterz* (velvet-ore) also known as *przibramite,* from Przibram in Bohemia. *Onegite* is acicular goethite embedded in amethyst from Lake Onega, Russia. This material is cut as a gemstone under the name "Cupid's darts" (fleches d'amour). As an enclosure in other gem-minerals gdethite is found in aventurine *[q.v.)* and sunstone. *Mesabite* is an ochreous variety abundant amongst the iron ores of the Mesabp Range in the Lake Superior district of Minnesota. The modes of occurrence of goethite are the same as for limonite, and it is present in many limonitic iron ores. Fine groups of crystals were formerly obtained in abundance in the Restormel iron mines at Lanlivery and in the Botallack mine at St. Just in Cornwall. Larger, but less perfect, crystals are known from the Pike's Peak district in Colorado.

Scaly forms of FeO(OH) include lepidocrocite and pyrrhosiderite (or rubinglimmer), which until recently were regarded as varieties of goethite. These are also orthorhombic, but they differ from the acicular goethite in their optical properties and in thSir crystal structure as determined by JC-rays; and they are now included under the distinct species lepidocrocite, which is dimorphous with goethite and isomorphous with boehmite *(q.v.).* Diaspore, isomorphous with goethite, is a fourth member of this isodimo-phous series. The dimensions of the unit cells are:

FeO(OH)			AlO(OH)		
Goethite	*a*	4-54A	Diaspore	*a*	4-40A
	6	10-OA		*H*	9-39A
	c	3-03A		*c*	2-84A
Lepidocrocite	*a*	3-87A	Boehmite	*a*	3-78A
	b	12-51 A		6	11-8A
	c	3-06A		*c*	2-85A

L. J. S.

GOLD. Au (Aurum). At. wt. 197-2,at. no. 79.

Historical.—Gold cannot have escaped the observation of the men of the Stone Age, but it could have been of little use to them until they had discovered the art of melting. Flint daggers with gilt handles have been found in Egypt, and gold was well known in that country about 3,600 B.C, when its value in relation to silver was fixed by law. It was first used for coinage in Lydia, about 700 B.C., in the form of electrum, a native alloy of gold and silver.

The earliest method of obtaining gold, other than that of collecting it by hand, was by gravity concentration. The auriferous sand was stirred in a shallow stream of water running over sloping rocks, the heavy grains of gold settling to the bottom. Sheep-skins were spread out for entangling the particles of metal and helping in its collection. Over 2,000 years ago, the methods o$ ore-crushing by stone hammers and also by means of grinding mills were adopted in Egypt to release gold contained in solid rock. The powdered ore was washed on sloping tables (Gowland, J. Roy. Anth. Inst. 1912, 42, 256). The use of sieves to separate the insufficiently crushed pieces of rock is also attributed to the Egyptians. Stamp batteries for crushing ore were established at Joachimsthal in 1519, and sieves set at the outlet of the mortars were described by Agricola in 1556.

The use of mercury for separating gold from other materials, by amalgamation, was described by Pliny, and referred to by Theophilus in the eleventh century in his description of the extraction of gold frqm the sands of the Rhine. The method used in the Tyrol of stirring crushed ore with large quantities of mercury in circular bowls is very old, but the practice of charging mercury together with uncrushed ore into the mortars of stamp batteries, and catching the gold amalgam on copper plates was not mentioned before 1850.

The cyanide process was invented by MacArthur and Forrest in 1887, and flotation was first applied to a gold ore in 1900 (J. S. Elmore, Trans. Inst. Min. Met. 1900, 8, 379) although little success was obtained until much later. The methods of refining gold by the cementation process and by cupellation are very ancient. Nitric acid for refining was in use in Venice in the fifteenth century and was not superseded by sulphuric acid until the nineteenth century. The electrolytic refining process was invented in 1888, and the chlorine process of refining in 1867.

Gold Ores.—Gold is widely distributed in nature and occurs in minute traces in many ores of other nutato. It has been detected in igneous and metamorphic rocks in almost every cone in which a careful search for it has been made, and sedimentary rocks are seldom quite free from it. The comparatively small quantities of gold in limestones which have been formed in clear water for from land, appear to indicate the land as tho place of origin of the gold, but it is also present in sea water.

Gold occurs in quantities large enough to pay for extraction in many quartz veins or lodes in rock formations. The gold is disseminated in the quartz and is accompanied by brown oxidtj of iron in the upper portions of the deposits and by sulphides in the deep-seated portions. It usually occurs as native gold, mainly because its compounds are easily reduced. Even when it is contained in pyrites or other sulphides, it is present in the free state. Native gold also occurs in many secondary or detrital (" placer ") deposits, such as river gravels, sea beaches, etc., in the form of nuggets, grains and flakes. The auriferous beds of conglomerate in the Transvaal are generally considered to be of this character.

Nuggets show crystalline structure when polished and etched, but rarely exhibit regular crystal faces or angles externally. Native gold always contains some silver and copper, and other metals are usually present in smaller proportions.

Telluride of gold is found in large quantities in Western Australia, Colorado and Transylvania, and has been reported frcjn many other localities. There is only one true compound of gold and tellurium, AuTe$_2$, which contains 43-6% of gold; but several mixtures consisting of various compounds of tellurium with gold and silver and other metals have been recognised as mineral species. The best known of these are (I) *calaverite* (?.#.), which has the composition AuTe$_2$, (2) *sylvanite* or graphic tellurium which is supposed to correspond to (Au,Ag)Te$_2$, (3) *petzite,* a telluride of silver, Ag$_2$Te, with part of the silver replaced by gold, and (4) *nagyagite* or foliated tellurium, which contains some lead.

Auriferous telluride is usually dark grey or black in colour, but occasionally is silver-grey. Sometimes it contains an admixture of metallic gold which gives it a brassy-yellow colour. It is soft and brittle but its density is high, usually between 8 and 9. When heated in air, it oxidises, fuming and giving off TeO$_2$, and fuses bclgw a red heat. If the roasting process is continued, most of the tellurium is removed and the gold is left in the form of spherical pellets which have solidified from fusion. Calaverite may contain as much as 44% of gold, but usually partly replaced by silver. A specimen of sylvanite from Cripple Creek, Colorado, contained Aw 7-64%, Ag 32-39%, Te 59-96% (F. C. Smith, Trans. Amer. Inst. Min. Met. Eng. 1897,26,485).

Extraction of Gold from its Ores.—The metallurgical treatment of gold ores is usually simple and cheap and owing to this circumstance and to the high value of the metal, ores containing very small proportions of gold can be worked at a profit. Thus the ores of the Witwatersrand, now being worked, usually contain less than 0001% gold, and auriferous gravels, which do not require crushing, mav be worked when considerably poorer.

Washing Aurijerous Gravel {see U.S. Bureau of Mines Information Circular No. 6786,1934).— The gold occurring in placers is obtained by washing away the lighter gravei from the gold disseminated through it, the material being carried by a shallow stream of «water through inclined troughs (sluice-boxes) or over eloping tables. The heavy particles of gold sink to the bottom of the stream and are caught by the rough surface of blanketing or plush, or in crevices which are formed by the Bupply of " riffles " of various kinds. Sometimes the riffles consist of wooden strips or poles, sometimes of iron rails or sheets of " expanded " metal. Mercury is sprinkled in the stream and accumulates in the crevices, where it assists in catching the gold as an amalgam. The gold-amalgam, recovered in the periodical " clean-up," is strained through canvas to remove the excess of mercury and afterwards retorted.

The gravel is mined in various ways, according to circumstances. It may be raised by the spade and thrown into the stream, or, when in high banks, it may be Hroken down and washed away by jets of water (hydraulic mining). Dredgers are largely used to recover the gravel from river beds and also on dry alluvial " flats." In the latter case, thi dredger floats in a pond, and travels slowly across country, scooping away the grqund in front and stacking it behind after it has bee^ washed. The gravel is usually washed on the deck of the dredger and Che gold may be further concentrated by flotation. For descriptions of modern dredgers, *see* Eng. and Min. J. 1934,135,486, and 1935,136,270. Placer mining is now of less^relative importance than formerly owing to the exhaustion of many of the known deposits.

Ore Crushing.—Ore from lodes and other compacted material is treated by crushing, followed by (1) Amalgamation, (2) Cyaniding, or (3) Concentration, either by gravity or by flotation. A combination or succession of two or more of these processes is usually employed. The object of crushing is to free the particles of gold and thus facilitate their separation from ithe gangue or remainder of the ore. Many different crushing machines are used, i The stamp battery *(see* Caldccott and others, " Hand Metallurgical Practice," Vol. 1,1926, Vol. II, 1919, C. Griffin), evolved from the pestle and mortar, was first applied to the industry early in the sixteenth century and is still in wide use. In modern practice it consists of heavy iron or steel stampers, ranging up to about 2,000 lb. in weight, which are raised and let fall in mortars kept supplied with ore and water. The height of drop is usually about 7 or 8 in. and the number of drops per minute about 100. Five stamps, ranged in line in a mortar, form a unit, and a battery may consist of any number of units. Wire mesh screens or steel plates perforated with holes are placed in tho side of the mortar through which the wet pulp is discharged. The screens were formerly of comparatively fine mesh, *e.g.* 40 holes to the linear inch (coarser screens are used now to increase output), and the finely crushed ore was passed directly to amalgamation or concentration tables. Amalgamation tables consisted of sloping copper plates on which mercury had been spread by scrubbing until it formed a completely amalgamated surface. A thin stream of pulp, often mixed with mercury which had been fed into the mortar, flowed over the plates, on which the gold amalgam was caught and retained and subsequently removed by rubbers or scrapers and retorted. Much finely divided gold usually escaped the plates, remaining with the pulp (now " tailings ") which wont to the cyanide plant. These practices have been discarded in general, as mentioned later.

Ore from mines, however, contains material too coarse for crushing by stamps, and this is separated beforehand by means of a " grizzly " (iron bars in parallel) or by a vibrating screen of say S in. mesh. The coarse material is crushed in rock-breakers to 3 in. size before going to the stamps. Jaw crushers with reciprocating motion (hinged plates opening and losing successively) And gy ratory crushers are both used. The latter, such as the Gates, Newhouse and Symons cone crushers, contain vertical revolving spindles set eccentrically to the outer casing and crush the ore between surfaces on the spindle and casing. These machines are of great capacity and besides being used to feel stamps, Symons cone crushers, for example, may take their place, ore being reduced to a maximum size of J-inch with crushers worked in series.

Fine crushing by stamps, previously mentioned, is no longer the *common* practice. It has been superseded by more gradual reduction in successive machines. Coarser screens are used with modern heavy stamps, giving a product of *i* in. to 1 in. in diameter. The stamp duty has become much Higher and may be over^ 20 tons per stamp per day. In one instance (Prentice, Trans. Inst. Min. Met. 1935, 44, 479) 45 tons of Rand ore were crushed per day through a screen of 1 in. mesh with a single Nissen stamp of 1,910 lb. Each Nissen stamp (Nissen, J. Chem. Met. Soc. S. Africa, 1911, 12, 111) has its own cylindrical mortar box with a large screen area. The product of such work is too coarse for amalgamation and is passed to some form of grinding machine.

Tube mills are much used for fine grinding. They consist of revolving horizontal cylindew, half-filled with large pebbles, steel balls or pieces of hard ore, by the impact and abrading effect of which, in falling, coarse particles of sand are finely crushed. The pulp enters through one trunnion and passes- out through the other which is fitted with a grid plate to retain the pebbles in the mill while allowing both sand and slime to pass out. The water in the pulp fed to tube mills is carefully regulated. There must be enough to make the particles of ore adhere to the pebbles but no " free " water. For Rand ores the usual proportion of water is 24-32% of the feed. The pulp coming from primary crushing machines usually passes through classifiers (described later) which remove both slimed ore and excess water, leaving clean we? sand to enter the tube mills. The product from the mills contains much material which is insufficiently crushed. This is separated from the fines by mean* of classifiers and returned to the tube mill ("closed circuit grinding^. The finished product will pass through a screen of about 90 or 100 mesh.

Among other fine grinders are (1) the Hardinge conical ball mill (Trans. Amer. Inst. Min. Met. Eng. 1908, 39, 336) in which a pear-shaped grinding chamber replaces the cylinder of the tube mill (the change of design is to obviate further grinding of ore already fine enough), (2) the Marcy ball mm, (3) the Marcy rod mill, in which steel rods, 2 or 3 in. in diameter and a few inches shorter than the mill, are used instead of balls or pebbles for crushing. In small-scale operations in outlying gold-fields, *e.g.* in Rhodesia, the Hardinge ball mill sometimes takes the place of stamps instead of being used in conjunction with them.

Classifiers are in wide use for separating sand from slime in pulp coming from tube mills. The earliest forms were inverted pyramids, which were superseded by inverted cones (Caldecott, J. Chem. Met. Soc. S. Africa, 1909, 9, 312), the pulp entering at the centre from above and the fine stuff overflowing at the periphery. The sand settles in the cone and passes through a spigot at the apex. A stream of clear water is introduced near the apex of the cone in many instances and, rising through the sand, cleans it to some extent and overflows at the top with the slime. The spigot product or " underflow " is returned to the tube mill. Cone classifiers, however, are of comparatively small capacity and are now little used on the Rand, where they were introduced, except as de-waterers. The Dorr classifier has taken their place on many mines. It consists of an inclined rectangular trough, open at the upper end. The pulp enters on a transverse line about half way down the trough. The sand settles in the pulp and is pushed up the inclined bottom of the trough by a scries of rakes which are lifted and lowered at opposite ends of their stroke. The sand presently emerges from the liquid and is then washed and discharged from the open upper end of the machine with about 26% of moisture. The slime is prevented from settling by the flow of the liquid and by the agitation caused by the reciprocating scrapers. It overflows the dam at the lower end of the machine.

The Dorr bowl ^classifier consists in the addition of a shallow circular bowl, with revolving rakes, to the ordinary rake classifier. The pulp enters near the centre and the slime overflows at the periphery of the bowl, while the sand settles to the bottom and is raked to a central discharge opening, whence it passes to the reciprocating rake compartment for further treatment before being returned to the tube mills.

Gravity Concentration.—The use of tube mills in a " closed circuit" with classifiers results in an " all-slimed " product, the sand going round the circuit until it has been sufficiently reduced to pass to the cyanide plant. Such fine grinding, however, is not required for gravity concentration, which can deal with unclassified pulp coming from stamp batteries fitted with 50 or 60 mesh screens, as at Morro Velho (J. H. French and H. Jones, Trans. Inst. Min. Met. 1933, 42, 189), or from stamps with J-in. screens, followed by a single passage through a tube mill, as in Borne mines on the Rand. The ancient method of catching gold on roughened sloping surfaces was for a long period of time Modified by adding mercury to the pulp and thus amalgamating the gold. This particular use of mercury is, however, being gradually abandoned. Amalgamation tables are becoming obsolete and have been widely superseded by blviket strokes (c/. Jason's Golden Fleece). These consist of strips of blanketing, canvas or more recently corduroy, stretched over sloping tables, with an inclination of 1J—2 in. per ft. The pulp flows over them in a thin stream of uniform depth. No mercury is used and the particles of gold, sinking to the bottom, adhere to the rough fibres of the corduroy or lodge against its ribs. The tailings pass to the cyanide circuit. The corduroy is removed and washed when necessary, usually every few hours. The concentrates thus obtained are fed to shaking concentration-tables such as the Wilfley table or the James table. (For description of these tables, *see* Rose and Newman, " Metallurgy of Gold," 1937, pp. 241 and 243.) In these, a number of strips of wood placed transversely are nailed on the surface to act as riffles. They retain the heavy particles which work to one edge of the table under the influence of a slight but rapid shake. The light worthless material is carried away by the water. (At Mono Velho, Brazil, the substitution of James tables for canvas strakes was completed in 1935, with improved results.) The concentrates are then ground and amalgamated in iron or steel revolving barrels containing steel balls, water and mercury. The amalgam is strained in canvas bags to remove excess mercury and retorted. Blanket recoveries on the Rand are from 25 to 60% of the gold in the ore, bringing this portion more quickly to account than if cyanide were used alone for treatment (Prentice, Trans. Inst. Min. Met. 1935,44,479).

The Cyanide Process.—The tailings from amalgamation plates or from blanket strakes or other concentrators contain some finely divided gold which is usually readily soluble in solutions of the cyanides of the alkali metals (*v.* Vol. III, 4866). Crushed virgin ore is also treated by cyaniding. The cyanide used at first was impure potassium cyanide, then mixtures of potassium and sodium cyanide and later sodium cyanide. Calcium cyanide containing an equivalent of 49% NaCN is also in use. It is still common practice to refer to the standard of these cyanides in terms of the potassium salt. Thus 97-98% NaCN is designated as 129-130% cyanide or potassium cyanide. The solvent action of cyanide on gold is very slow and requires the presence of an oxidising agent such as free oxygen. It may be expressed by the following equation, which represents the sum of the chemical actions:—

$$4Au+8KCN+O_2+2H_aO$$
$$=4KAu(CN)_a+4KOH$$

(J. S. MacLaurin, J.C.S. 1893, 63, 724). The equation, however, ignores galvanic action and subsidiary chemical changes which may have an important influence on industrial extraction (Allen, Trans. Amer. Inst. Min. Met. Eng. 1934, 112, 546).

The potassium aurocyanide remains dissolved in the water. The oxygen required is dissolved in the cyanide solutions from the air in contact with them. If the oxygen is exhausted owing, for example, to the cyanide solutions remaining for some time in contact with ore containing readily oxidisable sulphides or organic matter, dissolution of the gold is stopped, and it is necessary to aerate the pulp. Very dilute solutions of cyanide are used, containing from about 0-5% to as little as 0001% of potassium cyanide. The maximum solution rate is at about 0-027% KCN, when saturated with oxygen {H. A. White, J. Chem. Met. Soc. S. Africa, 1919, 20, 1; *see also* 'White, *ibid.* 1934, 35, 1). With Rand ores, the maximum strength in treating sands is 0-06% KCN and for slimes, solutions containing 0-01 to 0-025% KCN are used (Prentice, Trans. Inst. Min. Met. 1935. 44, 511).

In practice the ablution rate depends mainly on the amount of oxygen dissolved in the solution. In a mass of ore undergoing treatment it is difficult to maintain a sufficient quantity of oxygen in a free state. Hence the time required for treatment may be many hours or even days, although under favourable conditions, the gold could be dissolved in a few minutes or at most in 2 or 3 hours. Various oxidising methods have been applied, such as the passage of a current of air through the charge or agitation with air, or, more rarely, the addition of oxidisers other than air. The gold contained in sulphides is more difficult to dissolve than free gold, partly owing to oxygen deficiency, and rich sulphides are generally separated and treated in other ways.

Another difficulty in cyaniding lies in the waste of cyanide due to its destruction by certain constituents of the ore. Some sulphides and arsenides dissolve in cyanide and interfere with the efficiency of the solution. Moreover when pyrite, pyrrhotite on marcasite has been subjected to the action of air and water (weathering) before treatment, compounds are formed which are more prejudicial to the solution than the sulphides. The same decomposition occurs during treatment, especially in prolonged aeration and agitation. Ferrous sulphate and sulphuric acid are formed and react as follows:

$$FeSO_4+6KCN=K_4Fe(CN)_6+K_aSO_4$$
$$H_8SO_4+2KCN=K_2SO_4+2HCN$$

Many other reactions occur, some copper and zinc minerals being especially troublesome cyanicides. Certain cupriferous ores destroy so much cyanide that they cannot be treated profitably by the process.

The effect of acidity and of ferrous sulphate are overcome by the presence of sufficient protective alkali in the solution. This is provided by the addition of lime to the ore as it is fed to the battery, or at any grinding stage. The amount may be 2 of 3 lb. per ton. The protective alkali is kept as low as possible consistent with a reasonable consumption of cyanide (Robertson, *ibid.* 1924, 84, [i], 84) as an excess of lime may be fatal to extraction (Wright, *ibid.* 1933, 42, 239). Alkali does not protect cyanide from copper salts.

Crushed ore or tailings from other extraction processes are treated in large vats (containing as much as 850 tons of ore) with false bottoms provided with filter beds. Cyanide solution is run on to the ore and allowed to percolate through it. Fresh solution is added from time to time and finally the ore is washed with water. The solutions pass through the filter by which they are clarified and are conveyed to the precipitation boxes, where the gold is separated, as described later.

There are numerous modifications in the

cyanide process necessitated by the conditions or introduced as improvements. Of these, the variations in mechanical treatment are th* most important and complex. Liquids do not pass readily through unclassified pulp, which is accordingly separated into sand and dime in classifiers, already described, or is merely run into a large vat filled with Vater. Here the sojid settles and fills the vat and the slime is carried off in the overflow. The separation is, however, far from perfect. Either the saftd is cyanided where it settles, or it is drained and transferred to another vat for the purpose, thus becoming well mixed **and** aerated. A solution of lead nitrate, t& remove sohrble sulphides, is sprinkled on the charge before it is removed to the treatment vat. On foe Rand, the strong solution, containing from 0·05 to 0·1 % **KCN** is run on to sand charges first, followed by weak solutions containing 0·02 or 0-03% **KCN,** and finally by wash water. As frequently as possible during the process, which lasts from 4 to 7 days, the sand is permitted to drain to allow the entry of air. In some instances vacuum pumps are used to expedite leaching Qnd to assist aeration. The tailings are removed by sluicing or shovelling. They contain about 0-25 or 0-3 dwt. gold per ton or about 10% of that present in the sand before cyaniding, but part of the gold originally present has previously been caught on the 'blanket strakes. A large proportion of the residual gold is contained in the pyrites. The gold in the tailings could be further reduced in amount by finer grinding but it would not be profitable tt do so. A product just fine enough to pass through a 100-inesh screen is aimed at.

The treatment of sLgne is becoming the mosfe important part of the cyanide process. In *all-sliming* methods, the sand is reground until it can be included with the slime, so that no separate treatment is required. In many cases the gold is not completely laid open to attack until the ore is ground to slime and the recognition of this fact has led to a wide adoption of the all-sliming policy.

In practice the product of all-sliming operations usually contains from 5 to 35% of sand that will not pass a 200-mesh sieve. The slime, whether it- is the portion separated from sand by classifiers or is the product of all-sliming, is suspended in 5 to 10 parts of water and must be thickened before it can be cyanided. In order to promote its settlement a solution of lime is added, usually before or during grinding. The alkalinity is maintained at 0·002-0·025% **CaO.** This causes agglomeration or flocculation of the particles, "clouds of large and indefinite diameter are formed " and subside in the liquid. Heat assists settlement. With an alkalinity of not more than 0·005%, Rand slime settles at the rate of 2-4 ft. per hour with a clear overflow. The thickened slime contains only 35-45% moisture. The gold in it is readily dissolved by cyanide and the solution is separated from the slime either by decantation or filtration.

In the decantation method (Caldetott, " Hand Metallurgical Practice," 1920, Vol. I, p. 217), now little used, the settled slime is discharged from tho Bottling vat by a jet of cyanide solution and pumped into another *vat with a conical bottom. Circulation is continued by withdrawing the pulp at the bottom and discharging it in oblique jets at the top. As soon as the gold is dissolved, which may be in from 4 to 24 hours, the pumps are stopped, the pulp allowed to settle, and the clear supernatant liquid is drawn off and sent to the precipitation plant. The pulp is diluted with " precipitated solution " to its original volume, agitated in a second vat, again allowed to settle and the liquor decanted. The settled slime, still containing about one-sixteenth of the dissolved gold, then goes to waste. (The Rand slime generally contains 2 or 3 dwts. gold per ton.) In counter-current decantation, the cyanide solution enters at the bottom of the vat and overflows as a clear liquid at the top, the settlement of the slime generally more than keeping pace with the upward movement of the solution. The underflow of slime passes to another vat, and the action is continuous.

Slime is now, generally treated by agitation with cyanide and filtration, with many variations in detail. The slime is first de-watered or thickened by settlement. The continuous thickeners now in common use, of which the l)orr machine ib the best known, have scrapers attached to rotating radial arms which move the settle^ slime towards the centre of the vat, where it is discharged through a pipe. Pulp enters the vat at the centre and clear liquor over-flows at the periphery, the action being continuous in both cases. The thickened pulp is then agitated with cyanide solution in an " air-lift " machine such as the Brown or Pachuca tank. This consists of a tall cylinder of steel with a conical bottom. Inside the cylinder a central pipe is tixSd extending nearly to the bottom and top. Air is forced into the central pipe near its lower end, and, bubbling up through the column of pulp inside it, reduces the density of the column. The pressure of the outside pulp on the open lower end of the pipe causes the column to rise and overflow at the top. Fresh pulp enters at the bottom of the pipe and a perfect circulation results, as w$ll as complete aeration. The tank can be worked intermittently, being discharged as soon as the gold is dissolved, but in some Rand plants a series of agitators work continuously, each overflowing into the next, and the loot delivering a finished product to gravitate to the filter plant (Thurlow and Prentice, J. Chem. Met. Soc. S. Africa, 1928, 28, 258).

The Brown tank agitators are confined to the treatment of 150-niesh or finer material, if building-up of coarse particles at tho bottom is to be avoided. Coarser material or flotation concentrates may be treated in a Wallace agitator in which the air-lifts are assisted by a rotating impeller (S. G. Turrell, Chem? Eng. Min. Rev. 1934, 26, 312). This can deal with sand of 40 mesh.

The ore slime from the agitators, after being thickened by the removal of part of the liquid in raking machines, is filtered through canvas with the aid of a vacuum (as in the Moore, Butters, Oliver and other filters) or by direct pressure (as in the Merrill -and Dehne filter presses). The liquid passes through leaving the solid matter as a cake adhering to the canvas.

The difficulty is that even a thin layer of slime packs down and offers great resistance to the passage of liquids. In practice, layers of £-1 in. are allowed to build up with vacuum leaching and layers of 2-3 in. with pressures of 40-100 lb. per sq. in. given by pumps. An enormous area of filtering surface is required in operations on a large scale. This is obtained by using a number of parallel vertical filter plates or leaves placed near together and kept separate by wooden strips or perforated iron plates or wire screens. The filter leaves may be contained in a basket which is immersed in the pulp and then lifted out for washing and discharge (Moore filter), or they may be fixed in a vat which is alternately filled with and emptied of pulp (Butters filter). Continuous filtration is arranged in some later machines *(e.g.* the Oliver and Dorrco filters) by placing the filter leaves on the outside surface of a rotating drum which is partly immersed in the pulp. Filtration, washing a^d discharge of the slime cakes are then effected during each revolution of the drum. For details of some of these machines, *see* Rose and Newman, " Metallurgy of Gold," C. Griffin, 1937, pp. 357-369. The results are superior to those of the decantation method. For instance, Prentice (Trans. Inst. Min. Met. 1935, 44, 517) states tlutf. the loss of dissolved gold in the residue from a vacuum filtration plant on the Rand was 0-022 dwt. per ton of slime and that from a decantation plant 0071 dwt.

The recovery of gold from cyanide solutions is effected by precipitation with zinc shavings or zinc dust. The solutions, which may be turbid from suspended slimed ore, arc clarified by passing them through beds of sand or preliminary filters before precipitation. It is believed that the actual precipitant is nascent hydrogen produced by the dissolution of zinc, thus:

$$\begin{aligned}&\mathrm{Zn+4NaCN+2H_2O}\\&\qquad\mathrm{=Na_2Zn(CN)_4+2NaOH+2H}\\&\mathrm{2NaAu(CN)_2+2H=2HCN+2NaCN+2Au}\end{aligned}$$

Free hydrogen is, however, inert and if formed is removed as fast as possible. Precipitation is aided by coating the zinc with lead by means of a solution of lead nitrate, the lead-zinc couple increasing the rate of dissolution of the zinc. An excess of free cyanide is also favourable and it is usual to add cyanide to weak solutions on · their way to the zinc boxes. Dissolved oxygen is detrimental by checking precipitation and wasting zinc, the solution is therefore de-aerated in modern practice. Oxygen is removed either by a vacuum (Merrill-Crowe process) or chemically. The former is the more efficient, and is installed in many modern plant. A vacuum of 22 in. of mercury is maintained in a large cylinder fitted with filter leaves, having a capacity in one plant of 6,000 tons of solution in 24 hours (Wartenweiler, J. Chem. Met. Soc. S. Africa, 1932, 3& 143). The oxygen content is reduced from 60 to 0-5 mg. per litre. The chemical method involves the use of finely divided iron and highly pyritic sand in the clarifiers, or else the addition of manganese sulphate or tannin extract.

Zinc shavings when used are contained in long boxes divided into compartments through which the solution flows. The gold is precipitated in the form of black slime. In cleaning-up, the zinc is washed free from cyanide and the unbroken shavings are put back in the boxes. The gold slimes are digested in sulphuric acid or sodium bisulphate solution until all action has ceased. The residue, now freed from zinc, is washed, dried and fused in pots or tilting furnaces with bora:*, manganese dioxide, sodium carbonate and sand. After casting, the bullion is separated from the slag and sold* to refineries. An alternative method is to smelt the precipitate with litharge, charcoed and fluxes, und to cupel the base lead-bullion produced (Tavener process). In modern practice[1] • precipitation is usually effected with zinc dust which is mixed with the clear cyanide solution in a tank fitted with vacuum filter^leaves (Merrill-Crowe process). The amount of zinc consumed is much less than when zinc shavings arc used. The gold precipitate is washed off the filter leaves with jets of water and is sometimes smelted without previous acid treatment. Attempts to precipitate gold with finely ground charcoal instead of zinc have not had much success in practice. In recent years methods of regenerating the cyanide in spent liquors have been adopted on some mines. Sulphurous acid is added and the hydrocyanic acid thus formed is absorbed by lime (Halvorsen process, Min. and Met. 1925, 6, 136; Mills-Crowe process, Lawr, Eng. and Min. J. 1929, **128,** 688).

The treatment of sulpho-telluricle ores by cyanide presents special difficulties, as **NaCN** acts very slowly on these»ores. Either the ore is roasted in order to expel the tellurium before cyaniding, as at Cripple Creek, Colorado and elsewhere (U.S. Bur. Mines, Information Circular 1933, No. 6739), or an addition of bromocyanide is made to ordinary cyanide, as at some mines in Western Australia and Canada (O'Malley, Chem. Eng. Min. Rev. 1933, 26, 115). Bromocyanide readily dissolves tclluride of gold. The bromocyanide is usually made in contact with the ore, as at Kirkland Lake, Ontario (J. T. Wiley, Eng. and Min. J. 1928, **126,** 16). Here the concentrates are stirred with 0-05% cyanide solution, atfid then **NaCN,** " Dow's salts" (a mixture of NaBr and $NaBrO_3$) and $\mathbf{H_2SO_4}$ are added. Bromine is liberated by the action of the adid on Dow's salts and reacts with the **NaCN** forming bromocyanide *(v.* Vol. 11 [, 504c).

Sometimes telluride ores are roasted before treatment with bromocyanide (A. James, *ibid.* 1927, **124,** 1004). Gold ores containing antimony as stibnite are also refractory r the stiUnite dissolving in caustic alkali and * decomposing cyanide. Roasting is useless unless the temperature is kept as low as 450°. At higher temperatures antimonates are formed, locking up the gold and protecting it against attack by cyanide. Long weathering of slimed ore containing stibnite makes it amenable to cyaniding (V. E. Robinson, J. Chem. Met. Soc. S. Africa, 1921, 21, 117). The graphite in West African schist precipitates gold from aurocyanide but the difficulty in treating these ores is overcome by roasting before cyuiifding (A. James, *l.e.).*

Flotation (q.v.).—This method of concentration is the most recent development of importance in the treatment of gold ores. In flotation the finely ground ore is mixed with water, air and less than 1% of oil, the ratio of water to solid being usually 3 or 4 to 1. The oil coats the particles of gold and minerals rich in gold and enables globules of air to adhere to them, so that they float to the top in a permanent froth which is skimmed off. The gangue particles are wetted by water and sink to the bottom. Besides oil, a number of other compounds are used in froth flotation, with various objects in view. Pine oil and cresol are in common use to form the froth, which must be stable enough to last while it is being removed from the machine. The amounts required vary from 0·05 to 0·15 lb. per ton of ore for pine oil and 0·1-0·5 lb. per ton for cresylic acid. " Collecting agents " such as xanthates, thiocarbanilide and cresyl phosphate (" *aerofloat* ") are used to enable the free gold and auriferous minerals to be floated, the amounts required being of the order of 0·1-0·3 lb. per ton. They are used in conjunction with " activators," such as copper sulphate and sodium sulphide, which assist in this action on some minerals. Copper sulphate and xanthates, however, cannot be used together as they form insoluble copper xanthate which is inactive. Sodium sulphide is advantageous in the presence of oxidised minerals such as copper carbonate and iron oxide, and in ores in which the gold is mixed with pyrite. " Modifiers" such as lime and soda ash assist in the wetting of the gangue particles, thus causing them to sink; they also neutralize acidity. Lime in excess, however, acts as a " depressor," causing both free gold and pyrite to sink. Sodium cyanide also acts as a depressor. " Dispersion agents " such as sulphuric acid and lime cause the gangue particles to separate from the mineral particles.

In flotation machines, the pulp and air entering a cell together are violently agitated by means of a central shaft fitted with blades or other form of impeller and revolving at high velocity (200-500 or more revolutions per minute). The impeller usually drives the pulp upwards and the air bubbles coated with mineral float to the surface and are scraped over the side of the vessel by revolving paddles. Among machines used in treating gold ores are the Minerals Separation subaeration, the Denver subaeration, the Fagergren and the Kraut flotation machines. Several units or cells are used in series, so that the froth from the first cell may be treated again in " cleaner cells," and the gangue tailings in other cells. The whole series forms the " flotation circuit." The froth or concentrate containing the free gold and valuable minerals is usually sold to smelters, or treated by cyanidation.

Flotation supplements, rather than supplants, the older processes. It is recognised that there is an advantage in withdrawing as much gold as possible from the pulp at the earliest practicable stage of treatment, as may be done by flotation or gravity concentration. Free gold floats alone in the absence of sulphides (RVhards and Locke, Mm, Ind. 1932, 4t 590). Thus on a rich Californian ore a froth assaying some £2,700 per ton with 60% extraction could be obtained by using only small quantities of " *pentasol* " xanthate and other reagents. The addition of two drops of pine oil per ton increased the assay value of the concentrates to £5,000 per ton. With some ores flotation is followed by cyanidation of the tailings, with others the cyanide treatment comes first. The tailings from amalgamation are also subjected to flotation in some instances.

There has been a rapid increase in the application of flotation to gold since the change from acid to alkaline circuits and from oils to synthetic organic chemical reagents. The alkalinity generally used is very slight, the p_H value (logarithm of the reciprocal of the hydrogen-ion concentration) of the pulp ranging from 7·0 to 7·5, the neutral figure being 7·0. Flotation is in use at many mines in the Kirkland gold field Canada, in Western America, in West Australia and other countries. It is also being tried on the Rand on a large scale.

Smelting.—Gold ores containing appreciable quantities of lead or copper are usually smelted for the production of these metals, from which the gold is subsequently extracted. Other gold ores are sometimes useful as fluxes in the smelting operations (v. COPPER).

Refining.—Gold extracted from ores is usually impure and unfit for use in the arts until it has been refined. Preliminary refining or " toughening " operations are often carried out either at the refineries or at the gold mills before the bullion is sold. Sometimes the gold is melted in crucibles with oxidising agents such as nitre, or a blast of air is directed on the surface of the molten metal or even passed through it. The base metals are oxidised and form a dross which is skimmed off with the help of bone ash, or borax is added to form a fusible slag with the oxides of the metals. Toughened bullion contains little except gold, silver and copper.

Refining by Sulphuric Acid.—In this process, an alloy of gold and silver is prepared by melting gold bullion with *doré silver (i.e.* silver containing small quantities of gold) or Mexican dollars or, occasionally, with refined silver if no other is available. The parting alloy usually contains from 20 to 30% of gold and a few per cent. of copper. If a higher proportion of gold is present, some silver remains undissolved and is retained by the gold. The copper assists the dissolution of the silver but the amount of base metals present in the alloy is carefully regulated, as their sulphates are sparingly soluble in concentrated sulphuric acid and consequently are precipitated and interfere with the progress of the operation. Not more than 10% copper and 5% lead are allowed. A small quantity of lead is said to assist in the dissolution of copper.

The alloy is granulated by being poured into water while still molten and the granulations are boiled in concentrated sulphuric acid of sp.gr. 1·85 in cast-iron kettles. The amount of acid used is four or five times the weight of the granulations, but only about half this amount is added at first. The sulphur dioxide, which is formed in large quantities, is carried away through leaden pipes. Silver sulphate is retained in solution in the hot concentrated acid, but tends to be precipitated when the acid is cooled or diluted. When the evolution of sulphur dioxide is at an end, the liquid is transferred to a settling pot, and fresh acid added. After three boilings in acid, the " brown gold " residue is washed with boiling water, dried, melted with nitre and cast in open moulds into ingots of about 400 oz. each.

The acid solution of silver is poured into large lead-lined tanks containing hot water and sheet or scrap copper, and is heated by means of steam and stirred until the precipitation of the silver is complete. The silver precipitate is washed, dried and compressed into cakes by hydraulic power before being melted. The copper is recovered by electro-deposition or as copper sulphate by crystallisation. The gold produced by sulphuric -acid parting is usually from 996 to 999 fine, and the precipitated silver is about 996 to 998 fine.

Refining by Electrolytic Deposition.—In the United States, and in some refineries elsewhere, gold is refined by electrolysis. Two processes are used successively. In the *Moebius process,* a parting alloy containing about 30% of gold and 65-70% of silver, copper, lead, etc., including not more than 15% of base metals, is electrolysed in a solution containing about 2% of free nitric acid and 3% of silver in the form of nitrate. Silver, copper and some other metals are dissolved at the anodes, which are enclosed in bags, and silver is deposited at the cathodes which consist of rolled sheets of pure silver, slightly oiled to reduce adhesion. The current density is usually 20-30 amperes per sq. ft. of cathode. The silver may be deposited in a coherent form on the cathodes, with the help of a little gelatin in the electrolyte, and subsequently stripped off. Sometimes the cathodes are continually scrubbed with wooden brushes, working automatically, by which their surfaces are kept free from loose crystals of electro-deposited silver. The loose silver falls on to removable trays placed below. The gold remains undissolved at the anodes and retains some silver. The copper, lead, zinc, etc., accumulate in the electrolyte, which is kept in condition by the addition of acid and silver nitrate and by frequent renewal. The gold anodes are sometimes boiled in sulphuric acid, but if they contain as much as 950 parts of gold per 1,000, they may be melted at once and cast into anodes for treatment by the Wohlwill process. For observations on the conductivity of electrolytes used in the Moebius process, *see* Concord, Kern and Mulligan, Trans. Amer. Inst. Min. Met. Eng. 1926, 73, 108. The Balbach-Thum process is similar to the Moebius process, the chief difference being that the electrodes are laid horizontally in trays, instead of being suspended vertically in bags in the electrolyte.

In the *Wohlwill process* (Zt. Electrochem. 1898, 4, 379, 402, 421; Rose and Newman, " Metallurgy of Gold," 7th ed., 1937, p. 481), the anodes contain not more than 50 parts of silver per 1,000 and a few pipts per 1,000 of base metals. By the use of a " pulsating " current (a combination of a direct and an alternating current), gold with 15-17% silver can be refined, as the silver chloride is automatically detached from the anodes (Wohlwill, Met. and Chem. Eng. 1910, 8, 82; Downs, Metal Ind. 1930, 36, 141).

Under ordinary conditions with hot solutions at 60-70°, the electrolyte contains from 2-5 to 4% gold in the form of chloride and 3-5% HCl. At 20°, 10% HCl is used. With the pulsating current, less HCl can be used. The reactions at the anode are:

$$HCl+Au+3Cl=HAuCl_4$$

and

$$HCl+Au+Cl=HAuCl_2.$$

The hydrochloroaurous acid subsequently decomposes in part into hydrochloroauric acid and metallic gold, which is found in minute particles in the anode mud.[4] At the cathode the reactions are:

$$HAuCl_4+3H=Au+4HCl,$$

and

$$HAuCl_2+H=Au+2HCl.$$

Some chlorine is evolved at the anode, especially if the temperature is too low, the hydrochloric acid insufficient in amount, or the current density too high, and some chlorine is taken up by silver and other impurities. The result is that the electrolyte gradually becomes weaker in gold chloride and more must be added at frequent intervals. The gold chloride for this purpose is usually prepared by dissolving gold in *aqua regia.* The $AuCl_4'$ ions migrate from the cathode and it is necessary to stir the solution by air-blowing or by a propeller. In pulsating-current practice, with an alternating current of strength 1·1 times that of the direct current, a direct current of 125 amperes per sq. ft. of anode can be used without scraping the anodes. In practice about 80 or 90 amperes per sq. ft. is usual. The amount of gold passing into the anode mud is diminished by the use of the pulsating current.

Platinum and palladium when alloyed with gold pass into solution from the anode and are subsequently recovered by chemical precipitation. Iridium, osmiridium and rhodium do not dissolve. Lead at the anode is converted into peroxide and causes passivity. It may also reach the cathode, making the gold brittle. It is accordingly removed beforehand together with selenium, tellurium, arsenic, antimony and bismuth by toughening. When the electrolyte becomes foul, owing to an accumulation of copper and other impurities, it is drawn off and the metals recovered. The electrolyte is renewed, most conveniently, by withdrawing a pad of it each day and adding a solution of pure gold chloride. The anodes are made of such thickness (4-12 mm.) that they can be dissolved in 24 to 36 hours. The cathodes consist of fine gold and the deposited gold is usually from 999-5 to 999-9 fine. The residue at the anodes consists chiefly of silver chloride.

The process is particularly applicable to platiniferous gold, as in other refining processes platinum is left with the gold and lost.

Chlorine Process.—In Australia, South Africa and elsewhere, gold is refined by the passage of a stream of chlorine gas through the molten metal contained in a clay pot and covered with borax. The method was invented by Miller in 1867 (J.C.S. 1868, 21, 506). The chlorine is at first completely absorbed and combines with all the mptnls present except perhaps some of the platinum group. Gold itself ia attacked very slightly in the earlier stages. The chlorfSes rise to the surface and are baled out, together with the borax, when they have become inconveniently bulky. Some chlorides volatilise and pass out of the furnace. In, one modification, oxygen is added with the chlorine (**Kah&n,** Trans. Inet. Min. Met. 1918, 28, 35). When the gold approaches a fineness of 990, gold **chloride** ia formed in rapidly increasing amounts and begins to appear in appreciable quantities in the fumes which pass through the slag. The stream of chlorine, which has already been reduced to a mere trickle, ia stopped soon afterwards. The end-point is ^marked by a peculiar stain (caused by gold chloride) on a cold clay pipe-atem held in the issuing fume. The remainder of the chloride slag is th^fnjeem overt and the gold cast into ingots. It is usually about 996 fii?e, the residue being mainly silver. Platinum remains with the gold. Tellurium is difficult to eliminate. If present, it remains to the end and is removed by additions of nitre.

The chloride slag is found to contain about 2% of the gold, mainly in the form of minute crystalline particles, reduced from chloride of gold which has passed into the slag (Law, 54th Ann. Rept. Royal Mint, 1923, p. 97). The gold ia collected by the addition of carbonate of soda to the molten slag. Part of the silver chloride is reduced, and the metallic silver settles to the bottom, carrying the gold with it. This portion again passes through the process. The remainder of the silver is freed from the base chlorides and reduced with iron plates.

The process is especially suitable fnr refining bullion over 700 fine in gold, with the remainder mainly silver. Gold of lower fineness can be treated but the time of treatment becomes longer and tha coat greater *[see* 64th Ann. Kept. Royal Mint, 1933, p. 110). If the silver is below 6%. there is some difficulty in removing base metals. The process is obviously unsuitable for dor6 bullion or platiniferous gold. One great advantage is the rapidity of the process, as it brings 98% of the gold to account in a marketable form in a few hours. The plant costs little and the Tunning coats are low.

Properties of Gold.—The characteristic yellow colour of gold is made redder by tht< presence of copper and pal^r by the presence of silver. In certain proportions the effect of one of the two metals neutralises that of the other. In a finely divided state, when prepared by volatilisation or precipitation, gold assumes various colours, sueh BS deep violet, ruby and purple. " Faraday's gold " is a ruby coloured solution of colloidal metallic gold in water (Zsigmondy, Annalcn, 1898, **801,** 29; J.C.S. 1912,102, ii, 508). Molten gold is green.

Gold is the most extensible of all metals, and can be reduced by hammering to a thickness of 0-00008 mm. Its m»|le-:il>ility and ductility are reduced by the jresence of impurities, of which bismuth, lead and Mhirhini have the most •**taking effects. Gold containing** 0-26 per 1,000 of bismuth is brittle. TIIK melting-point of P»re gold is 10tt3°. but if it **oontafcu** 0-2% of tellurium, it softens at 432°, the melting-point of the eutectic of gold and the compound AuTe,. The presence of most other metals reduces the melting-point of gold, but it is raised by platinum. It begins to volatilise *in vacuo* in a quarts vessel at 1070° and boils at 1800° under the same conditions (Krafft and Bergfeld, Ber, 1905, 38, **264).** The density of cast gold in about 19-3, but that of precipitated gold js higher, and when gold is crystallised from solution its density is given as 19-43. It crystallises in the cubic system.

Gold is unaffected by the air at all temperatures and can be melted and solidified without being changed. In large pieces, it is not perceptibly attacked by alkalin or by nitric, sulphuric or hydrochloric acid, but, when finely divided, it is slightly soluble in boiling HCI and in boiling HNO.,. It is freely soluble in *aqua regia* or other mixtures, evolving one of the halogens, and more slowly in cyanide solutions in ths presence of air. Its compounds are generally formed with difficulty and decomposed very easily with the liberation of the metal.

Alloys of Gold.—The *gold-copper* alloys **are** harder, more fusible, of higher tensile strength and less malleable and ductile than pure gold. Tin" metals are mjsciblc in all proportions when molt^i mid on solidification separate only to a slight degree. The first additions of copper to gold cause a rapid lowering of the melting-point, the minimum of 884° being reached at the brittle alloy containing gold 82%, copper 18%. On cooling the solid solution of gold and copper which exists at high temperatures, gradual decomposition occurs with the formation of the compounds $AuCu_a$and $AuCu_3$ (Haughton and Payne, J. Inst. Metals, 1931, **46,** 457 j Kurnakov and Agcew, *ibid.* 481; Grube, Z. anorg. Chem. 1931, 201, 41). The transition point is not far below 400°. The compound AuCu is hard and brittle and alloys containing much of it cannot bo rolled or drawn. The effects are pronounced in the alloys containing 50-75% gold but are reduced by quenching (E. A. Smith, Metal Iml. **1932,** 41, 28). The densities of the alloy?when cast are as follows (Hoitsema, Z. anorg. Chem. 1904, 41, 65):

Proportion of gold, %.	Donrity.
100	19-30
91-66	17-35
BOO	17-17
750	14-74
58-3	12-69
250	1003

The densities of gold wares, which consist of triple alloys of gold, silver and copper, ars higher.

OoM-silver alloys are soft, malleable and ductile and all their propertied arc intermediate between those of goM and silver. The colour is dominated by the silver, the alloy containing 37-5% of gold being only just distinguishable in colour from pure silver. Alloys contuining not IPBD than 65% of silver are almost completely **p»rtod by boiling nitric** or sulphuric add, t In' silver being **dissolved** and an ullotropto form of gold left behind na a brown sponge or powder (**Hanriot,** Bull. **Sue.** chim. 19H. [iv], 9, 139, 339; C,mtii. **rand. 1912,**165, **10W).** The gold obstinately retains about 0-1% of silver, and on continued boiling in strong nitric acid, some gold is dissolved whilst the proportion of silver is reduced very slowly. The presence of copper facilitates the action of the acid but does not alter the final result.

Amalgams or alloys of gold and mercury are formed at ordinary temperatures by direct union of the two metals. Mercury dissolves Q-11% of gold at 0° and 0-126% at 100° (Kasantseff, Bull. Soc. chim. 1878, [ii], 30, 20), and gold absorbs mercury, forming a silver-white solid alloy containing about 40% of gold. .At 440° most of the mercury is removed by volatilisation, the residue containing about 75% of gold. At a bright red heat, almost all the remainder of the mercury is distilled off. In the alternative, the mercury can be removed by dissolving it in nitric acid. Parravano (Gazzetta, 1918, 48, ii, 123) states that gold amalgams contain at least two compounds, Au_2Hg_3 and Au_3Hg (*cf.* Paal and Steyer, Kolloid-Z. 1918, 23, 145); Plaksin (Am. Inst. Anal. Chim. Leningrad, 1928, 4, 336) gives the compounds as $AuHg_2$ and Au_2Hg. <

Odd-iron alloys are hard but malleable and ductile (Isaac and Tammann, Z. anorg Chem. 1907, 53, 281; Nowack, Z. Metallk. 1930, 22, 97). Alloys containing between 15 and 20% of iron are used in jewellery in France under the name *or gris.* Their colour is greyish-yellow and they melt at temperatures higher than that of pure gold. *Or bleu* contains 25% of iron. It melts at a temperature of 1,160°.

Gold forms a brittle purple compound with aluminium, Au AL (aluminiu/n21-5%) (Heycock and Neville, Phil. Trans. 1900, A, 194, 201; 1914, A, 214, 267). The compound AuZn, containing 25% of zinc, is of a pale lilac colour and is also brittle. The compounds Au_3Zn and $AuZn_3$ also exist (Soldau, J. Inst. Metals, 1923, 30, 351; 1926, 36, 454). Zinc removes gold from molten lead, and aluminium has the same property, the compound formed being $AuAI_2$.

Ustis of Gold .—Gold is used in the form of its alloys with copper, silver, etc., in the manufacture of coin, plate and. jewellery. Gold leaf is used for gilding by hand and potassium aurocyanide is used in gold plating baths. Gold is also used in photography (in the form of sodium chloroaurate); in dentistry (as alloys); in medicine (as the chloride); and in the manufacture of mirrors for reflecting purposes. In 'the form of Purple of Cassius, and as leaf it is used for colouring and decorating glasses, glazes and enamels. Gold lace consists of extremely fine strips of gold twined round silk and contains about 2-5% of gold by weight. A large proportion of tho gold production remains in the form of refined ingots which are used in international exchange.

Gold Wares.—Tho alloys used in the manufacture of gold wares consist of gold, silver and copper. The wares arc usually made from rolled plates whic^i are cut out by punc&s and struck between dies. The pieces are fitted together by hand, usually by means of soldering. Solders have fusion points lower than the gold objects with which they arc to be used. They usually contain gold, silver, copper, zinc and cadmium in proportions varying according to the colour of the alloy required. Decorative work is carfied out by hand-hammering, engraving, chasing, etc. The wares are " coloured" or pickled by a process which removes the'silver and copper from the surface and leaves a coating of pure gold, afterwards burnished. In pickling, the wares are heated to redness in air and the blackened surface is removed by boiling In dilutf sulphuric or nitric acid, after which the colour is improved by immersion in hot mixtures of nitre, common salt, ^lum, etc. In the United Kingdom the 18-carat alloy (*i.e. ii* gold) was introduced in 1^77, the 22-carat alloy in 1573, and the 15-, 12- and 9-carat standards in 1854. In 1932 the 15- and 12-carat alloys were abolished as legal standards and in their place a new standard containing 585 gold per 1,000 was adopted, closely approximating to 14-carat gold (583-3 parts of gold per 1,000). The 9-carat alloys are used for the greatest amount of jewellery. They offer much scope for variations in colour. In addition to silver and copper the alloying metals include zinc, cadmium, nickel and occasionally iron. A small quantity of zinc is frequently added in the form of brass (" compo "). The zinc acts as a deoxidiser and assists in producing sound metal. The 14-carat alloys are also much used. Annealing at too high a temperature, say above 650°, or for too long a time impairs the working qualities of these alloys. Quenching at above 500° results in a greater degree of softness. Zinc is often added to both 14- and 18-carat alloys as a deoxidiser and degasifier (Carter, Amer. Inst? Min. Met. Eng., Tech. Publ. 86; E. A. Smith, Metal Ind. 1931, 39, 123; 1932, 41,'28).

Imitation gold wares sometimes consist of alloys of copper with aluminium, zinc, etc. " Rolled gold " (E. A. Smith, J. Inst. Metals, 1930, 44, 175) is made by sweating or soldering a sheet of gold alloy to a sheet of silver or base metal and then rolling. In " gold filled " wares, a gold sheet is soldered on each side of the base metal before the rolling. Electro-gilding is carried out in baths containing potassium aurocyanide with anodes of pure gold. Various colours of the deposit may be obtained according to temperature and current density (Sizelove, Monthly l?ev. Amer. Electroplaters' Soc. 1931, 18,45). Gilding by simple immersion in hot aurocyanide solutions is also practised. In mercurial gilding, gold amalgam is brushed over the surface of articles and the mercury driven off by heat.

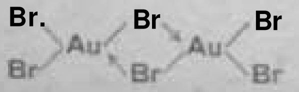
Gold Leaf contains from 90 to 98% of gold, the rest being silver and copper. The metal is cast into little flat bars which are rolled out with frequent annealings until about 0-33 mm. thick. The strip of gold is then cut into pieces of 1 in. square and these are interleaved with vellum and beaten with a 16-lb. hammer to 4 in. square. They are again cut up and beaten out between gold-beaters' skins. The book of 25 leaves, each about 3J in. (8-25 cm.) square, contains from 4 to 10 grains (0-26-0̣05 g.) of gold. The leaves are from 0-00008 to 0,0002 mm. thick.

T. K. It.

GOLD, THE COMPOUNDS OF.—Tho chief classes of gold compounds arc the aurous compounds in which the metal is univalent arid the auric compounds in which it is **tervalent.** There is an intermediate **clam,** auroauric compounds, in the molecules oP'whieh there are equal numbers of univaient :ind tcr-valentgold atoms. Whenever gold in *in* aqueous solution either in the aurous or auric conditions it is Always present as a complex ion and, as far as our present knowledgo^goes, there is no evidence for the existence in gold salts of the aurous (Au^+) and of the aurki (Au^{+*+}) ion. In its compounds gold is always co-ordinated. In the **typical** aurous and,auric compounds gold is 2-covalent ami 4-eoyaient, respectively, and then has the corresponding effective atomic **numbers** of 82 and 84. **Ii»,** ccrlain compounds which are exceptional aurous gold may be 4-cov.:.i I–lit and auric gold may be S-covalcnt; and in both cases gold then attains an effective atomic number of 8(5, corresponding to the atomic number of radon, the next inert gas (Dothie.Uewellyn, **WarcQaw** and Welch. J.C.S. 1039, **428j Brain and Gibson,** ***ibid.*** **1939, 762).** Recent investigations **indicate that** such coir-pounda as auric bromide, auric chloride, aurous bromide, aurous chloride atld aurous cyanido arc not salts but are **non-electrolytea.** They are co-ordinated compounds in which the gold atom has a co-ordination number of four or two, depending on whether it is iivthe auric or aurous **condition.** This conception involves a revision of the constitution of many gold compounds. This may involve in some cases a change of nomenclature and, to emphasise the non-electrolytic character of the above simple compounds, th*y may be given the alternative names of tribromogold, trichlorogold, mono-broniogoM, nionochlor9gold, monoiodogold and' monocyanogold respectively.

Gold Tribromide (auric bromide, tribromo-gold), is prepared by adding slowly at le:ist twice the theoretical quantity of pure bromine to a weighed amount of pure and finely precipitated gold con t a i net I in a wide mouth glass fiask provided with a ground stopper. The bromine and gold are brought **into** intimate contact and only sufficient cooling to avoid undue loss of **brom** ine ie employed during the mixing. When all the bromine has been added the contents are allowed to stand at the ordinary temperature for some hours in the stoppered ILisk. The flnssk with its Btopper removed is then allowed to stand over sodium hydroxide until **bwftttine** vapour **ia** BO longer evident in the apparatus. The **residue, a** compact dark-red crystalline mass, is pure gold tribromide. {Gibson and Colles, *ibid.* 1931, **8407).**

Gold tribromide is decomposed by water, aurous bromide Und hydrobromoauric acid being produced. It-is insoluble **in** ether, **in** the presence of **which** it undergoes decomposition, aurous bromide being **formed** and the ether becoming brominated. It is also insoluble in ether containing anhydrous **hydrogen bromide** and is sparingly soluble in bromine. Its **molecular** weight **in** boiling bromine indicates **that its molecular formula** is $(AuBr_3)_a$ and it> **constitution** is **conveniently represented**:



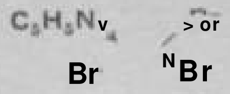
The magnetic susceptibility of gold tribromido at *V.r* is it—**0-23** X10-* e.m.u. On being **heated to** a closed evacuated tube, it **undergoes** dissociation below 100°; the evolved bromine does not wholly reef mi bine on cooling even after many months (Buniwoy and Gibson, ***ibid.*** 11*35, 217).

Gold tribromide is readily soluble in aqueous solutions of bromides and **chlorides** nnd **Buck** solutions afford the- most convenient sources of hydrobromoaurie aeid and its salts as well as of mixed eh lorobromoau rates.

Hydrobromoauric Acid, $HAuBr_4,3HjO$ (l.engfeld.Amer. Cliem.J. **1901,26,**824),**maybe** conveniently obtained by the careful evaporation, finally under reduced pressure, over potassium hydroxide at the ordinary tempi ratine, of a solution of gold tribromide in an aqueous solution of hydrobromic acid. It crystallises in long dark-red needles which are hygroscopic and soluble nofonly in water hut also in ether. When carefully heated it becomes anhydrous •mil **ia then** insoluble **in ether.**

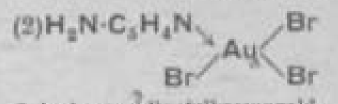
The salts of hydrobromoauric acid with inorganic bases are best prepared by dissolving pure gold tribromide in an aqueous solution containing the calculated amount of the inorganic bromi3e and **evaporating** the solution to crystallisation in a dust-free atmosphere. Although highly soluble, these deeply coloured salts, bromoaurates, can be recrystaliiscd from **wat**er. Many such salts are known and typical onea have the compositions: **$NH,AuBr_4$;** $NaAuBr_4,2Hj,O$; $KAuBr_4,2H_aO$; $RbAuBr_4$; $CsAuBr_4$; MgtAuBr^^eHjO (Gibson, privatE)communication); $Ba\{AuB,r_4)_2$. A comprehensive series of bromouuniU-s of organic bases has been described by Outbier and Hutier (Z. anorg. Chem. 1914, 85, 383). The X-ray examinations of the potassium salt have 1Men carried out by Cox and Webster (J.C.S. **1930,** 1635).

Co-ordination compounds of gold tribromide with suitable organic bases can be prepared cither by the direct interaction of the^gold compound and the base or by the following reaction: $MAuBr_4+B=MBrfB-AuBr_3$ (**M-univalent** metal) **(Gibson** and Colles, *I.e.).* The following aro the constitutional formula.* of some of these non-electrolytic 4-covalent auric compounds :

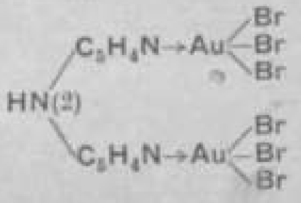


Fyrlclinotribroino-goM.

Qulnollmi- and *iso-* quinolino-tribrUII ogold.



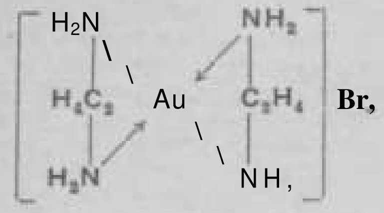
2-Aminopyridinotribromogold.



Dl-a-pyridylainlnotflbromugiihl

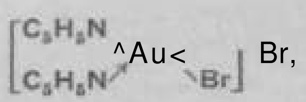
These co-ordination compounds are all deep red in colour and highly crystalline. They are stable and although sparingly soluble they can be recrystallisrd from solvents, *e.g.* chloroform and carbon tetrachloride which do not undergo oxidation or bromination.

When ethylenediamine is used in the above reaction the solution becomes pale yellow, and on addition of alcohol *diethytenediaminogold tribrwnide* (diethylenediaminoauric bromide)



crystallises in yellow glistening needles. This salt, in which auric and 4-covalent gold is part of a complex tervalent cation, lite the co-ordination compounds described above, is decomposed by hydrobromic acid, hydrobroruoauric acid and the hydrobromide of the baie being formed.

By re crystallisation of the compounds^of the type, *B*-Au Br_3, from the liquid base B, salts of the type $\{B_BAuBr_a)Br$ are formed. The compound *dipyrldinodibromogold bromide,*



is a dark-red, crystalline, soluble salt which on being heated first loses a molecule of pyridine and is converted into the non-electrolyte, pyridinotribromogold, already mentioned.

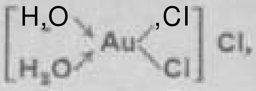
Diethylenediaminogold tribromide (diethylenediaminoauric bromide) is analogous to the colourless crystalline salt *lelramtninoauric nitrate,* $[Au\{NHa)J(NO_3)_3$ (Weitz, Annalen, 1916*, 410, 13 7} which to prepared by adding a dilute solution of hydrochloroauric acid saturated with ammonium nitrate to a saturated solution of ammonium nitrate, treating the mixture with ammonia and washing the precipitate with water. It can be recrystaUised from warm **water.** Examples of other salts which have been obtained are: the phosphate, RPO_4,HjO, the oxalonitratc, $RNO_3(C,O_4\}$, the perchlorate, $R(ClO_4)_a$. tlie oxaloperchlorate, $RClO_1(C_£O_<)$, the chlorate, $R(ClO;,)_3$, the aulphatonitratc, $R(NO,)(SO_4)$, and the oliromate, $R.(CrO_4L$ where $R=[Au\{NH_a),]^+$. All these salta are highly stable in the solid condition and retain their ammonia even in the presence of concentrated acids. The salts with halogen acids, hydtocyanic and thiocyanic acids have not been obtained.

Co-ordination compounds of gold tribromide with organic sulphides are also known. *Di-«e'i taMT. ramMgotd,mogold,* (C,H,>,S A.uABBr,, iapri-[iiti,Ti by the action of bromine on, di benzyl-s'phidomo nob romogold («<• *below).*] Us a deep-red highly rr.vBt.alli no **non-ei**ectrolyte, **ulnUa** m benwhe, ,,.;,. U9-U9 (tiewJ mp.) (Gibson and lyabji, private commun cation).

Gold Trichloride (auric chloride,[1] trichlorogoid} can be obtained by the direct action of a large;fixcess of chlorine on finely divided pure gold (Rose, J.C.S. 1885, 67, 905). The reaction can be carried out even at 1,100°, although in the absence of excess of chlorine gold trichloride is completely decoinpoaed at a lower temperature. The most conve^ont way of preparing the compound is by heating pure hydrochloroauric acid, $HAuCI_4,3H_aO$, at 200° in a current of dry **dhliftrae** (Diemer, J. Amer. Chem, Soc. 1913, 35, Kfcm

QOOI*

Gold trichloride foi'ois small, deep claret-red prismatic crystals (Pope, J.C.S. 1895, 67, 906). It is deliquescent a,tid dissolves in water; from this solution by careful evaporation at 'the ordinary temperatuie orange-red crystals of i" the so-called dihydrate, $AuCI_3,2H_aO$, separate. This in all ^probability is a salt,



diaquodithloToa-uric £tioride; it is not stable and tends to decompose, yielding auroua chloride {gold mono chloride, monochlorogold) and hydrochloroauric acid.

The molecular weight of gold trichloride between 150° and 260° corresponds with the formula $(AuCI_3)_£$ (W. Fischer, Z. anorg. Chem. 1029, 184, 333) and its constitution is antilogous to that of gold tribromide (p. llltf).

The volatilisation and dissociation of the compound have been studied by a n'imber of investigators, particularly Rose (f.c.)and Ephraim (Ber, 1919, 52, 241). At atmospheric pressure, gold trie! do ride dissociates into auroua chloride and chlorine at 254-256°, further decomposition of the auroua compound taking place at 2£H)°.

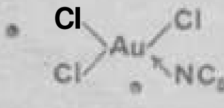
The statement frequently made that gold trichloride (auric chloride) i» soluble in alcohol, other and other organic solvents is not correct. Wil]statt«r((W. 1903, 86,1803), who stated that gold chloride is soluble in ether, was investigating the priin:i lirs of hydrochloroauric acid, $HAuCI_.,3H_aO$, and tlii.s compound *(see below)* is soluble in ether. Many of the properties formerly ascribed to gold trichloride are those of hydrochloroauric arid nrnl of sodium chloroaurate, and by " gold chloride" in certain **recipea relating to the** photographic process, etc., is frequently meant either hydrochloroauric acid or sodium chioroaurate. In the older literature " **a** solution of gold chloride " generally means " a solution **of hydrochteoaario** acid."

Gold trichloride is soluble in hydrochloric acid and *kydrochlloToauric acid in* fonntjd. When this solution is (tvajwrated and finally left in a desiccator over potassium hydroxide the red crystalline residue has the com position

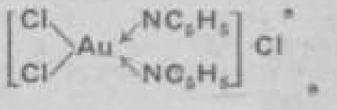
$$HAuCl_t.3H_aOf$$

this compound is soluble in ether but tbo anhydrous aoid is insoluble in that solvent. Theoretically, the chlorouuratcH may be obtained by **neutniiiing** & solution **of bydioahloroaiific** mid **with the appropriate baw,** In **prw Uoe,** th« chioroaurate iw **mon otmvenieiiuy** obtained when an **excett of** the appropriate cation present as provided by a solution of the chloride. The chloroaurates are also prepared by dissolving gold trichloride in a warm solution of the appropriate metallic chloride. A large number of chloroaurates have been described. The sodium and potassium salts, $NaAuCl_4,2H_2O$ and $KAuCl_4,2H_2O$ respectively, are both used for toning silver photographic prints (Kebler, J. Franklin Inst. 1900, 150, 235; Johnson, J.S.C.I. 1901, 20, 210). The ammonium salt has the composition $NH_4AuCl_4,5H_2O$. The brown orthorhombic crystals obtained by Pollard (J.C.S. 1920, **117**, 99) by adding ammonium chloride to a solution of gold in *aqua regia* containing ammonium chloride, to which silver nitrate has also been added, are evidently those of a complex salt having the composition $3AgAuCl_4(NH_4)AuCl_4 \cdot 7NH_4Cl$. The calcium, strontium and barium salts have the general formula $M(AuCl_4)_2,6H_2O$. Numerous other inorganic salts have been described; they are generally characterised by being highly crystalline, soluble in water and of a deep yellow or orange colour. Chloroaurates of many organic bases have also been prepared, since these latter compounds have, in many cases, been identified through their salts with hydrochloroauric acid.

Co-ordination compounds of gold trichloride with organic bases are analogous to the corresponding compounds of gold tribromide and are prepared by similar methods. A convenient method of preparing the yellow *pyridinotrichlorogold,*



(cf. Francois, Compt. rend. 1903, **136**, 1557) is by dissolving sodium acetate in an aqueous solution of hydrochloroauric acid (not necessarily free from hydrochloric acid) and adding 1 mol. proportion of pyridine for each molecular proportion of hydrochloroauric acid. This non-electrolyte may be recrystallised from non-oxidisable solvents which do not undergo chlorination. When recrystallised from pyridine it is converted into the orange-coloured salt, *dipyridinodichloroauric chloride,*

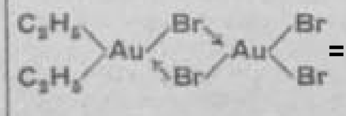


When this compound is gently heated it loses pyridine and is converted into pyridinotrichlorogold before undergoing more profound decomposition.* Co-ordination compounds with dibenzyl sulphide and aliphatic sulphides having the general formula $R_2S \rightarrow AuCl_3$ have been authenticated (Herrmann, Ber. 1905, **38**, 2813; Smith, J. Amer. Chem. Soc. 1922, 44, 1709; Kay and Sen, J. Indian Chem. Soc. 1930, 7, 37). The so-called salts of gold trichloride with sulphur tetrachloride, selenium tetrachloride and nitrosyl chloride are probably co-ordination compounds analogous to pyridinotrichlorogold. Gold trichloride also forms a complex compound with stannic chloride.

The evidence for the existence of the iodine derivative of tervalent gold is not conclusive. The early work on this substance as well as on the corresponding acid and salts, iodoaurates, needs repetition (cf. Johnston, Phil. Mag. 1836, [iii], 9, 206).

There is also little satisfactory evidence for the existence of the fluorine derivative of tervalent gold.

Gold Monobromide (aurous bromide, monobromogold) produced by heating gold tribromide or hydrobromoauric acid is always likely to be contaminated with the metal. It can be obtained in a state of purity by heating monoethyldibromogold (*see* p. 120) at 50° to constant weight (about 30 minutes) the following reaction taking place:



$=2C_2H_5Br+2AuBr$

As the molecular weight of the compound has not been determined the molecular formula should for the time being be written $(AuBr)_n$ and the constitution is probably best represented thus:

$$\rightarrow Au{-}Br \rightarrow Au{-}Br \rightarrow Au{-}Br \rightarrow$$

When the compound is prepared by the above method (Burawoy and Gibson, J.C.S. 1934, 860; 1935, 218) it is obtained in yellowish-green crystals. It forms co-ordination compounds in which, as in the original compound, the aurous gold is 2-covalent. Examples of such co-ordination compounds are *pyridinomonobromogold,* $C_5H_5N \rightarrow Au{-}Br$ (Burawoy and Gibson, l.c. 1935), the compound with phosphorus tribromide, $Br_3P \rightarrow Au{-}Br$; *dibenzylsulphidomonobromogold,* $(C_7H_7)_2S \rightarrow Au{-}Br$ (Gibson and Tyabji, 1937, private communication). The diammino compound is a salt having the constitution $[H_3N \rightarrow Au \leftarrow NH_3]Br$ and is described as *diamminoaurous bromide.*

Hydrobromoaurous Acid has not been isolated but it is present in theoretical quantity in the solution obtained by reducing an ethyl-alcoholic solution of potassium bromoaurate by means of sulphur dioxide, the reaction taking place being:

$$KAuBr_4+SO_2+2H_2O = HAuBr_2+KBr+H_2SO_4+HBr$$

The colourless solution is stable and if excess sulphur dioxide has been used it may be expelled by heating the solution on the water bath. It will be filtered from precipitated potassium bromide, and on long exposure to air, or considerable dilution with water, gold is precipitated and the solution becomes coloured owing to the formation of bromoaurate (Brain, Gibson and Imperial Chemical Industries Limited, B.P. 407740).

Gold Monochloride (aurous chloride, monochlorogold) has probably a constitution analogous to that of the corresponding bromine compound. It is a yellowish powder formed by heating the trichloride at 170-180°; at higher temperatures further decomposition takes place (Rose, J.C.S. 1895, 67, 881, 905; Campbell, Trans. Faraday Soc. 1907, 3, 103). It is insoluble in water and is slowly attacked by hydrochloric acid, gold and hydrochloroauric acid being produced,

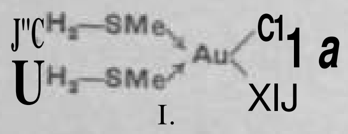
$$3AuCl + HCl \rightarrow HAuCl_4 + 2Au.$$

When an alcoholic solution of a chloroaurate is reduced with sulphur dioxide the solution becomes paler in colour but does not become colourless and gold separates after some time in quantitative amount. If hydrochloroaurous acid is formed it is evidently less stable than hydrobromoaurous acid (see *above).* Certain salts of hydrochloroaurous acid which have been described do not appear to have been definitely authenticated.

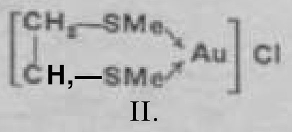
A number of co-ordination compounds of gold monochloride have been described; examples of these are the compound with phosphorus trichloride, $Cl_3P \rightarrow Au—Cl$, and compounds of the general formulae $R_3P \rightarrow Au—Cl$ and $R_3As \rightarrow Au—Cl$ (Mann, Wells and Purdie, J.C.S. 1937, 1828} where R=alkyl group. These alkylphosphine and alkylarsine derivatives are volatile and the former yield brilliant gold films when their vapours are heated. *Amminomonochlorogold* and *dibenzi/lsulphidomonoc/dorogoU* $(C_7H_7)_2S \rightarrow Au—Cl$ (Herrmann, Ber. 1905, 38, 2813) are compounds of similar type.

Diamminoaurous Chloride (Ephraim, *ibid.* 1919, 52 [B], 241) is analogous to the corresponding bromine compound and is a salt having the constitution $[NH_3 \rightarrow Au \leftarrow NH_3]Cl$. In all these co-ordination compounds the aurous gold atom is 2-covalent. Compounds containing 3 and 12 mol. of ammonia to each molecule of gold monochloride have been described *(see below).*

Sulphur compounds structurally analogous to diamminoaurous chloride have been investigated by Morgan *el al.* (J.C.S. 1922, **121,** 2882; 1928, 143). By adding dimethyldithiolethylene, CHaSCjH^SCHj, to hydrochloroauric acid dissolved in ether the yellow *dichlorodtmethylihioUtkyUneauric chloride (I)* is precipitated., and in the presence of moisture this is converted into *dimethyldithiolethyleneaur&u* chloride* (II).

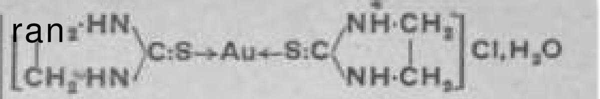


I.

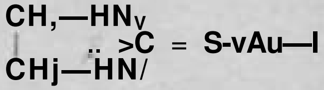


II.

By interaction of hydrochloroauric acid and ethylenethiocarbiwmde *HaCieAyhntthioearbamidoauTous chloride* (III) is obtained in colourless crystals. The corresponding nitrate (anhydrous) and bromide **(1H₂O)** and oxide are also described together **with** the non-electrolytj» *ethvUnethiocarbamidoiodogold* (IV). From thiocarbftmide, Morgan and Ledbury obtained the colourless crystalline *biatkiocarhamidoanrou* nitrate* (V) as well as tho anhydrous compound (c/. Reynolds, J.C.S. 1869, **1).**

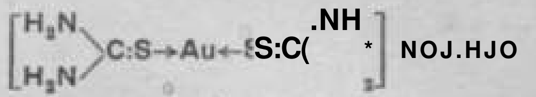


III.



$$\begin{matrix}CH_2—HN\diagdown \\ | \qquad\qquad >C = S \rightarrow Au—I \\ CH_2—HN\diagup\end{matrix}$$

IV.



V.

The constitutions of the non-electrolytes $(NH_3)_3AuCl$ (Meyer, Compt. rend. 1906, 143, 280), (NHa)a;P(6Me)3}AuCl {Levi-Malvano, Atti. R. Acad. Lincei, 1908, 17, 857) do not necessarily conflict with the stable 2-covalency of the aurous gold atom and such compounds may contain co-ordinated hydrogen atoms. On the otlierjuiml, certain investigators (*cf.* Mann, Wells and Purdie, *I.e.)* regard such compounds as containing 4-covalent aurous gold *(see below).* The substance stated to have the composition **AuCl·12NH₃** {Meyer, Compt. rend. 1901,**133,** 815) and prepared by the action of ammonia on gold monochloride at —28° easily loses ammonia and is converted into the stable diamminoaurous chloride mentioned above.

Fluorine has no action on gold at the ordinary temperature but is stated to corrode the metal at higher temperatures, *ft* is doubtful whether a compound having the empirical formula AuF_3 has been isolated and no corresponding aurous compound has been described.

Gold Mono iodide (aurous iodide, monoiodogold) having the empirical formula AuI is prepared by the action in aqueous solution of potassium iodide on potassium chloroaurate,

$$KAuCl_4 + 3KI \rightarrow 4KCl + AuI + I_2$$

The precipitated compound is freed from admixed iodine by gently warming (35°); unless special precautions are taken metallic gold is generally present. If excess of potassium iodide is used some gold remains in solution indicating the possibility of the formation of a salt, KAuI, or KAu • 4; but such compounds have not been isolated.

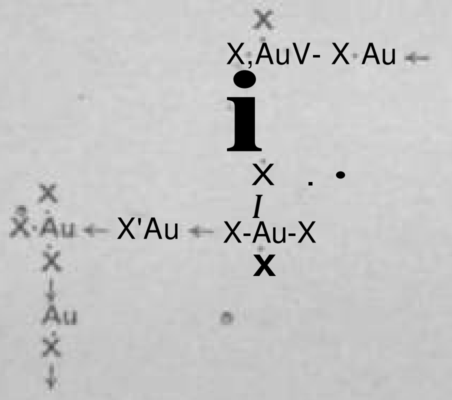
Aurous iodide is a yellow crystalline powder which is decomposed by hydriodic acid and by an aqueous solution of potassium-iodide, metallic gold being produced. It has been suggested that hydroiodoauric acid (or the potassium salt) may be present in the solution

$$3AuI + HI \rightarrow HAuI_4 + 2Au.$$

Like other aurous halides aurous iodide forms compounds with ammonia of which the most stable is *ammiiiomonoitxlugold',* $H_3N \rightarrow Au—I$ (Meyer, *I.e.). Triethylphoxphinomonoioilogotd,* ᶜ¥ᴴJiᴾ-* Au—I, m.p. 40°, *trin-ttvtylphoil>htn<miiinaiodogold.* $(C_4H_9)_3P \rightarrow Au—I$, b.p. 21io-225^/0'2 mm., and *tntnethylarsinomonoiodoV*d,* **(CH^As -+ Au—I,** m.p. 176-178° (Mann,

Wells and Purdie, *l.*c.) are stable compounds **and** afford further **examples** of the 2-covalency of nitrons gold.

There is some doubt concerning the existence of the so-called anrosoauric bromide and chloride, compounds having the general empirical formula AuXj. Neither of these compounds hits **been** Adequately described, but tAere is reason for believing that they raa-y be capable of existing under .certain conditions and if so it is suggested that their constitutions may be represented thus:



i.e. as a zig-zag chain containing alternate tervalent and 4-covalent auric gold atoms and univalent and 2-covalenfc aurous gold atoms. A formerly suggested constitution, Au[AuX.,|, representing the compounds as aurous salts ia much less **probable.**

Cyanides.—In the presence of air or oxygen **gold** dissolves in an aqueous solution of potassium (sodium) cyanide, the following reactions taking place:

$$2Au+4KCN+2H_2O+O_2 = 2KAu(CN)_2+2KOH+H_2O_2,$$

$$2Au+4KCN+H_2O_2 = 2KAu(CN)_2+2KOH$$

This is the basis of the Me Arthur-Forrest process (1887) most extensively used in gold extraction *(q.v.).* The gold goes into solution as the *potassium (sodium) aurocyanide* which can be obtained in colourless crystals by careful evaporation of a solution of gold monocyanide (auroua cyanide, monoeyanogold, *set below)* containing the calculated quantity of potassium (sodium) cyanide.

Gold Monocyanide (nurous cyaniQe, monocyanogold) was originally prepared by adding hydrochloric acid to an aqueous solution of potassium aurocyanido, carefully evaporating the solution to dryness and washing the **product** with water, it, ia **obtained puw u** a **nnmrhat** yellowish powder by gently heating the dialkyliminocyjinogold compounds («« *below)* above tli'ir melting-poinis. **[ti molecular** weight has not yet **been** determined and the **molecular** formula should be written as (AuCN),,, ita constitution being represented thus,

$$\rightarrow Au-C\equiv N\rightarrow Au-C\equiv N\rightarrow Au-C\equiv N\rightarrow$$

iSibf»' *K*TW- *R*o*y*- Soc- I!l;t<) At 173, 100; *cf.* West, Z. Krint. **1986,** 90. **856).**

Potassium Aurocyanide. **KAu(CN).** *[see above),* is obtained by **cryttalliiation of** the aurous solution prepared by dissolving gold in the presence of air or oxygen in an aqueous solution of potassium cyanide or by **crystallising** ft solution of aurous cyanide in aqueous potassium cyanide solution. It is present in the aqueous solution obtained by the addition of potassium cyanide to hydrochloroauric acid. It is a colourless crystallino salt which yields colourless solutions in water (solubility, 14*3 g. in 100 e,c. at the ordinary temperature and 200 g. in 100 c.c. at 100°). According to Rose and Newman {"The Metallurgy- of Gold," 1037. p. 73), the aqueous solution of potassium aurocyanide used for the electro-deposition of gold may be prepared (i) by dissolving the " fulminating gold." precipitated by adding ammonia to hydrocliloroauric acid, in potassium cyanide, or (ii) by dissolving purified auric hydroxide *(see below)* in aqueous potassium cyanide, or (iii) by passing an electric current through an aqueous solution of potassium cyanide using a gold anode.

The precipitation of gold from aqueous solutions of potassium (sodium) aurocyanide which c«n be represented in ita simplest form by the equation

$$Zn+2KAu(CN)_2=K_2Zn(CN)_4+2Au$$

is u&d industrially. Other metals more electropositive than gold may be used. Oxalie acid, sulphurous acid and mercurous chloride are stated to precipitate aurous cyanide from aqueous solutions of potassium fturocyanide,

Aurocyanides of sodium, ammonium, calcium, barium, zinc and cadmium have been prepared. Like potassium aurocyanide, alt these yield a precipitate of aurgus cyanide with evolution of hydrogen cyanide when treated with mineral acids. Co-ordination compounds of potassium aurocyanide with 2:2'-dipyridyl and 4:5-(o-)phenanthrolino in'which the auroua gold atoms are 4-rovalent have been investigated by Dothie, Llewellyn, Wardlaw and Welch (J.CiS. 1939, 426).

The cyano derivative of tervalent gold {auric cyanide) has not been prepared.

Potassium Auricyanide (potassium cyanoaumtc), **2KAu(CN)$_4$,3H$_2$O,** is **described** as being obtained in colourless crystals by adding art aqueous solution of potassium cyanide to sodium ehloroaurate until the precipitate formed redissolvcs.and carefully evaporating the solution which should be colourless- *{see* Potassium Aurocyanide). Derivatives of potassium auricyanide (cyanoauratc) in which the cyanogen radical is **replaced by** halogens (not fluorine) have been described (Limlbom, Her, 1877, 10, 172-1).

Oxides of Gold.—The lower oxide of gold, which would **be expected to** have the empirical formula **Au$_2$O,** docs not exist. A critical and experimental revic'V of the composition of tho material prepared as described by Kiguier (Ann. Chim, Phys. 1844, **[Hi], II,** 339), by Krnsa (Annalcn, 1887, 237, 270} and by his own more HuitiiMo method* has beer- made by Pollard (J.OJB. **1926,** 1347), who concludes that **material described aa** "aurous oxide" is a mixture of gold and auric oxide (Au_2O_3) and dcKis not exhibit reactions of auroua **compounds***

Gold Trihydroxide (auric **hydroxide) having** the empirical formula $Au(OH)_3$ is obtained (i) by heating an aqueous solution of hydrochloroauric acid with excess of magnesium oxide and washing the precipitate thoroughly with dilute nitric acid, (ii) by adding an aqueous solution of potassium hydroxide to one of hydrochloroauric acid until the precipitate just redissolves, boiling the dark brown solution until the supernatant liquid becomes pale yellow, adding a slight excess of sulphuric acid and washing the precipitate. It may be further purified by dissolving the precipitate in concentrated nitric acid, precipitating finally with water and drying under reduced pressure.

When allowed to stand over phosphorus pentoxide it is converted into a substance which has been described as *auryl hydroxide* but which may be the unstable *auric acid,* $H[AuO_2J$. When the trihydroxide is heated at 140° it is converted into auric oxide, Au_2O_3, a brown powder (Krüss, Annalen, 1887, 2S7, 290).

When auric hydroxide is warmed with alcoholic potassium hydroxide it is reduced to the metal, which is frequently deposited in small glistening scales used in mediaeval times in painting miniatures. By the action of hydrochloric and hydrobromic acids, auric hydroxide is converted into hydrochloroauric and lfydrobromoauric acids respectively.

Auric hydroxide is soluble in an aqueous solution of potassium hydroxide and this solution on evaporation at the ordinary temperature under reduced pressure yields small pale-yellow needles of *potassium aurate,* $KAuO_2,3H_2O$. Aqueous solutions of this salt are strongly alkaline. The corresponding barium* salt, $Ba(AuO_2)_2,5H_2O$, is sparingly soluble in water. Other salts are also known.

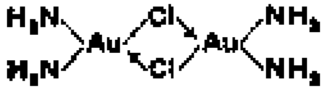
The so-called *auroauric oxide* having the empirical formula AuO, and which would correspond to halogen compounds having the general empirical formula AuX_2 *(see above),* is described as being produced by heating auric hydroxide at 160° (Krüss, Ber. 1886, 19. 2541).

Sulphides.—It would appear that the early work (Ditte, Compt. rend. 1895,120,320; Levol, Ann. Chim. Phys. 1850, [iii], 30, 355; Hoffmann and Kruss, Ber. 1887, 20, 2674) on the compounds of gold and sulphur having the empirical formulae Au_2S and AuS, respectively, and produced by the action of hydrogen sulphide on solutions of aurocyanides and chloroaurates, respectively, needs revision. The salt, *sodium aurosulphide,* $NaAuS,4H_2O$, corresponding to a sulphide, Au_2S, is obtained by heating metallic gold with sodium sulphide and sulphur, extracting the fused mass with water, filtering and evaporating the solution in an inert atmosphere at the ordinary temperature. The salt crystallises in colourless monoclinic prisms which rapidly become brown on exposure to air. The solution of gold in " liver of Bulphur " was known to Glauber and Stahl.

Auric Sulphide, Au_2S_3, was described as being obtained as* deep yellow precipitate by treating anhydrous lithium chloroaurate with hydrogen sulphide at -10° (Antony and Lucchesi, Gazzetta, 1890, 20, 601; 1891, 21, ii, 209), but this method of preparation seems unlikely to lead to a pure product. Gutbior and Diirrwächter (Z. anorg. Chem. 1922, 121, 266), who could not prepare the other sulphides *(see above),* obtained the pure auric sulphide by passing a rapid stream of hydrogen sulphide at -2° through a dilute (less than 2%) solution of hydrochloroauric acid in JV-hydrochloric acid, It is a dark-coloured powder soluble in sodium sulphide i forming sodium aurisulphide having probably the formula $NaAuS_2$ analogous to $NaAuCI_4$. It is also soluble in potassium sulphide solution.

Fulminating Gold.—There are several varieties of the explosive substances known by the historic neme of " fulminating gold." Earlier work on thib difficult subject (Dumas, Ann. Chim. Phys. 1830, [ii], 44, 167; Baschig, Annalen, 1886, 235, 341) has been the subject of a critical review and a detailed experimental study by Wutfc(i6id. 1915, 410, 117-222).

Some of the better known " fulminating golds'* (if individual substances) contain halogen in addition to nitrogen, which must ahvaya be present. The greyish precipitate obtained by the action, of excess of ammonia on an aqueous solution of hydrochloroauric acid appears to be a mixture *(A)* of two compounds to which the formulae $Au_2O_3>3NH_3$ *(sesquiamminoauric oxide)* and $HN:AuClNH_2$ *(aminoiminoauric chloride)* have been assigned. Assuming the correctness of such formula) for explosive substances, it is not surprising that they do not necessarily conform to the formulae of normal gold compounds. The yellow precipitate obtained by adding a dilute solution of hydrochloroauric acid containing ammonium chloride to a cold saturated solution of amfionium chloride containing ammonia is stated to be an individual and to have the formula $Au(NH_2)_2CI$ (diaminoauric chloride) and is not explosive. This compound is stated to contain water, but the compound itself may be a normal auric compound having the constitution :



Treatment of this compound with an excess of water furnishes an explosive compound containing no Tialogen and to which the empirical formula $3AuO$-$2NH_3,nH_2O$ has been assigned, and sucl\a formula cloes not appear to be that of a normal gold compound.

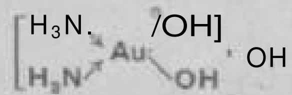
One of the most sensitive of the " fulminating golds" has been given the formula Au_2O,-2NH,. It is a black substance the constitution of which cannot be formulated as that of a normal auric compound. It is obtained by treatment with hot water of *sesquiamminoauric hydroxide,* $2Au(OH)_3$-$3NH_a$, which is itself obtained by the action of excess of ammonia on the mixture *(A)* mentioned above.

In the light of our present information, the proposed classification of " fulminating golds " into two types of compounds in which the atomic ratios of gold to nitrogen are respectively 1:1 and 2:3 cannot be adhered to rigidly. It is probable that more satisfactory knowledge regarding the constitution of " fulminating golds " may be obtained, an indicated by Weitz (*l.c.*). by [a] further study of tetramminoauric compounds some of which have been referred to above. Alkaline aqueous solutions of 4etram-mmoa-urio nitrate on standing yield explosive precipitates.

One variety of " fulminating gold " has been prepared by a reaction which may be represented thus:

$$HAuCl_4+6NH_3+3H_2O$$
$$=4NH_4Cl+[Au(NH_3)_a(OH\hat{\ }]OH$$

It is a yellow precipitate, explosive but not *no* sensitive as other varieties mentioned above. The compound may be dianiminodihytlroxyic hydroxide having tbi constitution:



Salts.—Since gold does not yield salts containing either aurous or auric ions the existence of such compounds as the so-called auroua sulphate, auric sulphate anc^auric chromata ia very doubtful. On the other hand, SchottliLnder (»6«t. 1883, 217, 312) by the action of concentrated sulphuric acid on "auryl nitrate" *{set below)* at 200° obtained yellow octahedra of wliat he described as *auryl hydrosulpkate.,* AuO'HSO₄. When this compound ia treated with one-tenth, of its weight of potassium hydrogen sulphate and the mixture evaporated at 200' it yields yellow rhombic crystals of what he described as *potassium disulphatoaurule.* He also prepared the corresponding silver salt. The constitution and systematic name of each of these substances maf be respectively, •

OxysulphatoaurJr arid.

Potassium dlsulphatoaurate.

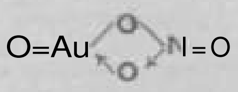
For similar reasons, the existence of compounds which have been described as aurous and auric nitrates must bejregarded as doubtful. Again, on the other hand, Schottla*tder *(I.e.)* obtained golden-yellow triclinic crystals of *hydrtmitratoauric acid* by cooling the solution of auric hydroxide in nitric acid (density, 1-5) in a freezing mixture. The same acid was obtained by Jeffery (Trans. Faraday Soc. 1916, 11, 172) by electrolysing nitric acid (1:2) using a porous pot and a gold anode and evaporating the yellowish-brown anodic solution over sulphuric acid and sodium hydroxide. The acid is decomposed by water and both authors assign to it the formula $H[Au(NO,)A3H_sO$, analogous to hydrothloroauric and hydrobromoaurie acids, $H[AiiX_4],3H.O$. The ammomum, potassium and rubidium salts have been described by Schottlandor

The *auryl nitrau* which 8chottlander (I.e.) obtained as on amorphous mass by dissolving auric hydroxide in nitric acid (density, 1*4) and to which he gave the formula

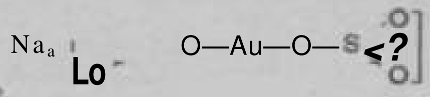
$$AuONO_3,5H_aO$$

may not be » salt in the strict sense of the term; in accordance with the 4-covalency of tervalent gold its constitution may be written as

or, less likely, aa



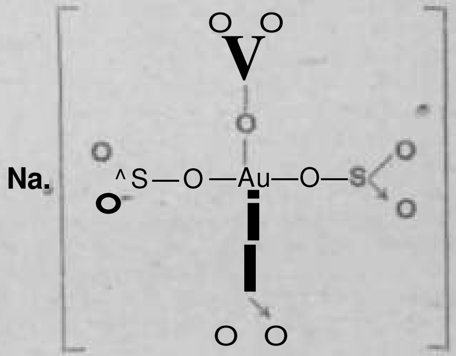
A number of complex sulphites have been described. One of these (Himly, Annalen, 1848, 59, 95) having fche formula $Na_3Au\,(SO_3)_t,2H,O$ may be aa aurous compound having the constitution:



The yellow compound having the formula

$$Na_BAu\{SO_{.,})_4,5H_2O$$

(Oddo and Mingoia, Gazzetta, 1927,57, 820; *cf.* Kosenheim, Hertzm.inn and Pritze, Z. anorg. Chem. 1908, 59, 198) and which ia prepared by neutralising hydrochloroauric acid with sodium hydroxide and adding a solution of sodium sulphite, filtering and precipitating with alcohol may, bearing in mind its colour, be an auric compound having the constitution:

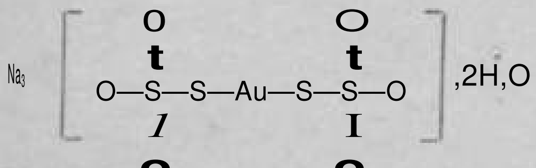


The corresponding potassium salt haa also been prepared.

Sodium Aurotniosulphate, FordoB and Gelis' salt (Ann. Cbim. Phys., 1845. [iii], 13.344), although long known as a complex auroua com* pound and used in, the toning of silver photographic prints, has been of considerable interest since 1924 when it was introduced by Mollgaord of Copenhagen under the name " *Sanocrystn* " for the treatment of tuberculosis. Later, along with ""many other complex aurous compounds, it has been used in the treatment of rheumatoid arthritis, and it ie not improbable that " gold therapy " may he extended considerably *{see below).* Its constitution has been expressed by the formula $3Na_2S_2O_3Au_aS_2O_3,4H_2O$ which cannot be correct since this colourless crystalline salt gives no reactions of a thiosulpliato and aurous gold doc3 not form salts containing aurous ions.

It was originally prepared by the gradual addition of a 2% solution of sodium chloro-auratc to an aqueous solution containing 4 mol. proportions of sodium thiosulphate. After the red liquid had become colourless the Bait was precipitated by the addition of alcohol and was purified either by repeated precipitation from its aqueous solution by means of alcohol or by recrystallisation from water. In the preparation just" described part of Jhe sodium thiosulphate reduces the auric compound to the auroua condition, being itself converted into tetrathionate. Consequently several modifications of the preparation have been introduced. These consist essentially in carrying out the reaction using suitable redwing agents whereby.all the sodium thiosulphate employed reacts with the reduced gold compound as soon as it is formed.

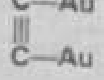
The constitution of the compound should be expressed thus:



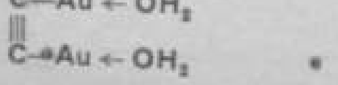
$$Na_3\left[\begin{array}{c}\quad O \qquad\qquad\qquad\quad O\\ \quad\uparrow \qquad\qquad\qquad\quad \uparrow\\ O-S-S-Au-S-S-O\\ \quad\downarrow \qquad\qquad\qquad\quad \downarrow\\ \quad O \qquad\qquad\qquad\quad O\end{array}\right],2H_2O$$

in keeping with the 2-covalency of aurous gold and with the fact that the compound does not give the usual thiosulphate reactions, The corresponding barium salt has been prepared by double decomposition between the sodium salt and barium chloride and the free acid has been obtained by treating the barium salt with the calculated quantity of sulphuric acid.

Sodium aurothiosulphnte is somewhat sparingly soluble in water at the ordinary temperature and possesses a curiously sweet taste It is stable but, as ordinarily prepared, when exposed *o air it becomes yellowish-brown, decomposition having set in. Its solution is not reduced by ferrous sulphate or oxalic add nor decomposed by hydrochloric acid. When [illegible] aqueous solution the so-called auro«* aottylidt, C_2Au_2, is produced as a yellow precipitate which is erosive when dry (Matthews and Watters, J. Amcr Owm Soc. 1900 22, 108; .Vol. II 28 [illegible]. The constitutional formula



is not in keeping with the 2-covalency of aurous gold, which would however be satisfied by the formula



Like other acetylides, it is decomposed by hydrochloric acid yielding acetylene and, in this case, gold mono chloride.

Complex Imido Compounds.—A number of complex succinimido derivatives mostly containing auric gold have been described by Pope (B.P. 338506/1929; B, 1931, 319). The compounds are prepared from auric hydroxide, chloroaurates, hydrochloroauric acid or fulminating gold and succinimide in the presence of ammonia or am-Ws. Among the compounds isolated are;

[(Nvl$_s$)jAuSiijlCI, diamminodisuccinimidoauric chloride,

[(N H$_3$)JAUSU,]AIJC1 j; diaraminodisueeinimidoaurie chloroaurate,

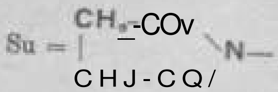
[(NH$_a$Me)$_a$AuSu$_z$]CI,dimonomct.hy]amminoaisuceinimidoauric chloride,

[(NHEt$_s$)jAuSu$_2$JC;, didiethylamminodisuceinimidoauric chloride,

[(N H Et,)$_?$ AuSu$_2$]AuSu$_s$, didiethylamminodrsuccininiidoauriceuccinimidoaurate,

NH$_3$AuSu$_3$, inonoamminotrisuccinimi'iogold,

SStr/? ff MnimidoauroM acid, H[AuSu$_2$], and salts of dichtorodisuecinimidoaurie acid, HfCl^uSu-J, where



Other examples of complex imido compounds belonging to this series are hydrodiphthalimidohydroxyaunc acid, H[Phth.Au(OH)$_a$], where

(Gibson and Tyabji, [illegible]) and iiydrodimethyiglyoxtminylbromoauric acid,

$$\left[\begin{array}{ll}CH_3-C=N-O\searrow & Br\\ & \quad\vert\\ CH_3-C=N-O\nearrow & BrJ\end{array}\right]$$

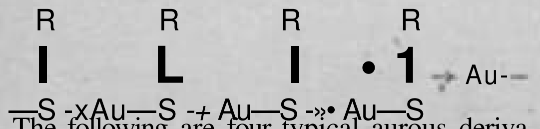
(Brain and Gibson, private communication). Complex derivatives (imidoaurie acids) of sueon unide, phthalimidc, 5;5-dicthylbin hit uric acid and o-bemoicBulphinide (sncchnrin) have also been described by Kharasrh and Isbcll (J. Amer. Chem. Soc. 1931, 53, **8069).**

Other InorganiCjGold Compounds Containing .Complex Organic Radicals.—In view of the use of complex (chiefly aurous} compounds in the therapeutical treatment of tuberculosia^faee Sodium Aurothiosulphate, "A'ajio. *crysin* ") and their increasing application in the treatmeptof other conditions, especially rheumatoid arthritis, a large and rapidly increaBing number of aurous derivatives of organic compounds have been prepared,generally by nx-thodB winch are the subjectR of patent* (c/.'" Handbuch der Cheraotherapie," Fischl and JScblossberger, [illegible] Leipzig. 19[illegible].

The compounds are generally prepared by the action of the organic compound (part of which act [illegible] reducing agent) on alkali halogenoaurates (usually sodium chloroaurate) [illegible] in the presence of a auit- rcdticfng [illegible] (Bodiura Bulphite, etc.).

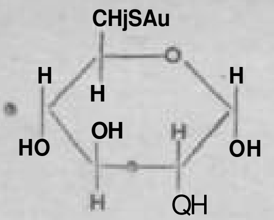
Many of the compounds are soluble in water and such aqueous solutions may be administered intravenously; others may not be soluble in water and these as well as the former may be administered intramuscularly in oil suspension.

Many of the aurous compounds which have been described are derivatives of substances (such as mercaptans) cont^ning the —SH group and in the literature are frequently given the constitutional formula of the general type —**SAu.** Such a general formula does not xllow for the 2-covalency of aurous gold and cannot be correct. The simplest aurous derivatives of mercaptans are generally highly insoluble compounds having high molecular •> weights. Their constitution may be written (R—S—Au)« or, in extended form, as <t



R R R R
I L I •1 Au-–
—S -xAu—S -+ Au—S -»• Au—S

The following are four typical aurous derivatives of organic compounds which (in addition to sodium aurothiosulpha+e, frequently known as "*Sanocrysin,"* but other proprietary names have also been allotted to it) have found considerable therapeutic application: "*Holganol B* " described as goldthioglucose and, in the literature, given the constitutional formula



" *Lopion* "ia sodium S-allylgoldthioureabenzoate and in the literature is given the formula (G.P. 651421)

$NaO_2C{\cdot}C_6H_4{\cdot}NH{\cdot}C(SAu){:}N{\cdot}CH_2{\cdot}CH{:}CH_2$

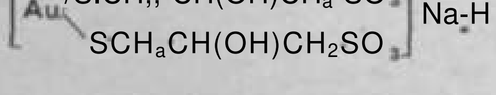
" *Myoehrysin "* is disodium aurotbiomalate and stated to have the formula

NaOOCCHfSAuI-CHjCOONa

" *Alfockryzine* " (Lumiero and Perrln, Compt. rend. 1927,**184,** 289) is given in the literature the constitutional formula „

$$AuSCH.CH(OH)CH,SO_aNa \\ + HS\text{-}CH_{i!}CH(OH)\text{-}CH_3SO_3Na$$

but thia compound may have a constitution analogous to that of sodium aurotbioeulphate thus;



$$\left[Au\begin{matrix}/S.CH,,\text{-}CH(OH)CH_a\text{-}SO_3\\ \backslash SCH_aCH(OH)CH_2SO_3\end{matrix}\right]Na\text{-}H$$

OEOAHIO COMFOUHDS OF GOLD.

Apart from the already known cyano compounds and the acetylido (*ee *above),* the first typical organic compounds of gold were prepared by Popo and Gibeon (J.C.S. 1907, 91, 2061); and their investigation has been carried out chiefly by Gibson *et al.* {*ibid.* 1930, 2531; 1931, 2407; 1934, 860; 1935, 219, 1024; 1937, 1690; 1939, 762; Ann. Report Brit. Assoc. 1938, 35).

Diethylmonobromogald, **(EtjAuBr),,** may be prepared starting from hydrobromoauric acid, $HAuBr_4,3H_aO$, gold tribromide, $(AuBr_3)_f$, pyridinotribromogold, CjHjNAuBrj, or, most conveniently, from the corresponding trichloro-eompound.

To a mechanically stirred suspension of pyridinotrichlorogold (19 g.) in dry pyridine (200 c.c.) at 0° is added a filtered solution of ethylmagnesium bromide (2-2 mol.) in ether (45 c.c). Water (100 c.c.) at 0° is then added followed by ligroin (b.p. 60-80°; 300 c.c.) and then hydrobromic acid {*&* 1-49 ; 300 c.c.) at such a rate that the temperature does not rise above 40". The liquid (two layers) is filtered from solid matter and the ligroin solution separated. The aqueous solution is extracted several times with ligroin. To the combined ligroin extracts, after washing with water, ethylenediamine is added until no further colourless precipitate (ethylenediamino-•diethylgold bromide, *see below)* is produced. The colourless precipitate is dissolved by shaking the ligroin suspension with water and the separated aqueous solution acidified with hydrn-bromic acid. The colourless precipitate, diethylmonobromogold, is separated, washed with water and dried at the ordinary temperature. It may be purified by dissolving in redistilled ligroin (b.p. 40-60°) and allowing the solution to evaporate at the ordinary temperature.

Diethylmonobromogold crystallises from li* groin in soft coloifless anorthic needles, m.p. 58° (decomp.). It is soluble in all the usual organic solvents and when pure is fairly etable, decomposing superficially (violet colour) on exposure to light. Its molecular weight in freezing benzene and bromoform shows that the molecular formula is (EtjAuBr), and its constitution may be conveniently expressed aa

the auric gold atoms being 4-covalent. This constitution is in agreement with the results of X-ray erystallographic investigation **which** has also shown that the four valencies attached to the 4-covalent auric atoms are planar. Diethylmonobromogold and certain related organic gold compounds when dissolved in a suitable solvent *(e.g.* ethanol) undergo an interesting spontaneous decomposition at the ordinary temperature on treatment with alkali or alkali metal alcoholate; brilliant gold films are produced which can be deposited on a variety of surfaces (Gibson, B.P. 49724t>).

The following derivatives among others have been prepared:

Ethjlenediaminodiethylgold bromide,

$[Et_aAuen]Br$,

a stable coolurless crystalline salt, decomp. from 182°, soluble in water («w *ahove).*

Monoamminodiethylbromogold,

$Et_2Au(NH_3)Br$,

a colourless crystalline non-electrolyte, insoluble in water and soluble in benzene.

PyridinodielhylbromogoU, $Et_2Au(C_5H_5N)Br$ a colourless crystalline non-electrolyte, very similar in general properties to the preceding ammino compound.

Dibenzylaulpkidodiethylmonobromogotd,

$Et_2Au\{S(C_7H_7)_2\}Br$,

a colourless crystalline non-electrolyte, m.p. 91*.

2:2'-DipyridyItelraetkyldibTomodigotd, also a colourless non-electrolyte which has m.p. 169° (decomp.); its constitution may be briefly written

$$Et_2BrAu \leftarrow NC_5H_4—C_5H_4N\rightarrow AuBrEt_2$$

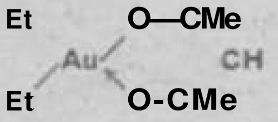
The compound *monoethyhnediaminotetra-n-propyldibromodigold,* a derivative of di-n-propylmono bromogold *(see below)* and analogous to the above dipyridyl compound, is also a non-electrolyte and its colourless solution in chloroform becomes cloudy owing to the following equilibrium being set up:

$$2Pr^a_2AuBrenAuBrPr^a_2 \rightleftharpoons Pr^a_2AuenJBr+HPrV^uBrJj$$

This compound has m.p. 110-111°, when gas is evolved; on further heating the product decomposes violently at 140°. The first of these changes also takes place when benzene or chloroform solutions of the substance are gently boiled, *meiiidkyUnediamiiiodi-n-pmpyldibromodigoid*—a typical example of a mixed auric-aurous compound in which the auric and aurous gold atoms are 4-covalent and 2-covalent respectively—being produced with the initial evolution of free w-propyl radicals, the reaction taking place being represented,

$$Pr^a_2AuBr\cdot en\cdot AuBrPr^a_2 \rightarrow Pr^a_2AuBr\cdot en\cdot AuBr+2Pr^a$$

By the interaction of diethylmonobromogold and thallous acetylacetone, *acetylacetonediethylgold* is obtained in colourless flat plates, m.p. 9-10°. Its constitution is represented thus:



The corresponding diuieihyl compound has been prepared. From the diethyl compound by the action of sodium iodide (chloride) *dietkylmonoiodo>(chloro)yoUt* is obtained and the corresponding salts *tthyUiwdiaminodiethylgold iodide* and *chloride* have been obtained from the latter compounds by the action of ethylenediamine"

Using magnesium methyl iodide and adopting a similar procedure *dimelhylrnvrtoiodogold,* colourless needles, melting and decomposing at 78-5°, has been obtained. It is more sparingly soluble than diethylmonobromogold and yields derivatives analogous to those of the latter compound.

Di'^propylmonvbromogoid (colourless liquid, crystallising below 0°) and *di-n-butylmonobromogold* (colourless liquid) have been prepared by the method used for the preparation of the other dialkyl compounds. These have also been converted into their colourless ethylenediamine co-ordination compounds. *Dibtnzitlmonobromogold* is much less stable than the above dialkyl compounds, hut its colourless ethylenediamine co-ordination compound, *ethylenediaviinodibenzylgold brotnVde,* is moderately stable (Gibson, private communication). Using methods identical with those first described by Pope and Gibson *(l.c.),* Kharasch and Isbell (J. Amer. Chem. Soc. 1931, 63, 2701) also prepared a number of dialkyl and diaryl gold halides; these authors did not determine the molecular weight a of any of the compounds which generally were characterised only by their gold content *(cf. Gibson et al., J.C.S.* 1931, 2409; 1935, 1024),

By the action of bromine (2 mol.) on the above dialkyl compounds (1 mol.) in a suitable solvent at the ordinary temperature deep-red crystalline compounds having the general empirical formula $RAuBr_2$ are obtained, and the ethyl and *n*-propyl derivatives have been investigated in detail. These *monoalkyldibro'moqold* compounds have been shown by physical investigation (molecular weights, dipole moments, etc.) to have the general constitution:

This constitution is in keeping with their chemical properties. When allowed to react with hydrobromic acid they yield the dialkylmono bromogold compounds and hydrobromoauric acid; with sodium bromide they yield similarly the dialkylmonobromogold compounds and sodium bromoauratc; with ethylpiiediainine they yield the etbykjiediuminodialkylgold bromides and diethylenediaminoauric bromide. This last reaction may be represented thus:

$$+3en=[R_2Auen]Br+[enAuen]Br_3$$

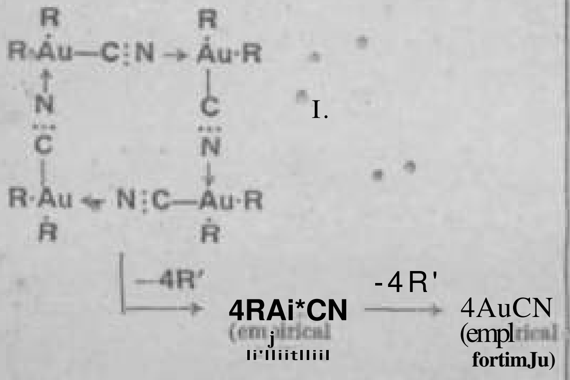
The monoalkyldibromogold compounds decompose on being gently heated. This decomposition has been shown to proceed quantitatively thus: .

$$=2RBr+2AuBr$$

\JKA liold Monobromide, p. 113c).

By the action of silver cyanide on diethyl and di-n-propylmonobromogold the corresponding colourless and highly crystalline cyano-compounds have been obtained. These compounds which are readily soluble in hydrocarbon, and other organic solvents have the molecular formula $(R_aAuCN)_4$ and their constitution is represented by (I). This has been completely confirmed by the resulta of dipole momerrt determinations and by X-ray crystallographic investigations (Phillips and Powell, Proe. Roy. Soc. 1939, A, 173, 147).

hiilliylmonocyanogold. when^ merely vigorously rubbed undergoes "explosiCs" decomposition and *di-n-propytmonocyanogold* undergoes a similar decomposition when heated above ita melting-point (94-95°), the decomposition taking place may be represented thus:

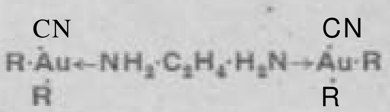

I.

Fre> radicals, ethyl and n-propyl {R') are evolved and have been recognised (from the diethyl compound) as n-butane and {from the di-n-propyl compound) as n-hexane.

Compounds having the empirical formula RAuCN are almost insoluble in organic solvents and have high (and at present unknown) molecular weights; they are also produced from compounds of type (I) by long standing at the ordinary temperature <<•/. Kharasch and IsbelT, *l.c).* They are mixed aurous and auric compounds in which the aurous gold atoms are 2-covalent and the auric gold atoms are 4-covalent, In view of the fact that the four valencies of. auric gold have a planar distribution, and that the two valencies of aurous gold have a linear distribution, the constitution of compounds having the empirical formula RAuCN cannot be represented by a planar ring structure which would also not be in keeping with their very low solubility. Their constitution can, however, be satisfactorily represented by a zig-zag chain structure;

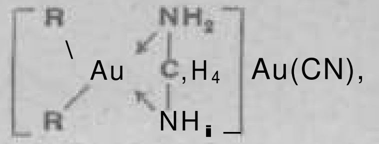
Such a constitution U in keeping with their insolubility and, unlike the parent substance, with their having no melting-points. Further and complete loss of hydrocarbon radicals results in the production of aurous monocyanidc (aurous cyanide) which, as pointed out above, probably possesses a straight chain structure (Gibson, 1'n.c. Roy. Soc. 1939, A, **173,** 100).

Compounds of type (I) yield ethylenediamine derivatives having the general formula



$$R\cdot\overset{CN}{\underset{R}{Au}}\leftarrow NH_2\cdot C_2H_4\cdot H_2N\rightarrow\overset{CN}{\underset{R}{Au}}\cdot R$$

These are colourless crystalline n on-electrolytes. When suspended in water and the mixture heated, solution takes place gradually; free radicals—identified as the corresponding hydrocarbons—are evolved initially, and the clear solution yields after evaporation a colourless crystalline salt having the formula



These aurocyanides of type IV may also be obtained by boiling benzene solutions of compounds of type HI and recrystallising the resulting solid products from water. On treatment with sufficient mineral acid to combine with the ethylenediamine they are converted into the compounds having the empirical formula RAuCN, type II.

The "phenylauric chloride," having ths formula PhAuCI, and m.p. 73-75°, which has been described by Kliarasch and I a boll, (J. Amer. Uitm. Hoc. 1931, 53, 3055) and which waB prepared by the addition of auric chloride, to an excess of pure benzene, does not appear to have **either** a constitution or properties analogous to those of the monoalkyldibromogold compounds (c/. J.C.S, *1964, Stilt* 1935, 1024 (footnote)). If such a compound does exist PhAuCI, would only represent its empirical formula. The compounds prepared similarly from toluene, diphenyl (decomp. at 66°) and methyl ealicylate (HI.p. 107° decomp.) contain a molecule of water in each case even after recrystalUsation from ether.

The compound *aurous chloride carbonyl,* classified by Kharaach and Iabell (J. Amur. Chem. Soc., 1930. 62, 2919) as an organic gold compound, was first prepared by -Mancliot and Gall (Bor. 1925, 68 [B]» 2175) by passing carbon monoxide over gold trichloride at 95°. Kharasch and Isbell prepared it from aurous chloride in beniene suspension (20-30") and from gold trichloride in totrachloroethylene (100-140°). It is a colourless Bubstance soluble in organic BolvenU and decomposed by water. IU molecular weight is normal in freezing benzene and the compound dissociates in hot solvents and when heated under reduced pressure yielding pure aurous chloride. It is suggested that its constitution should be expressed,

$$O \equiv C \rightarrow Au—Cl,$$

in keeping with the 2-covaiency of aurous gold and with the linear distribution of the two valencies. With pyridine and hexamethylenetetramine carbon monoxide is evolved and (presumably) co-ordination compounds of aurous chloride *(e.g.* H_5C_6N - Au—Cl) are formed.

Aurous chloride carbonyl reacts with arylmagnesium halides giving good yields of bis-aromatic, hydrocarbons (diphenyl, feo-tolyl, di-p-tolyl dibenzyl, aa'-dinaphthyl), carbon monoxide being evolved and gold precipitated.

C. S. G.

GOLD, MANNHEIM. A brass containing 80% copper and 20% zinc.

GOLD, MOSAIC. A fine, flaky, yellow form of stannic sulphide which is now used only to a limited extent to imitate bronze. It is prepared by gently heating a mixture of 7 parts of sulphur, 6 parts of ammonium chloride and 18 parts of a powdered amalgam containing 12 parts of tin to 6 parts of mercury, until the odour of sulphuretted hydrogen is no longer perceptible. The residue is then heated to low redness and a mixture of mercurous chloride, ammonium chloride and cinnabar sublimes, while the mosaic gold alone remains. A good product is also obtained by heating a mixture of 5 parts of stannous sulphide and 8 parts of mercuric chloride.

A pale yellow mosaic gold is produced- by heating 50 parts of crystalline stannous chloride with 25 parts flowers of sulphur; a reddish-yellow product is obtained on heating together 50 parts 50% tin-amalgam, 25 parts stannous chloride, 35 parts ammonium ohloride and 35 parts of sulphur (Lagutt, Z. angew. Ghem. 1897, 11, 557). The temperature used should not be too high, as the stannic sulphide, when strongly heated, loses one equivalent of sulphur and becomes black.

Mosaic gold is insoluble in nitric and hydrochloric acid, but dissolves in *aqua regia* and in alkaline hydroxides.

A brass containing 52-55% zinc has also been known by this name.

C. O. B.

GOLD NUMBER *(v.* Vol. Ill, 2876).

GOLD PURPLE *(Purple of Cassius).* This product consists of a mixture of metallic gold and tin oxide. An imperfect description of its preparation was given by Andreas Cassius (" De Auro," 1685). It is obtained as a fine flocculent purple precipitate on addition of a solution of stannous chloride, which contains some stannic chloride, to a dilute neutral solution of gold chloride. The presence of stannic chloride is essential as puro stannous chloride produces only a brown precipitate. T. K. Rose (Ghem. News, 1892, 66, 271) has shown that the formation of the colour is capable of detecting 1 part of gold ^100,000,000 parts of: water when the Lest is carried out under specifio conditions.

A very fine product is obtained by adding stannous chloride to ferric chloride until the solution is of a pale green colour and employing this mixture to precipitate the gold from solution. R. Zsigmondy (Annalen, 1898, 301, 361) prepared Purple of Cassius by mixing 200 c.c. gold chloride solution (3 g. Au per litre) and 250 c.c. stannous chloride solution (3 g. Sn per litre) with a very slight excess of HCI and 4 litres of water. After 3 days the purple was deposited, leaving a liquid free from gold and tin. The precipitate thus prepared contained, after ignition, 40-3% gold and 59-7% stannic oxide.

According to H. Moissan (Compt. rend. 1905, 141, 977), when gold-tin alloys, mixed with lime, are distilled in air, a finely divided mixture of stannic oxide, lime and gold is obtained having the colour and properties of Purple of Cassius. Similar deposits of varying tint can be obtained by substituting for lkne other oxides such as zirconia, silica, magnesia or alumina.

Purple of Cassius may also be obtained in great beauty by treating an alloy of gold 2 parts, tin 3*5 parts and silver 15 parts with strong nitric acid to dissolve the silver and oxidise the tin (Müller, J. pr. Chem. 1884, [ii], 30, 252). E. A. Schneider (Z. anorg. Chem. 1894, 5, 80) obtained gold purple by treating an alloy of gold, tin and silver with concentrated nitric acid. The resulting black powder was washed with ammonia when a ruby-red coloured solution was obtained which was dialysed until it contained no more ammonia. Potassium cyanide decolourises this solution and stannic oxide separates. With mercury, the solution becomes brownish-red and gold is extracted; with excess of hydrochloric acid, the solution becomes violet and yields finely divided gold on dialysis. According to this author, the soluble form of purple gold is possibly a mixture of the hydrosols of gold and stannic acid.

Purple of Cassius is used in the manufacture of artificial gems *(v.* Vol. V, 513c), and for imparting a red, rose or pink colour to glass, porcelain or. enamel; it varies in colour from a violet to a purplish-red or brown.

In the dry state, gold purple is insoluble in either strong or dilute alkalis, but when moist it dissolves in water in the presence of very small quantities of alkalis. Salts and excess of acids and alkalis precipitate the purple from these solutions. Whilst moist, it is also soluble in ammonia with the production of a purple colour from which the precipitate is redeposited on addition of an acid or on boiling, and in the latter case is not again soluble. The ammoniacal solution precipitates gold on exposure to light. The purple does not pass through the membrane of a dialyser.

When dried and triturated, the Purple of Cassius acquires a metallic lustre, but no gold is removed from it by the action of mercury. It retains water at 100°, but gives it up and acquires a brick-red colour when ignited, and loses its colour at the melting-point of gold .without the evolution of oxygen.

On adding a greater quantity of mercuroiw chloride to a solution of auric chloride than that required for the reaction:

$$3HgCl+AuCl_3=3HgCl_t+Au,$$

the characteristic colour of Purple of Cassius is obtained. If barium sulphate suspended in water is previously mixed with the mercurous chloride, the sulphate takes up the gold and acquires the purple colour. Antony* and Lucchesi (Gazzctta, 1896, 26, ii, 195) therefore regarded true Purple of Cassius as being not a compound but merely stannic oxide mechanically covered with gold.

M. Miiller (l.c.) also prepared Purples by several processes without the use of tin. A pale rose (containing 0·1 % gold) to deep carmine pigment is produced by igniting a well washed and dried mixture of magnesium oxide and gold chloride. A similar result is obtained by heating the mixture in a current of hydrogen. Lime, calcium carbonate, calcium phosphate, barium sulphate and lead and zinc oxides give similar but less satisfactory results.

The most intense purple is obtained by treating a mixture of aluminium hydroxide and gold chloride with grape-sugar solution. The mixture is agitated and heated until of a bright scarlet colour, but the colour must not be allowed to reach a purplish-red or the resultant product will be of inferior brilliancy.

Similar purples, but less brilliant than those with magnesia and alumina are obtained with tin; 11·5 g. of stannous chloride are dissolved in 200 c.c. of water, gold chloride added and the solution rendered alkaline by the addition of potassium carbonate. Grape-sugar solution is now added and the mixture is diluted to 300 litres and is then warmed until of the required colour.

C. O. B.

"*GOMENOL*" A trade name for an essential oil prepared from the leaves of *Melaleuca Viridiflora* Linn. (Fam. Myrtaceae), found in New Caledonia. It is similar to, if not identical with, oil of cajuput (*q.v.*).

C. T. B.

GONDANG WAX (? Getah Wax). A wax recovered from the latex of the Javanese wild fig-tree (v. Vol. V, 1716).

GOND BABUL (*v.* Vol. I, 585a).

GONIOMETER. The goniometer is an instrument for measuring the angles between faces in crystals. The constancy of the angle between corresponding faces in different crystals of the same substance is the most striking feature of obviously crystalline matter and was, naturally, the first to be studied quantitatively.

In crystalline matter the atoms or molecules are arranged in a regular pattern in three dimensions. Many crystalline substances develop external faces, the presence of which was commonly taken to be the distinguishing mark of the crystalline state but which we now know is not essential. But when a crystal has external faces these are parallel to planes of atoms in the structure so that the external faces are regularly arranged and define the internal regularity of construction of the crystal. Because of this symmetry the faces lie in zones, groups of faces in a "zone" being all parallel to a direction which is called the zone-axis. The measurement of the angles between faces is of fundamental importance in the study of the symmetry of crystals and is of great help in their identification.

The Contact Goniometer was invented by Wangeot in 1780 and was used by the crystallographers Rome* de l'Isle and the Abbe' Hatty. It consists of a semi-circular protractor graduated in degrees, with a straight bar pivoted at the centre. With this instrument it is possible to measure the angle between faces only if these are fairly large.

In 1809 Wollaston invented the Reflecting Goniometer, the principle of which is used in modern instruments although these have been greatly improved. The reflection of a fixed image is obtained over a reference mark from two faces in turn, and the angle through which the crystal is turned between the two reflecting positions is the angle between the normals to the two faces in question.

The crystal is mounted on a holder consisting of two movable arcs perpendicular to each other. It is so adjusted that one prominent face is parallel to the plane of one of these arcs. The arcs are then tilted until the zone-axis of the zone to be measured is parallel to the axis of the goniometer, i.e. perpendicular to the graduated disc. A fairly parallel beam of light from a distant source or from a collimator is reflected from the prominent face previously mentioned, and the crystal is set so that this reflected image lies over a fixed reference mark. The plane containing the incident and reflected beams and the normal to the face must therefore be parallel to the plane of the graduated disc. This procedure is repeated with another face using only the adjusting arc which will move the original face only in its own plane. In this way the crystal can be quickly adjusted so that the zone-axis of the zone to be measured is set parallel to the axis of the instrument. As the graduated disc is turned through 360° the settings at which reflection occur for the various faces in turn are noted.

The usual procedure is as follows:—

(1) A drawing of the crystal with lettered or numbered faces is made as it is essential to be able to recognise each face.

(2) The crystal is set up with a zone-axis parallel to the axis of the instrument as described.

(3) The angles between the normals to faces in this zone are measured, the readings being set out as below:

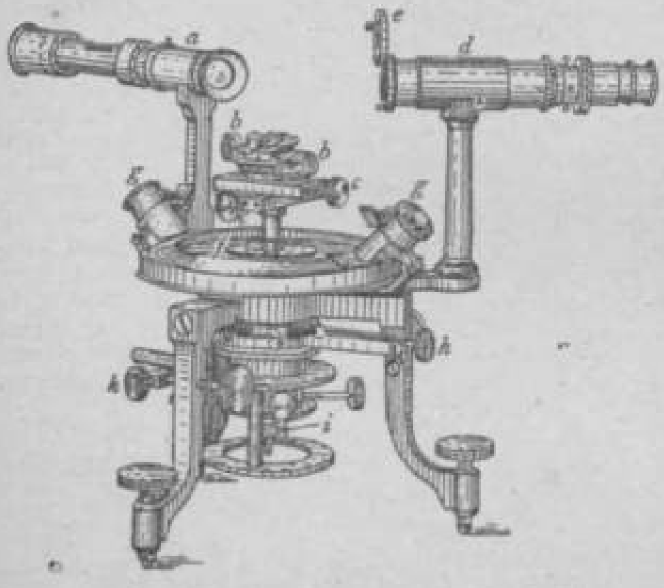
Face	Quality of Image	Reading	Differences of Pairs of Readings

(4) This process is repeated with other zones until sufficient data have been obtained to allow the directions of the normals to each face to be plotted on a projection (nearly always the stereographic).

(5) A consistent set of indices is assigned to the faces, and the forms present are noted. The axial ratio or morphological constants of crystals can be obtained after some simple calculations.

Although all Reflecting Goniometers employ the same principle, they are of different types. In the simplest Student's Goniometer the image of a distant source of light is used because the light must be as nearly parallel as can be obtained. This image is reflected from a fixed mirror and this provides a reference mark, while the image reflected from the crystal can be seen at the same time because the crystal is email compared with the mirror. The tilting adjustments carried on the graduated disc are very simple.

More accurate goniometers are fitted with collimators so that a fairly parallel beam can be obtained from a near source. They have also a telescope, the cross-wires of which provide the most accurate reference mark. Such goniometers are of two types. Vertical Circle or Horizontal Circle, Vertical Circle Goniometers are cheaper but Horizontal Circle goniometers have definite advantages; the crystal is much less likely to shift in the wax mount tinder its own weight and thus larger specimens can be measured; the large amount of possible movement of the telescope makes it easier to deal with difficult cases and also allows the instrument to be used for the determination of refractive indices as well as *of* crystal angles. A very good type of Horizontal Circle Goniometer is illustrated in the figure below.*



No. 2A FOESS REFLECTING GONIOMETER.

a. ColU (i) a Lor.	6, Tilting ecrewi.
e. Centering screw*.	*d.* Telescope.
e. Lens for changing telescope Into & microscope.	
/. Disc bearing graduated circle.	
9. Vernier microscopes.	*h.* Fixing screws.
i. Hutght adjusting »crvw.	

The accuracy with which angle measurements can bo made depends both on the instrument and on the crystal. The type of instrument illustrated can bo read accurately to hatf-mioutes. In the case of very good crystals this order of accuracy is required, although evea these will show* differences of as much as a whole minute owing to irregularities in crystal growth. But even greater accuracy is required in the study of the change of angle with change of temperature, which, is one way of determining Uw coefficient of thermal expansion of a gratal. *or this type of work a larger Horizontal Circle Uomometer, such as the Fuess No. 1a, which con be read to seconds is constructed. Cryitah vary from very good ones suitable for such accurate measurement down to very bad onca in which the irregularities of growth are such that the reflected image extends over two or three degrees.

Although a good Horizontal Circle Goniometer auch as that illustrated is adequate for nearly all crystallographic work, more complicated two- and three-circle instruments have been developed iil the last 50 years by Federov, Czapaki, V. Goldschmidt and Herbert Smith. These have the advantage that the crystal is set up dhce only and in canes where there are it large number of very small faces difficult to identify, this is useful. Of course only one zone can be measureS through 3tSO^{a}, but this IB not a serious disadvantage aJ crystals rich in faces are often those which have been attached by one end to a surface during growtft and so have only one end well developed. Both the practical and mathematical techniques required for handling these Theodolite Goliio meters with two or three circles are much more complicated than for the single circle instrument. But it must be emphasised that for almost all goiiiometrical purposes in mineralogical and chemical laboratories the •iingle circle instrument is entirely adequate and, also, that the technique of using it is easily learned. A very full description of the various types of instruments and of their use, with practical examples, is given by A. E. H. Tutton in " Crystallography and Practical Crystal Measurement," 2 Vols., *1922* (Macmillan & Co.).

In the course of the '-ast century mineralogists have built up a vast collection of dtta on the forms, angles and symmetry of minerals. The corresponding data for crystals of organic and of inorganic compounds which do not occur as minerals are very scanty. Such duta are useful in the rapid identification of crystalline substances and a good goniometer should bo a valued piece of apparatus in every chemical laboratory.

N. F. M. H.

GOOSEBERHY. The fruit of *Rxbea groasularia* (Kuropean species) Or of *R* hirtdlum (H. oxyacanthoidts),* the American gooseberry. The latter species produces reddish fruit, smaller • than that of Kuropean species. Among recorded percentage analyses of European gooseberries the following are typical:

	I*	II[1]
Totaj solids	120	**11-9-151**
Acid	1-95*	**l-S-2-3t**
Invert sugar	4-87	—
Sucrose	018	0-10-0-12
Glucose	—	1-2-3-6
LievttloM	—	2-1-3-8
Ash	0-43	—

[1] *O\\g{Z. Vatcn.* **A'*hr.-u. (tcnuiara.** ***1910.*** **l», 6M.**
[1] **HutUT *{'/,.* lindw. Wrsuchsw. Dtut.-Ooterr. 1900, •, 047.**
* **A» citric adii.**
t **As malic add.**

"Whidwch and Schmidt (Z. Unt«r«. Nah-r.

Genussm. 1909, 17, 584) give the average percentage composition of gooseberry juice as :

Total solids.	Protein.	Acid (as citric),	Invert sugar.	Sucrose.	Tannin.	Ash.
11*05	0-32	1-16	6*58	0-38	008	0-42

In earlier analyses the free acidity of gooseberry juice was regarded as due almost entirely to malic acid. It would appear, however, that citric acid in comparable proportions isaalso present. Thus Bigelow and Dunbar (Ind. Eng. Chem. 1917, 9, 762) report 1-72-2-63% of citric acid and 0-28-208% of malic acid in American species, and Muttelet (Ann. Falsif. 1922, 15, 453) finds 2-07% of citric add in red and 2-20% in white European varieties.

Gooseberries are notably rich in vitamin C, Kudrjavzeva and Ivanova (Voprosui Pitaniya, 1935, 4, 114) recording as muck as 500 units per kg. ©f berries, *i.e.* of the same order as in oranges and lemons.

The composition of gooseberry ash is given *by* Wolff as:

Total ash.	H_2O	Na_2O	CaO	MgO	P_SO_5	SO,	SlO.
0-38	0'15	0'04	0'05	0'02	0'07	0'02	0'01

expressed as percentage of the fresh fruit. According to Dodd (Analyst, 1929,54,15) the dry matter of the fruit contains 0-028% of boric acid.

A. G. Po.

GORLI SEED OIL *(v.* Vol. II, 5236).

GORLIC ACID (v. Vol. II, 5236).

GORSE^ FURZE or WHIN. *Vlex europceus* L. A leguminous shrub common on poor dry heath soils.^ The leaves develop as spines. The tender young shoots are readily eaten by cattle and horses as also is the older, harder growth after suitable crushing (Voelcker, J. Roy. Agric. Soc. 1899 and 1901). Other species, *U. nanus* and *U. gallii,* also occur in Britain. In some areas gorse is cultivated, more especially as a horse fodder, for which purpose its food value is approximately 40% of that of hay.

Girard (Ann. Agron. 1901, 27, 6) records the percentage composition of gorse as:

Water.	Protein.	Pat.	N-free extract.	Cellulose.	Ash.
62-7	4-6	0-9	26·0	14-5	1-6

The N-free extract includes sugars 1-4, pentosans 9 and pectin 1-6%. The ash contains:

HjO	CaO	M«O	Fe,O,	P.O,	SO_a
27'1	H-7	4-3	2-4	6-7	4-7

An alkaloid, " ulcxine," obtained from the seeds by Gerrard (Pharm. J. 1886, [iii], 17,101,*229) is identical with cytisine *(q.v.)* (Parthcil, Ber. 1891, 24, 634). From the flowers Bridel and Beguin (Bull. Soc. Chim. biol. 1926,8, 915) have isolated a glucoside, ulexoside, hydrolysable to invert sugar and ulexogenol.

A. G. Po.

GOSIO GAS *{v.* Vol. I, 479ef, 483c).

GOSLARITE, *Zinc Vitriol* or *White Vitriol*. Hydrated zinc sulphate, $ZnSO_4,7H_aO$, crystallising in the orthorhombic system and isomorphous with epsomite. It results from the weathering of zinc-blende, and usually forms white encrusting masses, or sometimes aggregates of fine, silky fibres. Being readily soluble in water it is not of common occurrence, but is occasionally found in the old galleries of zino mines. Considerable quantities were at one time obtained from the Bammelsberg mine near Goslar in the Harz Mountains. Varieties are ferro-goslarite and cupro-goslarite.

L. J. S.

GOSSIPETIN *(v.* Vol. Ill, 4056).

GOSSIPITONE *(v.* Vol. Ill, 405d).

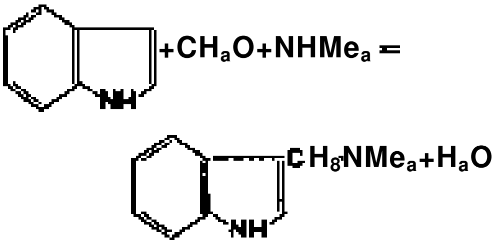
GOSSIPITRIN (*. Vol. Ill, 4066).

GOSSIPOL *(v.* Vol. Ill, 407d).

GOULARD'S EXTRACT, LOTION, WATER. Solutions of basic lead acetate.

"GRAHAM'S SALT," sodium hexametaphosphate *[v.* CALGON).

GRAMINE, $C_nHi_4N_2$, is a crystalline base discovered in certain chlorophyll-defective mutants of barley by Von Euler and Hcllström (Z. physiol. Chem. 1932, 208, 43; 1933, 217, 23); the yield was about 001% of the dry weight of the plants. The same base was next described as the alkaloid *donaxine,* which Orechoff and Norkina (Ber. 1935, 68 [B], 436) isolated in a yield of 0-57% from the reed *Arundo donax* from Central Asia; Madinavcitia (J.G.S. 1937, 1927)^obtained 0-28% from the same species growing on the coast near Barcelona. The constitution was investigated by Von Euler, Erdtman and Hellström (Ber. 1936, 69 [B], 743) but only fully established as 3-dimethylaminomethylindole by synthesis (Th. Wieland and Chi Yi Using, Annalen, 1936, 526, 188; Kiihn and Stein, Ber. 1937, 60 [B], 567). The second synthesis, ^-condensation of indole with formaldehyde and dimethylamine in the cold, is probably biological and gives a quantitative yield :



Gramine forms needles from acetone, m.p. 134°; *picrate,* m.p. 141°; *perchlorate,* m.p. 150°. Orechoff and Norkina describe a *methiodide,* m.p. 177°, but a " methiodide " melting above 350° and obtained by Wieland and Chi Yi Hsing, as well as by Kiihn and Stein, i*as in all probability tetramethylammonium iodide. Madinaveitia showed that in the presence of methyl iodide and potassium hydroxide in methanol solution, gramine is quantitatively decomposed into 3-methoxymetLylindole and tetramethylammonium iodide, and that, without alkali, the latter salt is also formed (along with 3-hydroxymethylindole ?). Ethyl iodide reacts normally with gaamine in neutral solution, but in alkaline solution dimethylethylamine is formed.

Arundo donax contains also a minute quantity of *donaxarine,* $C_{13}H_{ie}O_aN_2$, m.p. 217° (Madinavcitia). This second alkaloid is an indole substituted in the 2-position, for it gives neither the

Ehrlich nor the Hopkins and Cole reaction (both positive with gramine). Donaxarine contains one —NMe group, but no —OMe or —CMe, and is optically inactive.

G. B.

GRANITE. An acid igneous rock consisting of a granular (hence, the name) holocrystalline aggregate of quartz, felspar and mica. It contains about 65-75% of silica, which is present partly as free silica (quartz forming 30-50% of the rock), and partly in combination in the silicates. The felspar (36-68%) is generally a potash-felspar, usually orthoclase, but sometimes microcline: it may also, especially in the "soda-granites," be a soda-bearing orthoclase, anorthoclase or a plagioclase (albite to oligoclase). The mica (5-18% of the rock) is usually of two kinds, a white mica, muscovite, and a black mica, biotite.[1] The one-mica granite, biotite-granite, is sometimes distinguished as *granitite.* Less frequently, hornblende or augite may partly or wholly take the place of mica, as in hornblende-granite and augite-granite. In other varieties, especially those altered by pneumatolytic agencies, tourmaline may be present. Granites differ widely in their general appearance and character, owing to variations in their coarseness of grain, the occasional presence of larger porphyritic crystals embedded in a finer-grained groundmass, the colour of the felspars (dull white to pink), and the lack or predominance of the dark-coloured minerals, biotite and hornblende. Sp.gr. 2-6-2-8; weight per cu. ft., 160-175 lb.; crushing strength, 1,000, 2,000, 3,000 tons per sq. ft. Degree of porosity very low, 0-2-0-3%. The grain of the rock is sufficiently coarse for the individual minerals to be distinguishable by the unaided eye. It varies from fine-grained in *aplite* (a variety composed only of quartz and felspar) to very coarse-grained in *pegmatite* and *graphic granite* (the latter characterised by an intimate intergrowth of quartz and felspar). At times granite displays a more or less pronounced foliated structure (gneissose granite), passing imperceptibly into *gneiss.* This rock has the same mineral and chemical composition as granite, and to a certain extent can be employed for the same purposes.

The following analyses are of: I, Coarse-grained, red biotite-granite from Peterhead, Aberdeen (J. A. Phillips, 1880). II, Fine-grained, bluish-grey Muscovite-biotite-granite from Rubislaw, Aberdeen (W. Mackie, 1901). III, Biotite-granite with large porphyritic crystals of red felspar from Shap, Westmorland [illegible] 1891). IV. Grey muscovite-biotite-granite from Grcady, near Luxullian, Cornwall (J. A, Phillips, 1880). V, Dark red, medium-grained hornblende-biotite-granite from Mount Sorrel, Leicestershire (C. K. Baker). VI, Average of nine analyses of the grey, two-[illegible] Haughton, 1855). For a large collection of analyses of granite, , J. Roth, "Beitrage z Petrographie d. plutonischen Gesteine", Berlin, 1873-84; H. S. Washington, U.S. Geol. Survey, Prof. Paper, 1917, No. 99.

	I.	II.	III.	IV.	V.	VI.
SiO_2 .	73-70	69-01	68-55	69-64	67-10	72-03
Al_2O_3	14-44	[illegible]	16-21	17-35	16-19	14-46
Fe_2O_3	0-43	0-97	2-26	1-04	3-82	2-40
FeO .	1-49	2-05	n.d.	1-97	—	—
MnO.	trace	—	0-45	trace	—	—
MgO .	trace	0-48	1-04	0-21	1-58	0-10
CaO .	1-08	1-95	2-40	1-40	2-59	1-76
Na_2O	4-21	2-73	4-08	3-51	2-43	3-01
K_2O .	4-43	3-94	4-14	4-08	5-38	4-80
P_2O_5 .	trace	—	—	trace	—	
H_2O .	0-01	1-18	n.d.	0-72	1-02	0-01
	100-39	100-[illegible]	99-13	99-92	100-17	99-52
Sp.gr.	2-69	[illegible]	2-69	2-72	2-6[illegible]	2-63

Granites are of wide distribution as rock-masses of considerable magnitude. They are extensively developed and quarried in Cornwall and Devon, where they occur as a series of bosses protruding through the killas or clay-slate. The largest of these intrusions are, proceeding westwards, those of Dartmoor, Brown Willy or Bodmin Moor, St. Austell or Hens barrow, Cam Menelez or Pcnryn and the Land's End or Penzance districts. In addition to these principal exposures there are numerous smaller masses. The granite of Devon and Cornwall is usually grey and coarse-grained, but red granite also occurs, as at Trowlesworthy in the western part of Dartmoor. Although used locally since prehistoric times, Cornish granites were not systematically quarried until early in the eighteenth century; one of the first quarries to be developed was the De Lank quarry near Bodmin, which supplied the material for the exterior of the Eddystone Lighthouse in 1756. Dartmoor granite was sent to London in 1817 for the construction of Waterloo Bridge, and in 1831 for London Bridge. The granites of Scotland are of great industrial importance. Aberdeen granite was first brought to London for paving in 1764, but the great development of the trade dates from about 1850. The Aberdeen stone, valued for monumental work, is of a grey or blue tint, whilst that of Peterhead is usually of a fine pink colour. The Ross of Mull in Argyllshire furnishes a handsome pink granite, yielding blocks, of exceptional size. Granite is also quarried in Kirkcudbrightshire, the grey stone of Dalbeattie being well-known in commerce. Ireland is rich in granites. The very large Leinster mass, in the counties of Dublin, Wicklow, Wexford and Carlow was quarried as early as 1680. Other important occurrences are in the Mourne Mountains in Co. Down, and in Co. Galway and Co. Donegal. Other British occurrences are in the Stilly Islands, Jersey and Guernsey, Lundy Island, Maivem Hills, Mount Sorrel in Leicestershire, Skiddaw, Eskdalc, and Shap in the Lake District, the Sam district in North Wales, and Foxdule and Dhoon in the Isle of Man ; and in Scotland many other localities in addition to those mentioned above.

Granite is extensively used as a building and paving stone, and owing to its massive character and durability it is especially useful

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[1] These minerals carry part of the potash, each of them containing about 10% K [illegible] bulk of the potash is, however, [illegible] are potash-felspar containing [illegible]

where massive constructive work is required, as in the foundation of buildings, in docks, sea-walls, piers of bridges, lighthouses, etc. ^Taking a high polish, which is retained on exposure to weather, and being suitable for carving, it is much in demand for ornamental and monumental work. Refuse from the quarries is dressed as paving setts, or kerb stones, or crushed and screened for road metal, railway ballast and granite chips. Partly weathered granite from near the surface, especially when covered by a soil rich in humic -\cids, shows dull cloudy felspars and the darker silicates have a rusty appearance, and the rock itself is often quite crumbly. This surface weathering may sometimes extend to considerable depths, and under certain conditions china-stone or china-clay may result. The solid fresh rock is, however, little affected by weathering yrctesses when employed as a building stone. The most important cause of disintegration under these conditions is that due to the unequal degree of expansion and contraction of the different minerals with changes of,temperature ; coarse-grained granites are more affected by this agency than the finer-grained varieties. The handsome course-grained Rapakivi granite ol Finland lacks durability on this account Granite has further the defect that it does not resist fire well. The cracking and scaling of the surface is due to the presence in th(quartz of vast numbers of microscopic cavities, containing water and liquid carbon dioxide! Stone containing nodules and specks of iron-pyrites shoVld be avoided, since this mineral readily decomposes, ^producing free acid and unnightly brown stains. Of special varieties used for ornamental purposes mention may be made of *luxtillianite,* and orbicular or spheroidal granite. The former, from Luxullian in Cornwall, consists of largo porphyritic crystals of pink felspar set in a black matrix of tourmaline and quartz. A good set of large polished blocks and slabs of orbicular granite from several localities is displayed in the Mineral Gallery of the British Museum (Natural History). Gra'nite was used as an ornamental stone by the nnncnt Egyptians and the Romans.

Granite rocks are always divided naturally °y joints, which usually run in three directions, approximately at right angles, thus cntihling the rock to be quarried in roughly ttenboidal blocks. Those are sometimes of considerable *'*;• providing, for example, the obelisks up to 100 ft. in length obtained by the ancient Egyptians in the quarries of pink hornblende- biotitc-£u»to at Assouan (Syene) in Upper Egypt. -The blocks are split up by " plug and feather " wedges, the splitting taking place more readily in certain directions, known to the qunrrymen *s the "rift" or " grain " of the stone. This is sometimes due to the presence of flow structure »the rock with a parallelism of the flakes of mica but at other times it is apparently due «> the effect of stresses. When the surface is required to be dressed smooth, it is " rine-axed " <>y continual tapping, at right angles to the face, *uh a special form of axe. Slabs are cut by uumond saws, and OQIBOUM up to 8 ft. in dift-elor arfc turned in the lathe with diamond-w.*t tools. Tho.polishing of granite is effected by cast-iron planes worked over the smoothed surface, first with sand and water, and then with emery, the final polish being given with putty powder applied on thick felt. In this way even elaborate mouldings are polished. The name granite is sometimes incorrectly applied as a trade-name to stones of other kinds, *e.g.* " black granite " to a gabbro or other dark-coloured igneous rock of granitic texture, " Petit granit " to & black Belgian marble spotted with white encrinites, " Blendip granite " to a limestone, and " Ingleton granite " to a conglomerate.

Veins of metalliferous ores frequently occur in connection with granite masses, either in the granite itself or at its junction with the surrounding rocks. Tin ore, in particular, is almost always found only in association with granite. The pegmatite veins occurring in connection with granite often carry various gem-atones (tourrabline, beryl, etc.) and rare-earth minerals.

Reference.—G. F. Harris, " Granite and our Granite Industries," London, 1888. J. Watson, »" British and Foreign Building Stones," Cambridge, 1911. J. A. Howe, " Geology of Building Stones," London, 1910. G. P, Merrill, " BUtbM for Building and Itecoration," 3rd ed., New York, 1903. J. G. C. Anderson and M. Macgregor, " The Granites of Scotland," Mem. Geol. Survey, 1939. On the granites of the eastern United States, *see* T. N. Dale, Bull. U.S Geol. Survey, 1907, No. 313; 1908, Jfo. 354; 1909, No. 4W; 1911, No. 484.

L. J. S.

GRANITE-ARLITE (». Vol. I11, **32d).**

GRANITE-PEGMATITE (vol. I11, 32tf).

GRAPE. The fruit of *Vitis* spp. European varieties are normally derived from *V. viniftra* L. According to Winton, American viirí<ties have been bred from P. *labrusca* L. (the fox grape), *V. aealivalia* Mich*, (the summer grape) and *V, rolundifotia* Michx. (the Muscadine or sonthem fox grape). The famous American variety " Concord " is derived from *V. labrusca.* It is used for dessert and for the manufacture of grape juke, but is less favoured for the making of wine or of raisins. Typical analyses of the fruit include:

	H_tO.	Protein.	Kit.	Fibre.	Carbohydrates	Aali.
European (whole)[1]	781	0-7	—	2 1	Hi it	*Ob*
European (skin)[2]	765	1-5	DO	21	1«4	0-*
European (seeds)[2]	sa-7	6-5	80	276	18-0	0-7
American (whole)[3]	77·4	1·3	10	2-2	170	(I
American (skin and	BM	0-4	0-3	06	17 3	0-4
American (pulp)[4]	82-3	0-5	02	0-8	16·6	033

[1] Ktinlg/AmilyilBorFoodi."

[2] Dull" rid (Rev, Intvni. falsil. 1900, 13, 92).

[3] Atwutir ami Itryanl (U.8. Dept. Agrlc. OH. Kxp. 6u. Hull.. No. 28 rev, (iwiii)>.

[4] Miller ami Diixuuc (llawili Aeri*-. Exp. SU. Bull. No. 77 (1037)).

The composition of grape juice varies considerable with the stage of maturity of the harvested fruit and with growth conditions. Varietal differences may also be considerable. The storage quality and flavour of the fruit and the quality of preserved juice are largely controlled by the proportion of sugars and acids (mainly tartaric and malic) present in the juice. Among data for American varieties may be recorded the following percentage analyses of the juice :

	I.	n.	III.
Total solids . . .	18-5 -10-0		**J8**·3-22-2
Protein	**y-7-0-4**	IM	0-27-0-45
Total nvlds (as tart.aric ai-hl).	**0-4-0-8**	09	0 **T-l-0**
Tartratea (ditto) . .	**O-B-0-fi**	**0-7**	0-8-O-7
Invet sugar . . .	**12-3-13-4**	180	17 O-ltH)
Sucrose	0-0-1-9	...	0 0
Tannin		0-00	0-1-0-4
Asli	0-2	0-3	0-3

f. Varieties **from** F. *rotundifotia.* Gore (Ind. Eng. Chom. IIHJD, 1,430).
II. Cutawlm variety from *V. Inbrusca,* Gore *(I.e.).*
III. Uoirconl, Hiirtiiiiin and Tolman {U.S. Dept, Auric Bull. GJfi (11)18)).

In juice from European varieties Colby r*[1] ports variations in reducing sugar contents of* 19-8-23-1%. in total Bugars 21 0-23-5% and in free acids (aa tartaric) 0-36-0*65%. CaldwcU {J. Agric. Res, 1925,30,1133) in a study of the effect of growth conditions reports the analyses of 49 varieties of juice grown in the same locality during five successive seasons. Minimum and maximum percentage values obtained were:

Total solids. . . .	12-9-200
Free acid (as tartaric) . .	0-5-21
Invert sugar. . . .	8-9-24-8
Sucrose.	0-0-5-6
Tannin.	0-03-2-4

In Muscadine grapes, -which yield 3-5 gallons of juice per bushel, Armstrong *et al.* {Georgia Agruv Exp. Sta. Bull. 185, 3 (IS34)) report the following ranges in juice characteristic*: total solids **128-21** 3%, p_K 3-42-2-90, tannins 0-02-0-417%.

During the ripening of grapes the juice comisition shows a marked increase in sugar count and a diminution in acidity. Loss of acidity falls mainly on the roulic acid: the total tartaric acid content is not greatly altered (Gari « o^"CftS"ia:Alin-Acctd- Agric- Torino, 1914, SO, *2.U;* Ferre, Ann. Falsif. 1928, 21, 75), although there is some conversion of free taruric acid iiito titrates (Brunet, Rev. vit. 1912, 37, 15). The ratio sugar/acid in the juice serves •a a measure of ripeness of the fruit, complete **rir^nw «m*ponding** to a ratio of 30 (Hugues **and** Buffnrd$_f$ Ann. Falsif; 1930, 29, 270) and commercial maturity with a ratio of 26 (Mcurice and Boulle Bull. irwt. agron. et sta. recherche*

1047. 7, _*40) states that juico of ripodLrt gripe* shouldl show a sugar/acid ratio of not lew. than 25 and </„ not below 1070.

In ConcordI grapes Helaoa (J. Amer. Chem. Soo. 1925, 47, 1177) found the acida of the juice to consist of J-tartarie (4u%) and **i**-malic acid (60%). Small proportions of citric acid, however, are reported by Hartmann and Hillig \J. Assoc. Off. Agric. Cliem. 1928, 11, 257) and by Heiduschka and Pyriki (2. Unters. Lebensm. 1929, 58, 378). The flavour of wine from northern grapes is said to bo influenced by the presence of l-.ctic acid in the fresh **jmoe** (Schindler and H'ulae:, Cheru. Listy, 1920, 23, 73). Glyoxylic acid occurs in unripe fruit {Semichon and Flanzy, Rev. vit. 1933, 79, 197) and a hexuronic acid (m,p, 1G5°) is reported in purple grapes by Cahi[1]} (Bull. Soc. Chim. bio), 1933, 15, **1462).**

Fresh grape juice contains peotiu and a partial **clarification** of the j Jce results from the actvm of enzymes of *PeniciUiiitn glaucum* which convert part of the pectin into soluble compounds and precipitate the remainder together with suspcnsoidY^Wiuaman and Kerta-sz, New York Agric. Exp. Sta. Tech. Bull. 178, 1S1 (1331)). Barbera (Ann. tech. agrar. 1933, 6, Ko. 3, I, 229, 350) isolated from grape juice a pectin yielding on hydrolysis arabiitoHe, xylose, galaetose, galacturonic acid and methyl alcohol. Its methoxyl content was less than that of orange pectin.

The odour of grape juice is ascribed to the presence of methyl antlinmilate, **of** which 0-2-2-0 tug. per litre of juice is reported by Power and **Ghesnit** (J. Aiucr, **Chem. Soc1ft22,** 43, 1741).

Unformatted grape juice is preserved commercially by pasteurisation or is concentrated by low-pressure distillation. In the latter condition it is sometimes referred to as grape " honey," an analysis of which is recorded by Cascrio (Ind. ital. cons, aliment. 1936, **11,** 51) •as HgO 24, ether e>:tr«;:t 0-7, ash 0-9, total sugars (as invert) 72, reducing sugars (a« fructose) 6t>-8, protein 0-7S>$_t$ **total a.** id **(as malio)** 1-5%. Gachot (Prop. 5th Intern. Cong. Tech. Chem. Agric. Ind. Holland, 1937, 11, 445) describes the pasteurised juice as having *d* 1 -072, dry iNHtttr 19, sugars 15 b' and ash 0-29%.

The anthocyanin pigment of European grapes iscenin, C!3HJ,JO,3CK4H2O, a monoglucosidc **of** tliinethyldclphinidm **(oenidin)** chloride, $Ci,H,_BO_7Cl$ (Willstatter and Zollinger, Annalcn, 1915,408,83; 191(i, **412,** 195). Anderson (J. Hid. (hem. 1923, 57, 71)5; 1924, 61, 97) isolated from Concord grapes a monoglucoside of the nionomcthyl ester of delphinidin. Both iuithot y/inin and anthocyanidin pigments were obtained from Italian grapes (Pariai and Bniini, Staz. Hpcr. ngr. ital. 1920,59,130).

CRAI'E-SBKI) OIL *[q.i.).*

KAJSISS and CUKRAKTIS rcpresi'tit a wide range of varieties of drift! **pope*. BomMgor** {Z. Untersuch. Nahr.-u. iGenussm. 1890, 2. »7) *&ve** the average j>erceutage armlyscs of samples from several Mediterranean countries as :

Bone.	H.O.	Acldi.	**Siiciirs.**	Aih.
Spain (museiitc!) .	25-1	**L-88**	65-2	**1-7**
Italy (raisins) . .	**80*1**	**i:n**	(17-1	**1-5**
Palest**LOU ((airtins;.**	22-7	1-22	69-8	**1-5**
Syria (raisins) .	—	1 U	iil-H	**1-8**
Zimti (currantii) .	—	**I I**	OHO	1-7
S. Ma**ira (ourr**ants)	—	**1-4**	fUJO	**10**

	Kfllsina.	Ciinvmts.
Water	24·5	25·4
Nitrogenous **matter**	2·4	1·2
Fat	0·6	—
Free ackt	1·2	1·5
Invert sugar	59·3	61·8
Sucrose	2·0	—
Other carbohydrates	1·3	5.9
Crude fibre and seeds	7·0	2·4
A ah	1·7	1·8

Konig's average data for raisins And currants are given in tho table **Opposite.**

Average analyses for the edible portion of American raisins are given by Atwater and Bryant (Lc) aa H_5O **14*6,** protein 2*6, fat 3-3, N-free extract and fibre 70-1, aah 3-4%.

RAISIN-SEED on. (». GSAFE-SEKD OIL).

Recorded mineral anal; ses of gr apea and their products include:

	fc'resli fruit (EuropearV	J''resh fruit (Coneordl.[3]	Skin.*	a*„-	Juice.[5]	" Honey." *
K_2O	**019-0-36**	0-22	0-40	0-28	0-2£	0-1fi
Na_2O	001-O-06	• O004	003	003	0-01	—
CaO „	002-003	00:»	013	0-31	0-02	016
MgO	001-002	0-21	003	**0-Ofi**	0-02	—
Fe_aO_3	—	—	U-12	0-005	0-'00	0-003
Mn_3Oj	—,	—	0-005	0003	002	—
P_2O_5	0-08-O-US	0 0-1	016	0-22	0-05	0-61
SO_3	001-003	—	0-05	002	0-02	—
SiO_2	002-003	—	0-02	001	001	—
Cl	0-00-0-02	0001	0005	0-003	0-004	.–.

[1] Hiolettl. * Atwater and Bryant. [3] K **bog.** [4] Cawrto.

Boric acid and traces of copper, aluminium and zinc have been reported by various observers.

A. G. Po.

GRAPEFRUIT. The fruit of *Citrus decumam,* Murr,, sometime^ described as *C. grandis* Oabeck or *C. aura.nliu.vi* var. *grandis* L. The' common grapefruit *k* grown widely - in tho tropical and subtropical areas of North America and of Africa. The " pomelo " is a pear-shaped variety with thick rind. In Hawaii a similar variety is known as tho " shaddock." Wintou (" Composition of Foods") quotes the percentage analyses (shown opposite) for the **edible** portions of the fruita:

	Grapefruit.	Pomelo.	Shaddock.
Water.	88-1	87-7	88-5
Protein	0-0	0-7	1·2
Citric acid	5-7	1·1	0-3
Total sugar	6-6	9-2	8·1
Sucrose	3-9	6-2	7-3
Ash	0-43	0-63	049

Joachim and Panditteseker; {Trop. Agric, 1939, 93, 14) report analyses of grapefruit grown in Ceylon ud quote comparative data for the juice of fruit from a number of sources :

	I. Florida.	II. *a* Trinidad.	**m.** Puerto RICO.	IV. Texas.	V. S.Africa.	VI. Jamaica.	VII. Ceylon.
Juice, %	—	«_	–	35-9-58-9	––	–	30-5^55-2
Citric acid, g./lOO cc.	0-9-1-4	**1-0-1**-1	1·1	1-0-1-4	1·6	0-8-1-5	0-9-1-9
Total solids, g./100 cc.	6-0-9-7	S-ft-9-2	8·1	8-3-10-5	—	9-8-11-8	7-0-10-7
Total sugars, g./lOO cc.	4-8-0-2	6-5-7-3	4-8	6-7-7-0	5-5	—	4-2-7-5
Reducing sugars, g./JOO CO.	3-4-4-0	4-WH	3·1	2-3-3-2	4-6	—	2-1-4-0
Solids/acid	7-2-7-8	8-3-9-0	7-1	7-7-9-0	—	7-3-13-3	4-6-8-9
Vn.	3-0	3-1-3-3	—	3-2-3-a	3-(i	—•	3-3-4-0

I. Roberts and Undduin. **bid.** I-Jill. Chem. 103.. 29. 574.
II, *ill.* **Hardy tod Bodrfguw,** TwP-A^v ^..fr^fa"^o! **419.**
IV. Truut. Ud Friend. Texas Airrc Ejp. 8ta. Bull. B30 No
V. ,.uriu. **Union** B. .Urku. JR-pt. Agric. 3d. B^L 1925, No. 40,
vi (**Iroaoher,** Jamaifa. **D«pt.** Bd. A«ric. BiuirNo. 5.
VII. Joaclilin iiiul I'linaittesekerc, I.e.

The pomelo juice is rtonvwhat more concentrated, analyses ahdwing an average of: Boiida 12-2, **"trio uU** J-5, total sugar* 8-7, BUcrose 5%.

In addition to citric acid amallcr amounts of malic and traces of tarlaric and oxalic acids occur in the juice. In Palestine fruit, Mencbikowsky and Popper (Hadar, 1932, 5, 181) record: citric acid 0-67-1-15, tartaric acid 0·0003-0-0007, malic acid 0·007-0016 and oxalic acid 0-002-0-005%.

Nelson and Keenan (Science, 1933, 77, 561) report 0-0028% of inosite in grapefruit juice.

During the ripening of grapefruit the ratio of sugar/acidity in the juice increases and is an approximate measure of maturity for commercial purposes.. Hyatt (New Zealand J. Sci. Tech. 1936, 18, 409) considers the ratio of total solids (Brix) to acidity should be 5 or over in palatable fruit. Investigations of Zoller (Ind. Eng. Chem. 1918, 10, 364) and of Hawkins (J. Agric. Res. 1920, 20, 357; 1921, 22, 263) show that the change in sugar/acid ratio in normally ripening fruit is brought about by a relatively larger diminution in acid content than the increase in sugar. Storage of the fruit in warm conditions causes a marked increase in acidity with only a small change in sugar content, whereas during storage at 0° there is a considerable decrease in acidity, the sugar content again showing little change. There is a small increase in *py* of the juice during maturation, but the relationship is not sufficiently uniform to be of commercial interest (L. Smith, Florida, Dept. Agric. Chem. Div. Rept. 1933/4, 85). Grapefruit juice is a rich sauce of vitamin C and also contains appreciable amounts of vitamin B. Its vitamin A content is small.

The bitter principle of grapefruit rind is the flavanone glucoside *naringin* which gives on hydrolysis rf-glucose, Z-rhamnose and *naringenin* (5:7:4'-trihydroxyflavanone). The amount present ranges from 0-14-0-8% of the weight of the whole fruit.

Steam distillation of the rind produces 1-5% of a yellow essential oil, ng> 1-475-1-4785, d^{20} 0-845-0-860, consisting of d-limonene 90-92, citral 3-5, a-pinene 0-5-1-5, geraniol 1-2, and linalool 1-2%. The expressed oil from the rind, on distillation first *in vacuo* and then in steam, leaves 7-5% of a waxy residue (Nelson and Mottern, Ind. Eng. Chem. 1934, 26, 634). The wax contains solid fatty acids of molecular weight corresponding to $C_{3a}H_{M}O_{2}$, together with linolenic) imoleic and oleic acids, a sapogenic ketone, $C_{31}H_{62}O$, m.p. 253°, hydrocarbons (mainly $C_{*»}H_{eo}$ and $C_{31}H_{e4}$), a phytosterol, $C_{M}H_{47}OH$, m.p. 132°, and umbelliferone (Markley *et al.*, J. Biol. Chem. 1937,118,433). The pectin content of the peel frequently exceeds 10% of its total weight (*cf.* Poore, Ind. Eng. Chem. 1934, 26, [illegible]).

The colour of grapefruit rind ia due to a phlobatannin which darkens on exposure to air. Pink varieties contain lycopene and fl-carotene (Matlack, J. Bitf. Chem. 1935,110, 249).

From grapefruit pulp Fiwatari (J. Biochem Japan, 1927,7,169) has isolated glycine-betaine, stachydrine and putrescine.

Chace (U.S. Dept. Agric. Bur. Chem. Bull. 1904, No. 87) shows the ash of grapefruit to contain K_2O 44-2, CaO 7-3, MgO 3-9, Fe.O, 1-3, P_aO_5 11·1, SO_3 3-4 and Cl 1-4%, the total ash content being 0-39% of the weight of the whole fresh fruit.

In recent years the rapidly extending canning process has led to the accumulation of much grapefruit waste (peel, rag and seeds). Thomas (Citrys Ind. 1934, 15, No. 11, 8-9) reports this as being of value as a cattle food, its analysis being:

	%
Water	8-2
Protein	4-9
Fibre	11-9
N-free extract	69-6
Ether extract	1·1
Ash	4-23

A. G. Po.

GRAPEFRUIT, ESSENTIAL OIL OF (v. GRAPEFRUIT).

GRAPE-SEED OIL (RAISIN-SEED OIL) is obtained commercially from the residual pips recovered from the processing of the wine-grape (varieties of the old-world *Vitis vinifera* L., the American *V. labrusca, V. sestivalis* and *V. riparia,* and their hybrids) for tue manufacture of wine or of seedless raisins (especially in California). The pips contain from 6 to 20% of oil, which may be recovered partially by expression, or in higher yield by extraction with solvents; the crude grape marc from the wine-pressing may be distilled as usual if desired before separating the pips. Since the first commercial trials in Italy in about 1770, grape-seed oil, has been of occasional local importance (chiefly when other oils have been scarce) in many European wine-growing countries such as Italy, France, Germany, Austria and the Balkan States; recovery of grape seeds for oil manufacture was made compulsory in certain districts of Germany in 1938-39. The better qualities of the oil are used for edihle purposes, whilst the lower grades may be employed for the manufacture of soap, paints, linoleum, etc. In California refined raisin-pip oil is used as an edible (salad) oil, for the coating of seeded raisins to prevent stickiness and for the manufacture of cosmetic preparations, as well as in the soap-making and paint and varnish industries *(v.* A. M. Paul, Food Ind. 1934,6,444; Eaton, Soap Trade Rev. 1937,10, 497; Rabak, J. Ind. Eng. Chem. 1921,13, 919; H. A. Gardner, U.S. Paint and Var. Manuf. Assoc. Scient. Sect. Circ. No. 190 (1923); H. Scheiber, Farbe u. Lack, 1936, 17, and later papers; Brambilla and Balbi, Chim. e. l'Ind. 1936, 18, 353; 1937, 19, 10; *see also* Bonnet, Bull. Goc. d'Encour. 1927,126, 523 (review"of French industry): Fritz, Chem.-Ztg. 1935, 59, 704 (German production)). Grape-seed oil is not satisfactory for the manufacture of Turkey red oils, nor as a lubricant; Margaillan states, however, that blown grape-seed oil may be us 3d for the latter purpose (Bull. Soc. d'Encour. 1927, 126, 560; Compt. rend. 1927, 185,306).

Cold pressed grape-seed oil from fresh seeds is pale in colour and satisfactory in flavour; it is stated by Eaton, however *(see* Jamieson and McKinney, Oil and Soap, 1935, 12, 241), that both the freshly expressed crude oil and refined oils give a positive Krcis test. The technical oils vary in colour, acidity and taste according to the age and condition of the seed treated, but can be refined fairly easily.

The chemical constitution of grape-seed oil i» still uncertain, as the data rucoid-d for the oil by various observers are very conflicting *(cf.* collected data in reviews by Fritz, Seifens.-Ztg. 1927, 54, 704, and Balbi and BramWlla, Olii Alin., Olii e Grassi, Colori e Vernici, 1937, 17, Nos. 3-7). The fact seems to be that the character of the oil varies widely from sample to sample; the variety of the^plant (and there are supposed to be over 500 varieties of *V. vinifera),* the nature of the climate and of the soil are all factors which appear to influence the composition of the oil to a degree which is Unusual among vegetable oils: ^

On the whole, the evidence suggests the existence of three main types of grape-seed oil.

(a) The Hydroxylated en " Castor Oil " Type.—The early investigator Horn (Mitt. Gew.-Mus. Wien, 1891, 185) and later Paris (Staz. sper. agr. ital. 1911, 44, 669) reported iodine values of 94-96, saponification values of^ 178-179 and very high acetyl values, viz. 14£-5 and 143, which were regarded as characteristic of grape-seed oil and indicative of the presence of glycerides of hydroxylated acids of the castor oil type. Considerable doubt has been cast upon the validity of these early results, as the methods employed for the determination of the acetyl value are open to adverse criticism; also in most cases the oils were highly acid and it has been found that some grape-seed oils, at least, are liable to develop high acetyl values upon ageing *(cf. also* Delaby and Charonnat, Compt. rend. 1930, 191, 1011). Nevertheless, although such high acetyl values have never been observed again, the fairly recent examination of a large number *f grape-seed oils of different origin by Andre *(ibid.* 1921, 172, 1296, 1413; 1922, 175, 107; 1923, 176, 686, 843; André and Ca^il, Bull. Soc. d'Encour. 1927, 126, 542; Täufel, Fischler and Jordan, Allgem. Oel- Fett-Ztg. 1931, 28, 119; *cf.* Fettchem. Umschau, 1934, 41, 196) and Otin and Dima (Allgem. Oel-Fett-Ztg. 1933, 30, 71, 135; 1934, 31, 107; *cf.* Beal and Beebe, J. Ind. Eng. Chem. 1915, 7, 1054), seems to afford confirmation of the existence of a moderate amount of hydroxylated acids in certain grape-seed oils. Out of some 40 laboratory-prepared and 6 commercial samples studied by André, 6 Jiad acetyl values between 20 and 50, whilst one—a commercial sample from Oran, having 40% free fatty acids—had an acetyl value of the order of 66. Most of the 40 Rumanian oils examined by Otin and Dima had hydroxyl values[1] in the region of 40 (equivalent to acetyl values of c. 39), the figure being somewhat higher (50-60) in a few cases. They givo the following composition for an oil (iodine value 124, hydroxyl value 34-8) from Southern Bessarabia": hydroxy-acids 11-8%, oleic acid 31-0%, linolic acid 43-7%, linolenic acid 0·14%, palmitic acid 6-2%, stearic acid 2*2%, glyceryl residue (C_3H_6) 4-04%, unsaponifiablc matter 0-59%. •

Täufel reported hydroxyl values of 92 and 76 (equivalent to acetyl values of c. 80 and 71, respectively) for two oils of acid value 51 and 7, respectively: in both cases the fatty acids prepared by saponitication had hydroxyl values of 44-46 (acetyl values c. 45) which appears to confirm the existence of hydroxy-acids. Further evidence is supplied by André *(I.e.* 1921, 1923) who claims to have separated a mixture of a saturated and an unsaturated hydroxy acid (C_{14} or C_{16} ?) from a sample having an acetyl value of 49. Bicinoleic acid itself, however, is not present.

It must be noted that all these recent specimens had iodine values between 124 and 142 (mostly between 132 and 139) and saponification values between 186 and 192 (most 189-190), and it seems likely that the low iodine values found by Horn and Paris were a consequence of the oxidation of the oil, since it has been shown by Otin and Dima that the iodine value falls very considerably when grape-seed oils are stored in the presence of air. No correlation can yet be drawn between the acetyl value and the variety of the grape or ecological factors; there can even be considerable variation in the acetyl value of oil from seeds harvested in the same vineyard in successive seasons (André), but it appears on the whole that a hot dry climate and a dry lime soil favour the production of hydroxy-acids.

It is doubtful whether oils having acetyl values in 4he region of 18-25 *(cf.* Fachini and Dorta, 7th Int. Congr. Appl. Chem. 1909, Sect. IV, A 1, 128; André, *I.e.;* Jamieson and McKinney, *I.e.)* should be included in this group or under (c) *(below).*

(b) The " Erucic Add " Type.—The occurrence of erucic acid in grape-seed oils was reported by Fitz (Ber. 1871,4,442, 910) and again by Paris *(I.e.),* but was disputed by subsequent investigators including delTAcqua (Ann. chim. appl. 1914, 2, 295) and Jamieson and McKinney (Oil and Soap, 1935, 12, 241). Its presence, however, was again affirmed by Carrière and Brunet (Compt. rend. 1927, 185, 1516) and by Mikšid and Refček (oil from the American hybrid vine " Noah " grown in Jugoslavia: Bull. Soc. chim. Boy. Jugoslav. 1930, 1, No. 2, 32).

(c) *The Semi-Drying Type of Q rape-Seed Oil* is undoubtedly the most common. Erucic acid is absent, and as a rule the acetyl value is very low, although technical oils may show fairly high acetyl values owing to the formation of free fatty acids, mono- and di-glycerides by partial hydrolysis. The iodine values generally run from 130 to 140 (André records a maximal figure of 157); the saponification values are normal (c. 190) and the oils exhibit moderate drying properties which render them suitable as partial substitutes for more unsaturated oils in the paint and varnish industries, etc. The composition of the fatty acids of a Californian raisin-seed oil (iodine valuO 129) of this type (acetyl Value 18<$, acid value 0) is given by Jamieson and McKinney, *Lc. (cf.* Täufel *et al.,* *I.e.)* as follows: palmitic acid 6-3; stearic acid 2*9; oleic acid 33*5; linolic acid 52-7; linolenic acit.i 2*4%. Traces of aracl)idic acid and meh'sHic acid (probably derived from the wax on the seed coats) were also present *(cf.* Balbi and Brambilla, Olii Min., etc., 1937, *l.c. supra;* Kaufmann, Fette u. Seifen, 1938, 46, 288). An oil (iodine value 137*8) examined by Kauf-

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[1] The hydroxyl values were determined by Normanni method; the approximate equivalent acctyl values have been obtained by calculation.

mann and Fiedler (*ibid.* 1937, **44,** 286) contained 10-8% of saturated acids but no linolenic acid.

The phytosterols of grape-seed oil appear to consist chiefly of sitosterol with a small amount of a dextrorotatory sterol (Antoniani and Zanelli, Atti. R. Accad. Lincei, 1932, [vi], 15, 284).

The residual seed-cake after expression or extraction of the oil is fairly rich in protein and potassium phosphate and may be employed as an animal feeding-stuff or as fertiliser. In the case of raisin-pips, 15% of tannins can be recovered after extraction of the oil, leaving a residue suitable for cattle-feeding (Rabak, Bull. U.S. Dept. Agric. Bur. Plant. Ind. **276** (1936)).

Hitherto it has been usual to separate the pips from the grape marc before recovering the oil. The fruit pulp, however, also contains a certain amount of fatty matter of a more saturated character, so that a mixed fat, of which about one-half is derived from the pips and the rest from the skins and pulp, can be obtained by treating the unseparated dried marc. Such a fat examined by M. de Girves (Bull. Assoc. Chim. Sucr. 1937, 54, 140) had m.p. 51°, saponification value 182, acid value 26-8, iodine value 118 and unsaponifiable matter 5% (Fachini, Ind. Olii Min. e. Grassi, 1930, 10, 122; S. A. Fabr. Ghim. Arenella, F.P. 635628).

E. L.

GRAPHITE (*v.* Vol. II, 313d).

GRAPHITIC **ACID,** graphitic oxide, is formed on oxidising graphite, *e.g.* by treating it with potassium chlorate in nitric acid (Brodie, Phil. Trans. 1859, **149,** 249; O. W. Storey, Trans. Electro-chem. Soc. 1927, 53, preprint) or in a nitric-sulphuric acid mixture (U. Hofmann, A. Frenzel and E. Csalán, Annalen, 1934, **510,** 34), or by electrolytic oxidation of graphite anodes (U. Hofmann and A. Frenzel, Kolloid-Z. 1934, 68, 149).

Graphitic acid is a green-grey powder of composition approximating to $C_nH_4O_6$. It yields colloidal solutions on treatment with hot water and suffers complete disruption with evolution of water vapour, carbon monoxide and carbon dioxide on heating to 200°.

Attempts have been made to find a definite constitution and stoichiometric composition for graphitic acid (H. Thicle, Z. anorg. Chem. 1930, 1??' ^J KoUoid-Z. 1932, 56, 129). On the other hand it has been described as an adsorption complex of graphite, water, carbon monoxide and dioxide. Recent chemical, X-ray and other physical determinations have led to a different view. It now seems established that graphitic acid is formed by the insertion of oxygen atoms between the laminae of graphite and may be termed a two-dimensional macromolecule. The X-ray and other physical evidence for this structure includes the molecular uni-dimensional swelling in polar solvents di-cussed by Bruins (Rec. trav. chim. 1935, 54, 317). The chemical evidence for this conclusion is briefly: Graphitic acid may be reconverted into graphite by moderate heating (U. Hofmann and A. Frenzcl, Kolloid-Z. 1932, 58, 8); the carbon/oxygen ratio varies between 2-9 and 3-5 but oxygen is never expelled as such nor directly as water; further, oxygen may be replaced by sulphur yielding graphitic sulphide on reducing with hydrogen sulphide (Hofmann, Frenzel and Csalán, *I.e.*).

Graphitic acid has been used in the preparation of threads, films, etc., by evaporating colloidal solutions (G.P. 298605), which are reduced to graphite by phenylhydrazine vapour (G.P. 600768), and also as a binder for carbon and metal oxides in the manufacture of electric heating resistances (G.P. 512264).

GRAPPIERS (*v.* Vol. II, 1356).

GRASS-CLOTHS (*v.* **Vol.** III, **326).**

GRASS LAND. Attention has recently been directed to the high proportion of inferior grass land in Britain. R. G. Stapledon, "The Land, Now and To-morrow," Faber and Faber, 1935, discusses this aspect of our agriculture from a national point of view, and on the results, so far obtained, from the application of his research work to the Cahn Hill Improvement Scheme, Aberystwyth, has shown how each type of grass land can be improved up to the level of that next higher in the scale. In a further book entitled "A Survey of the Agricultural and Waste Lands of Wales," Faber and Faber, 1936, Stapledon and his colleagues have been able, on the basis of a botanical survey, to classify grass land and produce a map of the grazings of Wales. Amongst points of exceptional interest two are of outstanding importance: (1) good rye-grass grazings occupy only 16,000 acres or 0-4% of the agricultural area in Wales, and **(2)** ***Agrostis*** **pasture and** ***Molinia-Nardus*** **moor** together occupy 54*8% of the agricultural area. The 1,697,000 acres of *Agrostis* pasture probably represents the most easily improvable grass land.

The results of recent research into the possibilities of grass as a food for live-stock have opened up new problems in connection with grass land improvement. Earlier grass-land research dealt mainly with two aspects: the effect of fertilisers, especially lime and basic slag, and the production of new swards by sowing, mainly in the north of England and Scotland. Accounts of this work are available in the Guides to the experiments on the Northumberland County Council's farm, Cockle Park (King's College, Newcastle-on-Tyne), and the publications of the North of Scotland Agricultural College, Aberdeen.

Large areas of grass land have become so noticeably deficient in lime and phosphate that the basis of the Government's agricultural policy as approved by Parliament in the Agriculture Act, 1937, has been to subsidise the use of lime and basic slag.

LIME-DEFICIENCY.—In areas of acid soils, especially, on Coal Measures and Millstone Grit, the main factor limiting grass land productivity is lime-deficiency. The effects of lime-deficiency in the soil are accentuated in industrial areas by smoke pollution, which has an indirect effect on the crop through the soil and a direct effect on the plant itself. An abnormal accumulation of sulphur compounds in soil and crop is noticeable under such conditions, and the effect is worst on perennial crops such as grass. The application of lime quickly increases the calcium content of the herbage, but a change *in* the botanical composition is slower in appearing in permanent grass. It is usually more economical to plough out the old sward, incorporate lime with the newly turned soil, and re-sow.

PHOSPHATE-DEFICIENCY.—Most clay soils, but especially Boulder Clays, exhibit serious phosphate-deficiency when under grass. Phosphatic fertilisers differ somewhat in their effectiveness according to soil and climate, but correctly used they have a marked effect on the clover content of a sward and subsequently, through enhanced fertility, on the productivity as a whole. Phosphoric acid recovery in the herbage on seriously phosphate-deficient soils is low (E. M. Crowther, J. Roy. Agric. Soc. 1934, 95, 34). On Boulder Clay at Cockle Park the recovery from one application was less than 10% over a period of 3 or 4 years during which frequent cuts were taken. The balance of the P_2O_5 is still held in the surface soil. After regular applications of basic slag for 40 years the recovery is higher, and it appears as though a certain degree of soil saturation in regard to phosphoric acid has to be reached before a reasonable recovery of added P_2O_6 is possible in the herbage (J. A. H&nley, Proc. 4th International Grassland Congress, Aberystwyth, 1937).

Recent research has shown that the actual returns from the use of fertilisers depend very much on the efficiency of the " management " of the grass, *i.e.* the methods of utilising the crop. Methods of cutting and grazing can exert almost as big an influence on the sward as methods of manuring (Martin Jones, Empire J. Exp. Agric. 1933, 1, No. 1, 43-45). In fact the condition of large areas of our natural and semi-natural grazings is due entirely to management methods. The influence of extensive sheep grazing, the burning of heather grazings, the use of cattle, the stage at which grass is grazed or cut, and the taking of regular hay crops, all affect botanical composition and quality.

Quality may be affected to such an extent that herbage becomes seriously mineral-deficient. Overseas, in the Dominions and elsewhere, deficiency diseases are common and well recognised (J. B. Orr, " Minerals in Pastures," Lewis, 1929). In this country they are not so pronounced, but there is a good deal of evidence that mineral-deficiency is at least a predisposing cause of certain sheep diseases.

Moreover, the vast changes in methods of stocking grass land, *e.g.* the increase in the output of milk and of young stock and the slaughter of younger animals for meat, mean that a much bigger proportion of the live-stock carried is either milk-producing or young growing stock removing relatively large amounts of minerals.

The proportion of CaO in the dry matter of reasonably good grass is usually not less than 1% and of P_2O_5 not less than 0-75%. These percentages are greatly exceeded in many instances. Whilst 0-4% P_2O_5 is a low figure, less than 0·1% P_2O_5 has been observed in the herbage of some open hill grazings (W. L. Stewart and A. Phyllis Ponsford, J. Comp. Path. and Therap. 1930, 59, Part I, 49-U2).

Generally speaking, the grasses are not as mineral-rich as the clovers or the weeds, but properly managed grass, converted in the young leafy stage, has a high mineral content (T. W. Fagan and H. T. Watkins, Welsh J. Agric. 1932, 8, 144-151). Stapledon has advocated the use of such plants as daisy, plantain and buttercup to some extent on poor upland mineral-deficient grazings.

INTENSIVE MANURING AND GRAZING.—The nutritive value of pasture herbage depends very much on the stage of growth at which it is removed. The so-called " intensive management" of grass land is aimed at converting it as nearly as possible at its most nutritious stage of growth, *i.e.* with the maximum amount of leaf and the minimum of stalk. This stage is usually attained at 4-6 weeks growth from the previous close grazing or cutting. The herbage under normal conditions of growth is then about 6-8 in. high and contains about 20% crude protein in the dry matter. On analysis the dry matter is approximately equivalent to a balanced ration for milk production and can be kept at that stage throughout the season by regularly repeated grazings or cuttings. Such a method makes a heavy drain on plant nutrients in the soil and calls for correspondingly heavy manuring. It also calls for skilful management of the grazing since growth is uneven from month to month in all seasons.

The method involves " rotational grazing " over a series of fields prepared for grazing at intervals, live-stock being concentrated on each field in turn. Theoretically this method is sound but in practice it is interfered with by seasonal changes in rainfall and temperature, so that modifications of the original strict rotational plan are the rule.

The numerous experiments carried out in connection with this method have, however, furnished new and valuable information on the possibilities of grass, and made it clear that as a crop it offers food for live-stock of " production " as well as " maintenance " quality, and further, if it can be preserved at the right stage of growth, material for winter as well as summer " keep."

GRASS ENSILAGE.—Although special, crops have been grown for ensilage in this country it was not, until feeding stuffs became short during 1914-18, a popular method of preserving grass. If green grass is heaped in a pit or stack, fermentation processes lead to loss of dry matter which in some cases may result in a loss of nutritive value as high as 40%. It is estimated that the average loss is 25%. These processes can be artificially arrested and two methods for doing this have recently been tried :

(1) Increasing the soluble carbohydrate content by watering on molasses as the heap is made (usually in a silo), and
(2) Adjusting the p_H by use of hydrochloric or sulphuric acid (A.I.V. process).

The latter method gives the least loss under skilful control but, on the average farm, the method proves difficult to handle and the use of molasses is probably the easier and safer plan (W. M. Davies, G. If. Botham and W. B. Thompson, J. Agric. Sci. 1937, 27, 151).

GRASS DRYING.—It is, however, possible that artificial drying of young grass of high quality will take its place with other methods of copservation. Drying of green fodders, especially lucerne, has been practised for many years, but the drying of young grass was first tried in this country on a really important scale in 1936 when about 10,000 tons of dried grass were produced. In 1937 the process was extended and several new types of drier introduced. It has been established that young grass can be successfully dried without appreciable loss of protein, minerals, carotenoids or digestibility, and the success of the practice depends on :

(1) The production of an economical drier;
(2) The regular production of grass of a quality suitable for drying throughout the season; and
(3) The introduction of this now concentrated food into live-stock rations.

The driers now in use have a rather low output and an improvement of 20% in efficiency would do much to put the cost of dried young grass on a basis comparable with that of other concentrated foods like oil-cakes. Much research remains to be done on the timing of grass which is as dependent on temperature and moisture conditions and on strains of plants used as it is on fertilisers.

Much preliminary work has been done or the nutritive value of young grass (H. E. Woodman and D B. Norman, J. Agric. Sci. 1932, 22, 852-872). With efficient drying young grass loses little of its nutritive value in the process. High temperatures can be used so long as the grass contains sufficient moisture, but the grass is damaged if subjected to high temperatures after it is dry. Usually temperatures of 300-400°C. are used throughout and the grass takes from 10 to 15 minutes to pass through the drier.

Although dried young grass has a high crude protein content, it can scarcely be produced yet at a price to compete with other high-protein feeding stuffs, and the main commercial value depends on its carotene content. Most of the dried grass sold in 1937 was purchased by feeding-stuffs manufacturers and mixed in the form of meal in poultry rations, thus replacing, to some extent, lucerne meal. The carotenoids in dried grass are effective in maintaining colour in the yolk of eggs and in milk during the winter period when green foods are not available. The guaranteed minimum total carotenoid content has, in some cases, been 250 mg. per kg. of dry matter, but dried grass giving nearly 5 times this amount is not unusual.

Young grass after drying is usually stored in fairly air-tight bags as meal, or is tightly baled as it comes from the drier. Exposure rapidly reduces its carotene content.

For information on all aspects of grass drying *see* E. J. Robeits, Agric. Research Council Report, " Grass Drying," 1G37.

NEW STRAINS OP HERBAGE PLANTS.—Recent research into the nutritive value of herbage has given added importance to the plant breeder's work. The successful attempts of R. G. Stapledon and his colleagues at the Welsh Plant Breeding Station, Aberystwyth to breed grasses and clovers of greater persistency in the sward, with high proportion of leaf to stalk, particularly early or particularly late have provided a new and wide choice of plants for sowing land down to grass to suit modern needs for carefully " timed " production.

GRASSES.

Strictly speaking, grasses are meadow and pasture plants belonging to the *Graminem.* The term grass, however, is used by the agriculturist to denote the association of plants—grasses legumes and weeds—found in cultivated swards. The associations vary from soil to soil according to soil reaction (acidity) and general fertility.

Cultivation of grass land usually aims at a sward consisting of perennial ryegrass *(Lolium perenne)* and wild white clover *(Trifolium repent),* the two dominant plants in the befct British grazings. Modern seed mixtures for sowing land to grass contain relatively few (4 or 5) species. Strains bred to'persist and to produce a high proportion of leaf to stalk are available.

Young leafy grass is very digestible, -rich in protein, minerals and carotenoids, and is in general the most reliable and cheapest food for live-stock. Mature grass has a low protein and high fibre content.- The clovers and certain weeds *(e.g.* plantain, daisy, buttercup) are richer in minerals than the grasses.

" *GRAVOCAINE* •• (*v.* Vol. I, 369c). A" J, H,

G * fASES.-The term " grease," originally applied to all kinds of fat having a soft, buttery consistency, is now restricted to low-grade inedible fats (mostly of animal origin) recovered from waste products, such as slaughterhouse and packing-house waste, condemned carcases, hotel, restaurant and ships' food-wastes, bones, garbage, skins, etc. Lubricating greases, which mostly contain mineral oil products, are not considered in the present article.

In the United States the term " grease " was formerly used to denote inedible hog-fats, as contrasted with " inedible tallow " derived from cattle and sheep; but this differentiation is no longer strictly maintained, especially outside the packing-house,and in general American trade the distinction between " grease " and " tallow " is merely one of consistency, the titer (f.p. of ^££ty x. acid8: 37-3»-5°C for greases and [illegible] Allows) serving as a rough guide, Lard and tallow greases, however, can be recovered separately in the large packing establishments, and a distinction is made in the trade [illegible] Jee x1} /***««' *grease* or *packing-house grease* and other types; the first-named is sometimes accompanied by the statement that it consists wholly of hog fat and is graded in three qualities (of which the first two are further subdivided); viz. " white grease." "yellow grease" and " brown grease." *While grease* resembles lard in appearance and is prepared from cleaned, fresh material which for some reason cannot be put to edible purposes: *yellow grease* comes from condemned or decomposed material, or ununshed carcases, viscera, etc., whilst *brown grease* represents the lowest grade and is obtained from all kinds of offal, sweepings, catch-basin accumulations, etc.

[illegible] f J?ackine-ho"^. greaseH are re- from hotel and restaurant wanton *(kitchen grease* or *house grease* or *melted stuff).*

condemned carcases, bones, slaughter-house and butcher's wastes, etc., garbage *(see* GARBAGE FATS), etc.; all these greases must be looked upon as low-grade varieties or mixtures of lard, tallow, bone fat, horse fat, etc.

They are characterised by a dark colour, a high percentage of free fatty acids and a high content of unsaponifiable matter: t^ey also have an objectionable odour.

The bulk of the greases are obtained either by boiling out the fatty tissues with open steam under pressure in closed digesters (the Vet-rendering system; *cf.* BONE FAT) or by dry-rendering processes in which the comminuted raw material is heated indirectly in jacketed vessels, without the addition of extraneous water, and the liberated grease is recovered by straining and pressing the solid residue *(cracklings).* Any residual grease in the cracklings or in the solid residue *(tankage)* frcyn the wet-renderinz process may be recov&ed by extraction with solvents as *extraction grease.*

The best qualities of grease, notably the packing-house greases, are used as substitutes for lard and tallow in the soap and candle industries. According to I?. B. Zapoleon (" Inedible Animal Fats in the United States," Leland-Stanford Univ., Fats and Oils Studies, No. 3, 1929) the bulk of the grease in the U.S.A. is pressed to furnish *grease-(inedible - lard-) stearin* and *grease-(lard-) oil.* The latter is used as a lubricant, and in the preparation of cutting and cooling oils for the metal-working trades and soap emulsions for woollen mills, leather finishing, etc. The grease-stearin, like much of the unpresnd grease, is employed for the manufacture of soaps, lubricating greases (cup greases), and for the> manufacture of red oil (commercial oleic acid, for the preparation of textile' soaps, etc.), stearine (for the candle, cosmetic and rubber industries) and glycerin.

A further series of greases arises as by-products of the leather industry: *skin greases* are obtained in the cleaning (scraping) of the skins prior to tanning, whilst various greases may be recovered by extraction from tanned and tawed skins, leather-clippings, wash-leather trimmings, etc.

Stuffing greases comprise various mixtures of ctegras *(q.v.),* horse fat, skin grease, tallow, fish-stearin, egg oil, etc., which are worked into the tanned leather in the stuffing or currying processes. The excess of unabsorbed grease which is scraped off the leather after this treatment is known as *curriers' grease:* if the original stuffing grease consisted of fairly good tallow and whale-stearin, the *hard curriers'-grease* derived fronv it may be employable in the manufacture of low-class soaps, but if the-original Htuffing grease contained much unsaponifiublo matter, or considerable quantities of fish oils or whale oil, then the proportion of oxidised acids and unsaponifiable matter will be high and render the product useless for soap-making, and such grease will be sold as *animal grease,* or —if the consistency is very soft—as *animal oil.*

Whale grease and *fish-stearin,* which represent low-grade stearins or solid glyccrides separated from whalo oil or fish'oils, are chiefly worked up into stuffing greases and ddgras substitutes.

Fuller's grease or *seek oil* is the fatty matter recovered from the soap-suds which have served for scouring silk, woollen or cotton goods by acidifying the waste suds with mineral acid, and consists of a mixture of fatty acids derived from the soap employed, together with any grease present in the goods.

Wool grease (wool fat, recovered grease, Yorkshire grease, brown grease; known in the United States as "dégras," "English dégras" or "German dégras ") is the crude mixture of wool wax and fatty acids recovered from the soapy liquor used for the scouring of raw wool, by cracking the liquors with mineral acid *(cf.* black grease, *below)*; some wool grease is now recovered by mechanical means, and therefore contains less soapy material or fatty acids. Since the pure wool wax is a wax and not a fat, wool grease differs from the other greases considered in. containing no combined glycerin.

Crude wool grease is used as a lubricant (with or without the addition of mineral oils), as a stuffing grease and degras substitute; some is refined for use as " lanolin " (pure wool wax) in the preparation of cosmetics, ointments, temporary rust preventives, etc., but the bulk of the crude grease is distilled and worked up in the manner described under black grease *(below)* for the preparation of *distilled grease oleine* (chiefly used as a wool oil) and *distilled grease stearine* (employed as a " sizing tallow" or stuffing grease), and as an inferior material in the soap and candle industries. These products give the tiocholesterol reaction, and are characterised by the presence of considerable quantities of unsaponifiable hydrocarbon material, produced by decomposition of the neutral wax esters during the distillation.

"Black grease'¹ is the dark, almost black, fatty matter which is recovered from cottonseed mucilage (soap-stock) on decomposing this with mineral acid *(see* COTTONSEED OIL). This black grease is used in the manufacture of low-class candle materials after a purification by distillation with superheated steam and further treatment of the distillate in a manner similar to that practised for the working up of fatty acids in the candle industry.

E. L.

GREENALITE. A hydrated iron silicate occurring in the form of green granules in sedimentary rocks, and closely resembling glauconite *(q.v.)y* from which it differs in containing no potassium. The composition varies somewhat; one analysis gives the formula

$$Fe_2'''(Fe'',Mg)_3(SiO_4)3,3H_{J8}O$$

and another

$$3FeO\text{-}4SiO_a,2H_2O$$

It occurs abundantly on the Mesabi Range iu the Lake Superior district of Minnesota, and by its alteration has given rise to ferruginous cherts and immense deposits of iron ore (C. K. Leith, Monograph U.S. Geol. Survey, 1903, 43; F. JoUiffc, Amer. Min. 1935, 20, 405; J. W. Uruner, *ibid.* 1936, 21, 449). A greenalite-chert is found at Glenluce, Wigtonahire (W. Q. Kennedy, Min. Mag. 193G, 24, 433).

L. J. b.

GREEN-EARTH. (Ger. *Orünerde.)* A term loosely applied to a variety of earthy minerals of a bluish-green, or dark olive-green colour occurring as alteration products in basic igneous rocks. It includes more particularly the species *celadonite* (or *seladonite),* and various indefinite members of the chlorite group, *e.g.* delessite, chlorophfleite, kirwanite, viridite, etc. Many of these are of indefinite composition and probably mixtures. They are often met with as a green lining in the amygdaloidal cavities of altered basaltic rocks, and form the " skin " of agates and other secondary minerals filling these cavities. Crystals of augite in the same rocks are sometimes completely altered to a soft aggregate of green-earth still preserving the sharp outlines of the original crystals. Similar pseudomorphs after hornblende also occur. Larger irregular masses fill cavities and fissures in these rocks. The well-known green-earth of Monte Baldo near Verona is referable to celadonite (K. Hummel, Chem. Erde, 1931, 6, 468). An analysis of material from this locality gave: SiO_2 54-84, TiO_2 0-10, Al_2O_3 1-22, Fe_2O_3 19·16, FeO 4-39, MnO 0-28, MgO 5-34, CaO 0-24, Na_2O 0-82, K_2O 9-75, H_2O 3-77, total 99-91 (Gümbel, 1896). This composition is very similar to that 'of glauconite, with which celadonite is perhaps identical, differing cily in its state of aggregation and mode of origin and occurrence. This celadonite green-earth is worked commercially as a pigment in the Italian Tyrol; and similar material could be obtained from many other localities.

L. J. S.

GREEN EBONY. This yellow dyewood, a native of Jamaica or West Indies, is obtained from the *Excoecaria glandulona* Siv. or *Jacaranda ovalifolia* R. Br. The trunk of the tree is about 6 in. in diameter; the wood is very hard and of an orange-brown colour when freshly cut, and stains the hands yellow. Bancroft, " Philosophy of Permanent Colours," 1813, ii, 106, and O'Neill, "Dictionary of Calico Printing and Dyeing," 1862, mention the use of this dyewood in dyeing greens and other compound shades, sometimes in place of old fustic, but it does not appear at any time to have been largely employed. It was also used to some extent as a dye for leather and for greening blacks in silk dyeing

Perkin and Briggs (J.C.S. 1902, 81, 210) examined green ebony and isolated two crystalline colouring matters, *excoecarin and jacarandin;* these were distinguished by the fact that only the latter is precipitated by lead acetate. About 17 g. excoecarin and 3 g. jacarandin were obtained from 8 kg. of the wood.

Excoecarin, $C_{13}H_{12}O_5$, lemon-yellow needles, melts with effervescence at 219-221°, and is soluble in aqueous and alcoholic alkaline solutions, forming violet-red liquidswhich are rapidly oxidised on exposure to air and assume a brown tint.

The *tribenzoyl* derivative forms colourless needles, m·p. 168-171°, and the *dimethyl ether* yellow needles, m.p. 117-119°. On fusion with alkali, excoecarin gives hydroquinone carboxylic acid (2:5-dihydroxybenzoic acid) and a sub stance melting at 124° which is probably hydrcj toluquinone (2:5-dihydroxytoluene).

By the action of bromine, excoecarin is oxidised to *excoecarone,* $C_{13}H_{10}O_5$, flat copper-coloured needles or leaflets, m.p. about 250°, and this isnreconverted into excoecarin by the action of sulphurous acid. With an alcoholic solution of qumone, excoecarin gives the compound ?ZS4;VCi3Hi2O5» minute green leaflets, m.p. u (decomp.), from which sulphurous acid also regenerates excoecarin. Since the latter contains a quinol or toluquinol nucleus, ex-?!iCa^?o is thus proba*>ly a p-quinone (Perkin, *ibid.* 1913, 103, 657).

Excoecarin does not dye mordanted fabrics, but is a substantive dyestuff in that it has a weak but decided affinity for the animal fibres with which it gives* preferably in the presence of tartanc or oxalic acid, yellow shadesf

Jacarandin, C_{14}*;$_2O_6$, yellow plates or S S M m-P'i43-245°, dissolves sparingly in alcohol and the usual solvents to form pale yellow hqmder having a green fluorescence. With alkali hydroxides it gives orange-red solutions, with alcoholic lead acetate a bright o? 5 Pr®ctPitate» and with alcoholic ferric S 3 lde * dark greenish-black solution. It dyes mordanted woollen faorics the following shades:

Chromium.	Aluminium.	Tin.	iron
Dull yellow-brown.	Orange-brown.	Bright golden yellow.	Deep olive.

Diacetyljacaran : in pale yellow needle8, m.p. 192-194°, when i* digested with boiling alcoholic potassium acetate, yields the *sdU*

(C$_{14}$H$_{11}$O$_6$·C$_{14}$H$_{n}$O$_6$;)K

yellow needles. *Dibenzoyljacarandin,* yellow prismatic needles, melts a*. 167-169°.

As indicated by Bancroft *(op. cit.)*$_9$ the colours given by green ebony are similar in character to those yielded by old fustic. Employing mordanted woollen cloth, the following shades are produced:

Chromium.	Aluminium.	Tin.	Copper	Iron.
Dull yellow-brown,	Dull brown-yellow.	Golden yellow,	Pale brown,	Olive-green,

,,,,,, ' #A. G. P. and E. J. C.

GREENOCKITE. Cadmium sulphide, J<Jb, crystallised in the hexagonal system with nemimorphic development and isomorphous with *wurtzite* (ZnS)v This and the still rarer cadmiujr* oxide, and *otavite* (basic carbonate), are the only minerals that contain cadmium as an essential constituent. Distinct, though small, crystals have been found in Scotland, in the neighbourhood of Glasgow. They occur very spriringly with *prehnite* in amygdaloidul basalt in the Bishopton railway-tunnel, in the ISoyleston quarry at Barrhead in Renfrewshire, and in the Bowling quarry in Dumbartonshire, lhey are honey- to orange-yellow, transparent to translucent, and have a resinous to adamanhne lustre; the streak is orange- to reddish->n e''ow- 8p.gr.4-8-49; hardness 3-3J. Minute (00.» ram.) red crystal* have been found at Llallagua. Bolivia (8. G. Gordon, Not. Nat. Ac-ad. Nat. Sci. Philadelphia, 1939, No. 1). Traces of cadmium are often present in zinc-blcnde (up to 1*5%, and in the ores of the Joplin district in Missouri averaging 0-358%), and with the weathering of this mineral cadmium sulphide remains as a thin, powdery, canary-yellow coating (" cadmium-ochre "), or it may impart a tinge of colour to the secondary zinc minerals *hemimorphite* and *smithsonite* (" turkey-fat ore "). In this form the mineral is known from many localities, though never in large amount. Being colloidal, it does not agree with the definition of greenockite as given above; and, again, the possible existence of a cubic form of cadmium sulphide is suggested by the isomorphous presence of this constituent in zinc-blende, although this modification has not been prepared artificially. The name *Zanthochroite* (A. F. Rogers, 1917) has therefore been suggested for this colloidal form of cadmium sulphide. Hemimorphic hexagonal crystals of cadmium sulphide have been prepared artificially^ reid they are not uncommon as furnace products. The artificial crystals have sp.gr. 4-820 and the high refractive indices ϵ_{Na} 2-529, ω_{Na} 2-506.

L. J. S.

GREEN STONE (t^Vol. IV, 8a, 536).

GREGE (v. Vol. V, 94a).

GRIESHEIM CELL (*v.* Vol. III, *50d*).

GRIGNARD REAGENTS. Unsymmetrical magnesium compounds of type RMgX where R=an organic residue and X=halogen. The use of Grignard reagents in organic chemistry may be traced to the use by Barbier (Compt. rend. 1898, 128, 110) of magnesium in place of zinc when condensing methyl iodide with methylheptenone. After unsuccessful attempts to exploit this innovation Grignard (Ann. Chim. Phys. 1901, [vii], 24, 437), believing that the more electropositive magnesium should be more reactive than zinc, showed that alkyl iodides react at room temperature with magnesium, and since then such reagents have been widely used for synthetic purposes. They do not normally exist in the free form RMgX but are combined with one (Blaise, Compt. rend. 1901, 132, 839; Grignard, *ibid.* 1901,132,558) or two (Tschelinzeff, Ber. 1904, 37, 2084, 4534; 1905, 38,3664; 1906,39, 773) molecules of ether; the latter may be replaced by tertiary amines, sulphones or organic compounds of selenium, tellurium or phosphorus. These, secondary reactants are only catalysts and, using minor quantities of these, Grignard reagents may be obtained in the solid state from benzene, solution. When isolated they are inflammable in air but fortunately may, with few exceptions, be used in ether or other solution without isolation.

For synthetic purposes the reactions of Grignard reagents may be summarised as follows:

(a) Reaction with active hydrogen atoms

$$RH+R'MgX \rightarrow RMgX+R'H$$

When R' is a lower aliphatic group 1 mol. of gaseous paraffin is liberated for each carboxyl, hydroxyl or NH-group present; this reaction provides the basis of the Tschugaeff-Zerewitinoff determination of such groups (Pregl-Roth, " Die quantitative organische Mikroanalyse," 1935) and further reactions of the N-magnesium compounds afford valuable routes to C-homologues in the pyrrole, indole and other series.

(6) Reaction with reactive halogen atoms

$$R{\cdot}COCl+R'MgX \rightarrow MgXCl+R{\cdot}CO{\cdot}R'$$

When excess of the reagent is used the resulting ketone may react further to give a tertiary alcohol.

(e) Most of the synthetic applications depend on the addition of Grignard reagents to unsaturated groupings :

$$RR''CO+R'MgX \rightarrow RR''CR'{\cdot}OMgX$$

$$\xrightarrow{H_3O} RR''CR'{\cdot}OH$$

$$RCjN+R'MgX \rightarrow RCR':NMgX$$

$$\xrightarrow{H_2O} R{\cdot}COR'$$

Clearly when two such groups are present in the same molecule reaction becomes more complex although the entering Grignard reagent usually shows a preference for one of the centres of possible reaction.

Reviews.—Schmidt, Ahrens Sammlung, 1906, 10, 67, 146; 1908, 13, 357, 446; Hepworth, J.S.C.I. 1922, 41, 7; Courtot, " Traité de Chim. Org.", 1937, V, 86; the last is unusually complete and contains an exhaustive bibliography.

GRISEOFULVIN (r. Vol. V, 58c).

Gftl-SHI-BU-ICHI. Japanese name for an alloy of copper and silver of a rich grey colour.

GRISON TETRYLITE COUCHE (*v.* Vol. IV, 4876).

GRISOU NAPHTHALITE-ROCHE (*v.* Vol. IV, 474(Z).

GRISOUTINE COUCHE (*v.* Vol. IV, 5536).

GRISOUTINE ROCHE (*v.* Vol. IV, 5536).

GROG (*v.* Vol. V, 566a).

GROTTHUS-DRAPER LAW. Photochemical reaction can only be brought about by radiation which is absorbed by some component or components of the system in which the reaction occurs. Stated in these broad terms this may be taken as the fundamental postulate of photochemistry. Its first expression we owe to Grotthus (Ostwald's Klassiker, 1817, No. 152, p. 101) who deduced that only light which is absorbed by a substance can cause it to become chemically active. Grotthus' paper was, however, rather rapidly forgotten and his proposition was independently restated by Draper (Phil. Mag. 1841, [iii], 19, 195), who was also able to provide, in a series of later papers, an experimental verification of the law as a result of his studies of the photochemical union of hydrogen and chlorine. The law is accordingly associated with the names of both workers.

While the law is without exception, it is entirely qualitative, the nature of the reactivity, the spectral region which is effective (for the law's converse that all light which is absorbed produces chemical change is far from true), and the relation between the amount of chemical reaction and the energy absorbed, are all undefined and must be determined by experiment. Neither is it necessary that the absorbing substance be a reactant, as exemplified by the important phenomenon of photo-sensitisation, in which the light is absorbed by a molecule (*e.g.* mercury) which, after transferring the energy it has absorbed to a reactant molecule, takes no part in the subsequent chemical change.

Quantitative expression of the relation between the energy absorbed and the amount of chemical reaction, and, indeed, any coherent etudy of photochemistry, bad to await the development of the quantum theory and of the theory of chain reactions.

D. W. G. S.

GROUND NUT. A term often used to describe the tuberous roots of the earth nut *(JJunium* spp.) or the peanut *(Arackia Iiypogtxa)*. According to Wynton the term is more properly restricted to the dark brown root swellings of *Apios tuberosa.* These " tubers," which are of similar size and shape to a hen's egg, grow wild in many parts of America and are cultivated in central European countries as a substitute for potatoes.

Tyjiiea.1 analyses of the American ground nut and of a Japanese variety *(A.fortumi)* are:

	r.	II.
Water	70-7	68-6
Crude protein . .	4-06	419
True protein . . .	1-88	1-50
Fat.	1-00	**(My**
N-free extract . .	1865	24-54
Starch	702	**18*0**
Pentosane	2-60	1-46
Fibre	3-55	120
Ash	205	1-30

I. .1. *luberosa* (Brlgliutt), SUz. spur, agr, ital. 1900 33. 72>~

II. *A. Jortunei* {Hemml, J. Coll. Agric. HoLkiililo. 1918, 8, 88).

According to Henuni the carbohydrates of *A. fortunei* include reducing sugars 1*10, non-reducing sugars 2-85, dextrin 10 and galactan 1-02%. The hemi-cellulose of *A, luberosa* yields J-arabinoae and <f-galactose on hydrolysis.

A. G. Po.

GROWAN *{v.* Vol. I11, 32c).

GROWTH - PROMOTING SUBSTATICES are substances which have the power of regulating the form and rate of growth ;;i the plant world *(set* Auxin). They are sometimes referred to as " plant hormones," but the term is in many respects inappropriate. There is no evidence that gro wth-promo tin g*substances are secretions of special organs as is the case with animal hormones. The association of high (immitnLtions of auxin with rapid vegetative **growth** in the aerial parts of plants has already been referral **to** (AUXIN). The opposite direction wf growth with heteroauxin **(indole-S-aootio** acid) in stimulating root formation has now found its obvious horticultural application and commenial preparations of this and related substances are now marketed for inducing the rapid rooting of plant cutting. Tincker (J. Roy. Hort. Soc. llWti, 61, 51U; 1038,63,210; 1939, 64, 554) records the results of rooting trials with a large number of plant species, using a variety of pure and commercial samples of gnwlh-**promoiiofi** substances.

From time to timu additions lire made to the number of substances exhibiting growth-regulating ability and in some cases, e.y. that of naphthylacetic acid, activity exceeding that of the naturally-occurring heteroauxin is recorded (Pfahler, Jahrb. wiss. Bot. 1938, 86, 675). According to Koepfli, Thimann and Went {J. Biol. Chem. 1938, 122, 763), growth-promoting activity is dependent on a particular molecular structure which includes the following characteristics: (i) a nuclear ring system containing a double bond; (it) a side-chain containing a carboxyl group {or a group from which this ia^eaily derived) separated from the nucleus by at least one C atom; (iii) a particular space relationship between the side-chain and the nucleus. Other investigations by Thimann *tt al.* suggest thatfjthe effect of growth-promo ting substances within tha plant is initiated by :ts action in increasing protoplasmic stream ing, this being influenced by respiratory activity (oxygen supply) and by the concentration of growth-pronwtijig substance present. It would appear that heteroauxin acts upon the cell substance rather than on the cell wall. Went (Plant Physiol. 1938, 13, 55) advances the theory that in the higher plants growth-substances do not alone produce their characteristic effects on growth, but operate by controlling the distribution within the plant of other substances, described as " calines." *Caulocalim, rhizocaline* and *phyUocaline* are natural plant constituents essential for the elongation of stems and lateral buds, for root formation and for leaf growth respectively.

The action of heteroauxin on plant growth ia enhanced by the presence of accessory substances, *e.g.* certain amino-acids, notably proline, and by vitamin B. (aneurin), a minimal amount of which is probably essential for the action of the growth-promoting substances.

The sealing of plant wounds is brought about by the rapid production of new tissue by division of adjacent cells. English and Bonner (J. Biol. Chem. 1937,**121,** 791) ascribe this sudden stimulation of cell activity to the action of a growth-promoting substance (wound " hormone") which they name *Imutttatin,* the isolated methyl ester of which has the formula $Ci.H_{17}O|N$. A later paper by English, Bonner and Haagen-**Bmifc** (Proc. Nat. Acad. Sci. 1939, 25, 323) reports the isolation of a second wound " hormone," tt dibasic acid of formula $C_uH_{80}O_4$.

Bios, the growth-promoting substance associated with yeast growth for a number of years, is now regarded as containing at feast five constituent factors:

(a) fue#o-lnositol, a necessary growth factor for nearly all types of yeasts.

{b) Pantothenic acid, a complex of 0-alanine with an unidentified hytlrosy-acid, to the calcium suit of which Williams *tt at.* (J. Amer. Chem. Soc. 1939, 61, 454) assign the formula (CgH^OjNJjCa. Pantothenic acid *is* also of considerable importance in the animal world, in which it is actively concerned in carbohydrate inetubolism, and occurs in considerable amounts in the liver and muscles. Jukes *{ibid.* 1939, 61_f 975) records the close similarity between panto-therrit; acid and the chick anti-derniiilitis factor.

(c) *Anrarin [v.* Vitamin li_t*]* decelerates the fermentutiun activity of a number of yeasts, the pyrimidine rather than the thiazole component of the vitamin being associated with its activity.

(d) Vitamin B_e has also been shown (gchulz *et ah, ibid.* 1939, 61,1931) to stimulate fermentation activity and the reproduction in yeast.

(e) *Biotin,* isolated by Kögl, is a widely distributed and essential growth factor for yeasts (Chem. and Ind. 1938,57,49).'

Aneurin is also of importance in the growth ot a number of moulds. In this case also the physiological activity appears to be associated with the pyrimidine constituent, although the thiazole component musft also be present. In some cases organisms grow satisfactorily if either the vitamin or the thiazole component is a&ded to the nutrient medium but not if the pyrimidine constituent alcSie is given. In such cases it is presumed that the organism can synthesise the pyrimidine but not the thiazole portion of the vitamin molecule. <• O\her organisms appear to be able to synthesise the whole vitamin and others must be supplied externally with the vitamin or its constituent pyrimidine and thiazole derivatives. A possible scheme of classification of the lower organisms on the basis of their requirements in respect of aneurin, or its pyrimidine or thiazole components, or of a mixture of these is indicated by Bobbins (Proc. Nat. Acad. Sci. 1938, 24, 53).

Nicotinic acid and nicotinamide may also serve 'as growth factors for certain bacteria (Knight and Mcllwain, Biochem. J. 1938, 32, 1241) and are possible constituents of the bios complex.

A. G. Po.

GUAIAQETIN. Sodium salt of the o-hydroxphenyl ether of glycollic acid.

GUAIACOL ***(Mongmethoxycatechol),***

$$OHC_6H_4OMe,$$

is a distillation product of guaiacum resin (Herzig and Schiff, Monatsh. 1898,19, 95), and occurs in beechwood tar, from which it can be separated by treating the fraction of the tar that comes over at 200-205° with ammonia to remove acids; it is then again fractionated, and the lower boiling fraction is dissolved in ether and treated with potassium hydroxide. The potassium salt of guaiacol is filtered, washed with ether and recrystalh'sed from alcqhol, after which it is decomposed with sulphuric acid, and the guaiacol redistilled. (For other methods of separation, *cf.* G.P. 87971,56003,10041&; Chem. ^entr. 1899, I, 764.) Guaiacol is prepared from o-anisidine. 500 g. o-anisidine are diazotised, and the solution of the diazo salt is then poured into a boiling solution of 600 g. of copper sulphate in 600 c.c. of water. The guaiaco^is then separated by distillation in steam (G.P. 167211; Frdl. 1905-7, 128; *cf. also* G.P. 95339; J.S.C.I. 1898,17,269,314).

l*iire guaiacol can be obtained by dissolving catechol (55 parts) in ethyl alcohol (2,000 parts) and adding nitrosomonoinethyl urea. The mixJure is cooled to 0° and 20 parts of sodium hydroxide dissolved in a small quantity of water are added, drop by drop, with constant stirring. The solution is filtered, the alcohol distilled oil', and the residue is fractionated *in* [illegible] (G.P. 18U843; Frdl. 1U05-7, 1151).

Guaiacol is also prepared by heating an equimolecular mixture of catechol, potash and potassium methylsulphate under pressure at 17<M80°, or by heating catechol and methyl iodide in methyl alcohol. In another method a weak base, such as sodium hydrogen carbonate, is gradually added to a mixture of catechol with the alkali or alkaline earth salts of mothylsulphuric acid, in the presence of veratrole as diluent at 160-180° (ZoUinger and Röhling, G.P. 305281; J.C.S. 1918,**114,** i, 497). Thompson (B.P. 5284, 1893) suggests the purification of guaiacol by treatment with a freezing mixture.

Guaiacol made by the ordinary commercial methods is impure; it is hygroscopic and has a low m.p. Moser and Ver. f. Chem. Ind, A.-G. (U.S.P. 1651617 (1927); G.P. 484539 (1925)) have described an improved process. If an insufficient amount of alkali is added to the tar oils the monomethyl ethers of dihydric phenols are first dissolved, and this selective action enables them to be separated from the nonmethylated phenols. (For synthetic methods, *see* Bergström and Cederquist, Iva, 1931, 1, 14; Jakubowski, Roczniki Farm. 1933, 11, 1; Sumarokov, Lesokhimicheskaya Prom. 1933, No. 3, 2, 34; Bentley and Catlow, U.S.P. 19809Q1; Dominikiewicz, Arch. Chem. Pharm. 1934, 1, 1; Gubelmann, Welland and Stallmann, U.S.P. 1623949 (1927); Titherley and Hudson, U.S.P. 1878061 (1932); I.G. Farbenind, A.-G., Marx and Lehmann, G.P. 591534).

Guaiacol 'has a characteristic odour and crystallises in long vitreous transparent prisms, which appear rose-red in sunlight; m.p. 28-5°, b.p. 202-4°/738 mm. (Freyfe, Chem.-Ztg. 1894, **18,** 565); sp. gr. ·i-140 at 25°. When quite pure it is non-caustic and non-poisonous (Béhal and Choay, Compt. rend. 1893, **116,** 197; Kuprianow, J.S.C.I. 1895, 14, 57). Dilling, "Materia Medica," 1939,394, states that it is less toxic than phenol.

It is soluble in most organic solvents, and to a less extent in water. The solubility of guaiacol in glycerol is given by J. A. Roborgh, Dissertation, Amsterdam (1927): 905 fe. of guaiacol is dissolved by 100 g. glycerol (98-2%, Dutch and German Pharmacopoeias) at 20°; the figure in French and British Pharmacopoeias (sp.gr. 1-2612, 86-5%) is 131 at 20°. With a trace of ferric chloride its alcoholic solution gives a blue colour, which becomes emerald-green on the addition of more ferric chloride.

Guaiacol is employed in pharmacy as an expectorant and intestinal antiseptic; also in pulmonary tuberculosis, in cases of typhoid and other fevers, and for the relief of superficial neuralgia. For esters of guaiacol possessing therapeutic properties, *see* B.P. 316750 (1928); 317194 (1928).

Tents.—(1) 2 c.c., of guaiacol mixed with 4 c.c. of light petroleum should separate at once into 2 layers. (2) 1 c.c. of guaiacol should dissolve in 2 c.c. of iV-sodium hydroxide when heated; on cooling the mixture should congeal to a white saline mass, which gives a clear solution with 20 c.c. of water. (3) 1 c.c. of guaiacol shaken with 10 c.c. of sulphuric acid should give a pure yellow colour (British Pharmacopoeia, 1932). For other tests, *see*

Marfori, J.S.C.I. 1891, 10, 487; Fonzes Piacon, Bull. Soc. chim. 1898, [iii], 19, 191; Guerin, J. Pharm. Chim. 1903, [vi], 17, 173.

A solution of $SbCI_5$ in chloroform gives a light brown coloration (or olive-brown), changing to deep green, blue-green and finally deep blue. Guaiacol carbonate gives a lemon or sulphur yellow (Ekkert, Pharm. Zentralhalle, 1934, 75, 49).

Guaiacol (0-05 g.) is dissolved in 5-10 c.c. cone. HCI, a minute crystal of sodium nitrite added and the mixture very gradually heated nearly to boiling, then cooled or diluted and poured into excess of 10% ammonia. Guaiacol gives a green colour. (In the acid stage guaiacol and other phenols often give a red .colour.) (Ware, Analyst, 1927, 52, 1927.)

A micro test for guaiacol is the characteristic precipitate given by diazo-j>-nitraniline (Rosenthaler, Mikrochemie, 1935,19, 17).

Wischo describes colour tests for guaiacol with $FeCI_3$, Jorrison's reagent, aqueous ammonium vanadate, and V_2O_5 in dilute HCI, K_3PO_4, and oxalic acid, respectively (Phann. Monatshefte, 1928, 9, 169).

For the estimation of guaiacol by a coloric metric method, 0-5 g. of the sample is dissolved in a little water, 10 c.c. of alcohol added, and the solution made up to 1,000 c.c.; 20 c.c. of this solution are mixed in a test-tube with 1 c.c. of sodium nitrite solution (1:100) and 1 c.c. dilute nitric acid (1:200). A characteristic red-brown colour is produced, which is compared within about 10 minutes with the colorations given by suitable standard solutions (Adrian, £. anal. Chem. 1901, 40, 624). For the estimation of guaiacol in pharmaceutical preparations, *see* Dominikiewicz, Chem. Zentr. 1931, II, 284; Chernoff, J. Amer. Chem. Soc. 1929, 51, 3072; Christie and Menzies, J.C.S. 1925, 127, 2369.

Guaiacol (or its carbonate) may be estimated gravimetrically as the derivative precipitated by the action of iodine in KI *(cf.* aristol from thymol; François and Seguin, Bull. Soc. chim. 1933, [iv], 53, 711). *See also* Knight, J. Assoc. Off. A'gric. Chem. 1931, 14, 367, and Meldrum and Patel, J. Indian Chem. Soc. 1925, 5, 91.

For estimation of guaiacol in urine, *see* Schmid, Z. physiol. Chem. 1932, 205, 213.

Guaiacol, when treated with hydrogen cyanide, in the presence of sodium or zinc chloride, yields vanillin (Roesler, G.P. 189037; Frdl. 1905-7, 1280; Guyot and Gry, Compt. rend. 1909, 149, 928; Bull. Soc. chim. 1910, [iv], 7, 902). *Barium* guaiacolate is insoluble-in neutral solvents, 100 parts of water dissolve 4-4 parts at 20°; it is partly hydrolysed by hot water. The *calcium* salt has similar properties (Sumarokov, Lesokhimicheskaya Prom. 1933, No. 3, 2, 34). *Copper* salt, *see* $Takatsuka and Iinuma, Bull. Chem. Soc. Japan, 1936,11.358.

Guaiacolmonosulphonic acids can be obtained by treating guaiacol with sulphuric acid between 0° and 140°. The mixture of 2-methoxyphenol-5-sulphonate (ra.p. 106-108°), and 2-methoxyphenol-4-sulphonate (m.p. 97-98°) is separated by converting them into the basic salts of the alkaline earths, or of the heavy metals, the salts of the former acid being readily soluble in water, whereas those of the latter are insoluble or sparingly soluble. By the action of hydrogen sulphide, or some suitable acid, the salts are then converted into their respective acids (G.P. 188506; Frdl. 1905-7, 936; G.P. 132607; Frdl. 1900-02, 113; G.P. 212389; Hahle, J. pr. Chem. 1902, [ii], 65, 95; Lamière and Perrin, Bull. Soc. chim. 1903, [iii], 29, 1228; Rising, Ber. 1906, 39, 3685; Paul, *ibid.* 2773, 4093; André, J. Pharm. Chim. 1898, [vi], 7, 324). With nitric acid the latter acid forms yellow dini§roguaiacol (m.p. 122°), whilst the former acid merely gives a dark red coloration. It is important that when the former acid is used therapeutically, it should be free from the latter compound whifh gpves rise to secondary reactions (Ellis, J.S.C.I. 1906, 25, 335).

The alkali guaiacofeulphonates are employed as drugs (Alpers, U.S.P. 692588; J.S.C.I. 1902, 21, 364). Tagliavini has prepared salts of the sulphonates ^ith antipyretic and analgesic bases (Boll. Chim. farm. 1909, 48, 6).

Carbonyl chloride condenses with the alkali guaiacolsulphonates in alkaline solutions, giving derivatives such *as potassium carbonatodiguaiacol-disulphonate* $CO[OG_6H_3(OMe)SO_3K]_2$, and *potassium carbonatodiguaiacolsulphonate,*

$$C_6H_4(OMe)OCO_2C_6H_3(OMe)SO_3K$$

(Einhorn, G.P. 203754, 1909).

A number of compounds of o-guaiacolsulphonic acid with alkaloids are described by Schaefer (J.S.C.I. 1910, 29, 928).

Guaiacyl benzoate (*"Benzosol,"* benzoyl guaiacol), $C_6H_5CO{\cdot}OC_6H_4OMe$, is a colourless, odourless, tasteless powder, almost insoluble in water, readily soluble in organic solvents. It has m.p. 56°, and is used in the treatment of pulmonary tuberculosis (B.P. 5366, 1890; J.S.C.I. 1891, 10, 383; Walzcr, Chem.-Ztg. Rep. 1891, 15, 165).

Guaiacyl cinnamate (*"Styracol,"* cinnamyl guaiacol), $C_8H_7CO{\cdot}OC_6H_4{\cdot}OMe$, from guaiacol and cinnamoyl chloride. It forms colourless needle-shaped crystals, m.p. 130°, which arc employed in eatarrhal affections of the digestive tracts, and in the treatment of phthisis.

Guaiacyl valerate, $C_4H_9\text{-}CO\text{-}OC_6H_4\text{-}OMe$, a yellowish oily liquid, b.p. 245-265°, is used in medicine under the name of *Geosot* (Rieck, J.S.C.I. 18&7,16, 632).

Guaiacyl salicylate {guaiacol-salol),

$$C_6H_4(OH)COOC_6H_4{\cdot}OMe,$$

is a white crystalline, odourless, tasteless powder; m.p. 65°.

G?mmcyZ«Mrciwa/c, $C_2H_4(CO{\cdot}OC_6H_4{\cdot}OMe)_2$, fine silty needles; m.p. 136°.

"Guaiamar," the *glyceryl ether of guaiacol,* $C_6H_4(OMe)OC_3H_7O_2$, is formed by the action of anhydrous glycerol on guaiacol. It is a white crystalline body, m.p. 75°, soluble in -water and in most organic solvents. It was suggested as an antiseptic for internal and external application (J.S.C.E. 1900, 19, 371; 1902, 21, 1346).

Guaiasanol {guaiacyl diethylaminoacetate hydrochloride), $MeO\text{-}C_6H_4O\text{-}CO\text{-}CH_2NEt_2HCI$. m.p. 184° (Einhorn, Chem.-Ztg. Rep. 1900, 24, 33; 'J.S.C.I. 1900, 464). *By* the action of the monochloracctic esters of phenols with secondary amines of the fatty series, many compounds, similar to the above, have been prepared (Einhorn and Hütz, Arch. Pharm. 1902, 240, 131; G.P. 105346). They are non-poisonous, odourless and strongly antiseptic substances.

Guaiacyl ethoxyacetate,

$$MeOC_6H_4OCOCH_2OEt$$

is a colourless, odourless oil, b.p. 150°/10 mm. The corresponding methoxy derivative boils at 170-171°/10 mm., and has very similar properties to the ethoxy derivative. Both substances are non-poisonous, and can be used therapeutically as external remedies (G.P. 171790; Frdl. 1905-07, 933).

Guaiaform (Geoform) is produced by the condensation of guaiacol (2 mol.) with formaldehyde (1 mol.). It is a tasteless, yellow, non-irritant and non-toxic powder (Ehtert, Pharm. J. 1902, 68, 61). Guaiacol condenses with formaldehyde and $(CH_3)_2NH$ to form 2-hydroxy-3-methoxybenzyl dimethylamine, m.p. 46-47°, b.p. 127-129°, soluble in alkali (Décombe, Compt. rend. 1933, 197, 2£B).

Guaiacyl carbonate ("*Duotal*"),

$$CO(OC_6H_4OMe)_2,$$

is prepared by passing phosgene into a solution of guaiacol in sodium hydroxide. It is a white crystalline powder, m.p. 85-88°, soluble in most organic solvents, but insoluble in water. Its alcoholic solution yields no characteristic colour with ferric chloride. Therapeutically it is very similar to guaiacol (G.P. 99057, 58129, 117346, of 1898; G.P. 224160; Einhorn, Chem. Zentr. 1910, II, 518; *see also* Mazover, Russ.P. 35192 (1934); Ekkert, Pharm. Zentralh. 1932, 73, 504).

Guaiacyl thymyl carbonate, b.p. 222-225°/15 mm. is an emulsifying agent, also a solvent for dyes and lacquers (Hurwitz, Swiss P. 180056/1936).

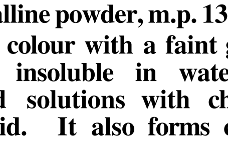
Guaiacyl chlorocarbonate is a colourless oil; b.p. 112°/25 mm. It is prepared by the interaction of antipyrine, carbonyl chloride and guaiacol (G.P. 117624 of 1899; Einhorn, G.P. 224108, 1908; Chem. Zentr. 1910, II, 517).

Guaiacol carboxylic acid,

$$C_6H_3(OH)(OMe)CO_2H,$$

is formed by the action of carbon dioxide on the previously heated sodium derivative of guaiacol; the free acid crystallises from water or dilute alcohol as a white, odourless crystalline powder, m.p. 148-150°. Its aqueous solution is coloured blue by ferric chloride. The acid and its salts have been recommended as antiseptics and anti-rheumatics (Pharm. J. 1890, 977).

Tetraguaiacoquinone, formed when guaiacol is oxidised with laccase,



$$\begin{array}{l} O(C_6H_3OMe)_2O \\ | \qquad\qquad\qquad\quad | \\ O(C_6H_3OMe)_2O \end{array}$$

is a fine crystalline powder, m.p. 135-140°, having a purplish-red colour with a faint green metallic lustre. It is insoluble in water, but gives mahogany-red solutions with chloroform and acetic acid. It also forms coloured solutions in alkalis (Bertrand, Compt. rend. 1903, 137, 1269).

Hexamethylenetetraminetriguaiacol crystallises in brilliant needles, which become soft at 80° and melt to a turbid liquid at about 95°. When distilled in steam it yields guaiacol (B.P. 24072, 1908; J.S.C.I. 1909, 28, 490).

Guaiacyl acetate, b.p. 123-124°/13 mm., readily undergoes intramolecular rearrangement, on which a new synthesis of vanillin has been based (Mottern, J. Amer. Chem. Soc 1934, 56, 2108).

Guaiacyl chloro-acetate,

$$MeOC_6H_4OCOCH_2Cl,$$

is prepared by treating a mixture of guaiacol, monochloroacetic acid and pyridine with phosphorus oxychloride. It forms white needles, m.p. 58-60° (Einhorn and Hütz, *l.c.*).

Guaiacol picrate forms orange-red needles; m.p. 88-89°.

Benzyl guaiacol is a yellow, beautifully fluorescent oil; b.p. 269-270°/436 mm. (Boscogrande, Chem. Zentr. 1898, I, 207).

Many other guaiacol derivatives have been prepared, some of which have been recommended for use in medicine (B.P. 5856, 1894; Ruhemann, J.C.S. 1902, 81, 421; G.P. 120558; Frdl. 1900-02, 1112; G.P. 157355; Frdl. 1902-04, 616; Knapp and Suter, Chem. Zentr. 1904, I, 391; Moureu and Lazennec, Compt. rend. 1906, 142, 894; Bischoff, Ber. 1906, 39, 3846; Gattermann, Annalen, 1907, 357, 313; Fourneau, J. Pharm. Chim. 1910, [vii], 1, 55, 97; Manchot, Ber. 1910, 43, 949; Wohl and Berthold, *ibid.* 2175; Hoffmann, G.P. 255924; Chem. Zentr. 1910, II, 1105).

A number of azo-derivatives of guaiacol are described by Leonardi (Atti R. Accad. Lincei, 1907, [v], 16, ii, 639); some nitro- and amino-derivatives by Reverdin and Crépieux, Ber. 1903, 36, 2257; 1906, 39, 4232; Paul, *ibid.* 2773; Kühling, *ibid.* 1905, 38, 3007; Fichter and Schwab, *ibid.* 1906, 39, 3339; PoUecoff and Robinson, J.C.S. 1918, 113, 645.

Thioguaiacol and *thioguaiacyl xanthate* have been prepared by Mauthner (Ber. 1906, 39, 1347).

Guaiacol forms mono-, di-, tri- and tetra-halogen derivatives (Cousin, Compt. rend. 1898, 127, 759; Tassily and Leroide, *ibid.* 1907, 144, 757; Bull. Soc. chim. 1908, [iv], 3, 124; Mameli, Gazzetta, 1907, 37, ii, 366; Robertson, J.C.S. 1908, 93, 791). The iodo-derivatives are said to be applicable in medicine (Mameli and Pinna, Chem. Zentr. 1907, II, 2044).

Guaiacyl phosphite, m.p. 75·5°, is a white crystalline powder, with a piquant non-caustic taste and slight odour, soluble in most organic solvents, but only sparingly in water (Bollard, G.P. 95578; J.S.C.I. 1897, 16, 632; B.P. 27527, 1896). Therapeutically similar to guaiacol. Another *guaiacyl phosphite,* m.p. 59°, is described by Dupuis (Compt. rend. 1910, 150, 622).

Guaiacyl phosphate, $(C_6H_4OMe)_3PO_4$, is prepared by the interaction of phosphorus oxychloride and the sodium derivative of guaiacol. It forms colourless crystals; m.p. 98°, insoluble in water and alcohol, but soluble in ether, chloroform and acetone. It has been proposed as an intestinal antiseptic.

A number of other phosphorus compounds of guaiacol are described by Auger and Dupuis (Compt. rend. 1908, 146, 1151), and by Dupuis (*ibid.* 1910, 150, 622; *cf.* F.P. 781019 (1934); G.P. 629952; U.S.P. 2023551 (1935). Smith, Engel and Stohlman discuss the toxicity of guaiacyl phosphate preparations (Nat. Inst. Health Bull. 1932, No. 160,1).

GUALACUM RESIN. This resin is obtained by extraction with alcohol from the wood of *Guaiacum officinale* or *O. sanctum,* members of the family Zygophyllacese. It is used to a small extent in medicine, but not to the extent it was some years ago, when it enjoyed an exaggerated reputation as a .specific for gout and rheumatism. It occurs in round or ovoid tears, or in large blocks, breaking with a vitreous fracture. Thin fragments are yellowish-green to reddish-brown.

A number of resin acids in guaiacum have been described, including guaiaretic acid,

$$\mathrm{C_{,0}H_{M}O_{s}(OH)}$$

a- and £-guaiaconic acids, $C_{20}H_{22}O_3(OH)_2$, and guaiacic acid, $C_{21}H_{19}O_4(OH)_3$. For details of these, *see* Dobner and Lucker (Arch. Pharm. 1926, 234, 590). Further evidence is necessary to establish the individuality of these- acids, the formulae of which are probably derived only from combustion data.

Good quality guaiacum resin should contain about 90% of matter soluble in alcohol, and ash from 3*5 to 5%. The acid value of the resin varies from 45 to 55, and ester value from 120 to 140.

Fresh alcoholic extract of guaiacum resin is a noted biochemical reagent for peroxidases; for a critical account, *see* Hawk, Bergeim and Coles, " Practical Physiological Chemistry," 11th ed., 1938, p. 393. Although it has been used for the purpose, guaiacum is not a specific test for blood stains *(see* Haldane, " Enzymes," 1930, p. 10).

E. J. P.

"*fäUAIAKINOL,"* Guaiachinol, the quinine /derivative of bromoguaiacol.

" GI/A/AMAR," monoglyceryl ether of guaiacol.

GUAIARETIC ACID (v. GUAIACUM RESIN).

GUAIASANOL (i\ GUAIACOL).

GUAIAZULENE *(v.* GUAIOL).

GUAICAMPHOL. Camphoric ester of guaiacol.

GUAIENE(v. GUAIOL).

GUAIOL.. The crystalline sesquiterpene alcohol, *yuaiol,* $C_{15}H_{26}O$, m.p. 93°, b.p. 147-148°/9 mm., *d*™ 0-9074, a},^{00} 1-4716, $[a]_D$-29-8° (in alcohol), is a constituent of Guaiacum wood oil (from, the wood of the tree, *Bulnesia sarmienti* Lorenz) (Schiramel's Report, 1892, II, 42) and occurs also in "the oils from *Callitris glauca* (Baker and Smith, " Pinej of Australia," 1910, pp. 63,118), *C. intratropica* (Trikojus and White, J. Proc. Roy. Soc. New South Wales, 1935, 68, 177) and from *(Jont/stylus miquelianus* (Evken, Rec. trav. chim. 1906, 25, 44). Guaof is a dicyclic tertiary alcohol, its. structure having been determined by Plattnercf *al.* (Holv. Chim. Acta, 1940, 23, 897; 1941, 24, 191, 1164). It yio da on catalytic hydrogenation the alcohoW*"-*hy<lroqmnol$_t$* m.p. 79-80^J, Ruzicka and Haagen-Smit, *ibid.* 1931,14, 1131) or the hydrocarbon, *tetrahydroguaiene,* b.p. 118-119°/17 mm., d^{20} 0-88Cō, rc_D 1-47840, $[o]_D$ +10-31^0 (Semmler and Risse, Ber. 1913, 46, 2305). On dehydration it yields a hydrocarbon or mixture of hydrocarbons known as *guaiene,* b.p. 128-130°/12 mm., *d** 0-9115, n_D 1-5021;, a_D -16-8° (Ruzicka, Pontalti and Balas, Helv. Chim. Acta, 1923, 6, 862), from whicji by dehydrogenation with sulphur die azurene, *guaiazulene,* b.p. 164°/H mm., *d}£* 0-9759, results (Ruzicka and Rudolph, *ibid.* 1926, 9, 140; St. Pfau and Plattner, *ibid.* 1936, 19, 866). The products formed by the oxidation of guaiol with pcfcassjtam permanganate and with ozone have been studied by Semmler and Mayer (Ber. 1912,45, 1391), Ruzicka and Haagen-Smit *(I.e.* p. 1122), and by TrikojWand White (Z.c). The main oxidation product with either reagent is a *dihydloxp-oxide,* $C_{16}H_{a6}O_3$, m.p. 218°.

J. L. S.

GUAIYL ACETATE. Guaiol *(q.v.)* has a slight odour suggestive of tea-roses, and is identical with the alcohol isolated from Champaca wood Uid formerly known as champacol (Merk, Arch. Pharm. 1893, 231, 123; Wallach and Tuttle, Annalen, 1894, 279, 391). The acetate has a definite tea-rose odour, and the following characteristics, $d^{16\cdot5}$ 0-988, nff 1-4890, $[a]_D$ -2-8°; ester value 210-220.

E. J. P.

GUANASE *(v.* Vol. IV, 315a).

" *GUANICAINE* " *(v.* Vol. I, *\20d).*

GUANIDINE, $HN:C(NH_2)_2$, occurs in small quantities in etiolated vetch seedlings, 3 kg. of dried material yielding 1 g. of the nitrate (Schulze, Ber. £392, 25, 658); in beet juice (Lippmann, *ibid.* 1896, 29, *2651);* in an edible mushroom, *Boletus edulis* (Winterstein *et al,* Landw. Vers.-Stat. 1913, 79-80, 541); and in the developing embryo chick (Burns, Biochem. J. 1916,10, 263). Guanidine and methylguanidine are found in urine, blood serum and other biological fluids, the quantities being increased in certain pathological conditions *(see* Burns and Sharpe, Quart. J. Exp. Physiol. 1916, 10, 345; Minot and Dodd, Amer. J. Dis. Children, 1933, 46, 522).

Guanidine was first prepared by Strecker (Annalert,' 1861, 118, 159) by oxidising guanine with potassium chlorate and hydrochloric acid; it is also obtained in small quantity by oxidising egg al&umen with potassium permanganate, or gelatin with barium or calcium permanganate (Lossen, *ibid.* 1880, 201, 369; Boudet, J. Pharm. Chim. 1857, [iii], 31, 32; Kutscher and Zickgraf, Sitzungsber. K. Akad. Wiss. Berlin, 1903, 28, 624);' it is formed synthetically (1) by heating biuret and hydrogen chloride at 160-170° (Finckh, Annalen, 1862, 124, 332); (2) from chloropicrin and alcoholic ammonia at 100° (Hofmann, Ber. 1868, *U* 145); (3) from ethyl orthocarbonate and aqueous ammonia at 150° (Hofmann, Annalen, 1866, 139, 111); (4) from carbonyl chloride and ammonia (Bouchanjat, Compt. rend. 1869, 69, 961); (5) from urea and ammonia under dehydrating conditions; ammonia and carbon dioxide or salts derived from them may be used instead of urea; finely divided nickel, aluminium, alumina or manganese dioxide have been proposed as catalysts for the reaction, which takes place at 250-300° under pressure or at lower temperatures in the presence of a non-aqueous solvent (Sander, G.P. 527237); (6) from ammonium chloride and alcoholic cyanamide at 100° (Erlerimeyer, Annalen, 1868, 146, 259), modifications of\his method using dicyanodiamide and various ammonium salts are frequently used for the preparation of guanidine salts; . (7) by the hydrolysis of dicyanod?«mide .with mineral acid, each molecule giving 1 mol. of guanidine (Davis, J.^Amer. Chem. Soc. 1921, 43, 668). (8) by the oxidation of dicyanodiamidine (Baumann, Ber. 1874, 7, 176C>; *cf.* the action *of aqua regia,* Ulpiani, G.P. 209431); (9) from cyanogen iodide and alcoholic ammonia at 100° (Bannow, Ber. 1871, 4, 161). Reduction of tetranitromethane with nickel-zinc and HCI yields guanidine hydrochloric}? ^Rakshit, J. Amer. XJhem. Soc. 1914, 86, 1221). Stāhler obtained this salt from CCI_4 and NK_3 at 140° in presence of Cu and I (Ber. 1914, 47, 909). Hydrogenation of carbamideimidoazide nitrate (Hantzsch and Vagt, Anpalen, 1901, 314, 339) in the presence of colloidal palladium gives guanidine and nitrogen (Wienhaus and Ziehl, Ber. 1932, 65 [B], 1461).

Guanidine, in the form of its salts, is usually prepared by modifications of Erlenmeyer's ((6) *supra)* or by the following method. Ammonium thiocyanate is heated for 20 hours at 180-190°, and the melt is extracted with water, the extract concentrated and the guanidine thiocyanate allowed to crystallise (Delitsch, J. pr. Chem. 187B, [ii], 8, 240; 1874, [ii], 9, 2; Volhard, *ibid.* 9,15; Krall, J.C.S. 1913,103, 1378; Sharpe, J. Biol. ChenJ. 1917,28, 399). *

Gluud *et al.* (Ber. Ges. Kohlentech. 1931, 4, 21; F.P. 728156; G.P. 568401) lead ammonia gas through molten ammonium thiocyanate at 170-180°. In Gockel's modification a metallic salt, *e.g.* of lead, is present (Angew. Chem. 1935, 48,430). Schopf and Klapproth have reported a violent explosion *(ibid.* 1936, 49, 23). The best methods of preparing guanidine salts depend on heating the corresponding ammonium salts with dicyanodiamide (Rathke, Ber. 1885, 18, 3107). Thus, Werner and Bell describe the preparation in 90% yield of tlie thiocyanate by this method (J.C.S. 1920, 117, 1133)/and Davis (9*g. Synth. 1927, 7, 46) similarly prepared the nitrate. Davis recommeifds heating dicyanodiamide and ammonium nitrate. Smith, Sabetta and Steinbach (Ind. Eng. Chem. 1931, 23, 1124) state the optimum conditions. Preparations: guanidine sulphate from dicyanodiamide, *see* Levene and Senior, J. Biol. Chem. 1916, 25, 623; Lidholm, Ber. 1913, 46, 156; t!aro, Z. angew. Chem. 1910, 23, 2405; guanidino phosphate, Jones and Aldred, Ind. Eng. Chem. 1936, 28, 272; guanidine salts from metallic cyanamides; G.P. 586446, 600869, and for the mechanism of the process, Gockel, Angew. Chem. 1934, 47, 555.

Guanidine is a deliquescent crystalline solid, readily soluble in alcohol and water; it is volatile and strongly alkaline, absorbs carbon dioxide from the air, and forms crystalline salts. According to e.m.f. measurements it is a stronger base than any other organic nitrogenous base recorded (Hall and Sprinkle, J. Amer. Chem. Soc. 1932, 54, 3469). The ultra-violet absorption spectrum shows only end absorption (Graubner, Z. ges. exp. Med. 1928, 63, 527). Guanidine is decomposed into ammonia and urea on boiling with barium hydroxide solution or dilute sulphuric acid (Ossikowsky, Bull. Soc. chim. 1872, [ii], 18, 161; Baumann, fcer. 1873, 6, 1376); and is completely decomposed into carbon dioxide and ammonia by heating with concentrated acids or alkalies. Guanidine is decomposed, evolving two-thirds of its nitrogen when mixed with sodium hypochlorite or hypobromite (Fenton, J.C.S. 1879, 35, 14; Von Cordier, Monatsh. 1926,47,327). When chlorinated at 0° in slightly acid solution buffered with NaOAc and AcOH, guanidine is converted into N-chloroazodicarbamidines (U.S.P. 2016257). Nitrous acid reacts with guanidine with liberation of nitrogen but only in the presence of strong acid (Hynd and MacFarlane, Biochem. J. 1926, 20, 1264). Cyanamide is formed when nitrous fumes are passed into aqueous guanidine sulphate (Bancroft and Belden, J. Physical Chem. 1931, 35, 2684). Guanidine and those of its derivatives containing a free amino-group react, on warming, with diacetyl or generally with" compounds containing the grouping -COCOCH,— with the formation of a violet coloration which has been made the basis for a colorimetric method of determining creatine and arginine (Lang, Z. physiol. Chem. 1932, 208, 273). Guanidine forms condensation products with dicarboxylic acids (Traube, Ber. 1893, 26, 2551; Ruheman and Stapleton, J.C.S. 1900, 77, 805; Kaess and Gruszkiewicz, Ber. 1902, 35, 3600); with 0-ketonic acids (Jaeger, Annalen, 1891, 262, 365); with β-diketones (Evans, J. pr. Chem. 1892, [ii], 45, 489; Wense, Ber. 1886, 19, 761); with malononitrile (Merck, G.P. 165692); with ethyl cyanoaceta'te (Traube, GJP. 115253). Guanidine reacts with mustard oils to form guanylthioureas, $RNH{\cdot}CSNHC(:NH)NH_2$ (Slotta, Tschesche and Dressier, Ber. 1330, 63 [B], 208). Glycine ester reacts with 2 mol. of anhydrous guanidine giving glycocyamidine (Abderhalden and Sicked, Z. physiol. Chem. 1928, 173, 51). Guanidine forms compounds with sugars containing 3 mol. of sugar and 1 mol. of guanidine; these exhibit mutarotation and have a lower optical activity than the sugars from which they are derived (Morrell and Bellars, J.C.S. 1907, 91, 1010; Przylecki *et* aJ., Biochem. Z. 1935, 277, 420, 424; *cf.* Giedroyd, Cichocka and Mystkowski, *ibid.* 1935, 281, 422). Combination with proteins also occurs under suitable p_E conditions. Thus, guanidine combines with ovalbumin and gelatin above the isoeleorric points, with casein and globulin below theii isoelectric points (Petrunkin, J. Gen. tfi/siol. 1927, 11, 101; Przylecki, Mystkowski and Niklewski, Biochem. Z. 1933,262, 260).

When guanidine hydrochloride is heated at 180°, ammonia is evolved and *biguanide* is formed, the reaction being similar to the formation of biuret from urea:

$$2HN:C(NH_2)_2 \rightarrow NH_3+HN:C(NH_2)NHC(:NH)NH_2$$

In its physiological action, guanidine is highly toxic; when fed to rabbits, it causes a considerable fall in the blood sugar, convulsions and death (Frank, Nothmann and Wagner, Arch. exp. Path. Pharm. 1926, **115,** 55). Doses smaller than poisonous ones were in rabbits excreted unchanged in the urine (Pommerrenig, Beitr. chem. Physiol. Path. 1902, i, 561; Garino, Arch. Farm, sperim. 1916, 22, 229, from Chem. Zentr. 1916, II, 1047). For other physiological data, *see* Dominguez, Proc. Soc. Exp. Biol. Med. 1927, 25, 57; Hurst and Hurst, J. Path. Bact. 1928, 81, 303; Camis, J. Physiol. 1909, 39, 73; Fühner, Arch. exp. Path. Pharm. 1920, **88,** 179; Langley, J. Physiol. 1916, 50, 419; Meighan, *ibid.* 1917, 51, 51). Although guanidine does not appear to be a normal oxidation product of arginine in the body (Pommerrenig, *l.c.*), guanidine intoxication occurs in certain clinical conditions (Minot and Dodd, Amer. J. Dis. Children, 1933, 46, 522). Many derivatives of guanidine, *e.g.* 1-guanido-4-aminobutane (" *Agmatine* "), the corresponding derivative of decane (" *Synthalin* "), the compound

$$EtOC_6H_4N{:}C(NHC_6H_4OMe)_2HCl$$

(" *Acoine*"), exhibit a marked insulin-like activity which has been applied in a few instances to the treatment of mild cases of *diabetes mellitus* (Frank, Nothmann and Wagner, Klin. Wochschr. 1926, 5, 2100; Cannavd, Arch. Farm. sperim. 1927, 44, 49; 45, 218; Kumagai, Kawai and Shikinami, Proc. Imp. Acad. (Japan), 1928, 4, 23; Gessner, Arch. exp. Path. Pharm. 1930, **147,** 366; Harwood, Iowa State Coll. J. Sci. 1932, 6, 431). Small quantities of guanidine, *0-01%,* are injurious to chlorophyllous plants, whilst fungi utilise it as a source of nitrogen but not of carbon (Kawakita, Bull. Coll. Agr. Tokyo, 1904, 6, 181; Kossawitz, Chem. Zentr. 1913, I, 1279). For its significance in plant physiology, *see* Tauböck and Winterstein, in G. Klein, Handb. Pflanzenanalyse, 1933, 4, 190; Chem. Zentr. 1933, II, 3321.

Tests and *Estimation.*—Many salts of guanidine give a yellowish-white flocculent precipitate with Nessler's reagent, even at a dilution of 0-01% (Schulze, Ber. 1892, 25, 661). Arginine gives a similar precipitate (Barger, " Simpler Natural Bases," 1914, 164; nephelometric determination of small quantities of guanidine, Rittmann, Biochem. Z. 1926, **172,** 36). A reagent made from 10% solutions of sodium nitroprusside and potassium ferricyanide mixed with sodium hydroxide just before use gives an intense red coloration with guanidine and its mono- and di-substituted derivatives. The guanidines are first separated as phosphotungstates or adsorbed on *"norit"* (WeW, Proc. Soc. Exp. Biol. Med. 1927, 24, 712; Pfiffner and Myers, *ibid.* 1926, 23, 830; J. Biol. Chem. 1930, **87,** 345; Ellis, Biochem. J. 1928, 22, 353; Weber, J. Biol. Chem. 1928, **78,** 465).

A test developed by Sullivan has also been used for the colorimetric estimation of guanidine. To guanidine in aqueous or 0·1N-hydrochloric acid solution is added a 1% solution of sodium 1:2-naphthoquinone-4-sulphonate and N-NaOH. After heating to 90° for 1 minute and cooling again, the solution is strongly acidified with hydrochloric acid. Addition of concentrated nitric acid now causes the formation of a red coloration or brown precipitate of 4-guanido-1:2-naphthoquinone (Sullivan, Proc. Soc. Exp. Biol. Med. 1935, 33, 106; Sullivan and Hess, J. Amer. Chem. Soc. 1936, 58, 47). Interference due to ammonia, methylamine, indole or benzidine can be eliminated by their removal beforehand. Certain synthetic derivatives of guanidine interfere (Braun and Rees, J. Biol. Chem. 1936, IK, 415), but these may be rendered inactive by addition of a little hydroxylamine immediately before acidification (Sullivan, *ibid.* 1936, 116, 233)."

The separation of guanidines from creatine and creatinine by adsorption on " *Doucil,*" a sodium aluminium silicate, has been suggested by Saunders (Biochem. J. 1932, 26, 801). The separation, of guanidine and methylguanidine can be effected by means of β-naphthalenesulphonyl chloride and depends on the fact that, under standardised conditions, methylguanidine does not react with this reagent (Hess and Sullivan, J. Amer. Chem. Soc. 1935, 57, 2331).

In the estimation of guanidine by precipitation with picric acid, the salt is dried at 110° and weighed (Vozdrik, Z. angew. Chem. 1902, 15, 670). Picrolonic acid has been used in preference to picric acid since the precipitates are not contaminated with creatinine (Kuen, Biochem. Z. 1927, **187,** 283). Flavianic acid can be used similarly (Müller, Z. physiol. Chem. 1932, **209,** 207). Guanidine phosphotungstate is soluble (22-8 parts) in 100 parts of a mixture of acetone (4 vol.) with water (3 vol.) (Wechsler, *ibid.* 1911, **78,** 141; Drummond, Biochem. J. 1918, 12, 5). 2-Nitro-1:3-indanedione *forms* a guanidine salt, m.p. about 258°, which is of use in the identification of guanidine (Wanag and Lode, Ber. 1937, 70 [B], 547). Choline and guanidine may be detected in organs by means of a histochemical test described by Hirosc (Mitt. Med. Ges. Tokio, 1931, 43, 888; Chem. Zentr. 1931 I, 654; Amer. Chem. Abstr. 1932, 26, 3812).

For the identification of the arylguanidines, used for the vulcanisation of rubber, by a colour reaction with cobalt oleate, *see* Shimada (J. Soc. Chem. Ind. Japan, 1933, 36, Suppl. binding 82), and for their estimation by titration with hydrochloric acid, *see* Mogoricheva and Korsunskaja, J. Rubber Ind. U.S.S.R. 1933, 10, 341; Minatoya, Nagai and Aoe, J. Soc. Rubber Ind. Japan, 1934, 7, 134; 1935, 8, 328; Kuznetzov, J. Chem. Ind. (Moscow), 1935, 12, 1265; Humphrey, Ind. Eng. Chem. [Anal.], 1936, 8, 153 (estimation as picrate after hydrolysis).

Salts.—Guanidine forms crystalline salts with mineral and organic acids, and also characteristic double salts. The *hydrochloride,* or *guanidinium chloride,* CH_6N_3Cl, crystallises in the orthorhombic system (Theilacker, Z. Krist. 1931, 76, 303) and forms double salts with *mercuric chloride,* $CH_6N_3Cl,2HgCl_2$ (Byk, J. pr. Chem. 1879, [ii], 20, 233) and *platinic iodide* (Datta and Ghosh, J. Amer. Chem. Soc. 1914, 36, 1017). The *hydrobromide,* CH_6N_3Br, forms orthorhombic bipyramidal crystals (Theilacker, Z. Krist. 1935, 90, 256). Both the bromide and iodide form addition compounds with *mercuric* cyanide of the type $CH_6N_3IHg(CN)_{.,}$, m.p. 261° (decomp.). The *ckloroaurate,*

$$CH_sN_aHAuCl,,$$

forms deep yellow, sparingly soluble needles (Hofmann, Ber. 1868, 1, 146); the *chlotoplalhiale,* $(CH_sN_3)(H_sPtCiV$, yellow needles solublo in water, sparingly so in alcohol (Strecfcer, Annnlen, 1861, 118. 160); the*plalinithiocyanate,* (CHjNjJjHjPtfCNSjg, forms beautiful red crystals which bkt:ken at 170-175* (Guareachi, Chem. 2entr. 1891, II, X>20). For the *palladuchloride, see* Gutbier and Fellner, Z. anorg. Chem. 1916, 95, 128. *The fiiriyanate,*

$$CH_{fi}N_3KCNS,$$

has m.p. 118^s and 100 parts of water dissolve 134-9 parts at 15° (Engel, Bull, Soc. ehim. 1885. [ii], 44,424). The oztftf $\mathbf{CH_sN_3HN_a}$. m.p. 93-5°, is formed by double decomposition between the chloride and silver azide. When treated with carbon di sulphide, it forms guanidinc azido-dithiocarbon&te, CH_4N_3-$HSCSN_3$ (Craik; Berger and Browne, J, Amer. Chem. Koo. 1934, 66, 2380). The *nitrate,* CH_5N_3,HNO_3, crystallises in large plates, m.p. (corr.) 217°; *25-ii* parts dissolve in 100 parts of water at 20° (Smith, Sabetta and Steinbach, Ind. Eng. Chem. 1931, 23, 1124). For the preparation of the nitrate from the tbiocyanate, *see* Jousselin, Bull. Soc. chim. 1880, [iij, 34, 497. The *nitrite,* $CH_5N_3HNO_2$, forms glittering prisms, ra.p. 76-78-5" (Loaaen, Annalen, 1891., 265, 129). The *sulphate,*

$$(CH_6N_3)_2H_2SO_4$$

(Bodewig, J. Ann. Physik, 1876,**157,**125), forma sdouble salt with *aluminium sulphate,*

$$(CH_6N_3)_2H_2SO_4{\cdot}Al_2(SO_4)_3,12H_2O$$

(Ferraboscbi, Proc. Camb. Phil. Soc. 1908, 14, 471). The *carbonate,* $(CH_5N_3)_2HXO_3$, priams, m.p. 197° (Schroder, Ber. 1880, 13, 1072); Burgers (Proc. Roy. Soc. 1927, A, **116,** 553) described uniaxkl, optically active crystals in which the activity was attributed to a special arrangement of the atoms within the unit structure. The(ril/it"ocor6«no(e,$(CH_sM_3)_2H_s$,CS_a, is prepared by heating the free base with carbon disulphide for 2 hours at 100° (Struck, 2. physiol, Chem. 1929, 180, 198). The *metaphottphale,* CH_SN_3-HPO_3, forma a fine crystalline precipitate (Pohl, *ibid.* 1889, 13, 296). *Viguanidine phosphate,*

$$(CH_sN_3)jH,PO_4,2H_aO, \quad „$$

« obtained by stirring the thioeyanate with silver phosphate and 20% phosphoric acid at 50° and evaporating to dryneas (G.P. 614818). -Ihe *didhylpyrophosphate,* results from the action ^f'hyl tuetuphoHpbato on thu carbonate in dry solvent:orm (PJimmer and Burch, J.C.S. 19-9, 279). Tho *kypopkosphate.* has been prepared and its magnetic susceptibility (-0-41 at **18-30"]** determinrf (lk<ll and **Snsdn,** *ibid.* 1933, 48>. The chlo•rote, CH_4N_3-$HC1O_S$, m.p. 100-101" (cf.• tho decomposition tem})erature 148° given **iMUa** «id Choudiiury, J. Amur. Chcni. Soc. 1916, 38, 1079), is less stable than the *perchlorate,* $CH_5N_3HCIO_i$, m.p. 245-246° (Uicewicz, Pmemysl Chem. 1926, 10, 56, **136).** According to Mazzucchcili and Kossi (Gazzetta, 1927, 67, 383), tho perchlorate oannot bo exploded with a hammer and when heated in the open it fuses and volatilises. The *mono-,* ***di-*** and *tri-chromates* are prepared by the action of chromic add on the carbonate. The nionofhromate forma triclinic, the di- and tri-L'hromates monoctinic crystals (Swaryczewski, Bull. Acad. Polonaise, Classe sci. math. nat. 1934, A, 246). Guanidino forms ealtn with a number of chromium complexes, *e.g.* the *niwekate,* $r(SCN)_4Cr(NH$-$]fJ$ $[CH_9N,]+$ [Carlsohn and Hathmann, J. pr. Chem. 1930, [ii], 147, 29, solubility data are given). The *acetate* forms shining needles, m.p. 229-230° (Ostrogovich, Gazzetta, 1897, 27, i, 223; *tf.* **Wielaad** *el al.,* Annalen, 1933, 507, 22(3). The *dioxalate,* CH_aN_3-$C_2H_3O_<,H_aO$, ia sparingly soluble 'Stracker, *I.e.).* The salt with acetylglycine has n.p. 105-110°. With 3:5-dinitrol>enj;oyl chloride *n* the presence of alkali, guauidine gives a di-3:fl-dinitrobenzoyl derivative which iainsoluble in sodium hydroxide (Saundera, Biochem. J. 19^4, 28, 580). *Thepierale,* $CH_1{:}N_{:(}$'$C_6H_5(NO_{1[})_3OH$ is a daringly soluble, yellow, crystalline salt, m.p. 333°; 1 part dissolves in 2,630 parts of water at 9° (Emich, Monatsh. • 1891, 12, 24). The precipitation of guanidine pierate is prevented by nucleic acid, owing to the formation of a more soluble complex pierate (White, Trans, Roy. Soc Canada, 1926, 20, Sect. V, **121).** According to Von Cordier (Chem. Zentr. 1906,1, 340), guanidine picrato-*tef. supra),* exists in two Btereoisomeric forms which are identical in specific gravity and **electric*)** conductivity but differ in solubility, Tho *p-toluenesulpko-?iate,* has m.p. 206°, and the *fi-naphtiudeiie' sulphonate,* m.p. 259° (Remsen and Garner, Amer. Chem. J. 1901,25,173). The *picrolonatt,* CH_sN_3-$C_{10}H_8O_sN_4$, is soluble in alcohol (Schenck, Z. physiol. Chem. 1905, 44, 427); the *m-bromopicroloHale* decomposes at* 275° (Zimmermann and Cuthbertoon, *ibid.* 1932, 206, 38). Many guanidinium salts of inorganic *ido-* and hetero-poly acids have been prepared (Gutbier, Mehler and Ottenstein, Z. anorg. Chem. 1014, 89, 313, 333, 343; Kosenheim *et al.,* ***ilnd.*** 1913, 79, 292; 1914, 89, 224; 1915, 91, 75; 1930, 193. 64; 1932, 204, 342; Ber. 1911,44, 1865; Z. Elektrochem. 1911, 17, ***mi;*** Fernandez *et al..* Atti K. Aefcad. Lincei, 1927, (vi], 6, 339; 1927, [vi], 6, 102; 1928, [vi]. 7, 49b'; Gazzetta, 1926, 56, U55; Brutl and Huliii, **Monstsh.** 1932, 59, 191; Kchranim, Z. nnorg. Chem. 1927, 161, 231; Weinhnd and Friede, Arch. **Rum.** 1928, 266, 9 53).

Acyl Derivatives.—*Formylguanidine,*

$$H_2NC(:NH)NHCHO,$$

has m.p. 17S° (decomp.); *acetylguanidine,* m.p. 18S°, *">hydrochtoride,* m.p. 145° (Korndorfer, \,rli. **Pharm. 1908,** 241, 449, givea m.p. 142°). (See ***alto*** **Traubo, Ber.** 1910, 43, 3586; Pierrow, Compt. rend. 1910, 151, 13B4; Wheeler and Jobnuon, Amer, ('Inui. J. 1901, 26, 417; Andreusch, Monatsh. 1926, 48, 639.)

Allylmalonylguanidine, m.p. 266-266°, crystallises from acetic acid in hexagonal plates (Johnson- and Hill, Amer. Chem. J. 1911, 46, 537). For *guanidino-glycylglycine* and the introduction of guanidine into the polypeptide molecule, *see* Clementi, Gazzetta, 1915, 45, i,56, ii, 276.

Alkyl and Aryl Derivatives.—*Methylguanidine,* **HN:C(NH$_2$)NHMe,** has been isolated from muscle (Gulewitsch, Z. physiol. Chem. 1906, 47, 471; Ewins, Biochem. J. 1916, 10, 103; Smorodintzev and Adova, Z. physiol. Chem. 1928, **181,** 77; Komarow, Biochem. Z. 1929, **211,** 326) and is considered by Mann to be a natural constituent of muscle *(ibid.* 1934,**268,**339). It has been found in milk (MüUer, Z. Biol. 1926,**84,**553). For its isolation from normal human urine, *see* Wada, Acta Schol. Med. Univ. Imp. Kioto, 1930,13,187, and from that of dogs, *see* Koch, J. Biol. Chem. 1913, **15,** 313; for its determination in blood, *see* Zappacosta, Boll. Soc. Ital. Biol. sperim. 1935, 10, 705; *see also* the methods of determining guanidine, many of which are applicable to its alky] derivatives. It can be prepared by several of the methods used for guanidine If methylamine is substituted for ammonia, *e.g.* Erlenmeyer's and Werner and Bell's methods (Erlenmeyer, Ber. 1870, 3, 896; B.P. 279884; Canad. P. 281121; Amer. Chem. Abstr. 1929,23, 3*143; Philippi and Morsch, Ber. 1927,60 B, 2120). The Rathke synthesis, consisting of the treatment of alkylitfothiourea salts with an amine, is general and applicable also to the preparation of polyalkyl-substituted derivatives (Lecher, *ZT* physiol.* Chem. 1928, 1<76, 43; Canad.P. 276107; Piovano, Gazzetta, 1928, **58,** 245; Phillips and Clarke, J. Amer. Chem. Soc. 1923, **45,**1755; Smith, *ibid.* 1929,**51,** 476). A special method of preparation of methylguanidine is by boiling creatine with mercuric or lead oxide and dilute sulphuric acid (Dessaignes, Annalen, 1854,92,407; 1856,97,340). For separation of guanidine and methylguanidine *(see* p. 144c). Methjlguanidine gives a characteristic red colour (Sagakuchi reaction) when treated, in alkaline solution, with a-naphthol and sodium hypochlorite. This reaction may be used for its colorimetric determination if the concentration is greater than 50 mg. per litre (Kuen, Biochem. Z. 1927, **187,** 283). The alkaline nitroprusside ferricyanide reagent (p. 1446) is also applicable to the colorimetric estimation of methylguanidine (Pfiffner and Myers, Proc. Soc. Exp. Biol. Med. 1926,23,830).

Methylguanidine is a strongly basic, volatile, deliquescent crystalline substance which readily decomposes; it decolorises permanganate, and liberates ammonia and methylamine on heating with potassium hydroxide. For the preparation ot the *chloride* and its conversion to other salts, [illegible] J. and Gorniak, Amer. Chem. Abstr. 1929, 23, 3443. The *sulphate,*

$$(C_2H_7N_3)_2H_2SO_4,$$

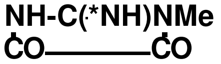
crystallised from water, has m.p. 238°; the *nitrate*!, from ethyl alcohol, m.p. 148-149° - the *mtr«e* m.p. if)0° and the *formate,* m.p. 122°. The *oxalate,* $(C_aH_7N_3)_8C,H_fO_4,2H_aO,$ is crystalline and soluble in water. The *chloroaurate,* **C$_8$H$_7$IM$_3$,HAuCl$_4$,** forms yellow crystals, m.p. 198-20u°; the *platinichloride,*

$$(C_2H_7N_3)_2H_2PtCl_6,$$

yellowish-red prisms, sintering at 186-187° and m.p. 194-195° (Schunck, Arch. Pharm. 1909,**247,** 466; Schenck and Kirchhof, Ber. 1927, 60 [B], 2412). The *reineekate,*

$$[(SCN)_4Cr(NH3)_2r[C_aH_8N_3f$$

has m.p. 228-230° (Smorodintzev, Z. physiol. Chem. 1930, 18Q, 7). The *picrate* crystallises from water in two distinct modifications, yellow plates or needles, m.p, 201-5° (Gulewitsch, *he).* The *picrolonate,* $C_2H_7N_3{\cdot}C_{10}H_8O_6N_4$, melts at 291° (Wheeler and Jamieson, J. Biol. Chem. 1904, 4, 111/, ^*cetylmethylguanidine* is **formed** by warming the base with ethyl acetate; it has m.p. 171-172°. *Benzoylmethylguanidine,* prepared similarly, has m.p. 156°; hydrochloride, m.p. 220-221°. *Oxalylmethylguanidine,*



$$\begin{array}{l}NH\text{-}C(\text{:}NH)NMe\\ \overset{|}{C}O\text{———}\overset{|}{C}O\end{array}$$

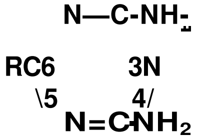
m.p. 2O&-2O7^0, is formed from the base and ethyl oxalate in alcoholic solution.

Alkyl derivatives of guanidine containing higher alkyl groups and also polysubstituted derivatives are usually prepared either by Erlenmeyer's or Rathke's method. For the preparation from alkyh'iothioureas of monosubstituted guanidines with alkyl groups higher than methyl, *see* Schenck and Kirchhof, Z. physiol. Chem. 1926, **158,** 90; Ber. 1927,60 [B], 2412; Piovano, Gazzetta, 1928, **58,** 245; and Amer. Chem. Abstr. 1933, 27, 1867, and for Erlenmeyer's method, B.P. 279884; Canad.P. 281121; G.P. 494918; B.P. 286196; *also* Davis and Elderfield, J. Amer. Chem. Soc. 1932, **54,** 1499. For polyalkylguanidines, *see* Klingner, Z. physiol. Chem. 1926, **155,** 206; Lecher and Demmler, *ibid.* 1927, **167,** 163; Schenck and Kirchhof, Ber. 1927,60 [B], 2412; Schotte, Priewe and Roescheisen, Z. physiol. Chem. 1928, **174,** 119; Davis and Elderfield, *I.e.;* B.P. 285873; and for peralkylated (pentasubstituted) guanidines, *see* Lecher *et al.,* Annalen, 1927, **455,** 139; U.S.i?. 1766755.

a-Phenylguanidine, **NH:C(NH$_8$)NHPh,** is conveniently prepared by heating aniline with methylt«othiourea sulphate until evolution of mercaptan ceases, it is purified by conversion to the carbonate which is only slightly soluble in cold water. The free base, m.p. 66-68°, crystallises in the monoclinic system, is soluble in alcohol and benzene and slightly soluble in water, ether and carbon tetrachloride, and absorbs carbon dioxide and water from the air. *a-Phenylguanidine sulphate* **forms** monoclinic crystals, m.p. 205°, is soluble in water and ^lightly soluble in 95% alcohol; the *carbonate,* monoclinic crj'stals, jn.p. 138-140°, is soluble in hot water; the *nitrate,* triclinic crystals, m.p. 118-119°, is soluble in hot water and alcohol but slightly in cold; the *picrate,* m.p. 218-220°, forms cither orthorhombic or triclinic crystals insoluble in water, and the *chloroplatinate,* m.p. 196°, triclinic crystals is slightly soluble in water (Smith, J. Amer. Chem. Soc. 1929,51, 476). *y-Benzoyl-a-phenylguanidine* has ni.p. 91-92°. For other arylguanidinss, *see* Braun, J. Amer. Chem. Soc, 1933, 55, 1280.

Diarylgiianidines are much used as accelerators for the vulcanisation of rubber (Elley and Powers, India Rubber WorH, 1926, 75, 143; Stoll, Gummi-Ztg. 1926, 41, 193; *diphenyV gua?iidinephthalate,V.S.V.* 1950067). ay-Derivatives may be prepared by desulphurising diarylthioureas in the presence of ammonia, *e.g.* with basic salts of lead, zinc, cadmium or tin (Naunton, Trans. Inst. .Rubber Industry, 1926, 2, 147; J.S.C.I. 1926, 45, 376T; q.S.P. 1630769, 1642180, 1662626, 1669242, 1672431; J3.P. 262155); or, in excellent^ yield, by the action of cyanogen chloride or bromide on anilines (Naunton, Z.c.jU.S.P. 1639724,1639725). Tor the preparation of *aa-diarylgwnidines,* see Paulson, U.S.P. 1575865; Arndt and Rosenau, Amer. Chem. Afcstr. 1918,12,1187. For reviews on the preparation of diphenylguanidine, *see* Hutin, Caoutchouc and Gutta-percha, 1926, 23, 13297; Drozdov, J. Chem. Ind. Russ. 1932, No. 7, 44. When aryl substituted gianidines are heated, rearrangements occur (Klingner, Z. physiol. Chem. 1926,155, 206). Additional references to substituted guanidines are: Strakosch, Ber. 1872, 5, 692; Tatarinow, J.C.S. 1880, 38, 233; Noah, Ber. 1890,23, 2196; Hofmann, *ibid.* 1869, 2,601; Fischer, *ibid.* 1897,30, 2414; Alway and Vail, Amer. Chem. J. 1902, 28, 158; Kampf, Ber. 1904, 37, 1681; Riedel, G.P. 66550; 104361; Schenck, Arch. Pharm. 1911, 249, 463, 1912, 250, 306.

Guanamines.—When the guanidine salts of the fatty acid serifs are heated at 220-230% water and ammonia are eliminated and 2:4-diamino-5-triazines,[1] formerly called *guanamines,* are formed, and afford excellent means of identifying volatile fatty acids (Haaf, J. pr. Chem. 1891, [ii], 43, 75):



The same series of compounds and also the aryl derivatives are formed when *dicyanodiamide is heated with amidincs or their salts or with nitriles at 200-250° with or without alcohol (Ostrogovich, Atti. R. Accad. Lincei, ft 11, [v], 20, i, 182, 249; Gazzetta, 1930, 60, 648; 1932, 32.317; Amer. Chem. Abstr. 1930, 24, 5752; Guanamines are also obtainable from biguanide and nitriles but the yields are lower. *Aceto-yuanamine,* (R CH_3) (6-methyl-2:4-dlamino-1:3:5-triazine), m.p. 265°.

Chloroguanidine, CH_4ClN_3, obtained by the action of bleaching powder solution on guanidine carbonate in ice-water, forms a pale y®J}ow crystalline powder that decomposes at ^0 (Kainenski. Ber. 1878, 11, 1602).

Bromoguanidine, CH_4BrN_3, formed from equimolecular proportions of bromine and guanidine carbonate, orystalliBes in yellow yeeaies. By the action of 3 mol. bromine on 1 mol. guanidine carbonate, the *compound,* $CH_5N_3{\cdot}HBr{\cdot}Br_2$, is formed, crystallising in dark red prisms. The corresponding *iodine compound,* CH_5N_3-HI*I_2, crystallises in prisms the colour of iodine (Kamenski, *l.e.).*

a-Cyanoguanidine *(Dlcyanodiamide, q.v.).*

Nitroguanidine,$HN:C(NH_2)NHNO_2$,was first prepared by Jousselin (1877) by the action of fuming nitric acid and nitric oxide on guanidine nitrate, and called by him nitrosoguanidine. Pellizzari (Gazzetta, 1891, 21, ii, 405) showed that it was the *nitro* compound and his results were confirmed by Thiele (Annalen, 1892,270,1), who also prepared it by the action of fuming nitric acid and sulphuric acid on guanidine thiocyanate. It exists in two modifications which differ in crystal form and habit and slightly in solubility, but are otherwise identical. The two forms are not interconvertible by solution in water, and may be separated by fractional crystallisation from that solvent. Either compound, dissolved in sulphuric acid and poured into water, gives the a-form. Neither appears to be an aci-form or a stronger *pseudo-acid* than the other since their solubilities in 0-1AT-KOH are essentially the same. *a-Nitroguanidine* is most conveniently prepared in 92% yield by adding pure guanidine nitrate, ground to a uniform fineness, to 3 parts by weight of concentrrted sulphuric acid cooled to below 0°. The reaction should not be prolonged for more than an hour, otherwise hydrolysis proceeds more, rapidly than nitration (Smith, Sabetta and Steinbach, Ind. Eng. Chem. 1931, 23, 1124). Davis (Organic Syntheses, 1927, 7, 68) describes a similar method giving a yield of 73%. It crystallises from water in colourless needles resembling phthalic anhydride, m.p. 246°, varying with the rate oT heating; 100 c.c. of water dissolve 0-271 g. at 19-5°. It is slightly soluble in ethyl acetate, acetone, ethyl alcohol, methyl alcohol and pyridinc, but insoluble in benzene, toluene, chloroform, carbon tetrachloride, ether and carbon disulphide (Devergnes, Rev. Chi in. Ind. 1929, 38, 265; Amer. Chem. Abstr. 1930, 24, 350). The heat of combustion ut constant pressure is +210-3 kg.-cal. and the heat of formation from its elements is +22 kg.-cal (Matignon, Compt. rend. 1892, 244, 1432). 0-*Nitroyuanidine* is produced in variable amount, usually accompanied by the a-form, by nitration of guanidine sulphate (mixed with (NH^SOj) which results from the hydrolysis of dicyanodiamide with sulphuric acid (Davis, Ashdown and Couch, J. Amer. Chem. Soc. 1925, 47, 1063). The j9-form crystallises from water in small thin elongated plates; for solubility curves of the two forms, *see* Davis, Ashdown and Couch, *I.e.* For the ultra-violet absorption, *see* Riegel and Buchwald, *ibid.* 1929, 51, 484; and for the explosion temperature (1,990°), *see* Muraour and Aunis, Mem. Poudres, 1932*25, 91. Nitroguanidine is decomposed by concentrated sulphuric acid, with a rapid evolution of nitrous oxide followed by a slower evolution of carbon dioxide and then by gases containing nitrogen. On long continued contact with water it decomposes with evolution of ammonia. When digested with ammonium hydroxide, it is converted to guanidine and urea, and with ammonium carbonate a 90% yield of guanidine carbonate may be obtained. Digestion at 60-

70° with methylamine gives *methylnitroguanidine,* m.p. 160-5-161°. Similarly the *ethylnitro-,* m.p. 147-148°, *butylnitro-,* m.p. 84-85° and *benzylnitro-* m.p. 183-185° derivatives may be prepared. For other alkyl nitro-derivatives, *see* Davis and Luce, J. Amer. Chem. Soc. 1927, 49, 2303. Reduction of nitroguanidine leads to the formation of, firstly,' nitrosoguanidine and then aminoguanidine *(v. infra).* The reversible system nitroguanidine^nitrosoguanidine has been studied by Smith and Sabetta *(ibid.* 1932, 54, 1034) who give 0-88 as the normal oxidation-reduction potential in acid solution. The *silver* derivative $\mathbf{CH_3N_4O_2Ag}$ is colourless and almost insoluble in water; the *nitrate* is crystalline and melts at 147°; the *hydrochloride* crystallises in plates or prisms. Two qualitative tests may be used for the identification of nitroguanidine (a- or *p-).* Nitroguanidine (0-01 g.) in cold water when treated with 2 drops of saturated ferrous ammonium sulphate and 1 c.c. of 62V-**NaOH,** allowed to stand 2 minutes and filtered, gives a fuchsin-coloured filtrate, fading in about half an hour. For the second test, nitroguanidine is reduced with zinc dust and 8% acetic acid and filtered. The aminoguanidine in the filtrate gives with $\mathbf{CuSO_4}$ solution an intensely blue solution, which, on boiling, evolves gas, and deposits metallic copper; it also reduces silver acetate in acetic acid solution. These reactions are also given by nitrosoguanidine, but the nitro- and nitroso-compounds are easily distinguished by their physical properties.

Nitrosoguanidine, $\mathbf{HN{:}C(NH_2)NHNO,}$ may be obtained by reduction of nitroguanidine with zinc dust and sulphuric acid or with zinc and 1*5% ammonium chloride solution (Sabetta, Himmelfarb and Smith, *ibid.* 1935, 57, 2478). For the catalytic hydrogenation of nitroguanidine to nitrosoguanidine in the presence of Raney nickel, which may be promoted with platinic chloride, *see* Lieber and Smith, *ibid.* 1935, 57, 2479; 1936, 58, 1417, 2170. It forms yellow needles which explode violently at 161°, is solvable in alkalis and reprecipitated by carbon dioxide. 100 g. of water dissolve 0-154 g. at 20°. The isoelectric point is at p_H 7. It gives the Licbcrmann reaction, and alkaline solutions give a beautiful purple coloration with ferrous salts *(cf.* Nitroguanidine). The estimation of nitrosoguanidine may be carried out by titration with potassium permanganate. For details of this and of other methods, *see* Sabetta, Himmelfarb and Smith, *I.e.* Aqueous solutions evolve nitrogen on boiling, but warming with concentrated hydrochloric acid gives nitric oxide (Davis and Abrams, Proc. Amer. Acad. Arts Sci. 1926, 61, 437). A cold acidified solution converts dimethylaniline and diphenylamine into their nitros\)-derivatives. The *silver salt,* $\mathbf{CH_3ON_4Ag,}$ is a colourless explosive precipitate ; the *copper salt,* $\mathbf{(CH_3ON_4)_2Cu,}$ is reddish-brown and the *nickel salt,* $\mathbf{(CH_3ON_4)_2Ni,}$ is vermilion red (Thiele, Annalen, 1893, **273,** 133). According to Hantzsch, Schumann and oEnglcr (Ber. 1899, **32,** 575, 1703), nitrosoguanidine is a true nitrosamine and its constitution is represented by the formula $\mathbf{HN{:}C(NH_2)NH\text{-}NO,}$ since it has a neutral reaction, yields mainly nitrous acid and not nitrogen when decomposed by acids, and does not react with phosphorus pentachloride or acetyl chloride. On the other hand, Whiteley (J.C.S. 1903, 83, 31) and Tschugaeff (Ber. 1906, 39, 3383) consider that the coloured metallic derivatives are salts of the tautomeric diazo-hydrate form

$$\mathbf{HN{:}C(NH_2)N{:}NOH.}$$

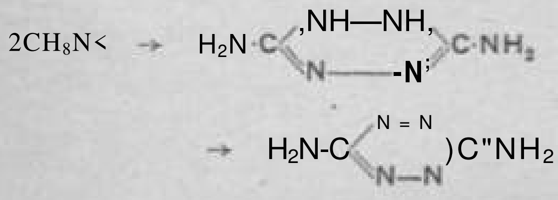
Nitroaminoguanidine,

$$\mathbf{H_2N\text{-}NHC({:}NH)NHNO_2,}$$

is obtained by treating nitroguanidine with hydrazine sulphate in aqueous ammonia. Its solubility in water at 20° is 0-34%, and at 70°, 3%. It melts with explosion at about 190° and reduces potassium permanganate and dichromate, Nessler's reagent, and ammoniacal $\mathbf{AgNO_3}$, and with Fehling's solution yields an explosive copper compound (Phillips and Williams, J. Amer. Chem. Soc. 1928, 50, 2465). Like other aminoguanidines and hydrazines ic readily forms derivatives with aldehydes and ketones, *e.g.* formaldehyde nitroguanylhydrazone; m.p. 169°, and the derivative from acetone, m.p. 164-165°; acetoacetlc ester, m.p. 130-131°; benzaldehyde, m.p. 188°; and salicylaldehyde, m.p. 213°. The reaction takes place rapidly in solution in water or aqueous methanol and the aldehydes or ketones may be recovered from the nitroguanylhydrazones by hydrolysis with 20% hydrochloric acid (Stoermer, Annalen, 1900, **312,** 273; Whitmore, Revukas and Smith, J. Amer. Chem. Soc. 1935, 57, 706; Smith and Shoub, *ibid.* 1937, 59, 2077). With nickel s>.lts and ammonium hydroxide, nitroaminoguanidine gives $\mathbf{NiO[HN{:}C(NHNO_2)NH\text{-}NH_2]_2}$ which is insoluble in water (hot or cold) but gives an intensely blue alkaline solution. This reaction may be used as a test for nitroaminoguanidine or for nickel. Reduction with zinc and acetic acid yields diaminoguanidine.

Aminoguanidine, $\mathbf{HN\text{-}.C(NH_2)NHNH_2,}$ was first obtained by Thiele by reduction of nitroguanidine with zinc dust in acetic acid at 40° until a test portion developed no coloration with ferrous sulphate and alkali (Annalen, 189S, **270,** 23). After filtering and evaporating excess of **AcOH,** a concentrated solution of aw, monium bicarbonate is added in the cold, thu. precipitating the bicarbonate of the base (G.P 59241). Modifications of Thiele's method have been described by Conard and Shriner (J. Amer. Chem. Soc. 1933,55,2867) and by Wyler (U.S.P. 1990511, 2123032). A 60% yield of aminoguanidine may be obtained by the reduction of nitroguanidine with sodium in solution in liquid ammonia, provided that a sufficient concentration of ammonium chloride is maintained (Fuller, Lieber and Smith, J. Amer. Chem. Soc. 1937, 59,1150). A yield of 81% by electrolytic reduction, with a tin cathode, of the nitro-compound suspended in dilute sulphuric acid is claimed by Boehringer und Söhne, G.P. 167637; but this has not been confirmed (Liebcr and Smith, Chem. Reviews, 1939, 25, 216, give a detailed summary of the chemistry of aminoguanidine). The catalytic hydrogenation of the nitro-compound was suggested by McGill (U.S.P 2033203) who used nickel on kicsclguhr at temperatures between 25° and 125° in the absence of a id, **but** Liober and Smith (J. Ainer. Chein. Soc. **1936,** 58, JIT(i) found the optimum concentration of add ia relatively high. In neutr&l and basic media nitrosoguanidine ia the first product, but Thiele found that zinc dust and acetic acid also reduce the nitroso- com pound to amino guanidine {Annalen, 1803, 2^3, **IS3).** Aminoguanidine may also be prepared by reftuxing an ak-oholic solution of **oyanamide** and hydrazine sulphate or hydro chloride (Pellizzari *zl^ ul,ₜ* Gazzetta, 1894. 24, i, 450; 1914, 44, ii, 72). Previously Hofmann and%Ehrhart (Ber. 1911,44, 2713) had used calcium eyanamide. Improvements in this method due to F^ntl and Silbermann (Annalen, 1928, **467,** 283) enable yields of 90-95% of aminoguanidine to be obtained from disodium cyanamidc-. Ecjuimolecular proportions of nitrosoguanidine and hydrazine hydrate react readily, with evolution o| nitrogen and water, to form aminoguaiiidine (Thiele, *ibid.* 1893, 273, 133). Aminoguanidine sulphate and its a-alkyl derivatives can be obtained in quantitative yield by treating S-alkyhaothiourea sulphates with hydrazine hydrate (Heyn, F.P. 618064; Scheriiig-Kahlbaum A.-G., O.P. 463576; Smith and Anzelmi, J, Amor, **Qhem. Soc. I**.*»3o, 57, 2730; Kirsten and **Smith** *ibid.* 193(5, 58, 800). a/9-Diary 1-y-aminoguanidines may be prepared from sywi-diarylthioureas and hydraaine hydrate in alcoholic potassium hydroxide (Busch and Bauer, Ber. 1900, 33, 1058).

Aminoguanidine cannot be prepared in the free * state; its salts when treated with an equivalent amount of barium or potassium hydroxide and evaporated *in vacuo* give reddish-violet prisms of fiyw^-diaminotetrazine whichi results from the condensation of 2 mol. of aminoguanidine and oxidation of the dianiinodihydrotetrazine so formed:



(Thiele, Annalen, 1892, **370,** 1; *cf.* Pinner, *ibid.* 1897, **297,** 258, and Ponzio and Gaataldi, Gazzetta, 1913, 43, ii, 1929; 1&14, 44, i, 257, 277). In boiling alkaline or acid solutions, amiitoguanidine is hydrolysed, yielding first semicarbazide and finally ammonia, carbon dioxide and hydrazine (Thiele, Annalen, 1892, 270, 1; Curtius, Ber. 1896, 29, 759); if sodium carbonate is used for the hydrolysis, semicarbazide ran be obtained in good yield. For the toxicity and Iliysiologieal effects of aminoguanidine, *see* Garino, Arch, Farm, sperim. 1916, 22, 229; AUes, J.- Pharmacol. 1926, 28, 251; Lettefl, Arch. exp. Path. Pharm. **1924,** 103, **100;** Anier. Chem. Abate. 1924, 18, 3224; Z. ges. exp. **Med.** J924, 40, ,52; Gollwitzer-Meier, Amer. Chcin. Abatr. I'liM, 18, :J42lj; ant] Nielsen and Wid»>ark, Upsala Lakareftir. Fiirh. 1927, [ii], 33, 327; Amer. Chem. Abstr. 1929, 23, 4973.

The determination of aminoguanidino. mu-y be ^aade by a volumetric method which is essentially an adaptation of the Jamteson method for hydrazine (" Volumetric Iodate Methods," Th© Chemical Catalog Co. Inc, New York, 1936, p. 36). The aminoguanidine salt is allowed to react with dilute sulphuric acid and a known volume of standard potassium iodate, potasaium iodide *in* then added and the excess of oxidising agent determined with thiosulphate. Aminoguanidine forms crystalline salts with mineral acids: *atoinoyuanidinium chloride,* forms large prisms, m.p. 163°. The *sulphate,*

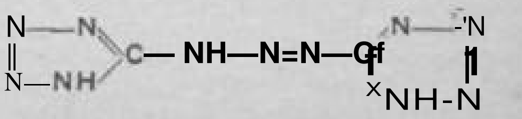
$$(CH_{fl}N_4)_2H_2S0_4,H_2O,$$

crystallises in needles, m.p. 207-208°; the *bisulpliate,* $CH_{fl}N_4{}'H_2SO$,, in large plates, m.p. Itil : -with absolute sulphuric acid, aminoguanidine gives the *sulphate* $[CN_4H_{10}](HSO_4)_1$ (Hantzseh, Ber. 1930, 63 [B], 1782). The *chloroplalinate* is yellow and insoluble, m.p. 145-146° (decomp.) (Thiele, Annalen, 1892, 270, 1). The *picrate,* $CH_{fl}N_4C_{fl}H_3O_7N_3$, is precipitated in yellow needles from hot water. Complex salts of "the type $[(CN_4H,)_{i!}Cu](NO_3)_{i1}$ are formed with copper and nickel. *In* the case of the topper salt, the complex is a deep violet-blue in i-olour and is insoluble in water (Thiele, *I.e.;* Smithy J.C.S. 1937, 1354). Aminoguanidine forms an addition complex with thiourea {Atkins and Werner, *ibid.* 1912,101, 1982) and with acid dyes it gives compounds insoluble in water (Suida, Z. physiol. Chem. 1910, 68, 381).

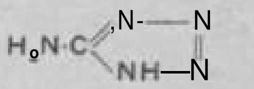
The oxidation of aminoguanidinium nitrate in dilute nitric acid with $KMnO_4$ gives a yellow substance, azodicarbamidine,

$$H_SN\text{-}C(:NHJN:N\text{-}C\{:NH\}NH_2.$$

which on reduction gives the hydrazoidcarbamidine. With nitrous acid, aminoguonidino reacts in three modes, depending on the conditions of reaction. In the presence of strong mineral acid, guanyl azide (N_3-C(:NH)NH_2) is formed; in solution in acetic acid the product is 1:3-ditetrazolyf triazene,



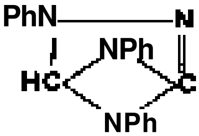
which results from the intermediate production of 5-aminotetrazole,



half of which is diazotised and coupled with the remainder (Hofmann and Hock, Ber. 1910, 48, 1866), If an aqueous solution of sodium nitrite and aminoguanidine nitrate is allowed to stand fl-7 days at 0-10°, the product M a white crystalline substance, l-guiinyl-4-nitroaoaminoguanylisotetrazene,

$$H_aN\text{-}C(:NH)NHNH\text{-}N{:}NC(:NH)NHNH\text{-}NO,$$

which forms readily hydrolysable salts many of which are extremely explosive. For details, *see* the review by Liebet and Smith *{I.e.).* Aminoguanidine and its derivatives containing the group —N H- N Hj are substituted hydrazines and as such readily form condensation products with aldehydes and ketones. The products are usually well-characterised crystalline compounds forming crystalline salts with acids (Thiele, Annalen, 1892, 270, 1; Thieleand Bihan, *ibid.* 1898, 302, 299). For the condensation products with aldehyde, chloraldehyde and chloral, *see* Thiele and Dralle *(ibid.* 1898, 302, 278); with aromatic aldehydes and ketones, *see* Thiele (Lc), ThieJe and Bihan *(Lc);* and Wedekind (Ber. 1897, 30, 444); with sugars, *see* Wolff *(ibid.* 1895, 28, 2613); with quinones, *see* Thiele and Barlow (Annalen, 1898, 302, 311); with a number of terpenes, *see* Baeyer (Ber. 1894, 27, 1919); with pyruvic acid, *see* Wedekind and Bronstein (Annalen, 1899, 307, 297); with glyoxylic acid, diacetyl, acetylacetone and acetonylacetone, *see* Thiele and Dralle *(Lc),* and Doebner and Gartner *(ibid.* 1910, 315, 1). With /3-diketones and 0-ketonic esters, pyrazole and pyrazolone derivatives are formed (De and Rakshit, J. Indian Chem. Soc. 1936, 13, 509; *cf.* acetylacetone) while aromatic a-diketones give aminotriazines (De, Quart. J. Indian Chem. Soc. 1927, 4, 183). Triarylaminoguanidines condense with formic acid directly or with higher aliphatic acids in the presence of phosphorus trichloride to give endoiminotriazoles ofewhich "*nitron,*"



has been applied to the gravimetric determination of nitric acid (Heck *et al.*, Analyst, 1934, 59, 18) *(v.* Vol. II, 598c).

Diaminoguanidine, $HN:C(NHNH_2)_2$, does not exist in the free state; the *hydrobromide* or *hydrochloride* is formed by the action of cyanogen bromide or chloride (1 mol.) on hydrazine (2 mol.) in ethereal or aqueous solution (Stollé, J. pr. Chem. 1907, [ii], 75, 423; Stollé and Hofmann, Ber. 1904, 37, 4524; PeUizzari and Cantoni, Gazzetta, 1905, 35, i, 291; PeUizzari and Repetto, *ibid.* 1907, 37, ii, 319; improved by PeUizzari and Gaiter, *ibid.* 1914, 44, ii, 72). A third method of preparation is by the reduction of nitroaminoguanidine with zinc dust and acetic acid (Phillips and Williams, J. Amer. Chem. Soc. 1928, 50, 2465). *Diaminoguanidinium bromide* crystallises in plates, m.p. 167°; the *chloride* has m.p. 185°; the *nitrate,* m.p. 143°; the *picrate,* $CH_7N_5,C_6H_3O_7N_3$, m.p. 191°; the *platinochloride,* m.p. 172-173°. All the salts reduce Fehling's solution and ammoniacal silver nitrate solution. *Dibenzoyldiaminoguanidine,* $NH:C(NHNH\cdot COC_6H_5)_2$, m.p. 210-211° KPeUizzari and Cantoni, *I.e.;* PeUizzari and Gaiter, *l.c*;* Gaiter, Gazzetta, 1915, 45, i, 450).

Triaminoguanidine, $NH_2N:C(NHNH_2)_2$, does not exist in the free state; its hydrochloride was first obtained by Stolid (Ber. 1904, 37, 3548) by the action of hydrazine hydrate on boiling carbon tetrachloride. It may be obtained by heating hydrazine hydrate with concentrated solutions of the salts of guanidine, aminoguanidine or diaminoguanidine or substances which yield them on treatment with hydrazine hydrate, *e.g.* S-alkylisothioureas (PeUizzari and Gaiter, *l.e.;* SchotU G.P. 501389; Amer. Chem. Abstr. 1930, 24,4524). Dichloroformoxime, $Cl_2C:NOH$, in ethereal solution reacts with an ether emulsion of hydrazine hydrate to give triaminoguanidine hydrochloride (Pi* ndtl and DoUfus, Ber. 1932,65 [ ], 754). The *hydrochloride* has m.p. 238-5°; *thiocyanate,* m.p. 136°; *picrate,* $CH_8N_6\text{-}C_6H_3O_7N_3$, m.p. 171°.

Dihydroxyguanidine Hydrobromide,

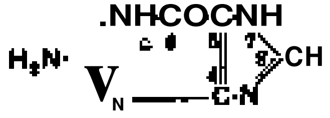
$$HN:C(NH\cdot OH)_2\cdot HBr,$$

is formed by the interaction of cyanogen bromide and hydroxylamine in methyl alcohol and ether at —20°; it forms colourless needles that decompose at 95°; alkalis convert it to the deep red dihydroxy derivative,

$$H_2N\text{-}C(:NOH)N:NC(:NOH)NH_2,$$

of azodicarbamidine; *see* aminoguanidine.

GUANINE, *2-amino-6-oxypurine,* $C_5H_5ON_5$



was discovered by Unger in guano in 1844 (Annalen, 1846, 51, 395; 58, 18; 59, 58), and although Hoppe-Seyler failed to find it in the excrement of fowls and geese, Haeter obtained it from the excrement of a heron *{Ardea cinerea)* fed on fish and flesh (Med. Chem. Untersuch.. 1871, 582); WiU and Gorap-Besanez found it in the excrement of a spider, in the organ of gBojanus of the mussel, and in the green gland of the crayfish *{cf.* Weinland, Z. Biol. 1889, 25, 390); and Pecile found 0-0068 g. of guanine per litre in the urine of a pig fed on bran, and in an unhealthy gouty condition (Annalen, 1876, 183, 141). In addition to its occurrence among the excretory products of animals, guanine is fairly widely distributed throughout the tissues; thus it is found in the liver (Smorodinzeff, Z. physiol. Chem. 1912, 80, 231; in muscle (Bennett, J. Biol. Chem. 1912,11,221); and it occurs, together with hypoxanthine, in the protamine from salmon roe, forming 6-8% of the ripe organ (Pitcard, Ber. 1874, 7, 1714); it occurs in the pancreas, spleen, liver and muscle of the ox, in quantities varying from 0-020 to 0-846%« (Braginsky, Z. physiol. Chem. 1883, 8, 395; Kossel, *ibid.* 404; Schindler, *ibid.* 1889, 13, 432); and it is found in the skin of fishes (Ewald and Kruckenberg, Chem. Zentr. 1883, 705; *see* Heller, Intern. Z. Biol. 1917, 8, 106. for possible connection between bioluminescence and guanine). Guanine is widely spread throughout the vegetable kingdom, Schützenberger found it, together with other purine bases, in yeast extract (Compt. rend. 1874, ,78, 493; Chem. Zentr. 1877, 73); Drummond and Funk in rice polishings (Biochem. J. 1914, 8, 598). Schulze and Bosshard isolated it, together with hypoxanthine and xanthine, from young potato tubers, sugar beet, leaf buds of plane and maple, bark of plane, from lupins, red clover, vetch, young grass and oats (Z. physiol. Chem. 1884, 9, 420). It has been found in the soya-bean

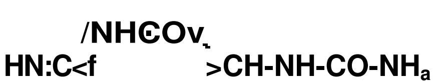
(Sasaki, J. Agric. Chem. Soc. Japan, 1932, 8, 417) and in the potato (Yoshimura, Biochem. J. 1934, **274,** 408). E. von Lippmann obtained it from beet juice (Ber. 1896, 29, 2645); molasses residues boiled with copper sulphate and sodium hydroxide yield about 0-04% guanine pentoside,

$$C_6H_9O_4C_6H_4OP4_6,2H_2O,$$

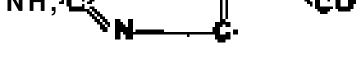
(Andrlik, Z. Zuckerind. Böhm. 1911, 85, 437). This js identical with the guanosine obtained from nucleic acid (Levene and Jacobs, Ber. 1909, 42, 2474; BiocTiem. Z. 1910, 28, 127); and with *vernine* (guanine-i-ribose), [a]J° —8-4° (Schulze and Trier, Z. physic! Chem. 1911-12, 7G, 145; Smolenski, Chem. Zentr. 1912, II, 769). According to Levene and Mandel (Biochem. Z. 1908, 10, 215; *see also* Jones and Richards, J. Biol. Ghem. 1915, 20, 25), guanine ·is one of the cleavage products of nucleic acid, when yie hydrolysis is effected by acetic acid in the presence of lead acetate at 150°; *cf.* Levene and Jacobs (J. Biol. Ghem. 1912, 12, 377); Scaffidi (Biochem. Z. 1912,**47,**215). Guanine nucleotide, CioH^OgNgP^HaO, has [a]?-13-6° in water and -48-5° in 5% **NH_4OH** solution. (BueU and Perkins, J. Biol. Ghem. 1927, 72, 21). It is found among the products of steam-heated soils (Lathrop, J. Amer. Ghem. Soc. 1912, 84, 1260).

Guanine exists in guano partly as the calcium compound, partly in substances like nuclein; from these it is liberated by boiling for 4 hours with dilute sulphuric acid, the liquid is cooled and filtered, and the filtrate made alkaline with sodium hydroxide and again filtered. The guanine and uric acid are precipitated in the filtrate by the addition of ammoniacal silVter solution, the precipitate washed with cojd and hot water and then decomposed by hot dilute hydrochloric acid, the silver chloride filtered off, the filtrate decolorised with animal charcoal and the guanine precipitated by ammonia, a small quantity of urea in hot nitric acid is added, and the mixture set aside to crystallise. The guanine nitrate, now'free from uric acid, is dissolved in dilute sodium hydroxide and the guanine precipitated by the addition of ammonium chloride, this last operation removing the xanthine (Wulff, Z. physiol. Chem. 1893, **17,** 468). It may be precipitated as the phosphotungstate—for the solubility of this in a mixture of acetone and water, *see* Wf chsler (Z. physiol. Chem. 1911, 73, 141).

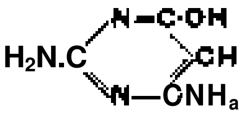
Fischer (Ber. 1897, 30, 559) has shown that guanine is 2-amino-6-oxypurine from the fact **that** ***imino-i/t-uric acid,***



obtained synthetically by Traube (Ber. 1893, 26, 2551) from guanidine and ethylmalonate, yields, on treatment with hydrochloric acid (jp.gr. 1-19), at 120°, the same 2-omfno-6:8-***aioxypurine,***



as is obtained from *bromoguanine,* **$C_6N_6H_4BrO$** (Fischer and Reese, Annalen, 1883, 212, 342) by the action of hydrochloric acid at 130°. Further, a synthetic guanine, identical in every way with the natural product, is obtained when ***6-oxy-2:%-dichloropurine*** **is heated with alcoholic** ammonia, and the resulting *cMoroguanine* reduced by means of hydriodic acid (Fischer, Ber. 1897, 30, 2226). The synthetic production of guanine has also been effected by Traube **(*ibid.* 1900, 33, 1371) from** ***2A-diamino-6-hydroxypyrimidine,***



obtained by the condensation of guanidine and ethyl cyanoacetate in the presence of sodium ethoxide. The nitroso derivative of this compound yields, on reduction with ammonium **sulphide,** ***2'A:5-triamino-6-hydroxypyrimidine,*** which, when heated with an equivalent amount of sodium formate and 8-10 times its weight of anhydrous formic acid, is converted into guanine. A similar synthetic production of guanine from ***2 - cyanamino - 4 - amino - 6 - hydroxypyrimidine,*** obtained by the condensation of dicyanodiamide tfhd ethyl cyanoacetate in the presence of sodium ethoxide, forms the subject of certain patents of Merck (G.P. 158591/1903, 162336/1904).

Guanine is an amorphous powder, insoluble in water, alcohol or ether, but soluble in acids or alkalis, forming salts of a di-acid base, or dibasic acid respectively. It can be obtained in the form of small rhombic crystals when the freshly precipitated compound is dissolved in a large excess of ammonia at 30-35°, and the filtered solution allowed to evaporate slowly (Drechsel, J. pr. Chem. 1881, [ii], 24, 44); or in crystals resembling those of creatinine zinc chloride, when a warm dilute alkaline solution (1:2000) is mixed with about one-third its volume of alcohol, acidified with acetic acid and allowed to cool (Horbaczewski, Z. physiol. Ghem. 1897,23, 226).

The administration of guanine as food to rabbits produces neither increase in purine excretion nor pathological changes in the kidney; but subcutaneous or intravenous injections of guanine dissolved in caustic soda, causes a great increase of purine substances, especially uric acid, in the urine (Schittenhelm, Ghem. Zentr. 1902,1, 1306; Schittenhelm and Bendix, Z. physiol. Chem. 1905,43, 365; Ewald, Z. exp. Path. u. Ther. 1900, 2, 348), and diminishes the arterial blood pressure (Desgrez and Dorléans, Compt. rend. 1912, **154,** 1109; Benelli, Arch. Farm, sperim. 1914, IT, 193-215); *see also* Desgrez and Dorléans (Compt. rend. 1913, **157,** 946) for the effect of injection of guanine previous to similar injection of adrenaline.

Guanine is converted to the extent of 60-70% into*xanthine when heated with excess of 25% hydrochloric acid for 32 hours (Fischer, Ber. 1910, 48, 805), and undergoes profound decomposition, yielding ammonia, carbon dioxide, formic acid and glycocoll on prolonged treatment with concentrated hydrochloric acid at 180-200° (Wulff, Z. physiol. Chem. 1893, 17, 468). A micro-organism belonging to the class of coccus bacteria and found in the excrement of pigeons, flourishes in a culture containing guanme, which ia decomposed into urea, ^unnidin^ and carbon dioxide (Ulpiani and Cingolani, Atti. R. Accad. Lincei, 1905, [v], 14, ii, 596); it is assimilated by a number of moulds aB a source of nitrogen and carbon (Kossowicz, Chem. Zentr. 1913,1, 1297).

The following derivatives of guanine have been described:

Salts.—(1) *With bases,* the *sodium,*

$$C_6H_3ON_5Na_2,4H_2O;$$

barium, $C_sH_3N_5OBa$; and *copper,*

$$C_6H_sN_sOCu_2O \text{ and } C_BH_SN_BO\ CuO,$$

derivatives. (2) *With acids,* the *hydrochloride,* $CjjH_5N_5O\text{-}HCt,H_2O$, forms double salts with zinc, cadmium, mercury, or platinic chloride; *hjdrobromide,* $C_5H_6N_S6\bullet HBr,2£H,,O$; *kydriodule,* $C_SH_SN_SO\ H\ 1,2JH,,O$, forms a doubk- suit with bismuth iodide; *-nitrates,*

$$C_{fi}H_5N_5OHNO_a,1iH_20;$$
$$C_SH_6N_SO2HNO,,2H,,O;$$
$$3C_{fi}H_5N_5O\text{-}4HN6_a,4H_2O; \text{ and}$$
$$3C_6H_6N_50\text{-}5HN0_3,5|H,O;$$

sulphate, (CJHSNSO^HJSO^HJOj *axalate,* $3C_6H_6N_5O\text{-}2C_2H_2O_{i;}$ *tarlrate,*

$$3C_5H_5N_5O{\cdot}2C_4H_6O_6;$$

dichromate, $C_6H_6N_sOHXr_2O_;$; *picrate,*

$$C_BH_BN_6OC_BH_3N_3O_7,H_8O;$$

picrolonale, $C_5H_5N_5O{\cdot}2C_{10}H_8O_5N_4$; *ferricyanide,,* $(C_5H_5N_5O)_4H_3Fe(CN)_6,6H_2O$; wi*tropnts&ide,*

$$(C_5H_5N_5O)_2H_2Fe(CN)_5NO,1\tfrac{1}{2}H_2O;$$

metapkosphaie, $C_SH_5N_6O\ HPO_3,xH_2O.$
{3) *Double sails, with mercuric chloride,*

$$C_5H_5N_5O{\cdot}HgCl_2,2\tfrac{1}{2}H_2O;$$

silver nitrate,* $C_BH_6N_6O\text{-}AgNO_3$. the *piaate of the silver salt,

$$C_£H_4AgN_5OC_BH_3N_sO_7,1iH_2O.$$

is insoluble in cold water; *(cf.* Unger, *Is.*; Strecker, Ai mien, 1801,118, 152; **Balke.J.pr.** Chem. 1 K!)3, [H], 47.539; Keu btitier and Kerncr, Annatea, 1857, 103, *-H'^; Vtvtff, /.* pfeyaio], Chem. 1893, 17. 4G8; Lev^ne, Biochem. Z. 1907, 4, 320). *Ouanine-d-glucoside,*

$$C,H_4N_{fc}O\text{-}C,H_uO,,$$

T;

m.p. 298" (cirr.) (Ki«rher and Helfcrich, Ber. **1814,47,210).**

Alkyl Derivatives.—*l-Hetliylguanlnc* forma a heavy colourlew, crj-italline powder which chars without melting (Traube and Dudley, Ber. 1913, 46, 3839). *1-Methylguanim* crystallises in slender, colourless needles which decompose at about 390°. 1:7*'-Dimeihylguanine.* crystallises with water of crystallisation, becomes anhydrous at 100° and melts at 343-345° (corr.); *l:"t-dimethylguanin&^ methiodide* -crystallises in large colourless plates, m.p. 330-333°. *Trimethylguanvnt methiodide* crystallises in colourless., slender needles, m.p. 295-300° (decomp.) (Fischor, Ber. 1897, 30, 2400; Traube and Dudley, *I.e.}.'*

Acyl Derivatives.—*AeetylgvanitK,*

$$C_5H_4N_5O(C_2H_3O),$$

ie crystalb'ne, sparingly Soluble in water, alcohol or ether, and may be heated at 260° without change. *PrapionylguaniTie,* $C_BH_4ON_S(C_3H_6O)$, is crystalline[1], snd remains unchanged when heated at 260°. *Benzoylguanine,*

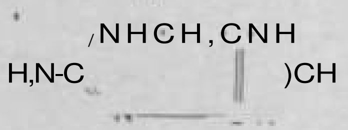
$$C_SH_4ON_6\{C_7H_6O),$$

is also crystalline {Wul^, *I.e.).*

Azo Derivatives.—Guanine and other purine bases that are riot substituted in position 7 react with diazobenzenesulphonic acid to form coloured *azo* compounds, in which the **-N:NR** group ia attached to carbon atom 8. Guanine and 7>-dichIorodi azo benzene chloride yield a dnrk red dye, which forms 8-aminoguanine when reduced. The ammo compound does not itself couple with diazo compounds, but can bo diazotised at 40°, and then yields a violet dye with an alkaline solution of R salt {Burian, Ber. 1904, 37, 696, 708; Hans Fischer, Z. phsyiol. CLem. 1909, 60, 69). Thfa reaction has been applied by Amatore de Giacomo (Z. wiss. Mikroscop. 1910, 27, 257) to a micro-chemical method for demonstrating the presence of guanine in the renal system of birds.

Bromoguanine, $C_6H_4N_6OBr$, ie a white crystalline powder, almost insoluble in wat<:r, alcohol or ether. It forms crystalline salts with **odds,** *e.g.* $C_6H_4N_BOBr,HCi$, and also unites with lead or silver to form crystalline compounds which, when heated with methyl iodide at 100°, yield bromocaffeine. Nitrous arid converts bromoguanine into bromoxanthine (Fischer and"Reese, Annalen, 1883, 221, 336).

Deoxyguanine,



$$H,N\text{-}C\begin{matrix}/NHCH,CNH\\ \quad\quad\ \|\ \ )CH\end{matrix}$$

is obtained whon pmninc is electrolyticalJy reduccd in 60% sulphuric ucid **sohrtkilij** it **oqr**sttllises in microscopic needles, melts and decomposes at 204' and has strongly basic properties, combining with atmospheric carbon dioxide. It is oxidised by bromine to *2-amino-**piirine,***

$$H_aN\text{-}C\begin{matrix}\text{-}N:CHCNH\\ \quad\quad\|\ )CH\end{matrix}$$

a crystalline base more readily soluble than its isomeride, *adenine.*

Guanine-Mononucleotide, GuanylicAcid, has been obtained from yeast-nucleic acid as a white amorphous powder, $[a]_D$ —2·4°. Its brucine salt,

$$C_{10}H_{14}O_8N_5P\text{-}2(C_{83}H_{26}O_4N_2),7H_2O,$$

has m.p. 203° (Read, J. Biol. Chem. 1917? 31, 47; Jones and Read, *ibid.'331;* Feulgen, Z. physiol. Chem. 1919, 106? 249; *ibid.* 1920, 108, 147 ; *ibid.* 1920, 111, 257). Levene has obtained the crystalline acid, $C_{10}H_{14}Q_8f?_6P,2H_tO_v$ from the Drucine salt, this has [a]™ —7·5° in aqueous solution; it yields the bruoine salt,

$$C_{5}[illegible]H[illegible]O_{14}N[illegible]P,7H_2O,$$

m.p. 233*, [a]*°-26·0° in 35% alcohol (J. Biol. Chem. 1919, 40, 171; 1920, 41, 453).

Tests.—Warm dilute solutions of guanine hydrochloride give with a saturated solution of picric acid an insoluble orange-red crystalline precipitate; xanthine and hypoxanthine give a similar reaction in very concentrated solutions only (S. Capranica, Z. physiol. Chem. 1880, 4, 233). It can be detected in animal tissue by treating it with a solution of diazobenzenesulphonic acid (sensitive to guanine) when, on addition of sodium hydroxide (after about 10 minutes), a red colour appears (de Giacomo, Z. wiss. Mikroskop, 1910, 27, 257)..

When guasine nitrate solution is evaporated it leaves a yellow residue, soluble in potassium hydroxide with a yellow coloration. On evaporating the yellow solution to dryness, it affords first a purple, then a violet coloration, and on exposure to air the original colour returns (Briicke, Monatsh. 1886, 7, 617).'

Estimation.—The formation of the insoluble picrate has been recommended by Wulff (Z. physiol. Chem. 1893, 17, 468) for the estimation of guanine. *See also* Hoppe-Seyler and Schmidt, *ibid.* 1928, 175, 304; Von Cordier, Monatsh. 1923, 43, 525; Grynberg, Biochem. Z. 1932, 253, 143; Engcl, Z. physiol. Chem. 1932, 208, 227.

GUANO (v. Vol. V, 63c).

GUANOSIN DEAMIDASE (lOVol. IV, 315a).

GUANOSINE *(v.* this Vol., p. 896).

GUANYLIC ACID *(v.* this Vol, p. 153a).

GUANYLNITROSOAMINOGUANYLTETRACENE *(v.* Vol. IV, 542d).

GUARA, *Casealotte.* The ground fruits of a variety of divi of South and Central America. The material contains 43-48% of tannins fcnd is used as a tanning agent (Callan, J.S.C.I. 1915, *•>» 645).

GUARANA. Guarana is a dried paste g*epared from the seeds of *Paullinia Cupana* tt-B. and K., a climbing shrub inhabiting the southern and western provinces of Brazil and oouth Venezuela. Generally the ground or powdered seeds are moistened and kneaded into a paste, made into cylindrical or globular musses and dried before fires, in chimneys or by the heat of the sun. They are usually found in commerce in cylindrical form, 1-2 in. thick and 5-10 in. long, with a rough, reddish-brown exterior and somewhat lighter colour inside. They have a chocolate-like odour and a bitter astringent taste. In South America guarana is an article of food used much in the same manner as we employ cocoa, and in European medicine it is administered as a nervous stimulant for the relief of certain kinds of headache. For further details as to its source, preparation and uses, *see* Cooke (Pharm. J. 1871, [iii], 1, 221); HaUawell *(ibid.* 1873, [iii], 3, 773)); Squibb *{ibid.* 1884-1885, [iii], 15, 165); Rusby *(ibid,* 1887-1888, [iii], 18, 1050); and Marsden (Ann. Trop. Med. 1898, 4, 105).

The physiological activity of guarana depends upon the presence of caffeine *(q.v.).* Of known drugs it is the richest in caffeine. For methods of extraction, *see* Greene (Pharm. J. 1878, [iii], 8, 87) who extracted a mixture of guarana and 3 times its weight of litharge with boiling water; C. J. Williams (Chem. News, 1872, 26, 97) who exhausted a moistened and slowly dried mixture of guarana and hydrate of lime with C_eH_6; Squibb (Pharm. J. 1885, [iii], 15, 165) and Bochefontain and Gusset (Ch. Tech. C. Anzeiger, 1886, 4, 322) who treated a mixture of guarana and magnesia with weak alcohol ana CHCIj successively. For estimation of caffeine in guarana, *see* Kremel (Pharm. Post, 1888, 21, 101). The following percentages of caffeine are selected from published analyses of guarana; 5-10, 5-04 (Stenhouse); 5-05 (Greene); 4-20-5-00 (5 samples, Feeinster, Pharm. J. 1883, [iii], 13, 363); 4-5 (B. and Gusset); 3·12 and 3-80 (Kremel); 3-4-3-7 (Ugarte, J. Pharm. Chim. 1921, [vii], 24, 387)s Thorns (Pharm. Zentralh. 1890, 31, 533), however, states thatthe proportion of caffeine in guarana has been overestimated and this has been confirmed by Kirmsse (Arch. Pharm. 1898, 236, 122), who found in 3 samples 2-68, 2-97 and 3-10%, respectively. For estimation of caffeine in guarana by an iodometric method, *see* Jermstad and Ostby, Amer. Chem. Abstr. 1933, 27, 5146. For micro-sublimation of caffeine from guarana, *see* Kutiak,' Amer. Chem. Abstr. 1935, 29, 291.

Besides caffeine, guarana contains gum, starch, an acrid green fixed oil, a more or less solid volatile oil, and tannin (Fournier, J. Pharm. Chim. 1861, [iii], 39, 291). The tannin further examined by Greene (Pharm. J. 1878, [iii], 8, 328) was found to behave towards reagents unlike previously known varieties, and the term *paullitannic* acid was therefore applied to it. It forms a yellowish-white amorphous mass, having an astringent taste. It is easily soluble in H_2O or EtOH. By the extraction of the crude tannin with Et_2O, crystals are obtained identical with those of the catechin of Pegu' catechu (Kirmsse, *l.e.).* Kremel *(l.e.)* found 1*3-2-0% of ash consisting chiefly of phosphates.

A specimen of guarana examined by Nierenstein, probably derived from *Paullinia trigonia* Veil., was found to contain an alkaloid, *p-*guaranine, $C_{40}H_{47}O_{fl}N_4$ (?). This work was repeated by Bertram! and Carneiro (Bull. Soc. chim., U)31, fiv], 49, 1093, where references can be found), but the above results could not be confirmed.

GUATANNIN, guaiaeol-tanno-cinnamate (G.P. 133

GUAVA is the fruit of *Piidivm guajava* L., Snail tropical tree or Bhrub grown largely in CenTra and South America. The fnnt » eaten Sw or may be preserved, or converted into the famous guava jelly. Other subspecrcs of guava include:

- *P caltkianum* Ndz., the strawberry guava of Brazil having round purptiah irmt;
- *P. friedrichslAalianum* Ndz., the yellow Costa Rican variety;
- *P. vtolk* Bertol. or guisaro, a smaller-fruited Mexican variety; and
- *P. guinetiue* Sw., or *P. anm* Raddi, the Brazilian guava with greenish - yellow fruit.

Thomson (Hawaii Agric. Exp. Sta. Ropt. 1914, 62) gives the following analysis:

	Common ffiiava.	Strawberry guava.
Solids	17-32	20-72
Protein	1-39	1-44
Fat	0-43	0-5&
Acid {aa citric)	0-51	1-23,
Reducing sugars	604	2-79
Sucrose	1-28	3-91
Fibre	4-66	fi-46
Ash	0-62	0-71

Later records by fc. D. Miller (Hawaii Ajric Exp. Sta. Bull. 1937fiNo. 77) include the following percentage composition:

	Water.	Protein.	Ether extract.	Crude Bbn.	Carbohydrate.	ABh.	Acid (us ettric).	Ca.	P.	Fc
Common guava, whole	81*8	0-7	0-2	70	9-8	0-5	1-37	0-010	0-022	00015
Common guava, seed removed.	84-9	0 3	—	2-3	Ll.fi	0-5	—	0015	0016	00003
Common guava, juice	93-9	0 1	—	—	5-7	0-3	0-88	0-006	0000	00001
Strawberry guava, whole	81-7	0-5	0-4	6 1	10-7	0-6	1-62	0034	0020	00003

Miller and Robbins (Hawaii Agric. Exp, Sta. Rept. 1933, 25) report the vitamin *C* content of guava juice to be approximately half that of orange juice.

Guava seeds have the following percentage composition (Azadian, Philippine Agric. 1925, 14, 57):

Water,	Protoln.	Fat.	Tannin,	Glucose.	Htaroh.	Fibre.	Ash.
10-30	15-25	14-31)	1-38	0-10	13-25	42-40	30

Sofcvent-extracted oil from the seeds in recorded by the same investigator to have the characteristics:

d^{li}	0-8243
W*f.	1-4632
Saponification value	197 1
Iodine, value	131-1
Reichert-Meissl value	0-26
Polenske value	0-25
Acid value	0-55
Volatile oil	0-26%

The following values for the seed oil from Indian-grown fruit *(Psidium guajava pi/rifcrtim)* are recorded by Vkrma, Godbole and Srivastava (Fettchem.-Umachau, 193J, 43, 8-9):

d^{30}	0-9365
n_D^{35}	1-4687
Saponification value	198-7
Iodine value	96-4
Reichert-Mciasl value	0-35
Polenske value	o-.i
Acid value	6-4
Unsaponiiiahle	0-68%

Of the fatty acids of the oil 16% are saturated (average molecular wt. 271), and the unsaturated acids (84%) include oleic 55-8, Uu6ieic 27-8 and linolenic acid 0-4%.

A. G. Po.

GUDMUND1TE. Sulphantimonide of iron, FeSbS, occurring as small silver-white to steel-grey crystals embedded in calcite. The orthorhombic crystals arc isomorphous with mia-pickt-I, FeAsS, and the two minerals, very similar in appearance, are associated together lll lead and zinc ore at Gudmundstrop near Sala, Sweden. Analysis[1] gave S 15-47, Sb 57-31, Fe 26*79, Nl trace, total 99 -57 (K. Johansson, Z. Krist. 1928, 68, 87).

L. J. B.

GUEdtARlTli *(v.* Vol. *U,* 518o).

GUHR(v. Vol. IV, 239b).

GUIGNET'S .GREEN *{v.* Vol. I1l, 1076).

GULAMAN DAGAT. A seaweed of the genus *OracHaria* (Philippine Islands) furnishing agar-agar *{q.v.).*

GUM BENJAMIN *(v.* Vol. I, 615a).

GUM FORMATION IN COAL GAS *{v.* VQ'. V, 4li8).

GUMMITE. An amorphous hydrated uranium oxide (UO_3 61-75%) with Bome lead, calcium, silica, etc. It occurs as an alteration product of *uraninite* (pitchblende), and forms yellow to reddish-brown gum-like masses, sometimes enclosing a nucleus of the unaltered parent mineral, and at times showing the external form of the original crystal. It in found together with other secondary uranium minerals at Johaniigeorgenstadt, Schnecberg, and Annaberg ui Saxony, in the Eliae mine *(diasiie)* at Joaohttusthai in jiuhejnja, and rather abundantly in the

Flat Rock and Deake mines in Mitchell Co., North Carolina. A gummite from Kambove, Belgian Congo, is a colloidal form of *cur&e (q.v.)* (A. Schoep, Bull. Soc. beige. Géol. 1937, 46, 309).

Related minerals are: *thorogummite,*

$$UO_3\text{-}3ThO_2\text{-}3SiO_2\text{-}6H_2O$$

from Llano Co., Texas; *pilbarite,*

$$UO_3 ThO_2 PbO\text{-}2SiO_2\text{-}4H_2O$$

from Pilbara, Western Australia; and *yttrogummite,* an alteration product of *clevcite (q.v.)* from Norway.

L. J. S.

GUMS. It is almost impossible to give an accurate chemical definition of a gum. At one time the gums were considered to be carbohydrates, but it is not correct to say more than that these plant substances are closely related to the carbohydrates. The word " gum " is, in commerce, frequently applied incorrectly to a resin; for example, the so-called " varnish gums " are all true resins, and have no chemical relationship with the gums.

Most of the gums of commerce are spontaneous exudations from plants, although some may be extracted from a plant, using water as the solvent. They may be regarded as combinations of metals, principally potassium, calcium and magnesium, with complex organic acids formed by the union of various sugars or allied bodies with hexose uronic acids.

Natural gums are characterised by either being soluble in water or having the power of absorbing a large quantity of water to form a glutinous mucilage. They are precipitated from such " solutions" by comparatively small amounts of alcohol. Such mucilages, when the water is allowed to evaporate, leave the gum with considerable adhesive properties and it is this property which is generally associated with the term gum.

In the case of the better known gums, such as gum arabic, it may be taken that one end of the molecular chain consists of the residual group (2-glucuronic or d-galacturonic acid, its carboxyl group being saturated by a metal. The aldehyde group of the uronic acid is joined by a glucosidic bond to an OH group of one of the sugars. A number of sugar groupings are similarly joined to the first one, and the sugars may be all alike or different. Usually at least two are present. When these bodies are hydrolysed the principal sugars obtained are galactose and arabinose. According to Butler and Cretcher (J. Amer. Chem. Soc. 1929, 51, 1519; 1930, 52, 4509) gum arabic is composed of 1 mol. of d-glucuronic acid, 3 mol. of *d*-galactose, 3 mol. of l-arabinose and 1 mol. of l-rhamnose.

Too much importance should not be attached to the quantitative results of any analysis of a given gum as there is no doubt that the proportions of the sugar and acid complexes, as well as the amount of the mineral matters, may vary considerably according to season, soil or climate for the gum obtained from any given species of plant.

Some gums contain as many as five different sugar complexes, and both pyranose and furanose ring structures may be present. The sugars, hitherto isolated after hydrolysis of gums, are glucose, mannose, galactose, fructose, xylose, arabinose, rhamnose and fucose. For an interesting summary of the chemistry of plant gums, *see* Hirst and Jones (Chemistry and Industry, 1937, 56, 724).

A certain number of gums are used in pharmacy for the preparation of pastilles, emollient medicines and emulsions, their emulsifying power being very considerable. In the arts considerable amounts of several gums find employment as adhesive agents, for finishing fabrics, in calico printing, ink manufacture and the manufacture of water colours. Gum tragacanth has come considerably into fashion in the manufacture of " hair creams."

The value of most gums for commercial purposes depends on the viscosity of their solutions in water. The determination of this value is usually of a quite arbitrary character. It can, of course, be determined on standard instruments, as in the case of oils, but in actual practice it is usually done by making up solutions of a satisfactory sample, and of the sample to be tested, of the particular strength which the user employs, and allowing equal volumes of the two solutions to flow from the same tube through a narrow orifice and noting the time of flow. Although this is a " rough and ready " test, the results are extremely useful for comparative purposes.

In addition to the viscosity test, the gum must be valued by the percentages of moisture and ash, and in many cases by the acid value of the sample. Naturally, the colour, taste and odour of a solution of a gum are very important. An unpleasant odour is obviously indicative of an unsatisfactory gum, and the odour will probably be found to correspond with its acid value. For many purposes it is highly important that the solution should be of a pale colour while for other purposes colour is almost immaterial. The higher the amount of water and ash, the lower is the value of the gum. The average values for water and ash will be found under the gums described.

Acacia Gum, commonly known as *gum arabic,* is amongst the best known and most generally used of the true water soluble gums. It is official in the British Pharmacopoeia, which authority requires it to contain not more than 15% of moisture, nor more than 5% of ash. Its principal constituent is araban, which yields arabinose, galactose and glucuronic acid on hydrolysis. The mineral matter consists of calcium, magnesium and potassium. The most esteemed variety is that collected in Kordofan, but Mogador and Senegal gums are also of excellent quality. It is, in the main, the gum by exudation of the stem and branches of *Acacia Senegal,* although allied species also yield the gum. Artificial incisions are usually made and the bark removed. In about 2 months the first collection of gum is made. In uncultivated trees the gum exudes naturally. The gum exists in small tears, and lumps up to the size of a walnut. The fragments break with a vitreous fracture and are often quite transparent.

Apart *from* the question of injuring the trees purposely, it appears that the Senegal trees yield most gum when they are in an unhealthy state, all attempts to improve their condition resulting in a smaller yield of gum.

Gum arabic is soluble in water and is precipitated by the addition of alcohol, or by basic lead acetate. The closely allied gums are of little commercial or scientific importance. An objectionable impurity in acacia gum is the so-called *Ghatti gum* which occurs in reddish tears or lumps less soluble than acacia; it is derived from various species of *Anogeissus* and the ash contains alumina and calcium phosphate.

Gum Tragacanth.—This gum is used in pharmacy to a considerable extent as it is a most useful emulsifier. It is also used in many other directions as a thickener, for example in thick sauces, chutneys, etc.

Tragacanth, as it is usually called, is the dried gummy exudation obtained by incision from *Astragalus gummifer* and other species. The plants are shrubs indigenous to Greece, Persia and Turkey. The exudation is collected and dried, when it forms flakes, which are graded according to their colour.

The gum is scarcely soluble in water, but swells up in contact with water to a gelatinous mass. Traces of starch are present. It is official in the British Pharmacopoeia, which authority requires that it shall not yield more than 4% of ash, and shall not acquire a pink colour with a solution of ruthenium red (ammoniated ruthenium hydroxy chloride) (absence of sterculia gum). The so-called Hog tragacanth is sometimes present in the lower qualities of tragacanth. This is probably the product of a species of ***Prunu8. Sterculia gum,* known as Indian** tragacanth, is obtained from *Sterculia wrens.* The particles are coloured bright pink by a solution of ruthenium red.

The composition of tragacanth has not been completely settled. According to Norman (Biochem. J. 1931, 25. 200), if a 0-1% "solution" be filtered, an insoluble portion, *bassorin,* remains on th£ filter, and a water-soluble portion, *tragacanthin,* passes through. This, on hydrolysis yields no sugar but arabinose. Norman considers tragacanthin to be a compound of arabinose and galacturonic acid only.

The early work of O'Sullivan on gum tragacanth and gum gedda laid the foundation for a good deal of the later work (J.C.S. 1884, 45, 41; 1890, 57, 59; 1901, **79,** 1164). From gedda gum he isolated an acid which he termed *geddic acid,* $C_{23}H_{38}O_{22}$, described as an isozner of arabic acid.

According to the British Pharmaceutical Codex, 1934, the soluble portion of tragacanth yields arabinose, galactose and geddic acid, but this is not in agreement with the work of Norman above quoted.

Bassorin, the insoluble portion, is probably a compound of bassoric acid with xylose and possibly a sugar to which the name tragacanthose Fellenberg (Chem. Zentr. 1914. II, 943) bassorin contains a methoxyl group. He considered that the bassoriii acid has the formula $C_uH_{20}O_{13}$, to which the name bassoric acid was assumed. Other acids are stated to be present.

The numerous other gums allied to acacia and tragacanth are of little or no commercial importance. But it should be mentioned that species of *Ceratonia* yield a gum, known as *carol gum* or *locust gum,* which is an excellent substitute for gum tragacanth.

For a description of methods for identifying common gums, *see* Jacobs and Jaffe (Ind. Eng. Chem. [Anal.] 1931, 3, 210; *cf.* Wildmar., J. Assoc. Off. Agric. Chem. 1935,18, 637).

Ma. J. P.

GUNARI (*v.* Vol. II, 439d).

GUN-COTTON (*v.* Vol. IV, 5066).

GURI-GINJA (*v.* Vol. I, 4c).

GURJUN BALSAM. This oleo-resia is the product of various species of *Dipterocarpus* of which about fifty exist in South and South-East Asia. One of the most important species is *D. turbimrius,* a tree found in Bengal, Burma and the Andaman Islands. A sample of this was Examined by Schimmel & Co. (Report, April, 1913, p. 68) and found to have sp.gr. 0-981 at 15°, and acid value 10-9. On steam distillation it yielded 46% of essential oil, of sp.gr. 0-927 at 15°, optical rotation —37° and refractive index 1-500 at 20°. The balsam is used to some extent as an adulterant of Copaiba balsam, but in the country of its production it is sold chiefly as a varnish.

Commercial samples of the balsam have the following characteristics:

Specific gravity at 15° . . .	0-960-0-985
Acid value	10-25
Ester value	1—10

They contain from 40-55% of essential oil which bas the following approxinate characteristics:

Specific gravity .	0-903-0-928 at 15°
Optical rotation .	Laevorotatory up to -130°
Refractive index	1-500-1-5050 at 20°.

The oil consists largely of sesquiterpenes (v. GURJUNENES, THE). The presence of gurjun oil (or balsam) as an adulterant can be detected, even in quite small amounts, by the following reaction: 3 or 4 drops are added to 10 c.c. of glacial acetic acid containing five drops of nitric acid. In the presence of gurjun oil a reddish-purple to violet colour will develop within a minute.

E. J. P

GURJUNENES THE. The oleo-resins,' Gurjun And Copaiba balsams, obtained from various species of *Dipterocarpus,* yield on distillation in steam an oil from which two sesquiterpenes, o-gurjunene and 0-gurjunene, have been separated (Deussen, Annalen, 1909, **369,** 59; Deusseif and Philipp, *ibid.* 1910, **374,** 105; Semmler and Spornitz, Ber. 1914, **47,** 1029; Semmler and Jakubowiez, *ibid.* 1144, 2253; Treibs, *ibid.* 1935, 68 [B], 1751). *a-Gurjunenc* has b.p. 114-116°/10 mm., d^{a0} 0-919, $«_D^{\circ}$ 1-501, a_D —90°, whilst *fi-gurjunene,* which can be freed from a-gurjunene by taking advantage of this hydrocarbon's facile oxidation with potassium permanganate, has b.p. 120-123°/13 mm., d° 0-9348, n_D 1-50275, a_D +74-5°. a-Gurjuneiic is tricyclic and gives a *monohydrochloride,* b.p. 165-170°/20 mm., from which an isomeric tri-oyclio hydrocarbon, V^{*a0} 0-819, n_D 1-502, a_D

— 19°, is obtained by treatment with alkali. On hydrogenation in presence of palladium black *dihydro-a-gurjunene,* d^{20} 0-89R, nff 1-4897, a_D -18° is formed, whilst dehydrogenation with sulphur yields an azulene. By the oxidation of a-gurjunenc with potassium permanganate Treibs *(I.e.)* has obtained succinic acid and a tricarboxylic acid, $C_9H_uO_e$, but it is not yet possible to assign a structure to the hydrocarbon. 0-Gurjunene, like a-gurjmene, is tricyclic and gives on catalytic hydrogenation *dihydro-P-gurjunene,* b.p: 120°/8 mm., d^{20} 0-9172, *n*^ 1-4922, a_D -42°. If repeatedly distilled over heated nickel p-cymene informed (Treibs), whilst when heated under pressure at 300° for some hours it yields a-te?pinene (Semmler and Jakubowicz). It is not improbable that *p*-gurjunene is closely related to ccdrene *(q.v.)*; it gives on oxidation with chron?'c acid an unsaturate^l *ketone,* $C_{16}H_{22}O$, m.p. 43°, b.p. 163-166°/10 mm., d^{20} 1017, w_D 1-527, c^ +123°, *temicarbazone,* m.p. 237°.

J. L. S.

GUTTA PERCHA^ AND BALATA

are plant products containing appreciable quantities of the gutta hydrocarbon, which like the rubber hydrocarbon, caoutchouc, is a polymer of isoprene and has the formula $(C_6Hg)n$ or $[—CH_2CMe:CHCH_2—]$„. At one time gutta pcrcha and balata were considered to contain different, although chemically related, hydrocarbons, but X-ray examination of the purified products suggests that both contain the same hydrocarbon and that it is a Btereoisomcr of caoutchouc.

The purified hydrocarbons of rubber, gutta percha and balata have the same general chemical properties, but the differences in spatial configuration are responsible for differences in physical properties which render the gutta and balata hydrocarbon particularly suitable for some purposes. At ordinary atmospheric temperature gutta percha and balata are much harder and less elastic than raw rubber, but soften markedly on heating and at temperatures approaching 100°C. are easily moulded, becoming hard again when cold.

Gutta pcrcha and balata differ from each other in that they arc obtained froiTi different trees growing in different countries and are associated with different 'resinous materials soluble in acetone.

Gutta pcrcha is the product obtained by coagulating the latex of certain species of *Palaquium* and *Payena* belonging to the natural order Sapotaceas which are natives of the Malay leninsula and Archipelago. The name is derived from two Malayan words " gctah " and pcrcha" meaning plant juice of Sumatra. l>alata » the product obtained by coagulating the latex of *Mimusops globosa,* a large forest tree, also belonging to the natural order Sapotacea*. A his tree is a native of many countries, among which are Brazil, Venezuela and the Guianas. Whereas gutta percha in a product of the East Indies, balata is chiefly a product of the tropical w«ion of South America.

A. he principal tree yielding gutta pcrcha of good quulity is *Palaquium gutta.* A number of other species of Palaquium furnish gutta percha of second quality, the chief of these being P. *obovatum, P. maingayi* and *P. oxleyanum.* Species of Payena such as P. *leerii* and P. *havilandii* are also sources of gutta.

Palaquium gutta is a largo forest tree which usually attains a height of about 60 ft. but sometimes reaches a height of 150 ft. and a diameter of 4-5 ft. The latex is contained in isolated sacs which occur chiefly in the inner layers of the bark and also in the leaves. On making incisions in the bark the latex exudes and quickly coagulates, so that only a small yield of gutta percha can be obtained at one tapping. The native method of obtaining gutta, therefore, is to fell the trees and ring them at' intervals of from 9 to 12 in. The latex exudes into the incisions where it quickly coagulates and can be rolled off on a stick or removed with a knife. The amount of gutta percha obtained per tree by the native method has been variously stated, but it may be as much as 10 lb. per tree.

Owing to the serious destruction of the trees involved in the native method, attempts were made as long ago as 1845 to establish plantations and to collect the product by tapping the standing trees, but the yield was too smalls Eventually mechanical methods were evolved for extracting gutta percha from leaves and twigs and a number of plantations, the chief of which is in Java, have now been established. The leaves hang on the branches for 10 to 18 months and are harvested when they are on the point of falling because they are then richest in gutta (2-0-2-7%). The average period between two picking rounds is about 40 days and the yield of gutta is about 250 lb. per acre per annum.

In order to separate the gutta percha the leaves are cut up, crushed and finally ground to a powder which is then mixed with water and allowed to ferment, after which the mixture is diluted with warm water and heated to 70°C. It is then poured into cold water when the leaf fibre sinks to the bottom and the flakes of :gutta percha, being lighter than water, are easily removed. The flakes are subsequently pulverised in cold water, washed in hot water and pressed into blocks.

The crude plantation product contains about 90% gutta hydrocarbon as compared with about 80% in 'the best of the wild grades. A still purer grade is prepared on the plantation by extracting the crude product with cold petroleum spirit to remove resins and then dissolving the gutta in hot spirit and treating with bleaching clay to remove pigments. On cooling the gutta is precipitated as a white, snow-like mass containing less than ^1% resin. The residual spirit is removed by steam distillation under a vacuum. This purified gutta readily oxidises when exposed to air and is therefore stored in evacuated tins or is treated with an antioxydant, such as p-toluidino, and stored in the diwk or under water. This highly purified gutta is in considerable demand for the outer cover of golf balls for which purpose it is usually mixed with a little rubber during manufacture.

Like gutta pcrcha, balata was first obtained by felling the tree, but is now obtained by tapping, a series of incisions being.made in the bark so arranged that the latex can run down to the base of the trunk where it is collected and poured into shallow dishes. This latex is remarkably stable, but on exposure to sun and air it coagulates and forms sheets which arc hung to dry in the air. In some districts these sheets are pressed into blocks. Sheet balata is produced chiefly in the Guianas, and block balata in Venezuela and the Amazon districts.

The latex of balata trees usually flows freely, and, in favourable circumstances, the yield from a tree 15-20 in. diameter, tapped to a height of 8 ft., is about 3 pints, representing from 1J to 2 lb. of dry balata.

The commercial brands of gutta percha and balata vary considerably in quality according to their origin. The quality mostly depends upon the hydrocarbon content. With the exception of the specially purified product already described, commercial material contains considerable quantities of naturally-occurring resin, as well as small quantities of foreign matter such as bark and sand. Good qualities of wild Palaquium gutta contain about 20% of resin, *but* balata usually contains 35-50%. For industrial purposes it is necessary to clean the commercial material by softening in hot water, washing in a masticator and straining through a fine gauze, after which it is dried by kneading and mixing under a high vacuum. For the manufacture of golf-ball covers, a solvent process, similar to that used on the gutta plantations, is employed to obtain a specially purified material.

The gutta hydrocarbon is a hard, horny, tough white substance wJhich progressively softens on heating until at 100°C. it becomes soft and sticky, rapidly regaining its original hardness pn cooling. When heated strongly in air it decomposes and burns with an odour characteristic of burning rubber. When destructively distilled it yields a mixture of hydrocarbons, including isoprene, similar to those obtained by the distillation of rubber. The guttai hydrocarbon exists in two forms, the a-form being stable below about 68°C, changing to the 0-form above that temperature. The hydrocarbon usually occurs in the /?-form and is converted into the a-form by heating at temperatures below the transition point. The 0-form is somewhat harder and slightly more dense and more soluble than the a-form. At normal atmospheric temperature the change from the metastable 0-form to the stable a-form is so slow as to be negligible, but occurs in a few hours at 60°C. (J. N. Dean, Trans. Inst. Rubber Ind. 1932, 8, 25). X-ray examination shows that gutta has a crystalline structure and that 'A,1S Probably a <ra?w-isomer of caoutchouc. (*or a review of the subject, *see* Davis and Blake, " Chemistry and Technologv of Rubber," Reinhold Publishing Corporation; New York, 1937, p. 120. The density of the hydrocarbon varies from 0-945 to 0-955 at 24°C. according to source and treatment.

The purified hydrocarbon is insoluble in ether, acetone, alcohol and cold petroleum spirit and is completely soluble in carbon clisulphide, chloroform, carbon tetrachloride and hot petroleum spirit. In general it is soluble in most aromatic hydrocarbon solvents, but is insoluble in saturated paraffin hydrocarbons when cold, becoming soluble on heating.

Gutta is not affected by weak mineral acids, strong hydrochloric or acetic acids, but is readily attacked by strong nitric or sulphuric acids. It is particularly resistant to hydrofluoric acid for which it is used as a container.

Gutta contains one double bond for each C_6hL_4 group present and forms addition products with halogens or nitrogen oxides closely resembling those prepared from rubber. Like rubber it slowly absorbs oxygen when exposed to air and light,tand in the process the gutta is converted into a Brittle resin. Gutta is not energetically attacked* however, by ozone, but it reacts in solution forming an ozonide which yields decomposition products similar to those from caoutchouc ozonide. The oxidation of gutta is of commercial importance since special precautions are required to prevent the deterioration of purified material. This deterioration is markedly accelerated by light and is retarded by the resins naturally occurring in the unpurified material.

Gutta is highly resistant to water, the purified material absorbing less than 0*2% over a period of 2 years.

Like rubber, gutta percha and balata can be vulcanised with sulphur and also by benzoyl peroxide and by m-dinitrobenzene, but the mechanical properties of the product are inferior to those of vulcanised rubber.

Analyses of commercial gutta percha and balata are necessary to assess quality, the most frequent determinations being resin, dirt and cnoisture. Moisture is Usually estimated by heating in nitrogen at low pressure; dirt (including protein) by dissolving in benzene and filtering; and resin by extracting with hot acetone. Gutta hydrocarbon can be estimated by difference or by precipitation of "the acetone-extracted material from filtered benzene solution by pouring into alcohol. The percentage composition of several representative samples of gutta percha and balata examined at the Imperial Institute or by Obach (J. Soc. Arts. 1897, 46, 125) is given in the table on the next page.

In comparison with these figures the following analysis oi leaf gutta from Java is of interest, viz. gutta 79, resin 7, dirt 4, moisture 10 (Ivan Lennap, India Rubber J. 1923, 65, 367).

The resinous bodies associated with the gutta hydrocarbon in gutta percha and balata are complex oxygenated substances. They were separated by Payen in 1852 into two portions: (1) a crystalline white resin, soluble in hot but insoluble in cold alcohol, which he named *albane*; (2) an amorphous yellow resin soluble in cold alcohol, which he named *fluavile.* It is unlikely that these are pure substances and it has been shown that the resin contains[1] appreciable quantities of a- and 0-amyrin esters (such as acetate), phytosterols such as lupeol, fats and fatty acids.

The introduction of gutta percha into commerce dates from 1843 when specimens were forwarded to London independently by two doctors resident in Singapore, William Montgomerie and José D[1] Almeida, and the

Variety.	Source.¹	(Jutta.	Hi-sin.	Protein and (or) dirt.	Mdstate.	Ask (included in ulrt).
Oeta taban merah * .	*Palaquium gutta*	701	139	1-2	14-8	095
„ „ „ .	„ „	68-3	13-4	8-1	10-2	0-89
„ „ putih , .	Uncertain	35-6	49-5	7-4	7-5	0-72
„ „ chaia . .	„	52-0	43-4	3*4	1-2	1-61
Geta Simpor . . .	*Palaquium maingayi*	44-9	45-5	8-4	**14**	213
„ feban Sutra,⁵ .	„ ***gvtla***	84-3	**10-7**	3-7	1-3	—
„ sundek * . . .	*Payena, hirii*	43-9	37-6	fi-I	13-4	—.
Sheet balata . . .	British Guiana	50-3	44-0	3-8	1-9	0-0
Block balata . . .	Venezuela	45-7	44-2	8-3	1-8	1-28
Balata	A.ʳostiy British Guiana	41-5	34-8	9-9	13-8	—
„	Dutch Guiana	43-5	3fi-9	14-3	**58**	—

[1] Obtained by tapping standing trees, n

* Analyses by Obacli.

remarkahje properties of the material at once attracted attention. At a meeting of the Royal Society in 1845 William Siemens suggested that it would make a suitable insulator fur underground telegraph wires and in 1847 his brother Ernst Werner von Siemens employed the material for thia purpose. In 1849 two umariroanta] lengths of submarine cable insulated with gutta percha were laid at Folkestone by Walter Breit.

The first submarine cable was not a auceess,. but many thousands of miles have now been successfully laid, nearly all of them insulated with gutta percha and a few with halata. The use of gutta pereha for submarine cables is based on the*eaee with which it can be extruded when warm, its low water absorption, good electrical properties and the ease of effecting repairs. Submarine cables are made by warming the gutta on hot rolls and feeding it to a hot extruding machine which forces it through a die over the metal conducting core, after which the cable is passed into a tank of cold water and rolled on to drums.

The second commercial use of gutta percha in order of importance ia foi the outer cover of golf balls. For this purpose balata is dissolved in hot solvent and a purified gutta precipitated on. cooling; this is freed from solvent and mixed with a little rubber and a white pigment on mixing rolls before moulding to the required shape. Owing to its excellent quality purified gutta supplied by the plantations has no* largely replaced that previously obtained from balata.

Largo quantities of balata were at one time J>wd for the manufacture of **belting,** but this naa been replaced to a great extent by rubber on account of cost.

Among the well-known substitutes for gutta pereha for the insulation of submarine cables are Para gutta and K. gutta. They consist °f mixtures of purified batata, deproteinifiprl rubber and hydrocarbon wax or petroleum jelly.

Small quantities of gutta percha are also used a* an adhesive, the best known being Chattelton's compound which is a mixture of gutta P«rcha, Stockholm tar and resin.

G. hi.

GUTZEIT'S TEST fo. Vol. I, **4706).**

GUVACINE f». Vol. 1,408a).

GUVACOLINE (*v.* Vol. I, 4586).

GUYACAN. A tanning agent obtained from the seed-pods of *Caesalpinia meianocarpa Grisab.* of the Argentine.

" *GYNERGEN" (v.* Vol. IV, 3304).

GYNOLACTOSE *(v.* Vol. I, 242a).

" *GYNOVAL."* isoBornyl wovalerato (" Ay-*sterol"),* b.p. 132-138°/12 mm. Used as a sedative.

GYhtOLITE *(v.* Vol. II, 227c).

GYPSUM (Fr. *Gypae ;* Ger. *Qips* ; Hal. *Gesso).* A common mineral composed of hydrated calcium sulphate, $CaSO_4 2H_2O$, crystallising in the monoclinic system.' The name *selenite* is sometimes applied to the clear cryMI Hi Bed variety, *satin-spar* to the finely fibrous variety, and *alabaster (q.v.)* to a compact, marble-like variety aised for caning. The low degree of hardness {no. 2 on the scale) is a very t'haracteristie feature; the mineral can be readily scratched with the finger-nail. Sp.gr. 2-32. The mineral is usually white, but sometimes greyish, yellowish or reddish j and the glistening cleavage surfaces are usually conspicuous on a broken ~ surface. The crystals possess a highly perfect cleavage in one direction parallel to the plane of symmetry; O:J the smooth, bnght cleavage surfaces **me hutn pearly,** and coloured bands (Newton's rings) are often to be Been. Cleavage flakes are flexible but not elastic (thus differing from mica), ami when bent a fibrous cleavage is developed parallel to the faces of a pyramid: this fibroua cleavage is *Been an silky* striations on the principal cleavage, and is a very cnaraeteristie feature of gypsum.

Single crystals of gypsum, with a rhomb-shaped outline, are of common occurrence embedded in clays. Fine groups of water-clear crystals arc found in the sulphur mines of Siiilyf the salt mines of Bex ^Switzerland and in many other localities. Enormous crystals, a yard in length, have been found in a cave in Wayne Co., Utah. Various types of twinned crystals are of common occurrence. The d-'posits of massive gypaum. such as arc miti<'<I for economic purposes, occur as thick beds and nodular masses in sedimentary rocks of various geological periods. Those of the midlands of Kngland are intcrbedded with the red marls and sandstones of Trtassic age; those worked near **Battle,** in Sussex, belong to the **later**

Purbeck beds; many of the deposits of the United States are of Palaeozoic (Silurian, Devonian and Carboniferous) age; whilst the important deposits in the Paris basin are of Tertiary (Eocene and Oligocene) age. These more extensive deposits of gypsum have been formed by the evaporation of water in inland lakes and seas; and they are often associated with beds of rock-salt. The mineral has, however, in many cases originated by the action of water containing sulphuric acid and soluble sulphates (produced by the weathering of iron-pyrites and other sulphides) on limestone and other calcareous rocks. It is also formed by the action of volcanic vapours on the surrounding rocks.

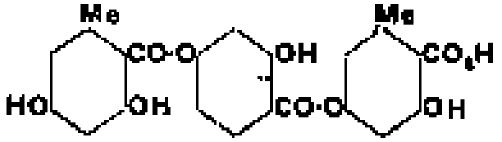
The output of gypsum in England amounts to about a quarter of a million tons per annum; about half of this amount is mined in Nottinghamshire, considerable quantities in Staffordshire, Sussex and Cumberland, and less in Derbyshire, Yorkshire, Westmorland and Somersetshire. The value ranges from 6 to 10 shillings per ton. In France, the output reaches 1£ million tons per annum, and about the same amount is produced in the United States. Nova Scotia and New Brunswick are also large producers. The French gypsum is remarkable in containing some admixed calcium carbonate and soluble silica, and for this reason it makes a harder plaster.

The principal use of gypsum is for the manufacture of plaster of Paris (*v.* Vol. II, 129-132), stucco and various kinds of wall-plasters and cements. Hence the popular name *plaster-stone.* The employment of plaster of Paris for making the moulds in the potteries has given rise to the name *potter's stone* for gypsum. In the tin-plate industry gypsum is used for polishing the plates; and it is added to water to give permanent hardness in brewing. The coarser grades of material are used as fertilizers (land plaster). Alabaster is used for carvings for inside decorations; and satin-spar is cut as beads and other small personal ornaments. Under the names " terra alba," "annaline" and "satinite," ground gypsum is used for adulterating paints, or sometimes as a legitimate constituent under specification, and as a mineral loading in the manufacture of paper (*v.* CALCIUM).

References.—R. W. Stones, "Gypsum Products, their Preparation and Uses," U.S. Bureau of Mines, 1918, Technical Paper 155; D. C. Winterbottom, V Gypsum and Plaster of Paris," Dept. of Chem. South Australia, 1917, Bull. No. 7; Special Reports on the Mineral Resources of Great Britain, Mem. Geol. Survey, 3, 2nd ed., 1918.; " Gypsum," Imp. Min. Res. Bur. London, 1923; G. I. Adams and others, " Gypsum Deposits of the United States," Bull. U.S. Geol* Survey, 1904, No. 223; W. F. Jennison, " Report on the Gypsum Deposits of Maritime Provinces," Canada, Dept. Mines, 1911, Publ. No. 84; L. H. Cole, " The Gypsum Industry of Canada," Mines Branch, 1930, No. 714; B. Wasserstein, "Gypsum in the Union of South Africa," Bull. Dept. Mines, S. Africa, 1935, No. 3.

L. J. S.

GYROPHORIC ACID, occurs in *Umbilicaria pustulata* Hoffrn., *Gyrophora* species and other lichens. It has m.p. 220° (decomp.). The structure of gyrophoric acid was first correctly postulated by Asahina and Watanabe (Ber. 1930, 63 [B], 3044)



and shortly afterwards confirmed by synthesis (*ibid.* 1932, 65 [B], 938; Asahina and Yoshioka, *ibid.* 1937, 70 [B], 200).

H

HAAS-OETTEL CELL (Vol. Ill, 65d).

HACKLIN-G (Vol. II, 11a).

H>EM (this Vol., pp. 1646, 165c).

" H/EMAROGEN," "HyEMOL" Trade names for albuminates of iron used as non-irritant assistants in the treatment of anaemia and chlorosis. These materials are frequently prepared from hemoglobin (Massatsch, Apoth.-Ztg. 1928, 43, 1307; sterilisation, Kirillow, Problems Nutrit. (Russ.), 1936, 5, No. 3, 55) though they then differ markedly from the iron compounds prepared from albumin. The term *hamatogen* was also applied to albuminates prepared by Bungc from egg-yolk and liver (Z. physiol. Chem. 1884, 9, 49; 1886, 10, 453).

H^MATIN (this Vol., p. 164).

H/EMATINIC ACID (this Vol., p. 1626).

H/EMATITE or HEMATITE. A mineral consisting of ferric oxide (Fe_8O_3), crystallising in the rhombohedral system, and an important ore of iron (Fe 70%). According to whether it is crystallised, massive, or earthy, it varies considerably in external appearance. In all cases, however, the mineral gives a characteristic brownish-red streak or powder; and it is on account of this colour (resembling that of dried blood) that the mineral receives its name haematite, meaning, in Greek, blood-stone. The sp.gr. of the Crystals is 5*2, but of the compact and earthy varieties it may be as low as 4-2;. hardness 6 (except in the soft, earthy varieties).

The crystals are iron-black with a brilliant metallic lustre, and they vary from rhombohedral to tabular in habit. This variety is distinguished as *iron-glance, specular iron* or *specular ite;* or, when the crystals are thin and scaly, as *micaceous iron-ore.* The compact varieties are distinguished as *red iron-ore* or *red hematite.* These sometimes exhibit a fibrous or columnar structure and a nodular surface, being then known as *kidney iron-ore*; or, when the fibrous structure is so marked that the mineral breaks into rods, as *pencil-ore.* In these cases the material is often dark-red with a dull surface, but sometimes it may be iron-black with a sub-metallic to metallic lustre. Earthy, ochreous varieties are brighter red in colour, and are often mixed with clay and other impurities; these are known as *reddle., ruddle* and *red iron-froi^.*.

Hipniutite occurs under a variety of conditions. The best crystals are found in connection with. in eta morphia silicate rocks and in mineral-veins, whilst the extensive masses *f red iron-ore occur as bedded deposits in sedimentary rocks, often in association with limestone. The deposits on **the** east coast of the island of Elba, which have been extensively worked since the time "of the Romans, consist of specular iron, whilst those of west Cumberland and north Lancashire, tilling large irregular cavities jn limestone, con«iat of red iron-ore and ldc&ney iron-ore.

Ik-sides being used as an ore of iron, hematite, in its harder, compact) varieties, is used, to a limited extent, aa a gem-atone, and it was the material employed for some of „ the ancient Babylonian cylinder-seals. The pencil-ore of Cumberland is cut and polished for mounting on scarf-pins, etc., and for the burnishing took used by jewellers and bookbinders. Ochreous varieties are used as a polishing material, and for making red paint andved pencils.

L. J. S.

H>EMATOGEN (Vol. II, 22a).

H>EMATOPORPHYRIN (Vol. II, 21a; this Vol., pp. 1616, *IQ'Zd).*

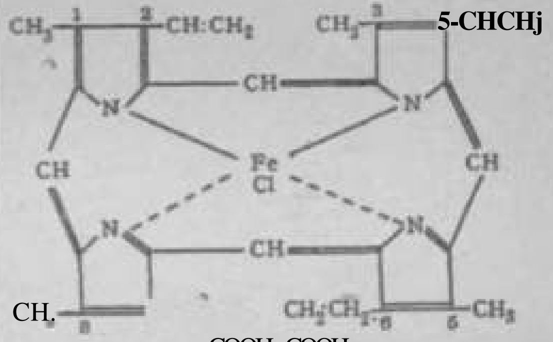
HvEMIN.CgaHaaO^FeCI. Hoppe-Seyler (Virchow's Arch. 18B2, 23, 446; 1864, 29, 233) first recognised that.the red pigment of the blood, for which he proposed the name haemoglobin, consisted of a protein combined with a coloured substance,*Jisematin.* Teichmann (Z, Rat. Med. 1857, 8, 141) obtained this pigment in a crystalline state by acetic, acid hydrolysis of blood. **Thifl** pigment, ***hfenun,*** can be readily obtained from blood by a modification of Teichmann's procedure.

Preparation.—200 ex. defibrinated blood is added dropwise with stirring to 1 litre 90% acetic acid containing 1 g. **NaC(,** at90-95"C. After a further 15 minutes at this temperature the mixture is allowed to cool slowly. Three days later the crystals are filtered off* through cloth and washed with water, alcohol and ether. 1 g. htemin is obtained. When carried out on a micro-scale this reaction Berves as a medico-legal test for blood. A small drop of blood, or a little dried blood plus a small drop of water, and a trace of NaCI are mixed on a microscope slide and evaporated to dryness, A cover-slip is placed over the residue and a drop of glacial acetic acid run beneath it. The slide is warmed until gas bubbles appear and is then allowed to cool. The warming is repeated with a second drop of acetic acid and, when cool, the characteristic crystals of htemiu can be recognised under the microscope.

Properties.— Htcmin is obtained as brown ot black rhombohedral needles or plates with a strong pale-blue reflex. It ia insoluble in water, alcohol, ether and dilute mineral acids, but in readily soluble in pyridine, in caustic alkali and in alkali carbonates. Concentrated **H_jSO_4** removes iron with the formation of *porphyrin.* Hsemin sinters at 240°C. but doea not melt below 300°C. {Fischer and Orth[1]).

L CHEMISTRY OF HJSMEN AND THE PORPHYRINS.

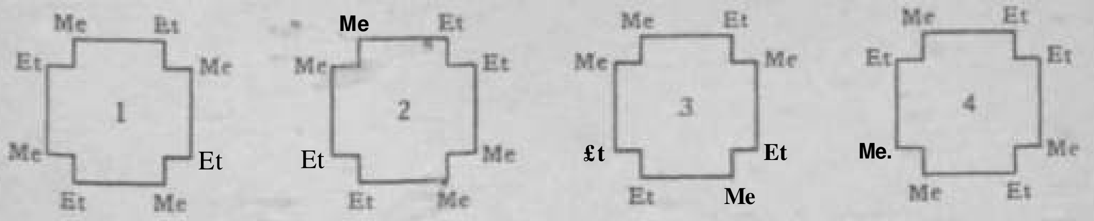
The chemical structure of hasmin, based on the work of Hans Fischer and his school, is given in



PIG. 1.

Fig. 1. Hsemin dissolves in alkali yielding a green-brown solution of *alkaline h&malin* (—Cl replaced by -OK). When now treated with a slight excess of HCI the colour changes to red-hrown and a brown precipitate of acid hiemattn is formed. In presence of a protective colloid *(e.g.* protein, gum arabic) tbo acid haematin remains in colloidal solution *(see.* Section II). If hremin is allowed to stand several days in presence of an excess of glacial acetic acid saturated with **HBr, the** iron **b removed** and a purplish solution of *dibromohmmntoporphifritt* ***tfdrobromidt*** in obtained in which the vinyl groups are replaced by **-CHBr-CH.,,** Crystallisation from HCI **ylekb** the hydrocbWide of ...matoporphyrin f-CH (OH)CHJ from which the free base is liberated by sodium acetate (Plimmur[8]). On heating in a vacuum, Ii;i-matoporphyrin loses 2 mol. of water and **yielda** *jtrotoporpht/rin.* The term *protohwmin* is fiimilift-ly used to characterise the litemin from blood {Fig. 1) with its characteristic substituents in the pyrrole nuclei.

The chemical structure of hwinin and the porphyrina is bused largely on the synthetic

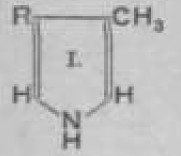


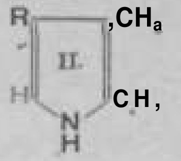
FIO. 2.

work of Hans Fischer and his collaborators. The problem is greatly complicated by the large number of isomers theoretically possible by rearrangement of groups in positions 1-8 (Fig. 1). In the case of ætioporphyrin, where the vinyl and propionic groups are replaced by ethyl groups, there are four possibilities and the naturally occurring porphyrins and derivatives can be grouped into two of the four classes (Fig. 2). Thus, while natural protohæmin is invariably of class 3, coproporphyrin and uroporphyrin, which occur in urine and fæces, have been identified in both the 1 and 3 forms. The brown pigment of hen's egg-shell is protoporphyrin 3. Fischer has been able to synthesise all four forms of these and of many other porphyrins. The structures (class 3) of the commoner porphyrins are summarised in Table I.

The different porphyrins, as well as the four classes of each porphyrin, can be distinguished by means of their absorption spectra in acid and in alkaline solutions (Oppenheimer,[3] p. 400; Fischer and Orth,[1] Vol. II). The bile pigments (q.v.) are derived from the porphyrins by oxidative degradation to linear tetrapyrrolic compounds (replacement of one methine group by two -OH).

Degradation of Porphyrins.—Nencki and Zaleski (Ber. 1901, 34, 997) heated hæmin with HI in glacial acetic acid, steam distilled the residue in presence of excess of alkali and obtained an oil, "hæmopyrrole." Later workers were able to fractionate the oil into four pyrroles (I—IV, R = Et) while from the residue were


I.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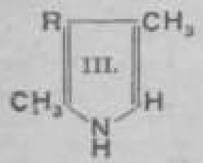
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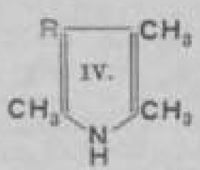
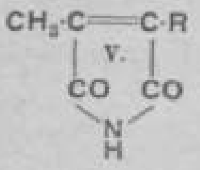

IV.


V.

isolated the four corresponding propionic acids ($R = CH_2CH_2{\cdot}COOH$). Küster and Weller (Z. physiol. Chem. 1917, 99, 253) obtained hæmatinic acid (V, $R = CH_2{\cdot}CH_2{\cdot}COOH$) by oxidation with chromic acid, while a similar oxidation of mesoporphyrin yielded hæmatinic acid and methylethylmaleimide (V, R = Et). The absence of the latter compound in the oxidation of protohæmin indicates that the unsaturated groups replace the C_2H_5 groups of mesoporphyrin. Evidence of unsaturation had previously been obtained by Willstätter and M. Fischer (ibid. 1913, 87, 410) who prepared an addition product with HBr which was readily hydrolysed to hæmatoporphyrin. Fischer and

	1	2	3	4	5	6	7	8
Ætioporphyrin	CH_3	C_2H_5	CH_3	C_2H_5	CH_3	C_2H_5	C_2H_5	CH_3
Deuteroporphyrin	CH_3	H	CH_3	H	CH_3	$[CH_2]_2COOH$	$[CH_2]_2COOH$	CH_3
Protoporphyrin	CH_3	$CH:CH_2$	CH_3	$CH:CH_2$	CH_3	$[CH_2]_2COOH$	$[CH_2]_2COOH$	CH_3
Hæmatoporphyrin	CH_3	$CH(OH){\cdot}CH_3$	CH_3	$CH(OH){\cdot}CH_3$	CH_3	$[CH_2]_2COOH$	$[CH_2]_2COOH$	CH_3
Mesoporphyrin	CH_3	C_2H_5	CH_3	C_2H_5	CH_3	$[CH_2]_2COOH$	$[CH_2]_2COOH$	CH_3
Coproporphyrin	CH_3	$[CH_2]_2COOH$	CH_3	$[CH_2]_2COOH$	CH_3	$[CH_2]_2COOH$	$[CH_2]_2COOH$	CH_3
Uroporphyrin	$CH_2{\cdot}COOH$	$[CH_2]_2COOH$	$CH_2{\cdot}COOH$	$[CH_2]_2COOH$	$CH_2{\cdot}COOH$	$[CH_2]_2COOH$	$[CH_2]_2COOH$	$CH_2{\cdot}COOH$

[1] Naturally occurring porphyrins.

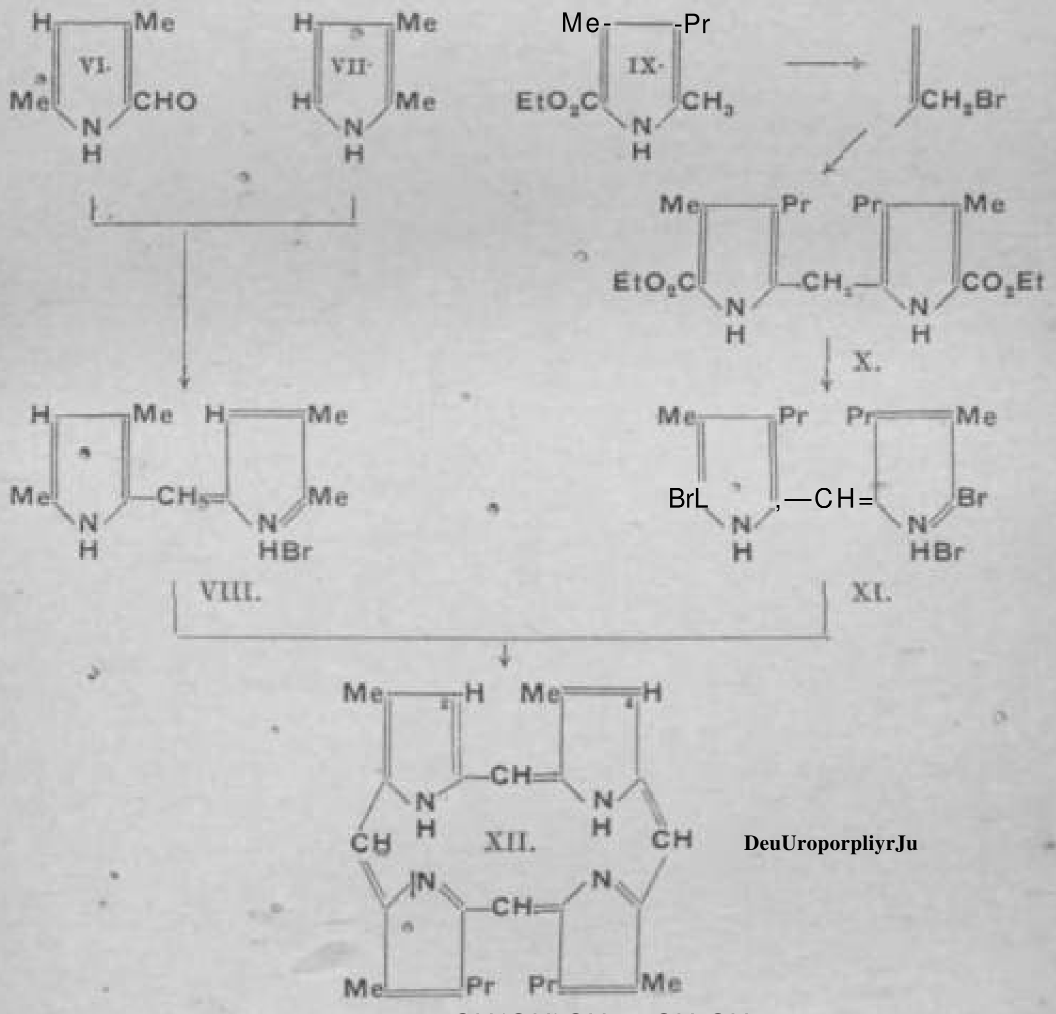
frequently transformed hæmatoporphyrin into protoporphyrin by heating *in vacuo.*

As early as 1912 Küster proposed a formula for hæmin identical with Fig. 1 except that CH_3 groups occupied positions 1 and 4 while the arrangement of the four vinyl C atoms was left indeterminate. Subsequent formulæ proposed by Willstätter and by Fischer were based on a tetrapyrrylethylene structure, but the present formula was established by Fischer and Stangier (Annalen, 1927, 459, 54) by synthesis of the corresponding mesoporphyrin (Fischer and Orth,[1] pp. 364-370).

Synthesis of Porphyrins and of Protohæmin.—The synthesis of hæmin *via* deuteroporphyrin is typical of the methods of porphyrin synthesis evolved by Fischer. 3:5-Dimethylpyrrole-2-aldehyde, VI, is condensed with 2:3-dimethylpyrrole, VII, in presence of alcoholic HBr to yield the basic component VIII. Carbethoxycryptopyrrolecarboxylic acid, IX

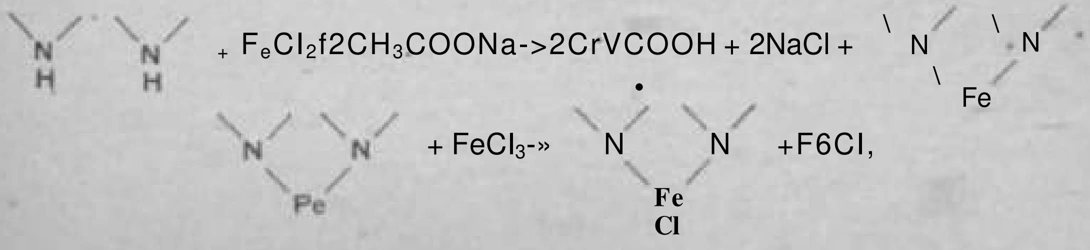
(Pr = $CH_2 \cdot CH_2 \cdot COOH$)

is brominated and condensed with itself (HBr in acetic acid) giving X which is hydrolysed and brominated to yield the acid component XI. By autoclaving in presence of HBr/glacial acetic acid, VIII and XI, condense to deuteroporphyrin, XII. Acetylation in positions 2 and 4 followed by reduction gives hæmatoporphyrin from which protoporphyrin is obtained by heating *in vacuo.* Treatment of protoporphyrin with ferrous chloride and sodium acetate gives rise to protohæmin in



In positions 2 and 4 H → CO·CH_3 → CH(OH)CH_3 → CH:CH_2

(Fischer, Naturwiss. 1929, 17, 611). Although the iron of protohæmin is in the trivalent state it is necessary to use a ferrous salt in the last reaction. In presence of air some ferric iron is always present and the reaction proceeds as follows:



For fuller details of porphyrin synthesis, see Fischer and OrtJi,[1] vol. II. For preparation of the intermediate compounds VI, VII and IX, *see.* Fischer and Orth,[1] Vol. I.

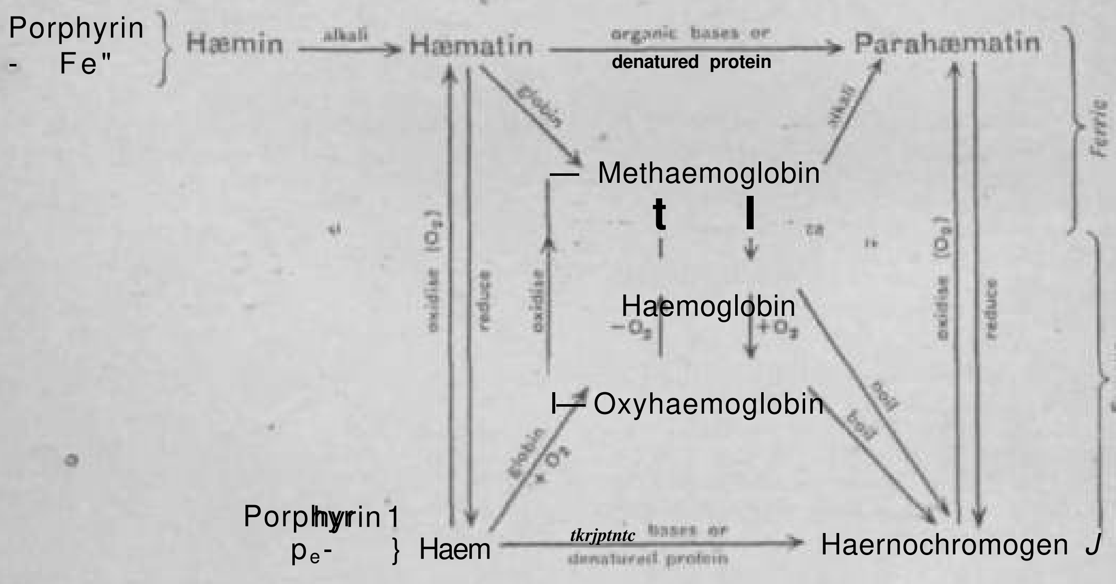
The parent substance*porphht* with H atoms in positions 1-8 has been prepared by Fischer and Gleira (Annalen, 1935, 531, 167) by heating pyrrole-a-aldehyde withformicacid.and by Stern and Molvig (J. Amer. Chem. Soc. 1936, 58, 625} by condensing pyrrole and formaldehyde in methanol solution. Porphin behaves as a normal porphyrin and forms a has rain in the usual way.

Porphyrins can be characterised not only by their absorption spectra but also by the " hydrochloric acid number." This property was defined by Willat&tter aa the concentration of HCI, expressed as a percentage, necessary to extract two-thirds of the porphyrin from an equal volume of ethereal solution. This principle can be applied to the fr&ctionation of porphyrin mixtures (Zeile and Rau, Z. physiol, Chem. 1937, 250, 197). A red fluorescence in ultra-violet light at very high dilution, especially in acid solution, is characteristic of porphyrins.

Porphyrins form metallic derivatives with a large number of heavy metals in addition to iron *{&.g.* silver, copper, tin, aluminium, manganese, cobalt, nickel). The iron, manganese and cobalt derivatives can be reduced to autox{disable compounds, involving change of valency, and the ferrous derivatives combine with CO. To this oiasa belongs the cod pigment *turadin* or coppor uroporphyrin which occurs in the wing feathers of the turaco *(Misopliagidm).* The pigment is readily extracted by dilute alkali, and the fact that it is slowly extracted by water indicates that the pigment may be produced as a means of excreting porphyrin (Church, Proc. Ruy. Soc, 1892,61,399; Keilin, *ibid.* 1926, B, 100,129).

II. REACTIONS oi[H^IATIN WITH OBOASIC BASKS AND PROTEINS.

The reaction between hieniatin and organic bases is of particular interest as the resulting compounds ^may serve as spectroscopic models of the natural hs&m-protein catalysts *{e.g.* haemoglobin), and also provide a simple -=neans of estimation of hsematin in tissues by speefcroscopic comparison with standard solutions of hremin. Fig. 3 summarises the interrelationships of these compotnds and their relationship to hemoglobin. For further details, ^ee Keilin **PA).**

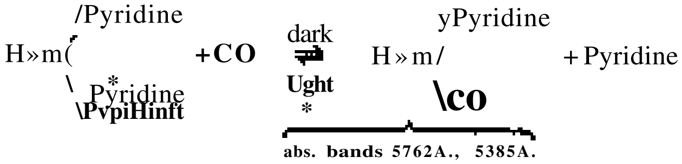


Flo. 3.

When treated with pyridine (or other organic bases) htematin forms an addition product *parahatmatin.* The solution becomes greener, but the diffuse absorption spectrum is not greatly changed. However, if the solution is now reduced ($Na_4S_sO_4$), the colour changes to pale red and the resulting *hwmockromogtn* has two sharp absorption' bands at 5590*. and 5257A. ; the former being more inter se. Hill and Holden {Biochem. J. 1926, 20, 132U) and luU-r Anson and Miraky {J. Gen. Physiol. 1930, 13, 4U9) succeeded in separating the protein of hemoglobin, or *gtobhi,* from the hs;matin without denaturing tho former. By adding this globin to an alkaline solution uf protoha-min, *metfurtnoyloijin* was obtairi.'d («ee Section VI) whirti wits reduced to bSBBM^ottn. Ol^hin has also been add«d to a number of other hremina, and of the resulting artificial hasmoglobina some exhibited the characteristic property of oxygenation. Methfcmoglobin may be prepared directly from oxyhicraoglobin by oxidation of the ferrous iron with $K_3Fe(CN)_{fl}$. During this reaction the combined r>xygsn of oxyhteruoglobin is liberated and the distinction between oxidation and oxygenation is clearly demonstrated.

If the mild procedures dcBmb<*d by the above author* are not Followed the protein become* denatured, and a para ha? matin or ha.[1] much ro mogen is formed according to the valency nf the iron. Thus if blood ia boiled, the h(rinochroinogen NjH-ti uni appears; if treated with alkali and dialyaed against water, parahiematin is formed.

All the ferrous compounds of Fig. 3 combine reversibly with CO, the absorption a[>ectruiu changing in each cast*. With hwra and hteuiochromogens the reaction is reversed by light and the following reaction takes place with reduced haematin (haem) and pyridine in presence of CO.



$$\text{Haem}\begin{cases}\text{Pyridine}\\ \text{Pyridine}\end{cases} + CO \underset{\text{light}}{\overset{\text{dark}}{\rightleftharpoons}} \underbrace{\text{Haem}\begin{cases}\text{Pyridine}\\ CO\end{cases}}_{\text{abs. bands 5762A., 5385A.}} + \text{Pyridine}$$

In absence of CO, haem and haemochromogen are autoxidisable.

III. OCCURRENCE IN NATURE.

Haematin is present in all animal and vegetable tissues, in yeast and aerobic bacteria, and is an essential constituent of all aerobic cells where it occurs either in the free state or, more usually, as haem-protein complexes functioning as respiratory catalysts, examples of which are described in this article. The concentration of haematin is greatest in tissues of high respiratory activity, or in a region where growth is very rapid. This is particularly noticeable in the case of the haem-protein *cytochrome (q.v.; see also* Keilin, Proc. Roy. Soc. 1925, B, 98, 312). Crude oils and bituminous minerals contain considerable quantities of haematin derivatives which can be observed with a direct-vision spectroscope. Most of these porphyrins are derived from chlorophyll but a small proportion of mesohaematin, a reduction product of protohaematin, can be detected. The porphyrins are present as metal derivatives; apart from iron, vanadium is commonly found (Treibs, Annalen, 1934, **510,** 42; 1935, **517,** 172).

IV. ESTIMATION.

The detection and estimation of free and combined haematin is most readily carried out by conversion to haemochromogen (pyridine and $Na_2S_2O_4$) which, of all haematin derivatives, has the most intense absorption spectrum *(see* Section II). The most convenient instrument to use is a Zeiss microspectroscope which has the necessary small dispersion and is fitted with a comparison prism to allow comparison of two spectra side by side. The solution or tissue extract to be examined is treated with alkali, to dissociate protein from haematin, followed by pyridine and $Na_2S_2O_4$. The absorption bands of haemochromogen can be observed in a 2 cm. depth of fluid containing only 0·001 mg. haemin per c.c.

The concentration of haematin can be determined to within 2-3% by comparing the spectrum with that of a variable depth of a standard solution of haemin crystals in sodium hydroxide similarly treated with pyridine and $Na_2S_2O_4$ (Hill, Proc. Roy. Soc. 1929, B, **105,** 112). The small dispersion of the Zeiss instrument permits accurate measurements with cloudy solutions. By the same method Elliot and Keilin *(ibid.* 1934, **114,** 210) were able to estimate haematin in intact vegetable tissue. A tube of the material *(e.g.* horse-radish root) was treated with pyridine and $Na_2S_2O_4$ in a vacuum when the root became sufficiently translucent for comparison of spectra. By this method the distribution of haematin in the entire cross-section of a plant can be rapidly determined.

The position of the absorption bands is determined by the chemical structure of the haematin nucleus rather than by the nitrogenous substance with which it is combined.

V. HAEMOGLOBIN AND MYOGLOBIN.

Haemoglobin *(v.* BLOOD).—This respiratory pigment is present in the blood of all vertebrates and is also distributed in a haphazard manner among the invertebrates where the oxygen supply is intermittent or irregular *(e.g.* ***Arenicola, Lumbricus, Planorbis, Chironomus;*** *see* M. Florkin, " Transporteurs d'oxygène," Paris, 1934). Haemoglobin is an intracorpuscular pigment in vertebrates but is in solution in invertebrate blood.

The haemoglobin molecule consists of 4 mol. of *haem* (reduced protohaematin) and 1 of globin *(see* Section II). It is a purplish-red pigment which combines reversibly with oxygen to give bright red oxyhaemoglobin, the equilibrium between the two forms being determined by the oxygen tension. The chemistry of the phenomenon of oxygenation has been investigated by a number of workers (Anson and Mirsky, J. Physiol. 1925, 60, 165; Barnard, Proc. Soc. Exp. Biol. Med. 1932, 30, 43; *see* J. Barcroft[4]) and its biological significance is discussed below.

Hill and Holden *(see* Section II) were able to examine the reaction between undenatured globin from haemoglobin and various porphyrins and metallo-porphyrins (Biochem. J. 1926, 20, 1326). They obtained spectroscopic evidence that native globin will combine with proto-, haemato- and meso-porphyrins (with a marked change in colour) as well as with iron derivatives of each. No evidence could be obtained that denatured globin or other proteins would react with the free porphyrins. Haurowitz and Waelsch (Z. physiol. Chem. 1929, **182,** 82) discuss the mode of combination of protohaematin and globin. They consider that the vinyl and carboxyl groups can play no part in the reaction, owing to the existence of artificial haemoglobins in which these groups are absent, and that the pyrrole N-atoms are too inert. They regard the reaction as complex-salt formation involving only the Fe atom and point out the similarity in behaviour of haemoglobin and inorganic complex salts towards acids, alkalis and organic bases. While this hypothesis may well hold for haemochromogens, the work of Hill and Holden as well as that of Warburg and Negelein (Biochem. Z. 1932, **244,** 9) does indicate that globin may also bo attached to other points of the hsematin molecule. These latter authors measured the O_a capacity of a number of artificial haemoglobins and found that it varied between 0 and 72% of the theoretical value, with varying subatituents in the hwmatin nucleus. The nature of the Fe-protein linkage has also been considered by Hill *[ibid.* **1928,** 19, 341).

Oxyhsomoglobin may be purified by crystallisation. The tendency to crystallise and the crystalline form vary considerably with the species (Abderhalden,[a]p. 185; Hawk and Bcrghcim[a]) while the positions of the absorption band.s vary slightly among vertebrate oxyhwmn. globing although invertebrate oxyhsemoglobinfi show larger variations. The average positions of the bands of vertebrate oxyhamoglobins are O-5770A. and J3-5240A,, the former being more intense. The spectrum of reduced or deoxygenatcd hemoglobin in very diffuse. If the O_2 of oxyhsemoglobin is replaced by CO the absorption maxima move slightly towards the blue as indicated in Table II [Anson, Barcroft, **Mirsky** and Oinuma, Proc. Roy. Soc. 1924, B_r 97, (il). If A and B are the positions in Angstrom I'nita of the a-bands of O_2Hb and COHb and A" is the equilibrium constant of the **reaction** CO | O.,Hb^COHb+Oj then, according to these aifthors, Iog.ff=005(A-B):

TABLE II,

Animal,	Position of a-band In Angstrom Units.	
	O_2Hb	COHb
Man	5,764	5,710
ArenicoUt. . . .	5,746	**5,698**
Lumbricus . . .	5,755	5,720
*Planorbi** . . .	5,746	5,708
Ohironotnui . . .	5,777	5,727
Pigeon	**5,782**	5,710
Carp	5,762	**6,7m**
Horse a	5,764	5,708
Tortoise	6,7(tfi	5,717
Fowl	5,769	5,718
Lizard	5,762	5,715

(Hb=h;einoglobin.)

Accurate measurements of, ware-length arc most conveniently carried out with the Hartridge reversion spectroscope (J. Physiol. 1922, **67,** 47),

Annlyaes of the amino-arids constituting globing from various sources have hcen recorded by J. Roche," Biouhimie generate et comparee des pigments res pirato ires," Paris, 1936.

Crystalline oxyhemoglobin is readily prepared by the following method .('Xeilin and Hartree, Proc. Roy. Soo. 1935, B, **117,** 1): 600 c.c. fresh di-nl.trina.ted horse-blood is centrifuged and the serum removed. The corpuscles are washed 3 times, by centrifuging, with 0-9% ^JaCI. 300 c.c, washed corpuscles are cooled to 0"C, shaken for •$ minute with 90 0.0, cold water and 90 e.c, cold pure ether and centrifuged. The **lower clew** layer is **dialysad for** 24 hours at 0°C. against distilled water and treated drop by drop with cold absolute alcohol until the solution contains 20% alcohol. Oxy haemoglobin Blowly crystallises out at 0°C. and can be recrystallised several times as follows: the cake of crystals is suspended in an equal volume of water, warmed to 37°C. and treated with the minimum of A^T-NaOH for complete solution. The solution is cooled, treated cautiously with JV-HCI equivalent to the NaOH used, centrifuged to remote impurities and set aside at 0° to crystallise. During recrystallisations the pigment becomes progressively less soluble in water. It is obtained as slender needles up to 2 mm. in length.

The determination of the molecular weight of hfcmoglobin has been recorded in a previous article (see BLOOD) and a value of 68,000 is now nrrnpted for vertebrate hemoglobin. The molecular size of invertebrate haemoglobins varies considerably

The estimation of oxyhiemoglobin can be carried out spectrophotometrically if o'Jher pigments are absent, but the moat reliable method is the measurement of the oxygen capacity. The hemoglobin molecule, containing 4 hremntm groups, takes up in rfir 4 mol. of oxygen. As already described (Section II) oxyhtemoglobin gives up its oxygen when oxidised to methajmnglobin, and it is only necessary to add an excess of $K_3Fe(CN)_g$ to a known volume of oxyhiemoglobiu solution in a suitable manomctric apparatus. For this purpose the manometers of Barcroft or Warburg are most suitable *(see* M. Dixon, "Manometric Methods," Cambridge, 1934). Thus, if 3 c.c. **OjHb** solution evolves *v* cu.mm. O« at N.T.P. on oxidation, then, as 68,000 g. Θ_tHb would combine with 4x22'4 I. Oj, the weight of **O_3Hb.** in 3 c.c. solution is

$$\frac{v \times 68{,}000}{4 \times 22{\cdot}4 \times 10^{4}} \text{ g.}$$

Myoglobin.—When blood is completely removed from an animal by perfusion it will bo found, on spectroscopie examination of thin slices of various organs, that a red pigment very similar to hemoglobin is*often present, and that it* concentration is greatest in tissues of high respiratory activity. If a perfused heart is finely minced, extracted with 0-9% NaCl and the extract clarified with kicsclguhr, a solution of this piginent, known aa *muscular kaunoglobtn* or *myoglobin* is obtained. The pigment combines reversibly wilh O_a (when the absorption maxima (horse-heart) are CI-5815A., /J-5440A.), and alwo with CO. The pigment forms a metmyoglobin andinitH gonenit properties is very similar to **hmoo^obin.** The pigment has beeft obtained in a crystalline state by Theorell, who has studied the Bpectroscopy of ita derivatives, it< reactions with O, and CO, and found the molecular weight, by ultraccntrifugal methods, to be 34,000 ; the molecule containing 2 mol. of protohajmatin (Biochem. Z. **L932,** 252,1; 1934, 268, 46). As a result of more recent measurements, a value of 17,000 is now accepted (Svedberg [7]). Hill has suggwtod (Proc. Roy. **8oa** 1930, B, **120.** 472) that " muscle haemoglobin indicates a presence of & reserve of oxygen not only in cases of **intermittent** «upply but nl in caeca **of intermittent** consumption of oxygen." Millikan *(ibid.* 1930, *[\\],* **120,** *\m;* 1937, [B|, 123, 218) using an apparatus in which reaction velocities could be measured by spectrum changes over very small intervals of time ($<10^{-3}$ sec.) showed that O_2 combines more rapidly with myoglobin than with haemoglobin. This author calculates that the oxygen stored by myoglobin in mammalian heart suffices for 10-15 seconds at rest or 2-3 seconds at high activity. This store could, therefore, tide the heart-muscle over from one contraction to the next. The oxidation of myoglobin (as distinct from its oxygenation) by molecular oxygen is also more rapid than that of haemoglobin.

Kinetics of Haemoglobin and Myoglobin.—Myoglobin was found by Hill (*l.c.*) to possess a higher affinity for oxygen than haemoglobin and the relationship is summarised in Fig. 4 (reproduced by permission of the author). This figure indicates the percentage of each pigment in the oxygenated form under various pressures of oxygen. Whereas the pressure of oxygen in the venous blood of man is 40 mm. Hg, the oxidase activity of the cell functions most efficiently at a lower pressure (*e.g.* 5 mm. Hg). At the former pressure myoglobin is 94% saturated and at the latter pressure 60% saturated with O_2. Myoglobin can thus act as an efficient oxygen carrier between the circulatory haemoglobin and the enzyme system of the cell. Hill has calculated that the oxygen made available from myoglobin by a drop in oxygen pressure from 40 mm. to 5 mm. would, in mammalian heart muscle, supply sufficient oxygen for 1 second's normal consumption, i.e. for approximately the duration of 1 heart beat.

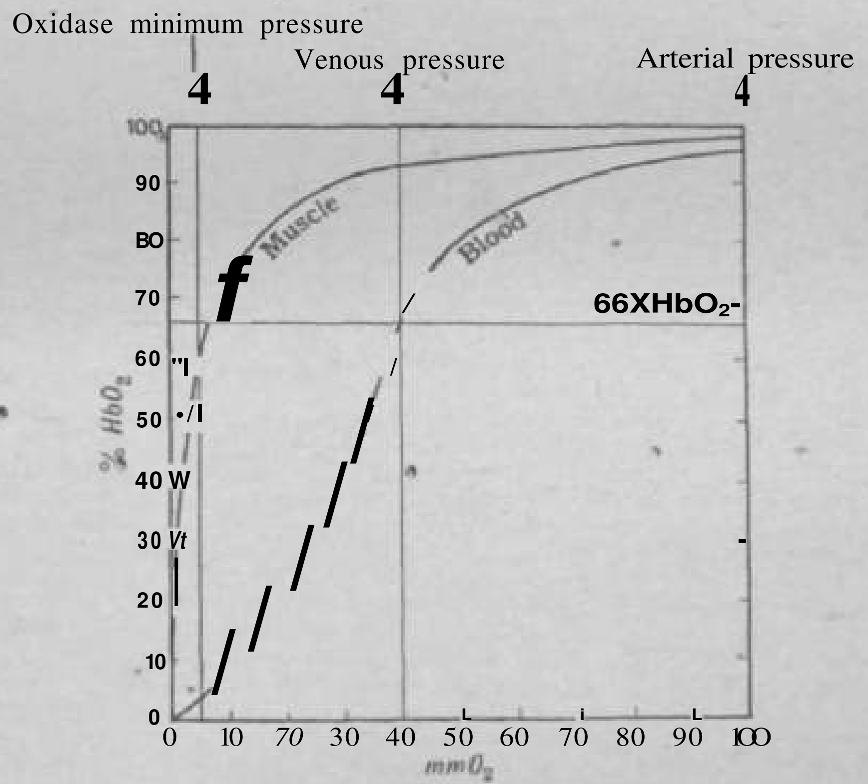


Fig. 4.

The relative affinities of these pigments for O_2 and CO is expressed by

$$K = \frac{[HbCO]\cdot[O_2]}{[HbO_2]\cdot[CO]}$$

Haemoglobin has a much higher affinity for CO than for O_2, and values of K between 100 and 600 have been found for various haemoglobins (Anson, Barcroft, Mirsky and Oinuma, Proc. Roy. Soc. 1924, B, 97, 61). The value of K for myoglobin is much lower; Theorell (Biochem. Z. 1934, 268, 64) finding values of the order of 20 for horse myoglobin.

VI. METHAEMOGLOBIN, PEROXIDASE AND CATALASE.

Methaemoglobin.—As previously mentioned, haemoglobin can be oxidised to methaemoglobin, the corresponding ferric compound, by means of $K_3Fe(CN)_6$ (see Keilin and Hartree, Proc. Roy. Soc. 1935, B, 117, 1). Below pH 7 a brown solution of acid methaemoglobin is obtained with absorption bands at 5040 Å., 5470 Å., 5820 Å. and 6370 Å. The last band is most prominent in visual observations. The spectrum is far less intense than that of oxyhaemoglobin, and a low-dispersion spectroscope is essential. Above pH 8 alkaline methaemoglobin is formed which is more reddish and has absorption maxima at 5750 Å. and 5450 Å. Methaemoglobin does not combine with CO or O_2 but forms a series of spectroscopically well-defined compounds with the respiratory inhibitors HCN, HN_3, H_2S, HF, NO, H_2O_2, and organic peroxides (*e.g.* C_2H_5OOH). In this respect methaemoglobin is closely analogous to the respiratory catalysts, peroxidase and catalase. The study of the formation of a definite compound between methæmoglobin and H_2O_2 (Keilin and Hartree, *l.c.*) led to the elucidation of the mechanism of the biologically fundamental reactions of peroxidase and catalase with H_2O_2.

Peroxidase.—This enzyme is very widely distributed in vegetable tissues but appears to be absent from animal tissues (except milk). It is a protohaematin-protein complex which has not yet been obtained in a pure state. It is obtainable most readily from horse-radish root and it catalyses the oxidation by H_2O_2 of many phenols and aromatic diamines (*e.g.* pyrogallol, hydroquinone, p-phenylenediamine), as well as of ascorbic acid (Willstätter and Pollinger, Annalen, 1923, 430, 269; Kuhn, Hand and Florkin, Z. physiol. Chem. 1931, 201, 255). Elliot and Keilin (Proc. Roy. Soc. 1934, B, 114, 210) demonstrated an approximate proportionality between hæmatin content and peroxidase activity during purification, while Keilin and Mann (*ibid.* 1937, B, 122, 119) were able to show that the activity was strictly proportional to the the spectrum intensity. The spectrum is very similar to that of methaemoglobin with bands at 4980 A., 5480 A., 5830 A., 6450 A. The latter authors recorded compound formation with the above inhibitors and the compound with H_2O_2 was the first example of an enzyme-substrate compound. Such compounds had always been postulated in studies of the mechanism of enzyme action. The same authors' purest preparation contained 1·5% hæmatin and may be considered as 40% pure on the assumption that peroxidase will contain the same proportion of hæmatin as methæmoglobin (0·38%). Haematin and all hæmatin derivatives possess a slight peroxidatic action and this fact has led to the reporting of heat-stable animal peroxidases. In such cases, the activity per milligram hæmatin is incomparably smaller than that of peroxidase which, like other hæm-protein enzymes, is destroyed by heating to 70°C.

ed as 40% pure on the assumption that

Catalase [*see also* CATALASE).—The occurrence of this enzyme, which decomposes H_2O_2 into molecular oxygen and water, is almost entirely restricted to animal tissues where it is very widely distributed. Considerable quantities occur in blood and liver. Like peroxidase it is a protohæmatin-protein complex with a 4-banded spectrum: 5065 A., 5440 A., 6800 A., 6295 A. (Euler and Josephson, Annalen, 1927, 452, 158; Zeile and Hellström, Z. physiol. Chem. 1930, 192, 171). Keilin and Hartree (Proc. Roy. Soc. 1936, B, 121, 173) described a simple method of preparation from horse liver and demonstrated a strict proportionality between the intensity of the catalase absorption spectrum and the hæmatin content of a series of catalases from horse liver, and later (unpublished results) found a similar proportionality between haematin content and catalase activity. The preparation of crystalline catalase from ox-liver (Sumner and Dounce, J. Biol. Chem. 1937, 121, 417) and the measurement of its sedimentation velocity in the ultra-centrifuge (Stern and Wyckoff, Science, 1938, 87, 18) showed that the molecular weight of catalase is of the order of 270,000 and hæmatin molecules occur per molecule. Recent work (Lemberg, Norrie and Legge, Nature, 1939, 144, 551) has cast some doubt on the equivalence of the four hæmatin nuclei and indicates that only three are protohæmatin. Catalase, like methæmoglobin, forms a series of compounds with the respiratory inhibitors (Keilin and Hartree, *l.c.*), while the mechanism of the decomposition of H_2O_2 into water and molecular oxygen has been explained by the same authors (Prop. Roy. Soc. 1938, B, 124, 397) as a reduction of $Fe^{\cdots}$ of catalase by H_2O_2 followed by its re-oxidation by oxygen.

$$4Fe^{\cdots}+2H_2O_2=4Fe^{\cdot\cdot}+4H^{\cdot}+2O_2$$
$$\underline{4Fe^{\cdot\cdot}+4H^{\cdot}+O_2=4Fe^{\cdots}+2H_2O}$$
$$2H_2O_2=2H_2O+O_2$$

VII. OTHER NATURALLY-OCCURRING HÆMATIN DERIVATIVES.

Cytochrome (*q.v.*).

Chlorocruorin.—Ray Lankaster (J. Anat. Physiol. 1867, 2, 114) [illegible] chlorocruorin [illegible] -protein pigment dissolved [illegible] certain polychaete worms. It acts as an oxygen carrier and its spectra in the oxygenated and deoxygenated forms are similar to those of hæmoglobin, though the bands are nearer to the red end of the spectrum.

The haemin was isolated and examined by Fox ([illegible] 1926, B, 99, 199) while, according to Fischer and von Seemann (Z. physiol. Chem. 1936, 242, 133), it is identical with the so-called *spirographishæmin*, *i.e.* [illegible] with [illegible] -CHO [illegible] 2. [illegible] hæmochromogen occurring during [illegible] hibernation. Its [illegible] in *Helix* [illegible] is unknown (Dhéré and Vegezzi, J. Physiol. Path. gen. 1917, 17, 44).

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HÆMOCHROMOGEN [illegible] HÆMOGLOBIN [illegible] p. 165c).

HÆMOPYRROLE (this Vol., p. 162a).

HAFNIUM. Hf. At. no. *72,* at. wt. 178-6.

In 1023 D. Coster and G. von Heveay detected in the X-ray spectra of a number of zirconium minerals six lines attributable to an element 72. They asserted that two of these lines were not identical with two lines observed by Dauvillier in 1922 in certain rare earth;?, and hence could not be identified with a new element " celtium " which had been claimed by Urbain to be present in the qame rare-earth preparation. Coste^and Von Hevesy proposed the name *hafnium* (from Hafnia, an old designation for Copenhagen) for element 72, and showed that it could be separated chemically with zirconium frem any accompanying rare earths, and that it did not yield the optical spectra assigned by Urbain to "celtium" (Nature, 1923, 111, 79, 182, 252, 462).

All zirconium minerals contain tufnium, although in greatly varying amounts; the oxides contain £-2%, the silicates such as zircon 2-6%. *Alvite,* a complex orthosilicate,

$$(Zr,Hf,Th)O_8,SiO_3,$$

from Kragero, Norway, contains 34% of zirconia and 16% of hafnia. The zirconium extracted from* the complex minerals *evxcnite* and *fergusoniU* contains i'rom 6 to 6% of hafnium. *Thortveitite,* from Madagascar, contains 3-2% HfiOj and 2% ZrO_a. Hafnium is as abundant in the earth's crust as thorium and about one-tenth as plentiful as zirconium.

Separation from Zirconium.—Hafnium exhibits a close chemical similarity to zirconium, and they rAnain associated when the latter is separated by the usual methods from the rare earths and thoria. Materials containing had nium and zirconium are fused with potassium hydrogen fluoride and the double fluorides KjXF.(X = Hf orZr) are separated by fractional crystallisation in aqueous solution. The hafnium salt is more soluble and in this way a product of 99-9% purity is obtainable. A convenient alternative consists in the fractionation of the ammonium double., fluorides, that of hafnium being the more soluble.

Hafnium ammonium sulphate is also more soluble than the corresponding zirconium double salt and may be used in these separations.

The phosphates $XO\{Hj_tPO_4)$, also serve for this separation, the hafnium phosphate WINJ.' appreciably less soluble in'concentrated acids than the zirconium compound. The freshly precipitated mixed phosphate dissolves in toaHo acid and on adding hydrochloric or sulphuric acid is reprecipitat«d in a readily filterable form. In this process hafnium accumulates in the less instead of in the more soluble fractions. This method is available on a large scale, and after about 26 fractionations the hafnium contains not more than 1% of zirconium (de Swr, Z.'anorg. Chem. 1926, 150, 210; with Broos, *ibid.* 1930, 187, 190).

A precipitation, method has also been recommended by Prandt" *{ibid.* 1932, 208, J20; 1937, 230,419} in which the solution of the hydroxides m dilate Bulphorio acid containing ammonium ""Ipli.'ite and oxalic add Ea trotted with sodium ferrocyanide; hafnium is enriched in the head fractions. Tlio presence of phosphate ions tends to interfere by causing co-precipitatiou of phosphates.

Sublimation and distillation methods have also been employed. The double compounds $2XC1_4$-PCI_S and $2XCI_4POCI_3$ (X-Hf and Zr), produced by melting together the mixed hafnium and zirconium tetrachlorides with the corresponding phosphorus chlorides, can be distilled under ordinary pressures and, in both cases, the hafnium compound, being the more volatile, is concentrated in the early fractions (Van Arkel and de Boer, *ibid.* 1924, 141, 289; B.P. 221802).

Metallic Hafnium, obtained by thermal decomposition of its iodide, has also beeu prepared from the double fluoride K_aHfF_e or the tetrachloride by reduction with metallic sodium ; the oxide may be used if a mixture of calcium and sodium is employed as the reducing agent (Van Arkel and de Boer, *ibid,* 1925, 148, 345; de Boer and Fast, *ibid.* 1030, 187, 193).

Physical Properties.—Hafnium is a highly lustrous, ductile metal reseinbb'ng zirconium in appearance and crystalline form (hexagonal system). The .Z-radiogram gives the side of the unit triangular prism as 3-32A. and its height as 5-4(SA., with axial ratio 1:1-64. It melts at 2220°G. while its density at room temperature is 13-3, the atomic volume being 13-42. Six isotopes have been indicated, weak lines at 174 and 176 with stronger lines at 177, 178, 179 and 180; the relative abundance of these is approximately 03, 5, 19, 28, 18 and 30%, respectively {Aston, Proo. Roy. Soc. 1935, A, 149, 896; Dempster, Physical Hev. 1939, |ii], 56, 794). The specific heat at low temperature has been measured by Cristeseu and Simon (Z. physikal. Chem. 1934, B, 25, 273) who find that there is an anomaly with a sharp peak at 75° abs. The resistivity of hafnium is 30-10* ohm-cm, at 0°C.; no evidence of superconductivity was noticed at 1-35° abs. (de Boer and Fast, Z. anorg. Chem. 1930,187, 193).

The spectrum of hafnium possesses a great number of lines, the persistent ones being ?5130, 2516-9, 2041-4, 2773-4, 2820-2, 2898-3, 2910-5, 3072-9, 3134-8, 4093-2A.

Chemical Proptrltet—Although falling between zirconium and thorium in the periodic classification, hafnium more closely resembles, but is more basic than, the former. Its reactions with acids, halogens and other reagents are similar to those of zirconium and it shows a like tendency to form complex salts.

COMPOUNDS.

Hafnium Dioxide (Hafnia), HfO_r—Obtained by ignition of the hydroxide, oxnlatr, oxychloride or sulphate. It is a dianiagnetic oxide, d^{i0} 8ti8, incandescent at high temperatures whil* its melSng-point is 3047±25° abs. Hafnia is an amphotcric oxide and strontium hafnatc, $SrHfO_3$, lms been made (Hoffmann, Naturwiw!. 1933, 21, 076).

Hafnium Tetrafluonde,HfF_4.—MoiKtchnic „-ismiitii- cryiitabobtatoedophcanagaranioniaiii I'li'niiiiifjriH-t' f ^J rl *Min* HI r if J11 & BvF^'ii 111 ^1 ILJIiO" gen at 500°. It may be purified by Kiblinmtioi! at 800% aiui this ptOOBH leads to a partial sftpva - tion from any zirconium present {Von Hevisy and Dullenkopf, Z. anorg. Chem. 1934,221,161; Schultze, Z. Krist. 1934,89, 477). When hafnia is dissolved in hydrofluoric acid and the solution is concentrated, crystals of the trihydrate $HfF_4,3H_2O$ separate, and these when recrystallised several times from water hydrolyse to form the *oxyfluoride* $HfOF_2 2HF,2H_2O$ (Von Hevesy and Wagner, Z. anorg. Chem. 1930, 191, 194). Hafnium fluoride very readily forms a series of double salts with alkali and ammonium fluorides of the types $M_2[HfF_6]$ and $M_3[HfF_7]$;. these are more soluble in water than the corresponding zirconium salts.

Hafnium Chlorides.—Hafnium burns fairly readily when heated in chlorine, producing the *tetrachloride* $HfCI_4$ as a white crystalline mass which can be further purified by sublimation in dry hydrogen. It begins to volatilise at 250° and any zirconium present will tend to collect in the first portion of the sublimate. The chloride is also formed when the oxide is heated in the presence of a reducing agent and chlorine. Water hydrolyses it to *hafnyl chloride,* $HfOCI_2$, while addition of ether to an alcoholic solution of the latter substance yields another *oxy-$_m$ chloride,* Hf«$O_3CI_2,5H_2O$. These compounds are less soluble in hydrochloric acid than the zirconium analogues and have been used fn the separation of the two metals (de Boer and Fast, Z.c).

Hafnium Oxybromide is formed as glistening tetragonal crystals on concentrating a solution of hafnia in hydrobromic acid. It is extremely soluble in the dilute acid, but increasing concentration of the latter causes a rapid decrease in the solubility. Thus in 0-35A^r-HBr at 25° the solubility is 3-3 g.-mol. "HfOBr, per litre while in 13-36JV- it is 0·0039 g.-mol. (Von Hevesy and Wagner, *I.e.).*

Hafnium Iodide *(see* de Boer, Z. anorg. Chem. 1926,150, 216).

Hafnium Sulphate, made either by the action of fuming sulphuric acid on the tetrachloride or by repeated evaporation of the fluoride with concentrated sulphuric acid, always seems to contain excess H_2SO_4 over that required by the formula $Hf(SO_4)_2$. This excess can only be removed at a temperature (500°) at which the salt begins to decompose (Von Hevesy and Cremer, *ibid.* 1931,195, 339).

Hafnium Nitrate.—This salt, mixed with tungstic oxide, is employed in making lamp filaments. The hafnium produced is stated to .prevent the recrystallisation of the tungsten filament.

Hafnium Phosphates.—When a solution of hafnyl chloride in 62V-HCI is added to one of disodium phosphate in the same medium a finely divided precipitate is produced corresponding to the formula $HfO_2,P_2O_5,2H_2O$. This might be either $Hf(HPO_4)_2,H_2O$ or«$HfO(H_2PO_4)_2$, but the well-known stability of hafnyl as compared with hafnium ions strongly favours the latter formula. When ignited, the salt loses 2 mol of water yielding hafnyl metaphosphate, <.

$$HfO(PO_3)_2.$$

Hafnyl phosphate is the least soluble of all phosphates in hydrochloric acid, the solubility in *ON*· acid at room temperature being 0-00009 g.-mol. per litre (Von Hevesy and Kimura, J. Amer. Chem. Soc. 1925, 47, 2540; Z. angew. Chem. 1925, S8, 228).

Hafnium Carbide.—Said to be obtained as a grey powder on heating an intimate mixture of hafnia and finely divided carbon in a graphite tube at 2,000-3,008°C. or by passing the vapour of the tetrachloride together with methane and hydrogen over a heated tungsten filament.

Hafnium Boride has also been prepared [Agte and Moers, Z. anorg. Chem. 1931,198,233; *see also* Vol. II, 44c).

Hafnium Acetylacetone, $Hf(C_5H_7O_a)_4$.—Monoclinic crystals, m.p. 194-195°, <£f 1;67, formed when acetylacetone and dilute soda solution are added to hafnyl chloride in water; the product is recrystallised from alcohol. It sublimes slowly in a high vacuum at 82° but at 87° decomposition sets in. Like zirconium acetylacetone and unlike the thorium analogue it does not combine with ammonia; it further resembles the former in giving a decahydrate $Hf(C_6H_7O_2)_4.10H_2O$ (Von Hevesy and L6gstrup, Ber. 1926,59 [£], 1890).

References.—Georg von Hevesy, " Das Element Hafnium," Berlin, 1927; J. W. Mellor, " A Comprehensive Treatise on Inorganic and General Chemistry," Vol. VII, London, 1927; H. Rose, " Das Hafnium," Braunschweig, 1926.

G. R. D.

HAGLUND PROCESS (Vol. I, 2686).

HAIPINGERITE (Vol. II, 2266).

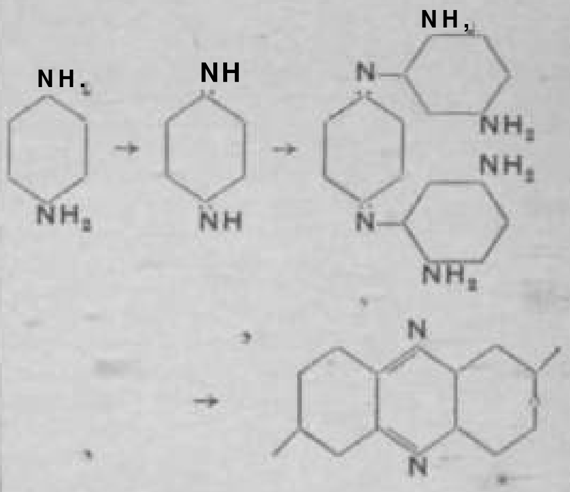
HAIR DYES (HUMAN). The practice of dyeing the hair has considerably increased of recent years, particularly since the introduction tf organic intermediates -auch as j?-phenylenediamine which can be oxidised to produce dyes on the hair. But the art is really of great antiquity; there are references to it in ancient Hebrew, Persian and Roman literature. The practice was common too in ancient Egypt and it seems that the use of mineral pigments such as kohl, and vegetable colours including henna, dates back several thousands of years.

Although hair has a general composition similar to that of wool, its dyeing present. peculiar problems because the affinity of human hair for dyes is very much less than that of wool, and the dyeing qualities of living hair differ somewhat from those of dead hair. Moreover, it will be obvious that only those substances can be used which will be effective at temperatures below about 37°C. and that the use of markedly acid or alkaline reagents will be fraught with serious consequences. There are three principal classes of hair dyes: (i) Inorganic dyes or pigments; (ii) Vegetable colouring mattera; and (iii) Oxidation dyes.

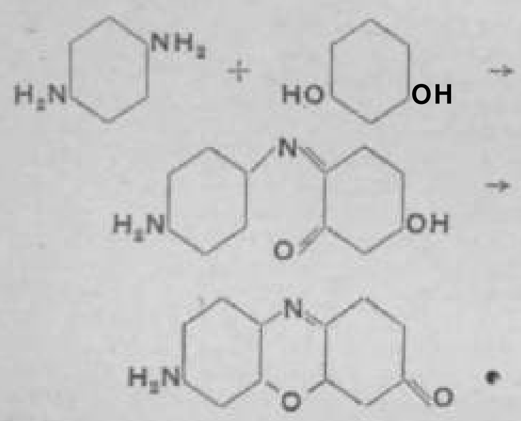
(i) In this class the most ancient material is kohl, the name covering a variety of black pigments, including charcoal and various forms of galena. It is not now used, save perhaps in some theatrical make-ups, in which the pigment is made into a paste or emulsion with resinous materials, gum or gelatin. Lead compounds are still used rather extensively, though they *tirv* more often described as hair restorers. Tin-chief ingredients in such mixtures are lead acetate, less commonly lead oxide, emulsified with a sulphur compound—either colloidal sulphur, sodium thiosulphate or a mixture thereof—in the presence of glycerin and oil. The proportions commonly present may be about 3% of lead acetate with an equal quantity of sulphur. These mixtures react slowly on the hair and form a brown or black coating of lead sulphide, part of which is adsorbed into the hair fibres. The mode of action is not quite clear, but it appears that the sulphur is first adsorbed and later combined with the lead. Silver forms the basis of another series of dyes; these differ from lead mixtures in that they require two separate solutions, one containing silver nitrate with or without ^.mmonia, and the other containing either an alkaline sulphide or a solution of pyrogallol. Sulphide mixtures give light brown shades, while the pyrogallol mixtures are darker or even black. Bismuth has enjoyed quite a vogue.-, The basis is usually bismuth citrate dissolved in a water-alcohol-glycerin mixture, and a separate solution contains cholesterol, sulphur and allmmiti. As in the case of the lead pigments, the reactions involve changes in the keratin of the hair with the liberation of hydrogen sulphide and the formation of a black bismuth sulphide on the hair. Various claims have been made as to the function of the cholesterol and albumin, but there is no evidence that they participate in the reactions. Preparations based on nickel, cobalt, iron, manganese and copper salts also appear in the literature, but are not in common use, though they may, as noted below, be used in admixture with henna and other vegetable compounds. Salts of these metals may be employed in conjunction with pyrogallol, with which they are said to produce good black dyes, B

(ii) The principal hair dyes coming within the second class, vegetable dyes, are henna, walnut, logwood, chamomile and indigo. Cutch and other tannin materials are used to a less extent. The dyeing properties of henna *(q.v.)* are due almost, entirely to 2-hydroxynaphthaquinone, known also as *Lawaont*; this substance is present to the extent of **1-1-5%** and^cta as an acid dyestuff. It is a pale yellow in acid solution and dyes hair a bright orange colour, the shade being considerably affected by metallic mordants. For use the powdered leaves, about S oz. for * head, are made into a paste with boiling water and applied to the hair for about 15 minutes; the presence of a*small amount of a wetting agent is of advantage. Many compounded hennas are sold; these contain copper salts, pyrogallol or even jj-phenylenediamine, and **serve** to give much darker shades than are obtainable from pure henna. Indigo finds use in conjunction with henna under the name of *tenna-reng, A* mixture of 2 parts of indigo with 1 part henna gives a **brown** and 3 parts of indigo give a darker brown. For the composition of henna powder and methods for the determination of 2-hvdroxynaphthaquinone, *see* H. E. Cox, Analyst, 1938, 63,397. Walnut ninnies and leaves which also find use as *&* hair **dye** resemble '"•mia in dyeing properties. The active ingPetlient in MiydmxyiifiphMinquuiom*, **j«#k>W***I* 't dyu« hair a durk brown but the colour takes **"'tin** time to develop fully. Walnut ic applied in the form of an extract, or the powdered leaves, with or without henna, are mixed to make a paste which can be applied hot. Extract of **walnut** should be freshly prepared as it does not keep well; commercial products may contain metallic additions, notably silver salts. There have been several attempts to apply logwood as a hair dye, but it is not very successful unless in admixture. The preparations for production of a satisfactory colour on the hair from the hsematoxylin present in logwood mixtures usually consist of powders containing the wood with additions of starch, chestnut or henna, and as o x idi se r an aci d sol uti on of dich rom ate. Chamomil.' flowers *(q.v.)* contain a rather feeble dyestuff of the flavone class called *ajtigcniu,* the glucosidal constitution of which is described by Power and Browning [J.C.S. 1914, 105. 1829). For practical application a hot paste made from powdered chamomile flowers diluted with fuller's earth or kaolin is applied to the hair and left in contact with it for half an hour or more. The colour produced on light hair is a warm blonde; it may be darkened by admixture with henna or walnut. Chamomile finds more extensive use as a shampoo or rinse than actually as a dye.

(iii) The most interesting development in hair dyeing began in 1888 when Erdmnim introduced the us~of p-phenylcnediamUic, the first and most important member of the oxidation class. Since that date a very great number of substances have been proposed or patented which claim to possess special merit, or to avoid the one disadvantage of y-phenylenediamine, namely its occasional irritant effect on the skin. Dye mixtures of this class involve two reagents, one being an alkaline solution of the base or bases, usually mixed with soap or other wetting agent and perfume, and the other a solution of hydrogen peroxide or tablets of urea peroxide. These two solutions are mixed immediately before use and are applied with a brush to the well-washed hair. When p-phenyfo&eduuaine is thus oxidised in alkaline solution the first product *in* Bandrow-* aki's base **(Bar,** 1894, 27, 480) possibly with quinonediiminc as an intermediate prxluct; this subsequently condenses with the **formation** of a complex azinc in and on the hair fibres (<•/.



H. K. Cox, Analyst, 1934, 59, 3). When p-**phmyleaadiunioe** is used alone the range of colours obtainable in limited to dull bruwu, greys and black, and there is considerable wastage. To extend the range and obtain auburn, light and dark brown shades, a dihydric phenol is added. This is usually resorcinol or caterhol, but a variety of other compounds may be used. In the presence of such phenols the course of the reaction is quite different; there is no formation of Bandrowaki's base but of indophenols of *a* red-brown colour, and having the oxygen in the ortfo-position to the nitrogen. These indophenols further condense to oxazonee on the hair (c/. Cox, *ibid.* 1040, 65, 393), and produce a pleasing variety of shades. The popularity of



these mixtures is such that it has \>*een* stated that 10 million packets per annum are sold in one European country, and as might be oxpectcd, there are many variants of the mixtures which give rise to particular colours or for which special virtues are claimed. The success of p-phenylenediamine as a hair dye is somewhat offset by the fact that it produces a troublesome dermatitis on some few individuals *who* are idiosyncratic or auperaensitive *(cf.* lugram, J. Derm. Syph. 1932, 44, 422; Cox, J. Med. Legal Soc. 1037, 123). For this reason •the Bubstance and ita honiologue p-taluylenediamine are included in Part **II** of the Poisons Rulesfin Britain and are subject to legislative restrictions in France, Germany and the U.S.A. It is customary, when these dyeB are to be usod, first to make a small patch test on the individual aiul only to proved if this test indicates that no supersensitivity exists. Perhaps it ia partly as a result of this difficulty that intensive search has been made for other oxidtsablc intermediates which might have the same or better tinctorial power and, in addition, possess all the virtues required of the ideal hair dye, viz. (1) it should provide n good range of colours and a silky lustre on **the** hair; (2) it must not make the hair brittle; (3) it must not irritate or stain the scalp • (4) it must not fade or produce " off " colours; and (5) it must not interfere with subsequent permanent waving of the htflr. Of the members of the same series p-toluylwii-cliauiine is used and jj-xylylenediamine has been suggested. Then **vulphonfc** acid groups **bCTO bMD** introijined to reduce toxkity but **snch** compounds are **oft** inferior tinctorial power, HO aluo ure the acet*y*\ **derivatives.** The metliyl-, ethyl- and diim'tbvl-dmvutivtt* of /t-plienylenediamine are rcn **good** d\e bases but, **0** far *tm* is known, they IN not leas toxic than tliu original hwc. The aminophenols, aminoanisoles and atninophenetoles are also used; p-aininophenol will produce a goodabrown. 2:4.-Diaminophenol is also useful. Another interesting series includes the nitroamines such as 2-iiitro-4-amino- and 2-amino-4-nitro-phetio)andnitro-p-phenylenediamine; the chemistry of the Oxidation of these compounds has not yet been elucidated. Various diphenylderivatives also find use; such are the p« aniiijodiphcnylamineH, #p'-diaminodiphenylamine and their substitution products and the naphthalenedia mines. These are also blended with a dihydric or trihydric phenol to give the required range «f colours. Any of these compounds may be present in mixtures together with a number of other substances whose names appear in the now voluminous list **of patents.** Ready-formed synthetic dyea may also be present. c

In view of what has been said it is clear that no simple methods of analysis can "be prescribed which will cover all cases. Mixtures will contain in addition to the foregoing bases suitable quantities of wetting agents, ammonia, soaps or sulphonated Compounds, perfumes and sometimes glycerin or oils. Before applying specific teat* therefore it is necessary to separate the ingredients, as dia mines form addition compounds with dihydric phenols and various interactions are possible in the solutions, thus rendering colour reactions most unreliable. Much can bo effected by judicious selection of solvents; petroleum spirit extracts any fat or fatty acids from the acidified xuiVture and subsequent treatment with ether will reropve most of the dihydric phenol, after which addition of alkali in the presence of (t mild reducing agent will enable any diamine to ho extracted. These various fractions can be further separated and examined. In checking by means *of* nitrogen determinations it should be borne in **mind** that some of these derivatives give markedly low results with the Kjeldahl process. J. Carol {J. Assoc. Off. Agr. Chem. 1940,23, 821} gives a good method for tho, separation of j>-pnenylenediamine in such mixtures.

In general finished dyes suoh as are useful for textiles have very limited affinity for living hair under tho conditions which must bo observed in hair dyeing. There are, however, considerable numbers of tinting mixtures or rinses which find extensive use for fancy purposes. It is important that dyes used for this purpose should be of a good degree of purity.

References.—Redgrave and Bari - WoohVs " Hair Dyes and Hair Dyeing," W. Hcinemann, Ltd.. London, 1039, and various papers by Cox (U). • ^ H. *E.* C

"HALARSOL" (Vol. 1,4896).

" *HALAZONE* " (Vol. IV, 20c).

HALBERG-BETH system of dry gasckanuig (Vol. V, :177).

HALF VALUE PERIOD. This term {or the equivalents " half life period " and " half time ") is used with reference to processes which take place at a mensurable **ipwd,** itnd represent* HM **tima aeOHMty** for sonic quantity which i« being measured to decrease to one-hall' of its original value. Tho commonest IILSO *in* that of a chemical reaction, where tho hulf value period

(H.V.P.) is the time necessary for the concentration of one of the initial reactants to be reduced to one-half. If, as is often the case, the course of the reaction is being followed by measuring the value of some property (*e.g.* pressure, volume, colour, conductivity, etc.) which is proportional to the concentration of the reactant, then the H.V.P. is also equal to the time necessary for this value to become halved. This criterion is often applied to radioactive changes, where the activity of the specimen is the property measured; similarly, in a racemisation the H.V.P. is the time required for the initial optical rotation to become halved.

The dependence of the H.V.P. on the initial concentration, and its relation to the velocity constant, depend on the kinetic order of the change. If *a* is the initial concentration of the reactant and x its concentration after time t, then for *first order reactions* (which include simple radioactive changes)

$$\frac{dx}{dt}=-k_1x, \quad k_1t=\log_e\frac{a}{x}, \quad t_{\frac{1}{2}}=\frac{1}{k_1}\log_e 2,$$

so that the H.V.P. is independent of the initial concentration and inversely proportional to the first order constant k_1. In this case the reaction velocity can be defined equally well by either k_1 or (j, and in the case of radioactive changes the latter is more often used. For a *second order reaction*,

$$\frac{dx}{dt}=-k_2x^2, \quad k_2t=\frac{1}{x}-\frac{1}{a}, \quad t_{\frac{1}{2}}=\frac{1}{ak_2}.$$

The H.V.P. is now inversely proportional both to the initial concentration and to k_2. In general, for a reaction of the nth order ($n>1$),

$$\frac{dx}{dt}=-k_nx^n, \quad k_nt=\frac{1}{n-1}\left(\frac{1}{x^{n-1}}-\frac{1}{a^{n-1}}\right),$$

$$t_{\frac{1}{2}}=\frac{2^{n-1}-1}{(n-1)a^{n-1}k_n}.$$

Thus, for all reaction orders, the H.V.P. of a reaction of the nth order is inversely proportional to a^{n-1}, where *a* is the initial concentration (or, in the case of a gas, the initial pressure). The dependence of the H.V.P. upon the initial concentration or pressure can thus be used as a method of determining the kinetic order of a change, though it is usually desirable to supplement this by measurements on the course of single reactions.

P. P. B.

HALITE or ROCK-SALT (Fr. *Sel gemme*; Ger. *Steinsalz*). Sodium chloride, NaCl, crystallised in the cubic system. Although known as a mineral since remote times and of very wide distribution, the name halite (from ἅλς, salt) is comparatively recent (E. F. Glocker, 1847). Well developed crystals with the form of simple cubes are not uncommon, but those of octahedral habit are quite rare. The faces of the cube sometimes show sunken depressions, though not so marked as in the hopper-shaped crystals produced artificially. Small square pits or etched figures are readily produced on the cube faces by solution. Silky, fibrous masses also occur. But most frequently the mineral is found as granular or sparry masses with bright cleavage surfaces. This perfect cleavage, parallel to the faces of the cube, is an important character. In addition, the crystals sometimes break along surfaces (glide-planes) parallel to the rhombic-dodecahedron. This effect is, however, secondary, and is only produced after the crystal has been subjected to pressure, either naturally by earth movements or by artificial means. If a cleavage cube of salt be placed diagonally in a vice so that two cube edges are held by the jaws, it can be broken in this direction. The plastic deformation of rock-salt and the percussion-figure (a four-rayed star with the rays parallel to the diagonals of the cube face, which is produced on a cleavage surface by a smart blow with a blunt point) also depend on the presence of these planes of gliding.

Crystals are usually colourless and transparent, but occasionally they are of a deep blue or violet colour. This colour disappears when the salt is dissolved in water or when heated; and it can be produced artificially by the vapour of alkali metals or by the action of cathode or radium rays. It has been variously ascribed to the presence of metallic sodium, sodium subchloride, Na_2Cl, or sulphur. Sp.gr. of pure crystals, 2·17; hardness 2½; specific heat, 0·219. The mineral is a non-conductor of electricity and is highly diathermanous. It is therefore used as blocks and lenses for experiments on radiant heat. The best crystallised material is obtained from Stassfurt in Prussia, and from Wieliezka and Kalim in Poland; good, clear cleavage blocks have been found at Meadow bank in Cheshire. Crystals are very nearly pure sodium chloride, and mixed crystals with potassium chloride (sylvite) do not occur. Massive material contains impurities of various kinds. A variety known as *huantajayite,* containing AgCl 11%, is found as small cubes at Huantajaya near Tarapaca in Chile.

Rock-salt is most frequently found as bedded deposits in sedimentary rocks, such as sandstone, shale, clay and, less often, limestone, and is frequently associated with beds of gypsum and anhydrite, and sometimes with petroleum. Such deposits have evidently been formed in inland seas and lakes under desert conditions; they are of world-wide distribution and are met with in formations of all geological periods, as indicated below:

Geological formation.	Localities.
Recent	Dead Sea, Caspian Sea, Great Salt Lake of Utah, California, etc.
Pliocene	Yiiltcrra iii TuHeany, Parajd in Transylvania.
Miocene	Wieltczkaand Kntusz in Poland, Bukovina, Minglam'lla in Spain.

Geolo lcal lurmntiDns.	Localities.
Oligocene.	Eastern Carpathians in Tnuisylvania, Witteleheira in Al-Bace.
Eocene	Cardona near Barcelona, Caucasus, Rumania.
Cretaceous	Unna in Westphalia, Medea in Algeria, Texas, Louisiana, Peru.
Jurassic .	Bex in Switzerland, Kodcnburg in Hesse-Nassau, Peru.
Triasaic—	
Keuper.	Cheshire, Worcestershire, Lancashire, north-east Yorkshire, Durham, Isle of Man, Antrim, Pyrenees, Lorraine, Cclte in Hanover, Berchteagarden in Bavaria, Hall in Tyrol, .Halluin in Salzburg, Iflchl and Hallstatt in Upper Austria, rtnimon in Styria.
Muschelkalk	**Priedrichahall** in Wiirttemberg, Ernsthall in Tluirtngia.
Bunter .	Schoiiingcn in Brunswick, A rush a 11 in Thuringia,
Permian •	Staasfurt, Halle, etc., in Prussian Saxony, A r tern in Thuringia, Sperenberg near Berlin, Segeberg in Holstein, Inowrazlaw in Posen, Orenburg in Russia, Kansas.
Carboniferous	Pennsylvania, Virginia, West Virginia, Michigan, Ohio, New Brunswick, Nova Scotia.
Devonian.	Westphalia, Baltic provinces of Russia, Siberia, China.
Silurian .	New York, Michigan, Ohio, Ontario.
Cambrian.	Salt Range in Punjab.

I n addition to these bedded deposits of rock-salt, which are the only deposits of economic importance, mention may be made here of some other modes of occurrence. The microscopic cavities present in vast numbers in the quartz of granitic igneous rocks often contain minute cubes of halite together with water and liquid carbon dioxide. The saline encrustations of active volcanoes (e.p. Vesuvius), produced either by direct sublimation or by the action of acid vapours on the scoria, contain sodium and pot us stum chlorides, usually in a powdery form, but occasionally as distinct crystals of halite and sylvite.

References.—For a detailed *risumi* of the mineralogical characters and occurrence of halite, *see*, C. Hintze, ^{L1} Hsndbuch der Jlineralogie," Leipzig, 1yi1, Vol. I, pp. 101-231; on the deposits worked commercially, *see* J. 0. von Buschman, " Das Salz, dessen Vorkommen und Verwertung in samtlidten Staaten der ,Erde," 2 vols, Leipzig, 190G-9 ; A. P. Culvert, " Salt in Cheshire," London, 1915.

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HALLOYSITE. A clay-mineral with approximately the composition uf kaolinttu *(q.v.)* but containing rather more water (about 19%). It forms compact masses with a slight greasy feel awl lustre, and **may** be white, grey or shades ufvariouscolours; sp.gr. 20-2-2 ; hardness 1-2. It occurs as beds in sedimentary rocks and as masses in mineral -veins, and has sometimea been observed as a decomposition product of granite and other rocks containing felspar. Possibly the minute amorphous granules of china-c&y and some other clays may be referable to this **KfeOBB**. *(See* H. Ries, " Clays, their Occurrence, Properties and Uses," 3rd ed., 1927; *also* Vol. I1l, 190a).

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HALOGEN ACETIC ACIDS. Derivatives of acetic acid in which the hydrogen of the methyl group is partly or wholly replaced by a halogen.

CHLOROACETIC ACIDS.

MonochloroaceticAcid.CHjjCI-COOH.- The acid may be prepared by passing chlorine into 100 g. glacial acetic acid, 1 g. iodine, 2 g. red phosphorus and: 2 g. phosphorus pentachloride at 100° contained in a flask fitted with a leading tube, a" condenser and mechanical stirrer (Bruckner, Amer. Chcm. Abstr. 1930,24, 61; Lyubarskii, *ibid.* p. 827; Shilov, *ibid.* p. 827). Sulphur, phosphorus, sulphur monochloride and acetic anhydride may also be used as catalysts (U.S.P. 1757100). Many patents protect the preparation from trichloroethylcno by heating with sulphuric **acid** (I/.S.P. 1304108, *1*322898; B.P. 132042; *set also* J.S.C.I. 1922, 41, I91K). Q-Trioxymethylone and sulphuryl* chloride at 170° in the presence of zinc chloride also give Ihe a-acid (Fuchs and Katscher, Ber. 1924, 57 LB], 1250).

The acid crystallises in three modifications: *a-,* prisms, m.p. 61-3°; j9-, plates, m.p, 56*18°; *y,* m.p. 5020° (Muller, J. Physical Cheni. 1914, 86, 197); b.p. 189°/77 mm., 104-105720 mm.; $d*^{s}$ 1-3518 (Grinakowski, Chem. Zentr. 1913, II, 2076). For hydrates, *see* Collea **(J.CJ3.** 1906, 89, 1252J; heat of solution, Pickering *{ibid.* 1895, 67, 665) and Louguinino (Ann Chim. Phys. 1879, [v], 17, 251); heat of combustion 171-0 kg.-cal., Berthelot (Ann. Chim Phys. 1893, [Tiff 28, 567); electrical conductivity, Kortright (Amer. Chem, J. 1896, 18, 368); magnetic rotation^ Pcrkin {J.C.S. 1896, 69, 1236); i for the esterification velocity constant, *see* Sudborough and Lloyd *(ibid.* 1899, 75, 476); for electrolytic dissociation constant, A =1-55 x 10-', ««. Ostwald (Z. physikal. Chem. 1889, 8, 176).

The ^cid is soluble in cold water, but decomposes on heating the solution into hydrochloric and glycollic acids {Buchanan, Ber. 1871, 4, 340, 8(>3; Jfittig and Thomson, Annalen, 1880, 200, 75; Senter, J.C.S. 1907, fll$_f$ 460). Metallic hydroxides of the type **R'OH** decompose it, **£#j£?8** BlywUie acid, whilst those of **the** type ^{R}, ($^{\circ H}$)e y«l(l diglycollic acid (Schreiber, J. pr. Chem. 1876, lii], 13, 346). The anhydride is produced by distilling the acid m *vacua* with phosphorus pc-ntoxide (Biscuoff and Walden, Ber. **1894,** 27, 2S49). **With** nmmonui glv cine is produwd (Kraut, Ogldbcrg and Kuna, AunaUn, 1891, **286,** 295), and phenols in the presence of alkali give aryloxy-acetic acids (Giacosa, J. pr. Chem. 1879, [ii], 19, 396).

By reaction with sodium sulphide and sulphur in alkaline solution, dithioglycollic acid is produced which on reduction yields thioglycollic acid (G.P. 180875; J.C.S. J4)O7, 92, i, 1008). The sodium salt or the ethyl ester reacts with potassium cyanide to yield the corresponding derivatives of cyanacetic acid (Phelps and Tillotson, Amer. J. Sci. 1908, [iv], 26, 267, 275). The *acid chloride,* b.p. ca. 105°, *d*° 1-495 (Wurtz, Ann. Chim. 1857, [iii], 49, 61) may be prepared from the acid and thionyl chloride (de Barry Barnett, Chem. News, 1921,122, 220). The use of methyl (b.p. 133°), ethyl (b.p. 143-145°), *iso*propyl (b.p. 147-155°) and aec-butyl (b.p. 165-170°) esters as fumigants has been investigated (Roark and Cotton, Ind. Eng. Chem. 1928, 20, 513; Nelson, *ibid.* 1380). The esters are obtojned by passing the vapour of the alcohol, or a mixture of the alcohol and acid, through the molten acid, Ti, Th or AI salts promoting the reaction (Jap. P. 43731).

Dichloroacetic Acid.. $CHCl_2COOH$.—This acid may be prepared in 80-85% yield by the action of copper powder on trichloroacetic acid in water or benzene (Doughty, J. Araer. Chem. Soc. 1925, 47, 1091; 1931, 53, 1594); or by the interaction of sodium cyanide (2 mol.) and chloral hydrate (1 mol.) in boiling aqueous solution, acidifying and extracting (A. 1929, 63). Also from asymmetric dichloroacetone with nitric acid (U.S.P. 2051470; Chem. Zentr. 1936, II, 3468).

Colourless⁰liquid, b.p. 194°; 144°/164 mm.; 125°/70 mm.; 102°/2Q,mm.; 94°/11 mm. *K*= 6-14 x 10-*.

Methyl Ester.—B.p. 143-144°; 49-8-50°/2 mm.

Ethyl Ester.—B.p. 158°. Prepared by treating chloral in alcoholic solution with potassium cyanide (Chattaway and Irving, J.C.S. 1929, 1038) or from alcohol and dichlorovinyl ethers (G.P. 209268, 210502, 212592; J.C.S. 1909, 96, i, 453, 694,873).

Trichloroacetic Acid, CCl_3COOH.—Prepared by chlorination of acetic acid at 120° in the presence of sulphur, phosphorus or iodine as catalyst; or by the oxidation of chloral with fuming nitric acid (Kolbe, Annalen, 1846, 54, 183) or chromic acid (Clermont, Compt. rend. 1873, 76, 774) or potassium permrnganate *(idem., ibid.* 1878, **86,**1270).

Deliquescent crystals, m.p. 58°, b.p. 196-5°; 141-142°/25 mm. JC=1-2; sp.gr. 1-6298 at 60-6°. Heat of combustion (constant pressure) 92-8 kg.-cal. (Berthelot, Ann. Chim. Phy?» 1893, [vi], 28, 569). Electrical conductivity (Rivals, Compt. rend. 1897, **125,** 274 ; (Mwald, Z. physikal. Chem. 1887, 1, 100; 1889, 3, 177). The acid, is readily hydrolysed to chloroform and carbon dioxide by heating with water or alkalis (Dumas, Annalen, 1839, 32, 101).

The acid has been used with success as a protein precipitant (Cristolef *al.,* Bull. Soc. Chim. bio). 1922, 4, 267) and also in toxicology for the isolation of alkaloids which might be destroyed by sulphuric acid (Florence, Bull. Soc. chim. **1927,** [iv], 41, 1097). IU distribution coefficients between water and various organic solvents have been determined (Anderson, A. 1929, 908) and also its solubility in different solvents (Kendall, Davidson and Adler, J. Amer. Chem. Soc. 1921, 43, 1487). Treatment with zinc in aqueous solution gives a quantitative yield of zinc dichloroacetate (Doughty, *ibid.* 1929, **51,** 852). The sodium or zinc salt yields on electrolysis trichloromethyl trichloroacetate (Elbs and Kratz, J. pr. Chem. 1897, [ii], 55, 502). It forms compounds with aldehydes and ketones (Koboseff, J. Russ. Phys. Chem. Soc. 1903, 35, 652; Plotrikoff, *ibid.* 1904, 36, 1088; 1905, 37, 875; Ber. 1906, 39, 1794). For molecular compounds of trichloroacetic acid with alcohols, phenols and ethers, *see* Pushin and Rikovski, Annalen, 1935, **516,** 286.

The acid has been shown to undergo the Reimer-Tiemann reaction with phenols, but the yields are poor (Van Alphen, Rec. trav. Chim. 1927, 46, 144).

Methyl Ester.—B.p. 152-3-152-57763-3 mm. (Schiff, Z. physikal. Chem. 1887, 1, 379; Anschütz and Haslam, Annalen, 1889, 253, 124); *d* **LV; 4892 <HeMy' JÇS.- IMfc 48, 1121).**

Ethyl Ester.—B.p. 164°; d™ 1-369 (Claus, Annalen, 1878, **191,** 58; Bruhl, *ibid.* 1880, 203, 22; S-hiff, *ibid.* 1883, 220, 108).

The cobalt, manganese and cadmium salts of the chloroacetic acids have been prepared by neutralising the acid with the metal carbonate and evaporating in a vacuum desiccator (Amer. Chem. Abstr. 1929,23,3900), and also the uranyl salts (A. 1926, 372).

BEOMOACETIO ACID£.

Monobromoacetic Acid, $CH_2BrCOOH$. Prepared in 80% yield from 20 g. acetic acid, 58 g. bromine and 0-1 g. red phosphorus as catalyst, at 100-105° (Amer. Chem. Abstr. 1922, **16,**2842); m.p. 50°; b.p. 203°; 168°/250 mm.; 118°/15 mm.; J5C=l-38 x 10"³ at 25°C. For electrical conductivity, *see* Ostwald, Z. physikal. Chem. 1889,3,178; Kortright, Amer. Cl^em. J. 1896, **18,**368.

The aqueous solution decomposes slowly on heating, giving glycollic acid (Senter, J.C.S. 1909, 95, 1828). The sodium salt heated *in vacuo* yields glycollide. Much work has been done on the physiological action of the acid and its esters.

Methyl Ester.—Prepared by heating the acid and alcohol in scaled tubes at 100° (I'erkin and Duppa, Annalen, 1858, **108,** 109); b.p. 144° with decomposition.

***Ethyl Ester.*—*Yrcv&rcd* as the methyl ester or** from ethyl alcohol and bromoacctylchlorido (Gal, Annalen, 1864,**132,**179); b.p. 159°.

***p-Nitrobenzyl Ester* has m.p.«8-89°.**

Dibromoacetic lAcid, $CHBr_2COOH$.—May be prepared by dropping bromine into boiling acetic acid to which 5% of sulphur has been added, and finally raising the temperature to 150° (Gcnvressc, Bull. Soc. chim. 1892, [iii], 7, 365); m.p. 48°; b.p. 232-234° (with decomposition); ^95-197°/250 mm. Easily soluble in water and alcohol.

Ethyl Ester.—Prepared from anhydrous sodium acetate (1 mol.), broinalcyanhydrin (I mol.)

and absolute alcohol (Klebs, Z. physikal. Chem. 1896, 19, 303); b.p. 192-194°; 120-121°/74 mm.

Tribromoacetic Acid, CBr_3COOH.—Prepared by gently warming bromal with fuming nitric acid and allowing the mixture to stand for 1 hour (Schaffer, Ber. 1871, 4, 370).

Monoclinic prisms, m.p. 130°, b.p. 246° (with decomposition). The acid is decomposed by water to give bromoform and carbon dioxide exclusively (De Groote, Bull. Soc. chim. Belg. 1928. 37, 225).

Ethyl Ester.—Prepared by passing hydrogen chloride into a cooled alcoholic solution of tribromoacetic acid (Broche, J. pr. Chem. 1894, [ii], 50, 98); b.p. 225°; 148°/73 mm.

CHLOROBROMOACETIC ACIDS.

Chlorobromoacetic Acid,

$CHClBrCOOH$.

Prepared by heating equimolecular quantities of monochloroacetic acid and bromine in sealed tubes at 160° (Cech and Steiner, Ber. 1875, 8, 1174). Also prepared by the hydrolysis of the acid chloride obtained by the action of bromine on αβ-dichlorovinyl ether (Backer and Mook, J.C.S. 1928, 2125). Also by heating chlorobromomalonic acid at 130° until evolution of CO_2 ceases (Read and McMath, *ibid.* 1926, 2183); m.p. 31-5°, b.p. 214-5° (decomp.), 103-104°/11 mm. (Backer and Mook, l.c.); m.p. 38° (Read and McMath, l.c.); b.p. 210-212° (Vanderstichele, *ibid.* 1923, 123, 1227). It is extremely deliquescent. Backer and Mook (*l.c.*) completed the resolution of this acid, employing quinine for isolating the dextro and brucine for isolating the lævo isomer, respectively.

Amide, m.p. 126°. *Ethyl ester,* b.p. 174°. *Phenyl ester,* m.p. 46-5°, b.p. 266° (Crompton and Triffitt, *ibid.* 1921, 119, 1874).

Monochlorodibromoacetic Acid,

$CClBr_2COOH$.

Prepared by heating monochlorodibromoacetaldehyde with fuming nitric acid (Neumeister, Ber. 1882, 15, 603); m.p. 89°; b.p. 232-234° (with decomposition). Potassium hydroxide converts it, on heating, into monochlorodibromomethane.

Dichloromonobromoacetic Acid,

$CCl_2BrCOOH$.

Prepared from dichloromonobromoacetaldehyde and fuming nitric acid (Neumeister, *ibid.* 1882, 15, 603); m.p. 64; b.p. 215° (decomposition).

IODOACETIC ACIDS.

Monoiodoacetic Acid, CH_2ICOOH.—Prepared from monochloro- or monobromoacetic acid and sodium iodide in acetone (G.P. 230172, Chem. Zentr. 1911, I, 359), or from potassium iodide and chloroacetic acid in water at 50° (Kailan and Jungermann, *ibid.* 1934, II, 3240). Also by hydrolysis of the ethyl ester (*q.v.*) with baryta water (Perkin and Duppa, Annalen, 1859, 112, 125); m.p. 82°.

Ethyl Ester.—Prepared by the interaction of ethyl chloro- or bromo-acetate, potassium iodide and alcohol (Perkin and Duppa, *l.c.*); b.p. 69°/12 mm.; 75-78°/16 mm. The acid and its ester possess marked poisonous properties (Chlopin, Amer. Chem. Abstr. 1928, 22, 127, 649).

Methyl Ester.—Prepared in a manner analogous to the ethyl ester; b.p. 169-171°. *sec-Octyl Ester,* b.p. 146°-147°/17 mm. (Rule and Mitchell, J.C.S. 1925, 3202).

The neutral ammonium salt (McMaster and Pratte, J. Amer. Chem. Soc. 1923, 45, 2999) and a basic ferric salt (A. 1926, 949) have been prepared.

Di-iodoacetic Acid, CHI_2COOH.—Prepared by the interaction of 1 part of malonic acid with 1 part of iodic acid in 4 parts of water; carbon dioxide is evolved; the solution is cooled, filtered and allowed to stand. After 2 or 3 days crystals of tri-iodoacetic acid separate; these are filtered off and, after heating the filtrate, the di-iodo compound separates on cooling; m.p. 110° (Angeli, Ber. 1893, 26, 596).

Ethyl Ester.—Prepared by the interaction of ethyl dibromoacetate and potassium iodide in alcoholic solution (Perkin and Duppa, Annalen, 1861, 117, 351), or *of* ethyl dichloroacetate and calcium iodide (Spindler, *ibid.* 1885, 231, 273). Yellow liquid, which cannot be distilled unchanged under atmospheric pressure.

Tri-iodoacetic Acid, CI_3-COOH.—For preparation, *see* di-iodoacetic acid. Yellow plates, m.p. 150° with decomposition. By heating with acetic acid, iodoform and carbon dioxide are produced.

FLUOROACETIC ACIDS.

Trifluoroacetic Acid, CF_3COOH.—Prepared by the oxidation of trifluorotoluidine (Swarts, Bull. Acad. roy. Belg. 1922, [v], 8, 343; Chem. Zentr. 1923, III, 918).

For the preparation of the *ethyl ester* (b.p. 126°) of trifluoroacetic acid, *see* Ray and Ray, *ibid.* 1937, I, 3627. Electrolysis of trifluoroacetic acid gives hexafluoroethane (Swarts, Bull. Acad. roy. Belg. 1931, [v], 17, 27). Treatment of the silver salt in ice-cold 30% solution in benzene with iodine gave the anhydride (Swarts, Amer. Chem. Abstr. 1930, 24, 589).

Ethyl Fluorodibromoacetate.—Prepared by the reaction of 1 mol. ethyl tribromoacetate and 4 mol. silver fluoride at 190-200°. It is an insoluble liquid and readily hydrolysed by water (Rathbury, Ber. 19, 18, 51, 669).

HALOTRICHITE,

$FeSO_4Al_2(SO_4)_3$-$24H_2O$,

occurs naturally as silky, fibrous, efflorescent masses of a yellowish-white colour; named from *£\s,* salt and *Bpt{₉ rpl\o's₉* hair. It results by the action of the products of decomposition of pyrite on surrounding aluminous rocks, as at Hurlet and Campsie near Glasgow; and also by the action of volcanic gases on rocks, as at the Solfatara di Pozzuoli near Naples, and in Iceland, where a variety called "hver-salt" is found. A large deposit occupies the crater of an extinct volcano near the source of the Gila river in Grant Co., New Mexico. At Urmia in Persia the mineral has been used for making ink.

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HALOXILINE (Vol. IV, 4636).

HALPHEN-HICKS REACTION (Vol. 111, 295a).

HALPHEN TEST (Vol. 11, 1676).

HALVORSAN PROCESS (Vol. I, 268c).

HAMAMELIN. (*Extract of Hamamelis B.P.C.*) A solid extracted by alcohol from the dried leaves of *Hamamelis virginiana* Linn, and used in medicine as an astringent, principally in the treatment of piles. The drug occurs in the form of a green or almost black powder; the brown substance formerly appearing in commerce under this name was prepared from hamamelis bark. Berry (Pharm. J. 1936, 2, 247) suggested improvements in manufacture to ensure maximum solubility and activity.

A.D. P.

HAMAMELIS. The dried leaves of the witch-hazel, *Hamamelis Virginian** Linn., a shrub indigenous to North America. The drug contains *tannin, gallic acid* and a trace of a *volatile oil.* Liquid and solid extracts prepared from the drug are used in medicine as astringents (*v.* HAMAMELIN). The fresh leaves of the witch-hazel are used to prepare a distilled extract (*Liquor Hamamelidis B.P.C.*), a weakly alcoholic, colourless liquid, possessing the characteristic odour of witch-hazel, but practically devoid of tannin. It is used externally in medicinal and cosmetic applications for the treatment of sunburn and other skin troubles. *Hamamelis bark (Hamamelidis Cortex B.P.C.)* is no longer an official pharmacopceical drug, but is still used in medicine in the form of a tincture (*Tinctura Hamamelidis B.P.C.*). The bark contains about 6% of *tannins,* including crystalline *hamamelitannin, gallic acid, resin, fat* and *phytosterol.* For description of hamamelitannin and its derivatives, *see* Freudenbcrg and Blttmmel (Annalen, 1924, 440, 45); Schmidt (*ibid.* 1929, 476, 250).

A. D. P.

HAMAMELOSE (Vol. II, 288(2).

HAMBERGITE (Vol. I, 685a).

HAMLINITE (Vol. V, 263c).

HANSA YELLOWS (Vol. IV, 235a).

HARDEN AND YOUNG ESTER (Vol. V, 20d, 22d).

HARDENED OR HYDROGENATED FATTY OILS. The scarcity of natural solid fats compared with the relative abundance of liquid oils is one of the outstanding features of the fatty oil trades. This unequal distribution has caused a greater value to be attached to the solid fats, and, with increasing demand for edible oils, there has arisen a desire for methods of producing solid fats from liquid material. Chemically the main difference between these two classes of fatty product is a preponderance of saturated long chain fatty acid esters (glycerides) in the solid fats and of corresponding unsaturated compounds in the oils.

The successful reduction of the unsaturated esters by catalytic hydrogenation is probably the most important development in the oil industry of the last 30 years. Prior to the introduction of this process various methods had been tried, Varrcntrapp's reaction forming the basis of one of the most interesting. According to this oleic acid is converted to palmitic acid by fusion with alkali hydroxide. In practice the process was limited to the treatment of fatty acids and was not applied to neutral glycerides. It yielded material of poor colour and the large volumes of hydrogen liberated were a source of danger.

Schmidt's process of heating oleic acid with zinc chloride at 185° requires a distillation of the product, and this is attended by partial decomposition of the /9-hydroxystearic acid formed in the reaction, into oleic and *isooleic* acids. Better results were obtained by methods in which oleic acid was treated with sulphuric acid at a low temperature, and the resulting sulphonated compound decomposed by means of water into hydroxystearic acid and free sulphuric acid. By distillation of the hydroxystearic acid a mixture of oleic acid and its solid isomeride twoleic acid was obtained, the latter being of commercial value as a candle material.

In 1897 Tissier (F.P. 263158, 1897) claimed a process of converting oleic acid into stearic acid by means of the nascent hydrogen liberated when fats are heated, in an autoclave, with water and finely divided zinc, but Freundlich and Rosauer (Chem.-Ztg. 1900, 24, 566) found that the process did not produce the result* claimed for it.

Electrolytic methods of hydrogenating oleic acid are claimed in the patents of Magnier, Brangier and Tissier (B.P. 3363, 1900) and of Hemptinne (B.P. 1572,1905). According to the latter, oleic acid is spread in a thin layer on metallic plates, between which is passed a silent discharge, whilst the air in the vessel is replaced by hydrogen. Under these conditions hydrogen is absorbed, with the formation of a considerable proportion of stearic acid and other substances of higher melting-point, and the process is repeated until about 20-30% of the oleic acid has been converted. The solid products are then separated by chilling and filtering the mixture.

Better yields were obtained in Bochringer's process (G.P. 187788,189332,1906) in which the cathodes consisted of platinum coated with a layer of spongy platinum, or palladium coated with palladium black.

These methods are of historic, rather than practical, interest and their application on a commercial scale has not achieved notable or lasting success, later catalytic methods having proved to be superior. Recently, however, attention has again been directed to methods of converting olein to claidin or other twoleins as a means of hardening oils. A process of *b.H.* Bertram (Ole, Fette, Wachse, Scife, Kosmetik, 1938, No. 7, 1-4) claims that the conversion may be accomplished by means of 0;1-1% of selenium at 150-240°C. with formation of a product of satisfactory colour.

DEVELOPMENT OF HYDROGENATION PROCESSES.

The modern methods of catalytic hydrogenation are based on the investigations of Sabatier and Senderens, who showed that the unsaturated bonds in organic compounds could be made to combine with hydrogen by passing a mixture of gases, *e.g.* ethylene or acetylene mixed with hydrogen, over heated finely divided nickel; cobaltT iron and platinum were less effective (Compt rend. 1897, **124,** 1358; 1899, **128,** im ri900,**130,**1628, 1761; **131,** 40,187).

A German patent for the hydrogenation of oils on these lines was taken out- in 1902 by LePrince and Siveke, G.P. 141029, whilst in 1903 Normann (B.P. 1515, 1903) claimed a process of catalytically hydrogenating oils either in the form of vapour or as liquid. He stated, for example, that by suspending nickel powder in oleic acid heated in an oil bath, and passing a current of hydrogen, or of a gaseous mixture rich in hydrogen, through the liquid, the oleic acid could be completely converted into stearic acid.

Sabatier (Ann. Chim. Phys. 1909, [viii], 16, .73) converted oleic acid vapour into stearic acid by means of hydrogen and nickel, but believed that the vapour state was necessary for the reaction.

Successful technical hydrogenation of fats dates from the Normann patent. As was inevitable many difficulties were .encountered in developing the method and it was not until the process was acquired by Joseph Crosfield & Sons of Warrington that it became, with Dr. Normann's assistance, a practical success. By 1910 several hundred tons of hardened oil were being produced per week and.the process enabled substitutes to be produced at a price between £10 and £20 a ton cheaper than tallow. Economic changes, however, have affected the position considerably and it may now be said that the development of hydrogenation and the consequent increase in production, of whale oil have caused the value of almost all edible oils to depend mainly on the value of whale oil.

The development of hydrogenation may be traced from the following account of some of the more important processes which have been patented since 1903.

An exhaustive account of these and other processes, and indeed of everything connected with oil-hardening, will be found in C. Ellis, " The Hydrogenation of Organic Substances, including Fats and Fuels," 3rd ed., D. van Nostrand Co., New York, 1930.

In Day's process (U.S.P. 826089, 1906) catalytic hydrogenation of hydrocarbon oils is employed to effect deodorisation, palladium black being used preferably as the catalyst.

- Treatment of hydrocarbon oils by catalytic hydrogenation is now carried out on a large scale to produce greater proportions of valuable fractions from mineral oil*. Complex mixtures of oxides and sulphides of various metals are employed as catalysts, and the reaction is conducted at high temperatures and pressures (*v.* HYDBOGKNATTON OF COAL).

An apparatus claimed By Schwoerer (G.P 199909, 1906) consists of a vessel containing a helical trough the underside of which is coated with asbestos impregnated with nickel. The oily substance, *e.g.* oleic acid, is brought«into a fine state, of division by means of supcrhchtcd steam, and passed, together with hydrogen, into the vessel, where the mixture is heated to 250-270°. Under these conditions the hydrogen is absorbed, and the stearic acid deposited to a large extent in the trough. Bedford and Williams' process (B.P. 9112, 1908) is concerned with the hydrogenation of oleic acid in the form of spray, the mixture of acid and hydrogen passing through two separate layers of catalytic material in a verfjcal tower, the internal temperature of which is maintained at about 200° The reduction is carried out under ordinary pressure, vacuum is then applied and the productodistilled over into a receiver connected to the tower.

In his processes described in G.P. 211669, 1907,221890,1909, Erdmann claims a method of hydrogenating cftls in the form of a fine spray in presence of a nickel or other catalyst. Thus'tne oil may be finely divided by means of a jet of hydrogen ·in a chamber containing a rotating cylinder covered with a layer of the catalytic agent, and9s then made to pass through a bed of pumice impregnated with nickel. Or the oil may be introduced as a spray into a tower nearly filled with porous catalytic material, and there meet a ·current of hydrogen from another inlet, the temperature beinp maintained at 170-180°. The solid product is preferably purified by treatment with steam under reduced pressure.

In the Kayser process, which is stated to be employed on a large scale in the United States, an inert powder such as kieselguhr is used as the carrier for a nickel catalyst, the oil being agitated with this at about 150-160°. One form of apparatus, used for effecting an intimate admixture of oil and catalyst, consists of a horizontal cylinder in which revolves a paddle wheel the skeleton blades of which"are covered with wire gauze. Hydrogen under pressure is introduced at one end of the cylinder, and the unabsorbed gas is drawn off at the other end.

Hydrogenation under pressure is also a feature of Testrup's process (B.P. 7726, 1910), the mixture of finely divided oil and catalyst being pumped into a vessel containing an atmosphere of hydrogen. For example, a mixture of oil and palladium, or preferably nickel, may be heated to about 460° in a jacketed chamber, containing hydrogen under 12 atm. provided with a stirring device, and then forced through spraying nozzles into a second chamber, where the temperature is maintained at about 160-170°, and in which a hydrogen pressure of 9 atm. is maintained. If still harder products are required, the process may be repeated in another chamber into which hydrogen is admitted at a pressure lower by 3 atm., or a whole series of connected vessels may be used.

The use of autoclaves for hydrogenating oils has the advantage that the conversion is effected at a relatively low temperature (100-160°) thus obviating the risk of injury by overheating. In Wilbuschewitsch's process (F.P. 426343, 1910) an intimate mixture of the oil and catalyst is pumped or injected into a series of connected autoclaves, through which circulates a current of hydrogen in the opposite direction. The gas may be admitted in such a way that it disperses, in the form of a spray, the oily mixture accumulating in the bottom of thr vessel, which is pumped into connected nut«»-claveH, where the process is repeated until tin-product has the desired melting-point; or th.

hydrogen passes counter-current through reducing valves into successive autoclaves with corresponding diminution **of pressure.**

In the process claimed **by Bedford** and Williams (B.P. 29612, 1910) about 1% of a metal oxide catalyst *is* added to the oil, which is heated by means of a steam coil, in a closed vessel, to about 250°, while hydrogen is intro**duced** through a perforated pipe at the bottom of the vessel. By using a mixture of hydrogen and oxygen in place of pure hydrogen, hydroxy-fatty acids, or their compounds, may be produced by this process.

In order to effect the hydrogenation in stages at different temperatures Ellis has devised a **method** whereby the mixture of oil and metal **catalyst** is made to pass in a continuous stream through a long tube, divided into a series of compartments, and encounters a current of hydrogen travelling in the opposite direction. Different temperatures are maintained in the different compartments, *e.g.* 1!50° in the first, 1(S5° in the second, and 180° in the last (B.P. 24084, 1912). In Pictet's process (F.P. 472OKO, 1913) the oil, with or without the addition of a catalyst, is made to pass by gravitation through a series of communicating tubes, the walls of which are composed of catalytic metal. Hydrogen is **introduced** under suitable pressure, and the oil is finely divided and brought into **intimate** contact with the gas by means of rotating devices **which brush continually** against the walls of the tubes.

In order to obtain a large surface of catalytic material Kayser and Liebmann (B.P. 156'68, 1*J14) distribute the catalyst over fibrous material such as **yarn, which** for strength may be enclosed between sheets of wire gauze. Or the fibrous **material** may be supported on frames attached to the agitator, or **wound** round the **blades** of **the agitator in the** hydrogenating **apparatus.**

In Calvert's hydrogenation process the oil is **mixed** with **the** catalyst and treated with hydrogen in **a** closed vessel containing a comb-shaped rotating agitator to subdivide **the** oil, whilst a centrifugal propeller at the base flings the mixture upwards to be beaten again (B.P. **5967,** 1914).

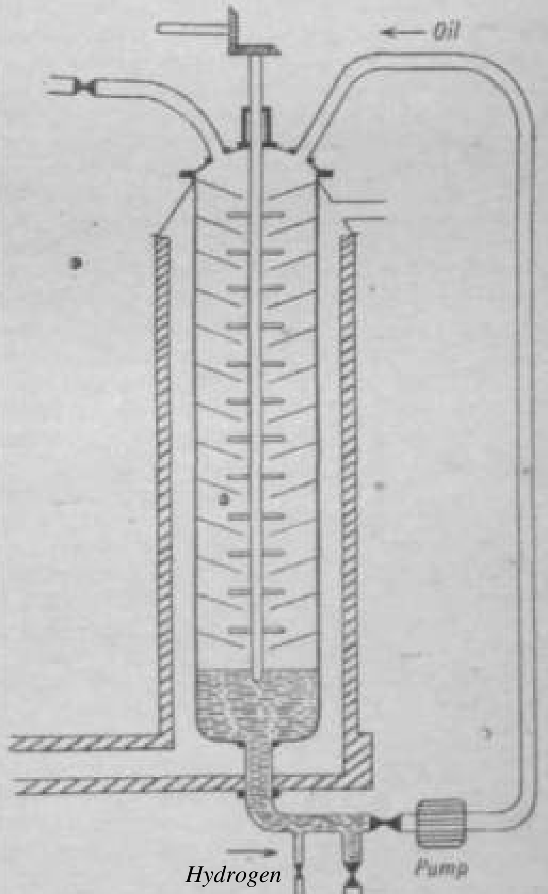
The method **of** effecting minute subdivision of the oil adopted by Moore (U.S.P. 112I80O, **1»14)** is to pass it together with the hydrogen through catalytic **material** which may be **contained in** a **diaphragm** porous to the oil and gas, but not **to the catalyst.**

Lane's **apparatus** (**B.P. 968,** 191.1) consists of a **vertical cylindrical vessel** which is **heated by means of a steam jacket or otherwise.** Beaters **rotating horizontally round** a central shaft alternate with annular sloping shelves on the sides of the vessel, so that the oil and catalyst, entering at the top, are alternately sprayed out**wards to the** sides and **guided** to the centre of the beaters next below; and so on, until they reach the **bottom** and are then pumped again to the top. The hydrogen **enters** by a pipe at the base of the apparatus.

In **Walker's process (U.S.P. 1128962, 1915) the mixed fatty acids or glycerides are sprayed** by means of hydrogen under pressure against heated, finely divided, catalytic material, in presence of an electric discharge.

The essential features of the **process** of Bh'keland and Devik (U.S.P. 1125259, 1!)15) are that the oil is mixed with the catalyst and a portion forced from a jet into an atmosphere of hydrogen, and thence downwards into the body of the oil, whereby hydrogen is conveyed by suction to the bottom of the vessel and is absorbed on rising through the oil.

McElroy (U.S.P. 1157993, 1915) claims the use of an emulsifying process. Freshly reduced nickel is mixed with the oil, and hydrogen is made to circulate through the liquid in minute ascending bubbles in **a special form** of apparatus, in such a way as to produce a gas-liquid emulsion.



LANE'S APPARATUS.

The apparatus devised by Maxted and Bidadate (U.P. 1W9O3, 191(i) **consists of a** vertical column provided with baffle plates, so arranged that a **mixture** of oil, catalyst and hydrogen, projected into the top of **the vessel,** is rotated alternately first in one direction and then in **the** other on its passage to the bottom.

The essential feature of the process of Wells (**U.S.P.** 1383887, 1921) is the vigorous agitation of the reaction mixture by the introduction of a stream of hydrogen from beneath.

In the apparatus described by Mellersh Jackson (U.S.P. 175021, **1920),** hydrogen is admitted through a distributing **plate** of **porous material** and rises in uniform bubbles through **the** oil. In another type of apparatus (Ellis, **U.S.P 1480861,**

1924) the oil is made to circulate in vertical planes in a long horizontal cylindrical tank by means of convection currents produced by heating coils placed in suitable positions. In another patent, also of Ellis (U.S.P. 1476330, 1923), the hydrogen is made to bubble through the oil at 150-200°, and is arrested by the nickel catalyst which is contained in a finely divided powder of inert material.

A new type of apparatus and process is claimed by Ruben (U.S.P. 1554296, 1925), in which a liquid with a high dielectric constant is passed upwards through a metal cylinder, containing a suspended porous pot with a dielectric constant lower than that of the liquid under treatment. This pot, which has a conductive inner surface, is supplied with a high frequency alternating current of high potential, whilst the conductive wall of the outer cylinder is connected with the other pole. Under these conditions hydrogenation of the oil is effected without the use of a catalyst.

In B.P. 341153, 1929, claim is made by the I.G. Farbenind. A.-G. for resistant zinc alloys, m.p. above 500°, for constructing or lining the hydrogenation vessels and connections.

In 1922 E. R. Bolton (J.S.C.I.1922,41, 384R) noted that the technical application of an apparently simple catalytic reaction had already inspired the subject-matter of 300 patents. This number has been largely increased since, and it may be said that the processes now in operation are all based on the fundamental concept of Sabatier-Senderens and differ only in method of catalyst production, mechanical details of admixture of oil, catalyst and hydrogen; reaction conditions of temperature and pressure, and after-treatment of products. A comparatively small weight of hydrogen is required (less than 0·7% by weight) but its volume is such that the efficiency of the process necessarily depends largely on the degree of admixture of the reactants with the catalyst and on the efficiency of the latter.

CATALYSTS FOR HYDROGENATION.

In the original investigations on catalytic hydrogenation by Sabatier and Senderens finely divided platinum or palladium was used as the catalytic agent, but as nickel is a much less expensive catalyst than those metals it is now almost universally employed for the hydrogenation of oils and fats. The use of other metals such as palladium, cobalt, iron and copper as catalytic agents has also been claimed in several of the patent processes of hydrogenation.

In preparing a nickel catalyst the usual method is to precipitate nickel hydroxide or carbonate from a solution of a salt such as nickel sulphate, in the presence of inert material such as kieselguhr, to dry the Sludge and to reduce it in a current of hydrogen at a temperature of 300–325°.

In Lane's process (Engineer, 1917, **128,** 511) solutions of nickel sulphate and of sodium carbonate are prepared in separate tanks provided with steam jets, and are transferred into a third tank provided with a mixing apparatus [illegible] support material such as mixture of precipitated nickel carbonate and kieselguhr is dried, ground and roasted to convert the carbonate into oxide, after which it is heated in a current of hydrogen.

One form of apparatus used for this purpose is a vertical vessel provided with external means of heating, and containing a series of reciprocating grids. The powdered material is introduced at the top and falls on to the successive grids, the movement of which exposes fresh particles to the current of hydrogen, which is admitted at the base, and rises through the grids to the outlet at the top of the apparatus. The reduced material falls into a vessel containing oil of the same kind as is to be hydrogenated, and, after being thoroughly mixed, the oily mess is ground until of the desired consistency.

The method of preparing the catalyst has a considerable influence on its activity and its resistance to external influences. For example, nickel which has been reduced at as low a temperature as possible is more effective than that reduced at a higher temperature, but, on the other hand, is also more sensitive to the action of catalyst " poisons." Ellis (J.S.C.I.1912,31, 1163) gives 300-325° as a suitable temperature for the reduction. According to Kelber, however (Ber. 1916,49,1868), a catalyst prepared by reducing basic nickel carbonate with hydrogen at 450° is more sensitive to poisons than one prepared at 310°. On the other hand a catalytic agent prepared by reducing the basic carbonate on Florida earth (Kelber, *l.c.,* p. 60) at 450° proved remarkably resistant to the action of hydrocyanic acid, hydrogen sulphide and carbon disulphide.

Nickel catalysts may be prepared from carbonates and oxides of the metal by reduction at temperatures as low as 150°C. and will remain active in use for long periods with suitable oils.

The activity of a catalyst has also some determining effect on the nature of the reaction, suppressing or promoting the formation of isomeric glycerides of oleic acid which always accompanies hydrogenation of unsaturated fatty oils. M. G. Barradas (U.S.P. 2014999, 1935) claims to control the selectivity of hydrogenation by admixing various proportions of an inert gas with the hydrogen used.

Reduced iron, sodium chloride, sodium sulphate and sodium nitrate have no influence on the activity of nickel catalysts, but sodium sulphide gradually impairs the efficiency, and sulphur destroys it immediately (Moore, Richter and Van Arsdel, Ind. Eng. Chem. 1917, 9, 451). Nickel may also be rendered inactive by traces of chlorine and of decomposition products in the oils undergoing hydrogenation. For this reason low-grade oils, such as whale and fish oils, may speedily render a nickel catalyst inactive. Heating and agitating the oil with freshly-precipitated copper hydroxide has been found an effective means of removing the poisonous constituents from such oils, especially after a preliminary treatment with sodium carbonate solution (Ellis and Wells, *ibid.* 1910, 8, H8(j). In some cases, however, it is necessary to hydrogenate the oil in two stages, filtering off the catalyst after it has become inactive. Veno (J. Chem. Ind. Tokyo, 1918, **21,** [illegible]) has shown that powdered metals (not reduced by hydrogen), such as nickel, tin, zirconium and copper, have but little injurious action on catalytic hydrogenation, but that iron, zinc, lead and mercury act as poisons.

For a detailed study of the effect of various catalyst poisons on platinum^*see* Maxted (J.C.S. 1925,127,73; 1928,1600; 1931,2203).

Catalysts resistant to poisoning by sulphur are prepared, according to B.P. 415203/1923 of I.G. Farbenind. A.-G., in the form of sulphides of the heavy metals of groups V and VI and Re, Ni, Co. The best results are obtained with Mo or W sulphides singly or as a mixture.

The efficiency of a catalytic metal, being at any Ata partly determined by the extent of its surface, is considerably increased by distributing it over a porous non-catalytic support such as charcoal, powdered pumice or kieselguhr, and the method of impregnating the support with the metal forms the subject-matter of numerous patents. In Crosfield's process (B.P. 30282, 1910) an inert medium, such as asbestos or kieselguhr, is impregnated with a solution of nickel sulphate, and then treated with a solution of an alkali hydroxide. The mass, which now contains nickel hydroxide, is washed, dried and heated in a current of hydrogen; and the resulting product should contain about 30% of metallic nickel.

Kayser (U.S.P. 10040?4, 1911) saturates the porous support with a solution of a nickel salt, and incorporates therewith molecular proportions of powdered sodium carbonate. The mixture is then treated with boiling water, dried and the nickel salt deduced. In a later patent (U.S.P. 1001279, 1911) Kayser claims a method of preparing a catalyst which may be exposed to tto air for several days without undergoing oxidation and losing its catalytic activity. In this process nickel oxide is reduced at about 500-600°, and a current of carbon dioxide passed through the material until the gas leaving the apparatus is no longer inflammable.

In Bolton and Lush's process (B.P. 162382, 1920) the poisoning of the catalyst through the formation of nickel soap is prevented by adding mono- or diglycerides to the oil. These combine with any free fatty acids present and so prevent the nickel being attacked. Bolton has also claimed a method of restoring the activity of the catalyst by washing it in the apparatus, first with hot oil to remove soap and then with a solvent to remove the oil (B.P. 162370,1920).

Leasing (B.P. 18998, 1912) claims the use of a catalyst composed of nickel carbonyl or other metallic compound which undergoes decomposition at the temperature of hydrogenation.

Reduction of nickel formate in the oil itself is described in a process of Brochet (Bull. Soc. chim. 1920, [iv], 27, 899). Processes based on this method have acquired considerable technical importance.

Bedford and Erdmann (B.P. 27718, 1912) make use of metallic oxides in a form suitable for catalytic agents. They assert (J. pr. Chem. 1913, [ii], 87, 425) that nickel oxides are much jess sensitive than metallic nickel to external influences, and that they effect more rapid hydrogenation. The activity of the catalytic agent is increased by the presence of the oxides of other metals. In carrying out the process the oil is heated to 180° in a cylindrical copper vessel fitted with an agitator, while a slow current of hydrogen is passed through it. A small quantity of nickel oxide is introduced, the temperature raised to 255-260°, and, after the addition of more catalyst, the supply of hydrogen is increased. It is claimed that the hydrogenated product is free from hydroxy-acids, and that nickel soap is formed only to a very limited extent.

Erdmann and Rack attribute any activity of nickel borate to the formation of nickel oxides at 260°. Contrary to the claim of Schönfeld, they find that nickel borate does not convey hydrogen to unsaturated fats at 175°. Normann, however, attributes the catalytic activity of nickel borate to the formation of metallic nickel produced by the hydrogen during the hydrogenation process, and finds that there is no positive evidence of the presence of nickel suboxide.

Meigen's experiments (J. pr. Chem. 1915, [ii], 92, 390) are opposed to the view of Erdmann and Bedford, that an oxide or suboxide of nickel is the catalytic agent. He concludes that while it is conceivable that their view may be correct, it is a hypothesis which is lacking in experimental proof.

In Byron's method of preparing a stable catalyst (B.P. 13382, 1913) the solution of a salt of a catalytically active metal, such as nickel sulphate, is treated with a solution of an alkali silicate, and the precipitate dried, and, if desired, reduced in a current of hydrogen.

Richardson (U.?.P. 1151718, 1915) claims the use of an oleate of nickel or other metal; whilst Bacon and Nicolet (U.S.P. 1152591, 1915) prepare a catalyst containing nickel hydroxide and aluminium hydroxide, in which the nickel has been rendered active by reduction with hydrogen. Catalysts composed of aluminates of nickel or other heavy metals have also been patented by De Nordiske Fabriker De-No-Fa A/s. (B.P. 140371, 1919).

Catalysts are prepared by Raney (U.S.P. 1628190,1927) by alloying nickel and aluminium and submitting the alloy to the action of alkali. The resulting material having a cellular microstructure is of a very active nature and has been much employed—chiefly in research—under the name of "*Raney nickel.*" If the action of the alkali is restricted to the surface of turnings of the alloy the catalyst may be used in massive form, thus leaving only traces of metal to be removed from the oil after hydrogenation.

L. G. Jenness (Oil and Soap, 1934, 11, 131) prepares *"foraminate"* catalysts by selective corrosion of aggregates of the catalytic metal and other material,* claiming such catalysts to be of superior activity.

A catalytic agent claimed by Ellis (U.S*P. 1156068) is prepared by incorporating hydrated nickel*hydroxide, $Ni(OH)_2,H_2O$, with an oily medium, reducing the nickel compound with hydrogen, and removing moisture from the product. In another process, also patented by Ellis (U.S.P. 1159480, 1915), a basic compound of nickel is partly reduced with hydrogen to obtain a catalyst consisting of nickel and a lower ide of nickel.

^Catalysts described by Ellis (U.S.P. 1378336-7-8, 1921) are prepared by incorporating organic salts of nickel, etc., with an oily medium, and heating the mixture at reduced pressure, *e.g.* heating nickel oleate in the presence of non-reducing inert gases ; and by reducing mixtures of metallic salts of nickel, copper and cobalt in an oily medium.

Armstrong and Hilditch (Proc. Roy. Soc. 1922, A, 102, 27) investigated the influence of copper in promoting the activity of a nickel catalyst. They found that a lower temperature (180°) was required for the reduction, whereas the nickel compound by itself was not reduced by hydrogen below 300°. Grote (Seifens.-Ztg. 1920, 47, 713) found that by using a catalyst consisting of a colloidal double nickel and magnesium (or aluminium) silicate, dried and reduced in hydrogen, the time of hydrogenation could be reduced to 10 minutes and the temperature to 160°. The addition of a phenolic substance (quinol, guaiacol or resorcinol) is claimed to accelerate hydrogenation (Lever Bros., Ltd., and R. Thomas, B.P. 208189, 1922).

Metallic soaps and other impurities which act as "poisons" to the catalyst may be removed by treatment with Japanese fuller's earth (S. Ucno, J. Soc. Chem. Ind. Japan, 1920, 23, 1028).

CONTINUOUS PROCESSES.

A scries of processes were devised for the continuous hydrogenation o£oils by Bolton and co-workers from 1920 onwards in which the catalyst is used in massive form and oil is passed over it at suitable temperatures in an atmosphere of hydrogen. Thus E. R. Bolton (B.P. 162370, 1920) activates nickel wool by treating it with nitric acid in liquid or vapour form, then roasting it and reducing adhering oxides with hydrogen. Oil and hydrogen are passed in counts-current over the catalyst which may be reactivated by treatment with hot oil and solvents.

A great advance was made by the introduction of Bolton and Lush's continuous process (Lush and Technical Research Works, Ltd., B.P. 203218, 1922), which is successfully worked in many countries by licences from Technical Research Works, Ltd. The catalyst consists of nickel wire or turnings enclosed in cages of metallic gauze. The cage and its contents are coated with a film of nickel peroxide in an electrolytic bath, with the cage itself as the anode, whilst n 5% solution of sodium carbonate forms the electrolyte. The cages are inserted into the apparatus and the nickel peroxide is reduced to nickel by means of a current of hydrogen at 200-250°, after which the temperatuie is allowed to fall to 180°, and the oil is made to flow over the catalyst. When the catalyst becomes inactive (after periods^up to (J months), the residual oil is extracted from the cages *in situ,* the solvent is removed, and the cages and their contents are re-activated by anodic oxidation in the electrolytic bath and returned to the plant for further use. A description of the plant on an industrial scale is given by Lush (Ind. Chem. 1927, 3, 249). Mandetstam (Oil and Soap, 1939, 16, 166) deals with later developments. In addition to the advantage of the process being continuous, it is claimed that ther$ is no hydrolysis of the oil, that the period of initial heating is short, and that the cost of production is lower than in the older powder processes.

Reference may also be made to the "T.R.W. Interchange Process," in which a saturated body (*e.g.* butyl alcohol) is mixed with an unsaturated body (*e.g.* olein), and the mixture is passed over the catalyst under conditions similar to those employed for direct hydrogenation. Hydrogen is transferred from one body to the other, with the formation of *e.g.* butaldehyde and stearin. According to the patent of Technical Research Works and Lush (B.P. 221000, 1923) the spent catalyst is freed from oil, and is then oxidised at the surface with hypochlorous acid and reduced with hydrogen.

HYDROGEN FOB CATALYTIC PROCESSES.

One of the main essentials for the successful hydrogenation of oils is a supply of pure hydrogen. The gas must be free from sulphur, chlorine, arsenic and phosphorus, and contain only negligible quantities of oxygen or oxides of carbon.

In some of the larger works (Sieinens-Schuckert, Ateliers Oerlikon) a very pure hydrogen, containing as impurity only 0-2% of oxygen, is prepared by the electrolysis of alkaline distilled water. In other works water gas or producer gas is used as the source of hydrogen. The methods of Linde-Frank-Caro and of the Soc. de l'Air Liquide are based on a fractional distillation of the liquefied components of water gas. The resulting hydrogen is of 97-98% purity, and is brought to 99-99*5% by being passed over soda-lime heated to 180°.

In Lane's process[1] (Anon., Engineering, 1917, 123. 546) steam is decomposed by means of reduced iron, and the resulting iron oxide is reduced by purified water gas. Spathic iron ore (ferrous carbonate) is used as the original source of iron. This, when heated, yields a porous mass of ferrous oxide, which is packed into a retort, where it is alternately reduced and oxidised. The cost of hydrogen made by this process was about *4s. 2d.* per 1,000 cu. ft. (Ellis, J.S.C.I. 1912, 31, 1164). A mixture of steam and water gas is used by the Soc. Lyonnaise du Gaz and the Griesheim-Elektron Co., the decomposition being effected by means of a mixture of lime and iron. These methods yield hydrogen of 97-5-98-5% purity.

Where petroleum is readily obtainable the method of Rincker-Wolter is used, in which the hydrocarbons of oil gas are decomposed at a high temperature into carbon and hydrogen.

Electrolytic hydrogen is now largely used for catalytic hydrogenation, the processes* and plant of Knowles (International Electrolytic Plant Co., Ltd.) and Bamag-Meguin A.-G. (Berlin) being widely used. The Knowles cell produces 8 cu. ft. per kw.-hour of hydrogen of 99-9%

purity at an economical voltage (E. F. Armstrong, Chem. and Ind. 1932, 51, 02).

TECHNOLOGY OF HYDROGENATION.

From a consideration of the foregoing outlines of patent processes it will be^seen that the main conditions for successful hydrogenation are a suitable temperature, fine state of subdivision of the oil, an active catalyst and the absence of injurious substances.

E. F. Armstrong and K. A. Williams (Chim. et Ind. 1939, 42, 2; Chem. and Ind. 1940, 59, 3) point out that tho technology of hydrogenation has now advanced to a stage where the older processes have all become more or less standardised in operation. The many difficulties encountered in the early development have mostly been eliminated, so that while in 1910 several hundred tons of oil were^treated per week, the output of hydrogenation plant had risen by 1939 to the order of 1,000 tons per day and the process had become applied to many substances other than fatty oils. Chemicals, such as phenol, cresols, naphthalene and pyridine, are treated in limited quantities, while with coal and petroleum oils the industry is conducted on an enormous scale.

In order to avoid catalyst poisoning extremely careful refining of fatty oils is necessary before they are hardened.

" Powder " or " batch " processes are applied in autoclaves, tho nickel catalyst usually being prepared by suspending an inert carrier in a solution of nickel sulphate to which is added sodium carbonate. The precipitate is thoroughly washed and dried, and reduced in a current of hydrogen at 250°C. *%T* more, according to the degree of activity required, the temperature used affecting also the robustness. After cooling the catalyst is flooded with oil and stored until required. Hydrogenation is conducted in autoclaves at about 180°C. in an atmosphere of hydrogen, under pressures in excess of atmospheric. The reaction occurs at a rate that can readily be controlled, and acapid examination of the product at intervals enables the reaction to be stopped at any desired stage.

Nickel formate catalyst is also used, with or without support, in a similar manner and is reduced *in s\}u in* the oil at about 26T)°C, saving plant, labour, and operating costs by combining the catalyst reduction and hydrogenation processes.

In batch processes, the oil is cooled and the catalyst filtered off after the reaction has proceeded far enough. The oil generally requires further refining and bleaching and will almost always require deodorising.

The " continuous" system of Technical Research Works, Ltd., is applied as described above, and in this case the hardened oil emerging from the plant contains less than 1 part of nickel per 10 million of oil. Subsequent filtration and refining are unnecessary but deodorisation is usually applied. In practice it has been found that the oil suffers from continual contact with the heated Malls of the vessel, and the short time of contact of oil, hydrogen and catalyst employed in this system is therefore advantageous.

It is believed that with oils, such as whale oil, cotton-seed and ground-nut oils, the powder systems involve running costs of from *25s.* to 30s. per ton and the continuous system of about one-half this sum. The latter system requires less labour and floor-space.

Fatty alcohols are now produced on a large scale by catalytic hydrogenation of oils or fatty acids under very high pressures, such conditions promoting the reduction of the carbonyl group. The products find use after sulphonation as wetting agents.

PROPERTIES OF HYDROOENATED OILS.

The degree of hardening depends upon the extent to which the hydrogenation process has been carried, so that products ranging from the consistence of a soft butter to a hard tallow may be obtained from the same oil.

Provided that the reaction is carried far enough, fish oils and whale oils are deodorised during hydrogenation owing to the conversion of the clupanodonic acid (to which, as Tsujimoto has shown, the odour is mainly due).

For edible purposes the chief oils hydrogenated are whale oil, cotton-seed, maize,. soya bean, arachi's and coconut oils, though any edible oil is suitable for the process. Products such as margarine and artificial lard, which formerly consisted of a vegetable oil mixed with sufficient oleostearin to give a semi-solid mass, are now prepared from oils such as cotton-seed oil or whale oil hydrogenated to a sufficient extent to give the required consistence; or by a mixture of hardened oils with liquid oils. In the opinion of Ellis (J.S.C.I. 1912, 31, 1165) the use of hydrogenated oils by themselves is preferable to the method of some manufacturers of blending hydrogenated oils with untreated oils, since the resulting product has a better flavour and keeps better.

With regard to the effect of hydrogenation on oils it has been found that the acid and saponification values are not materially affected, but the refractive index and iodine value are lowered and the melting-point raised to an extent corresponding with the degree of hydrogenation.

The acetyl value of hydroxylated oils such as castor oil is lowered by hydrogenation at the usual temperatures, but Jurgens and Meigen have shown that when esters of ricinoleiu acid are hydrogenated below 200° the OH group is not attacked and practically only the double bond is saturated.

While the catalytic hydrogenation of many chemicals consists in the simple addition of hydrogen at the double bonds, in some cases there is preferential action. If a compound contains more than one double bond all may react but more generally the reaction is limited to specific bonds? Thus E. J. Lush (J.S.C.1.1927,46, 454) has shown naphthalene to produce tetralin if treated in the vapour phase and decalin when in the liquid phase. Unsaturation in aromatic nuclei is generally less easily removed than in straight chains, and in a straight chain containing two or more double bonds one will be more readily reduce, than another.

E. F. Armstrong and K. A. Williams (Chim. et Ind. 1939,42, No. 2,234) point out that fatty oils consist of complex mixtures of glyceryl esters of fatty acids. The fatty acids are all of similar chain length but may be saturated, or contain one, two, three or more double bonds. Three acid radicals are attached to each glyceryl radical in a manner even now incompletely understood, though T. P. Hilditch and his co-workers continue to throw light on the problem. It is not known how the arrangement of the acids on the glyceryl residue affects the relative ease of reduction but it is believed that this has little effect in most cases. R. G. Pclly (J.S.C.I. 1927, 46, 449T) has shown, however, that in mixtures of fatty acids and neutral fats the unsaturated free acids are preferentially reduced. Further complications occur through side-reactions. There is a notable formation of isomers of oleic acid in batch hydrogenation; this can be largely suppressed in the continuous process.

Experiments on the hydrogenation of cotton-seed oil by Moore, Richter and Van Arsdel (Ind. Eng. Chem. 1917, 9, 451) have shown that linolein is hydrogenated more rapidly than olein at 200° and upwards, so that olein tends to accumulate in the fat. To obtain a hardened product with the same iodine value as another but containing, relatively, inpre saturated glycerides and linolein, it is necessary to effect the hydrogenation under conditions of lower temperature, greater pressure, more vigorous agitation and a larger proportion of catalyst.

It was found by E. F. Armstrong and T. P. Hilditch (Proc. Roy. Soc. 19£0, A, 98, 27) that in the hydrogenation of linseed oil in the presence of a nickel catalyst, a curve results the initial portion of which (30% of the whole curve) corresponds with the hydrogenation of the whole of the linolenin and most of the linolein; there is then a very abrupt change in the curve, and this is followed by an approximately linear curve at a much lower slope.

In a* further communication by the same authors *(ibid.* 1921, A, 100, 240) on the influence of pressure on the hydrogenation of liquids in the presence of nickel, it was shown that, in the absence of disturbing factors, an increase in the pressure of the hydrogen causes a proportionate increase in the rate of reduction. According to Lush (J.S.C.I. 1924, 48, 53T), the rate of hydrogenation is approximately proportional to the square root of the pressure.

Varying the mass of oil in relation to the catalyse has a pronounced effect on the nature of the products, and hydrogenated oils containing different proportions of foooleic acid may thus be obtained (Lush, *ibid.* 1923, 42, 219T). The influence of the concentration of the catalyst on the selective •hydrogenation of cotton-seed oil has also been studied by Dhingra, Hilditch and Rhead (J.S.C.I. 1932, 61, 195T); *see also* E. R. Bolton, *ibid.* 1927, 46, 44T, and " Oils, Fats, and Fatty Foods," 1928, pp.»302-316.

R. Thomas (J.S.C.I. 1920, 89. 10T), studying different aspects of the mechanism of the hydrogenation of unsaturatcd glycerides in the presence of a nickel catalyst, found that the influence of foreign gases on the catalyst and on the velocity of hydrogenation might be either purely physical or chemical. He confirmed the observation of Armstrong and Hilditch that linolein absorbs hydrogen much more rapidly than does olein* Kaufmann's thiocyanogen method of determining the degree of unsaturation of fats has also afforded proof of the selective character of hydrogenation (Kau&nann and Hansen-Schmidt, Ber.. 1927, 60 [B], 50). In experiments with a nickel catalyst at 200° in an autoclave the linolic acid in a fat had disappeared after 135 minutes.

The effects of tone temperature of hydrogenation on the selective action and upon the melting-point and iodine value of the product have been studied by K. A. Williams (J.S.C.I. 1927, 46, 446T, 448T) over * range of 120-200°.

The formation of *isooleic* acid is dealt with by Moore *{ibid.* 1919, 38, 320T); Hilditch and Moore *{ibid.* 1923, 42, 15T); Richardson, Knuth and Milligan (Ind. Eng. Chem. 1924, 16, 519; 1925, 17, 80) Cocks,,Christian and Harding (Analyst, 1932, 56, 368); Lush (J.S.C.I. 1923, 42, 219T; 1924, 48, 53T; 1925, 44, 129T); Hilditch and Vidyarthi (Proc. Roy. Soc. 1929, A, 122, 552).

Elaidic acid is the predominating isomer formed but a number of others also appear. The total proportion of isomers formed depends on temperature, possibly on pressure, certainly on the degree of activity of the catalyst, the relative degree of mixing of oil and catalyst, the rapidity of desorption of reacting' molecules from the catalyst and the nature of the catalyst. It is most marked with platinum, less with palladium, still less with nickel and least with copper. It is promoted by high temperatures and is least marked in the continuous process. Under constant conditions, the ratio of solid *isooleic* acid to liquid oleic acid in the product tends to a constant value after the reaction has proceeded to a fixed extent, this value being maintained until saturation is complete. Unpublished researches of K. A. Williams suggest that the proportions and the reactions themselves are controlled by excess electronic energy acquired by hydrogen in its sorption by the catalytic metal and subsequent transfer to the oil molecule.

The theory of the catalytic action is dealt with by Rideal and Taylor, "Catalysis in Theory and Practice," 1926; Falk, "Catalytic Action," 1922; Sabatier, "Le Catalyse en Chimie Organique," 1920; various reports of the American Committee on Contact Catalysis, 1922-26; Nyrop, "Treatise on the Catalytic Action of Surfaces," Copenhagen, 1934; Hilditch, " Catalytic Processes in Applied Chemistry," 1929; H. S. Taylor (Proc. Roy. Soc. 1925, A, 108, 103; J. Phys. Chem. 1926, 80, 150); Bloeinen (Fettchem. Uinschau, 1934, 41, 95, 151); Berkman, Morrcll and Egloff, "Catalysis" Reinhold Publishing Co., New York, 1940, Hydrogenation, pp. 809-887.

Arachidio acid may still be detected in hardened araehis oil, but a modification of the usual test is necessary *(see* Kreis and Roth, Z. Untcre. Nahr.-u. Genussm. 1913, 25, 81).

Leimdörfer (Chem. Zentr. 1914, I, 304) has shown that the stearic acid formed in the hydrogenation of oils is chemically identical with natural stearic acid.

Marine animal oils yield a much smaller proportion of insoluble bromides after hydrogenation, and the distinctive colour reactions of the original oils are either modified or no longer obtained.

Bellier's reagent (nitric acid, sp.gr. 1·4, and resorcinol in benzene) also gives different colour reactions with hardened sesame, cotton-seed and arachis oils from those given by the original oils. The Baudouin test for sesame oil is intensified by hydrogenation, but Halphen's test for cotton-seed oil is inhibited, the chromogenic substance giving the reaction being destroyed after hydrogenation for 15 minutes with a nickel catalyst at 150-160°.

The amount of phytosterol is not materially reduced by hydrogenation at 200°, but cholesterol is resinified at 200°, and after treatment at 250° will no longer yield a crystalline derivative (Marcusson and Msyerheim, Z. angew. Chem. 1914, 27, 201).

Analytical data for hydrogenated oils are given by Boiner and Leschly-Hansen (J.S.C.I. 1912, 31, 996); E. Mellana (*ibid.* 1914, 33, 701); Sudborough, Watson and Athawale (*ibid.* 1923, 42, 103A); Myddleton and Barry, "Fats Natural and Synthetic," E. Benn, Ltd., 1924; Williams and Bolton (Analyst, 1924, 49, 460); Williams (J.S.C.I. 1927, 46, 446, 448T); and in other communications already referred to.

The hydrogenation of tung oil is referred to by H. I. Waterman and C. van Vlodorp (Chem. Weekblad. 1934, 31, 420) who point out that the course of the reaction varies with temperature and pressure and with the nature of the catalyst. T. Moore (Biochem. J. 1839, 33, 1635) has found that the strong spectrographic absorption at 270μ drops, while the originally small value at 230μ first rises and then drops, both reaching negligible values at saturation. He compares the formation of an acid with absorption maximum at 230μ, indicated by this observation, with the formation of the same acid by hens and rats fed on tung oil. He also notes that the hydrogen absorption and drop in iodine value do not correspond in the hydrogenation of tung oil, ascribing this discrepancy to the effect of conjugated bonds.

For a study of the alteration in glyceride structure produced during the progressive hydrogenation of olive and cotton-seed oils, *see* Williams and Bolton (Analyst, 1924, 49, 460) and Hilditch and Jones (J.C.S. 1932, 805): and investigations of the course of hydrogenation in the continuous process of Technical Research Works, Ltd., *see* Lush (J.S.C.I. 1923, 42, 219T; 1924, 43, 53T); Hilditch and Rhead (J.S.C.I. 1932, 51, 198T). Williams and Bolton (Analyst, 1924, 49, 460) base a method for detecting hydrogenated oils on the determination of wooleic acid, using the insolubility of the lead salt of the latter in ether and alcohol as a means of separating it in admixture with saturated acids from the liquid acids. This test affords a much more trustworthy indication than the presence of nickel, which is now practically eliminated from the products of hydrogenation. J. Grossfeld and J. Peter (Z. Unters. Lebensm. 1934, 68, 345) have extended the applicability of this test.

NICKEL IN HYDROGENATED FATS.

The presence of a trace of the metallic catalyst was at one time of frequent occurrence in hydrogenated fats, especially those of continental origin. Bömer (Chem. Rev. Fett. u. Harz-Ind. 1912, 19, 221) found 0·01% of ash with 0·006% of nickel oxide in hydrogenated sesame oil, and 0·006% of ash with 0·0045% of nickel oxide in hardened whale oil. Hence, the detection of nickel in a fat indicates the presence of a hardened oil, although a negative result in the test does not necessarily prove that such products are absent, since means, such as treatment with dilute hydrochloric acid, are often employed to remove the residual metal. In experiments to ascertain the effect of traces of nickel upon the human system, Offerdahl (Ber. deut. pharm. Ges. 1913, 23, 558) found that 0·5 g. of nickel could be taken daily without any injurious effect, 99·8% of the metal being rapidly excreted from the system.

Modern edible hydrogenated fats do not usually contain more than 1 part of nickel per 10 million and often much less.

For the detection of traces of nickel the dimethylglyoxime test may be used (*see* Knapp, Analyst, 1913, 38, 102), but certain untreated oils, free from nickel, may show a similar coloration if the test is made directly on the oil. The test should therefore be applied to the ash of 100 g. of the oil for better results (Prall, Z. angew. Chem. 1915, 28, i, 40). A still more sensitive reagent for nickel is α-benzildioxime, as suggested by Atack (Analyst, 1913, 38, 316).

To obtain products relatively free from nickel, Ellis (J.S.C.I. 1912, 31, 1165) lays stress upon the importance of using the catalyst in metallic form rather than in the form of oxide, since metallic nickel will not readily combine with free fatty acids to form a soap in the presence of free hydrogen. Too rapid hydrogenation should also be avoided, so as to prevent decomposition of the fat, with liberation of water, which might cause hydrolysis of the fat and liberation of free fatty acids.

For the mechanism of the addition of hydrogen to unsaturated glycerides in the presence of nickel, *see* Thomas (J.S.C.I. 1920, 39, 10T); and for a study of the relation between the occlusive power of palladium for hydrogen and its activity in catalytic hydrogenation, *see* Maxted (J.C.S. 1921, 119, 1281).

NUTRITIVE VALUE OF HASTENED OILS.

The digestibility of hydrogenated fats is dealt with by Langworthy (Ind. Eng. Chem. 1923, 15, 276) who describes researches of the U.S. Department of Agriculture. The conclusion is drawn that soft hydrogenated fats are as well assimilated as natural fats, but if the melting-point is raised beyond 40-45° the digestibility fails rapidly.

The food value of hydrogenated fats is much the same as that of natural fats, but commercial hardening processes almost always destroy any vitamins in the raw material. Diets containing a considerable proportion of hydrogenated fats are widespread and lead to no harmful effects provided that other sources of necessary vitamins are included.

K. A. W. and C. A. M.

HARGREAVES-BIRD CELL (Vol. III, 5[illegible]].

HARMALA, ALKALOIDS OF PEGANUM HARMALA. *Harmaline, Harmine, Harmalol, Harman, Norharman.* The seeds of the wild rue, *Peganum harmala* Linn. (Fam. Rutacese) or harmal seeds have been employed from the earliest times in Eastern medicine as a stimulant, anthelmintic, or even narcotic. They are said to be the source of a red dye produced in Southern Russia and they have been used in the manufacture of oil. Wild rue is an odoriferous herbaceous plant, 1-3 ft. high, and inhabits Southern Europe, Asia Minor, Egypt, North-western India and Southern Siberia (Fliickiger, Pharm. J. 1872, [iii], 2, 229).

The seeds and root of the plant contain four alkaloids, *harmaline*, $C_{13}H_{14}ON_2$, first isolated by Goebel (Annalen, 1841, 38, 363; 39, 289), *harmine*, $C_{13}H_{12}ON_2$, obtained by Fritzsche (*ibid.* 1847,64, 360), *harmalol*, $C_{12}H_{12}ON_2$, first prepared by Fischer (Ber. 1885, 18, 402) and *vasicine* (also called *peganine*), belonging to a quite different chemical type of alkaloid.

From the South American plant "yage," "caapi," "aya-huasca" or "pilde\" used for the preparation of a native intoxicant (Perrot, Bull. Sci. pharmacol. 1923, 30, 107) and which has been identified as *Banisteria caapi* (Fam. Malpighiacese) an alkaloid has been isolated by various workers and named "telepathine," "yageine," or "banisterine" (literature: *see* Rouhier, *ibid.* 1926, 33, 252; Raymond-Hamet, Compt. rend. 1927, 184, 1266). All three alkaloids are identical with harmine; for yageine, telepathine, *see* Elger, Helv. Chim. Acta, 1928, 11, 162, and Wolfes and Rumpf, Arch. Pharm. 1928, 266, 188; for banisterine, *see* Briickl, Amer. Chem. Abstr. 1930, 24, 4680 and Lewin, Chem.-Ztg. 1928, 52, 357.

Harmal seeds contain about 4% of alkaloids, of which half to two-thirds is harmaline. The alkaloids are found for the most part in the outer portions of the seeds.

Extraction.—Fritzsche (l.e.) extracts the seeds with H_2O containing acetic or sulphuric acid. The extracts are concentrated to one-third and the phenolic harmalol separated from the other bases by precipitating the latter with a small excess of caustic potash. Harmaline and harmine are re-dissolved in acid and precipitated as hydrochlorides by a saturated solution of common salt. Harmaline and harmine are separated either by fractional precipitation with ammonia from their hydrochlorides or by fractional crystallisation from MeOH-C_0H. [illegible] These fractionations are not accurate (*cf.* Hasenfratz, Ann. Chim. 1927, [x], 7, 151); for an interesting separation of the two alkaloids by buffer solutions, *see* Elgazin, A. 1933, 408.

Harmaline, (I) $C_{13}H_{14}ON_2$, optically inactive, m.p. 239-240° (decomp.), from MeOH prisms or small tables, from EtOH rhombic octahedra, is very slightly soluble in cold H_2O or Et_2O, moderately soluble in cold and readily soluble in hot EtOH. For ultra-violet-absorption curves, *see* Kharash (Amer. Chem. Abstr. 1936, 30, 2706); dissociation constants, *see* Orlow (Chem. Zentr. 1932, II, 70); microchemical identification, *see* Amelink (Pharm. Weekblad, 1931, 68, 221).

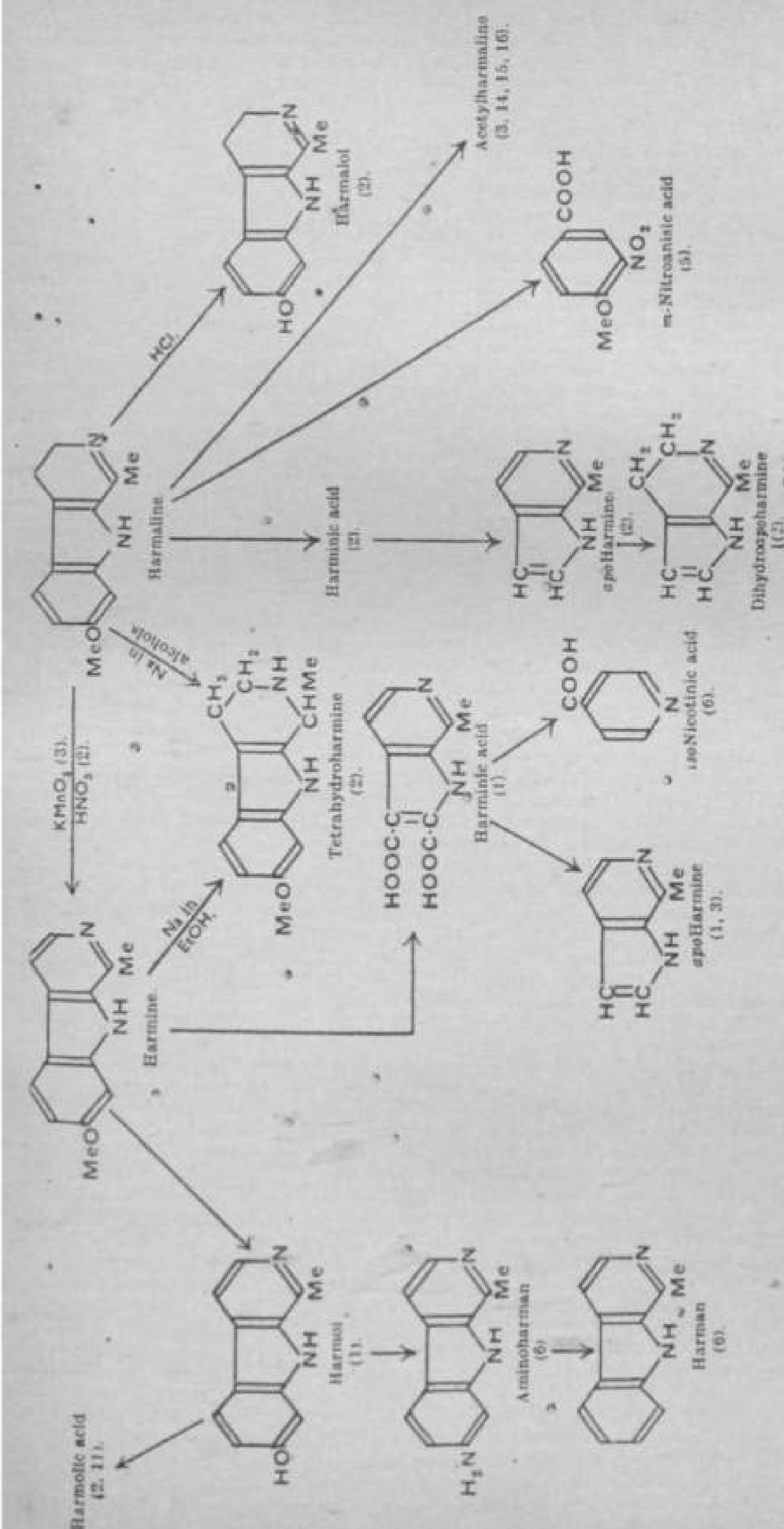
The salts are yellow: $BHCl,2H_2O$, slender needles; the platinichloride is microcrystalline; typical salts are the mercurichloride and the acid chromate, insoluble in H_2O. The hydrocyanide, B*HCN, is still a base and combines with acids to form crystalline salts. *Acetyl derivative,* colourless needles, m.p. 204-205°, easily affected by acids. By treating (I) with CH_3I, *N-methylharmaline hydriodide* and *dimethylharmaline hydriodide* are obtained (Fischer, Ber. Idl4, 47, 102). *N-methylharmaline,* m.p. 132°, easily soluble in EtOH, $CHCl_3$, MeOH-, sparingly soluble in Et_2O or C_6H_6. N-methylharmaline and acetylharmaline are derivatives of a tautomeric form of (I) (Perkin, Robinson *el al.,* J.C.S. 1924, 125, 657).

Harmaline heated in a sealed tube with HCl yields *harmalol,* $C_{12}H_{12}ON_2,3H_2O$; by gentle oxidation with HNO_3 or $KMnO_4$ (Fischer, Ber. 1889, 22, 640; Elgazin, A. 1934, 1117) harmine is obtained; sodium reduction in alcohol yields *dihydroharmaline (tetrahydroharmine).*

Harmine, (II) $C_{13}H_{12}ON_2$, optically inactive, m.p. 260-261 -5°, colourless prismatic needles from MeOH, easily subliming, is insoluble in H_2O and sparingly soluble in EtOH and Et_2O. For ultra-violet absorption, dissociation constants and microchemical identification, *see* Relevant references under (I); for crystallography, *see* Briickl *(l.e.). Harmine hydrochloride, platinichloride, oxalate* and acid *chromate* crystallise well. The salts are colourless but show a deep blue fluorescence in dilute solution (Ismailov *et al.,* Chem. Zentr. 1938, II, 3276). *Methylharmine* has m.p. 209°. On treatment with cone. HCl like (I) *(see* above), (II) yields *harmol,* $C_{12}H_{10}ON_2$, m.p. 321°, not occurring in nature.

Harmalol, (III) $C_{12}H_{12}ON_2,3H_2O$, m.p. 212° (anhydrous) may be either extracted from the natural material or prepared from (I) by demethylation. Red needles, sparingly soluble in H_2O, soluble in $CHCl_3$ and acetone. For preparation, see Fischer (Ber. 1889, 22, 638). The alkyl ethers of harmalol and harmol are of some importance in chemotherapy; for their preparations, *see e.g.* Coulthard, Levene and Pyman (Biochem. J. 1933,27,727; B.P. 359180, 38212$; G.P. 568675).

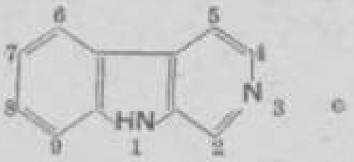
Constitution of (I) *and* (II).—(I) is dihydro-(II); both bases on reduction yield the same tetrahydro-(II); for catalytic re-oxidation, *see e.g.* Akabori and Saito (Chem. Zentr. 1930, II, 3257). Research on the constitution of the harmala bases was initiated by Fritzsche (Annalen, 1848, 64, 360; 68, 351; 1849, 72, 306; 1853, 88, 327; 1854, 92, 330) and by O. Fischer (Ber. 1885,18, 400[1]; 1889, 22, 637[s]; 1897, 30, 2481[3]; 1905, 38, 329*; 1912, 45, 1930*; 1914, 47, 99[6]) and finally concluded by the more recent researches of Perkin, Robinson *et al.* (Part I: J.C.S. 1912, 101, 1775[7]; Us



(The figures in brackets below the formulæ refer to the references in the text.)

BIS, 103, 1&TIl"; III: 1919, **115.** 933; IV: 1919, 115, M7[10]; V: 1921, 119. 1601[11]; VI: 1922, **121,** 1872[12]; VII: 1924, 125, 2ti[13]; VIII: 1924, 125, 657"; IX: 1927, 1[18]; X: 1929, 2942[16]). The arrangement of the three rings, of which two are heterocyclic, created unusual difficulties (cf. Perkin, Robinson *et al.*, Parts I and II); the scheme on p. 187 (in which the formulæ are written in the correct way) covers the work of Fischer and the earlier contributors.

Perkin, Robinson *et al.* (*see above* Parts III and IV) identified *harman* with a product which Hopkins (J. Physiol. 1903, 29, 451) had obtained synthetically by **oxidation** of tryptophan with ferric chloride (Perkin, Robinson *et al.*, Part *V*, l.c.). These findings settled **the** arrangement of the three rings in the **harmala** bases and demonstrated that they are all derivatives of 3-(or β-)carboline or *Norharman* (4-carboline of the earlier literature): cf. Perkin, Robinson *et al*, Part IV; for changes of nomenclature, *see* J.C.S. 1929, 2926, footnote.



Harman has not been found in any of the plants yielding harmine or harmaline, but Späth has found that the two bases *Aribine* (from *Arariba rubra,* Fam. Rubiaceæ) and *Loturine* (from *Symplocos racemosa,* Fam. Symplocaceæ) are identical with harman (Monatsh. 1919, **40,** 351; 1920, 41, **401).** Being of the nature of a proto-alkaloid, it is easily understandable that **harman** occurs in different families. Harman and norharman proved also to be the keystone in the elucidation of the structure of *Yohimbine.* *See* EVODIA RUTAECARPA, ALKALOIDS OF.

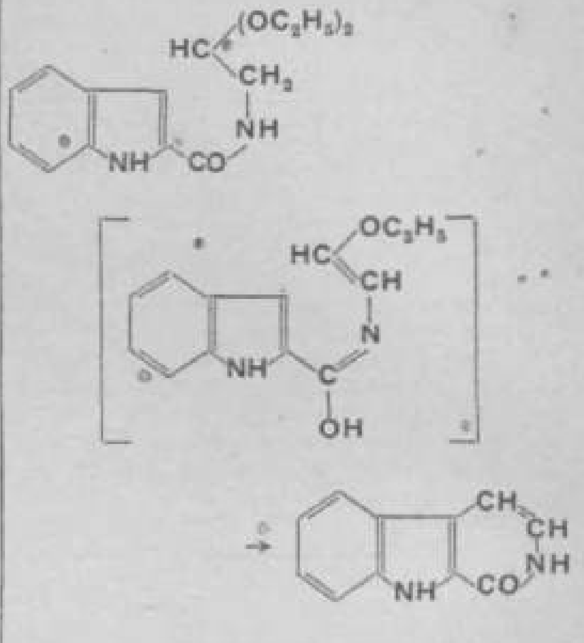
Harman, $C_{12}H_{10}N_2$, m.p. 238°, prisms from benzene; the sulphate, radiating clusters of short needles; the mercurichloride crystallises from dilute **HCl** in long slender needles. For other salts, see Späth (*l.c.* 1919); the ordinary salts show an intense bluish-violet fluorescence.

Norharman, $C_{11}H_8N_2$, crystallises from hot benzene in colourless slender needles and melts **at 188-9°,** sparingly soluble in cold C_6H_6 or light **petroleum,** moderately soluble in **Et_2O** or ethyl [illegible], readily soluble in **MeOH and EtOH,** also fairly soluble in hot water. A dilute **acid solution** exhibits a vivid fluorescence. For synthesis of norharman, *see* Perkin, Robinson *et al.*, Part V, p. 1638. The attribution of the correct position of the methoxy-group in (I) and (II) as well as the position of the **double-bond** in (I), *is* also due to these authors (see Parts VI and IX).

Several syntheses of the harmala alkaloids or of their **derivatives** have been described, they are essentially of the following types:

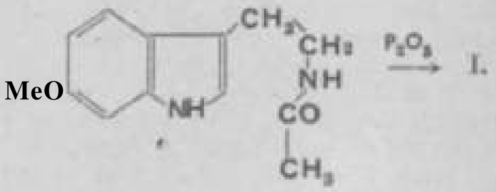
(*a*) Condensation of tryptophan with aldehydes and oxidation **with** chromic acid to harman (**Perkin, Robinson *et al.*, Part V**) and of **6-methoxytryptophan to harmine (Harvey** and Robson, J.C.S. **1938,** 97; *cf.* also Jacobs and **Craig,** J. Biol. Chem. 1936, 113, 760).

(*b*) Formation of an *iso*carbostyril by ring-closure of an indole-2-carboxy-acetalamide followed by vigorous reduction:



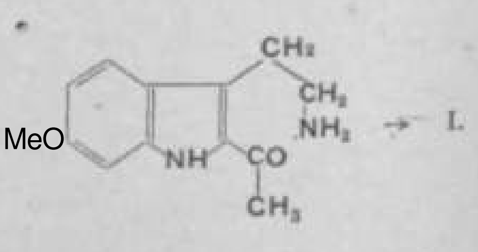
similar to the Pomeranz-Fritsch synthesis (*cf.* Fritsch, Ber. 1893, 26, 421). Synthesis of norharman, Perkin, Robinson *et al.*, Part V; condensing agent alcoholic **HCl** at 40°, *idem.* Part VI. Synthesis of N-methyltetrahydronorharman, *idem.* Part VI, with the same condensing agent.

(*c*) Formation of a dihydroharman derivative, similar to the Bischler-Napieralski synthesis of *iso*quinolines:



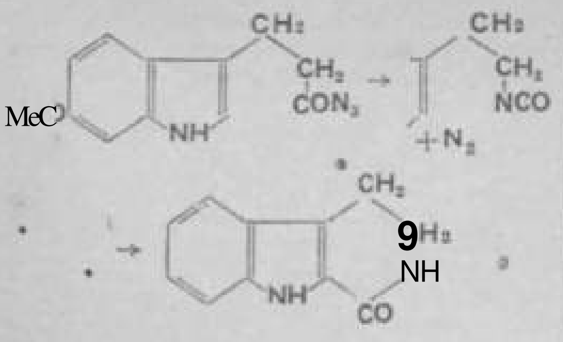
Syntheses of harmalan, harman, harmaline and harmine, *see* Späth and Lederer, Ber. 1930, 63 [B], 124, or Akabori and Saito, *ibid.* 2245; also Späth and **Lederer,** *ibid.* 2102; Asahina and Osada, Chem. **Zentr.** 1927, I, 1479; **Tatsui** *ibid.* 1928, II, 068,

(*d*) Formation of a dihydroharman derivative by ring-closure of *a* δ-aminoketone, viz.



[Perkin, Robinson *et al.*, Part IX).

(*e*) Formation of a ketotetrahydrocarboline by decomposition of the azido of indole-propionic **acid**



(Manske and liobinson, J.C.S.*1927, 240; and Efcrkin, Robinson *ei <d.,* Part X).

For formation of barman derivatives under " physiological " conditions, *see* Habn *el ah,* Ber. 1934, 67 [B], 2031; Annalen 1935, 520, 107, 123; Ber. 1938, **71** [B], 2103,^2175. tfor interesting but unsuccessful attempts at the synthesis of harnian derivatives, see *also* Spilth and Burger, Monatsh. 1928, 49, 2«5; for the synthesis of *apohtnmine, &te* Perkin, Kobiiitton *tt aX.,* Part VIII.

For the pharmacology of the harmala bases, *see* Henry, " Plant Alkaloids," 3rd ed., 1939, p. 453 if. where the literature is cited.

Schl.

HARM ALINE, HARMALOL i. HABMALA ALKALOIDS.

HARMAN *9.* HAKMALA ALKALOIDS and Vol. I, 46M.

HARMINE *v,* HAHMALA ALKALOIDS.

HARMOTOME (Vol. I, *GUI).*

HASHA3(Vol. I, lid).

HASHISH (Vol. 11,209c).

HATCHETTOL1TE (Vol. J, 685c).

HATCHETT'S BROWN (Vol. I1l, 471a).

HAUSMANN1TE. A manganese oxide. Mn_3O_4, crystallised in the tetragonal system, and tho richest ore of manganese (Mn 72%). It forms pyramidal crystals with a good basal cleavage, and with very much the aspect of regular octahedr*. They are opaque with a sub-metallic lustre and a <&rk brownish-black <>r black colour; the streak is chestnut-brown. Sp.gr. 4-7-4-8; hardness 5-5$. Well-developed crystals are found at Ilmenau in Thuringia, Ilfcld in the Harz, Langban in Sweden, IJigrigg in Cumberland and Miguel **Bonier** in Brazil. The massive black orea of manganese consist of mixtures of various manganese oxides, and doubtless hausmanmte ii often present, tliough not readily recognisable in the massive condition.

L. J. S

HAWKITE(VoI. IV. B56J).

HAWK'S EYE (Vol. HI, 430«).

HAWTHORN *(Craixgus* «pp.). The fruit or " haws " of the specie* are sometimes utilised "} tuakfng sweetmeats and preserves. Otto and hooper *(Z.* Unters. Nahr.- u. (jenussm. 1910,19, >»-8) give tho following composition of the haws of C• **COOCMtt**: wat*r, 7^-74 ; acids (atf malic), "'18; invert sugar. 7-84 ; nucrose, 012%.

A. G. Po.

HAWTHORN PERFUME. The natural **perfume** of the hawthorn, *or* May **bio**ssom, characteristic of *Cralxgu* oxyi*•cantha, one of the Rosaceae, is not an artido **oi** commerce. AU **uwtbora** perfumes arc miiture« of eyntbetic perfumes, which may, **in the** most c^ pensive lypcs, be iiiodilict] by a Hi tie of the natar&I porfumo of some other flower which Ucndo with the hawthorn odour. The dominant note in hawthorn **perfume** it **struck** by **aoiftaldehyd*** ('/-'-J **withotrt** which no hawthorn peri'mue ***a*** i>os.siljte. **AcetO'**phenone is the **uoond** most important constituent. Anisaldehyde is a licjiiid, but for " ***a*** n-venience," or probably greater profit, certain German msinu facturers offer crystal **aubepiiii**, a compound of the **aldehyde,** which is mity half as strong as the true aldehyde, and far less economical.

Numerous modifiers and fixntivi-s are **used,** *am* the following may serve us **a** lja.sk- formtiln which can be modified an **required.**

	r.m •
Anisaldehyde	**IOO**
Acetophenone	r>-8
Coumarin	2-5
J)i methyl - hyd ro (j u i n on r; . .	i-:t
Heliotropin	G
Vanillin	II ;,
Liimlol	g
Geruniol	5
rhenylacetaldchyde	1 i'

Traces of benzaldehyde and amyl **ealicylato** are useful, and synthetic neroli oil in small quantity is an effective modifier. Artificial musk is rather too pronounced to be used as a fixative, but a small quantity of dnnamic alcohol or tincturo of benzoin may bo employed for this purpose.

E. J. P.

HAZELNUT 'OIL. The seed-kernels of the European hazel (filbert) *t'onjlvs* ***aveQana*** *L.* contain about 50-65% of oil, of which **the balk** can be recovered **b]** expression as a **golden-** 0T lemon-yellow oil having the **characteristic odour** of hazelnuts, which assists in its **identification** in **admixture** with other oils. The oil i> **used** in perfumery and pharmacy and is pmcd in Switzerland M an edible (salad) oil. It fyps also **bean** used as a **lubricant** for fine machinery, and, on occasion, to adulterate **almond** nil, or as a substitute for peach kernel oil *(cf.* Bennett. Chemist and Druggist, **1008,** 72. 89). Thi- possible prescrvse of haze**bmtoilin the** B3d racted fat must be taken into **consideration** in tin-•nrialvsi.s of chocolate rontnmin;,' iiut'Crngmcntg (ef. Fincke, "Handburh der **Ka&ao*£ree**ug-nisae," Berlin, 193»ij.

The following **ralwM** for **genuine** samples of hazelnut oil are drawn fn'in **recent** noser vat ions *(ef.* **Pritekerand JttOgkunz,Z. Oaten.** Nilir.-u, Genussm. 1921, 42. 232: **Bchaette** and Chung. J. Amer. *Cttm* Soc. **1983,** 56, 3333 ; Bertt am, Ole, Fette Wach.se, **1986, Nb. L4.** p. 2): d_{15}^{15} 0-9152-0-915fi, rf!!J ft-9Hi, $H^{!0}$]-4(iS*l-l-4S98 J acid value 0-3-1-7; »aponificiitiou valuf 1S9-192; iodine value 84'7-80'8; thiocyanogi-n value 82'1 (S. and <!.); **Reichert-Meiwl** value 1-5 (Pf **and** J.), -•"' 5-0 (8. a»<l <-'.); Polermke **7afaiaO*5-O˃7;** unsaponifiable matter 0·35- W>8%-The **coaponUon** of the fatty acids **of** an **oil** expressed from fresh nuts of Italian **origin** was determined *U* 8chuette and Chang **aa foUowi**: (calculated toper cent, fatty acida on oil) myristie acid 0-2, palmitic acid 3-1, stearic acid 1-6, oleic acid 88-1 and linolic acid 2-9. (The residual oil in the nuts, subsequently extracted by light petroleum, contained a slightly higher proportion of linoleic acid (4-6%) and palmitic acid (3*6%)-) Bertram records somewhat different proportions for an oil extracted by light petroleum from French nuts, viz. saturated acids 8%, oleic acid 78-2% and linoleic acid 9-1%. Arachidic acid is absent; hence the isolation of this acid serves as a means of detecting adulteration with arachis oil (Pritzker and Jungkunz, *I.e.).* Adulteration of hazelnut oil with olive oil may be detected by the high freezing-point of the sample, for the pure oil has a solidification point of -17 to -20° C. *(cf.* Fabris and Settimj, Atti VI Cong, intern. Chim.appl. (Rome), 1907,5, 755; Girard, Monit. Sci. 1889, 3, 1181). Owing to the low content of linoleic acid, the separation of the saturated acids by the Twitchell method is attended with considerable difficulty (Bertram, *I.e.).*

E. L.

HEATHER or CALLUNA **VULGARIS.** In former times the common heath or heather, then named *Erica vulgaris,* was used as a dyestuff for producing a yellow colour on woollen goods (Crookes, " Dyeing and Calico Printing," 1874, p. 511). All the five species of *Erica* or heather found in Great Britain were believed by Bancroft (" Philosophy of Permanent Colours," 1813, II, 108) to be capable of giving yellows much like those obtained from dyer's broom. The experiments of Hummel, however, showed that *E. tetralix* (bell heather) and *E. cine'rea* contain only traces of yellow colouring matter. Heather possesses tanning property and, according to H. R. Proctor, contains 6-4% of tannin. The colouring matter, *quercetin,* was isolated by Perkin and Newbury (J.C.S. 1899, 75, 837) from an aqueous extract of the green portion of the plant, in which only it appears to exist.

The dyeing properties of heather are similar to those of quercitron bark; it is necessary, however, to employ 36 parts of the heather to obtain the effect given by 10 parts of quercitron bark.

A. G. P. and E. J. C.

HEAVY ALLOY. The " *G.E.C. Heavy Alloy* " which is 50% heavier than lead, has a tensile strength about equal to that of steel, with excellent machining properties. Its percentage composition is : 90 tungsten, 7-5 nickel, 2-5 copper (Nature, 1941,**148,** 507).

HEDENBERGITE (Vol. Ill, 573a).

HEDGE-MUSTARD **SEED** OIL (Wild Radish-, White Charlock-Seed Oil) occurs to the extent of 20-35% in the seeds of the common European >ield weed *Raphanus raphanistrum* L., which belongs \p the same Family, *Lructferae,* as the rape and ravison plants. Hedge-mustard seed was collected, and the oil was expressed on a large scale for the first time in Hungary in 1880 on the occasion of the lailure of the rape-seed harvest. The crude expressed oil has a dark olive-green colour; in odour, taste and chemical and physical properties it closely resembles rape oil, and fre- S l ta p ? W on the market in admixture this oil, or even under its name. The following figures indicate the analytical characteristics which have been recorded by various investigators: *dN* 0-9175-0-9186; n^{20} 1-4722, f.p. -13 to -14° C; acid value 2-16; saponification value 174-179; iodine value 105-109 *(N.B.,* thrs value lies on, or just above, the upper limit of the iodine value of rape oils) ; Reichert-Meissl value 0-7-1-4; Polenske value 0-7-0-95. *(Cf.* Valenta, Dinglers Polytech. J. 188$ **277,** 36; Grimme, Chem. Rev. 1012, 19, 104; Klimont, Z. angew. Chem. 1911, 24, 254; Knorr, Seifens.-Ztg. 1917, 44, 234; Bureš, Chim. et. Ind. 1933, §pec. No. (12^e Congrès de Chim. ind., Prague (1932), 1073)).

According to Bureš, the fatty acids from* the oil include arachidic acid *(ca.* 1-5%), linolenic acid *(ca.* 6%), linoleic acid *(ca.* 9%) with large amounts o£ " rapic acid " and small amounts of oleic and erucic acids. The content of erucic acid (1-5%) suggested by Bureš appears to be too low, in view of the saponification value of the oil and of the composition of oils from allied members of the same plant family. The identification of the i" rapic acid " (which was based upon its low freezing-point as compared with pure oleic acid) requires confirmation, since it has been shown (Hilditch, Riley and Vidyarthi, J.S.C.I. 1927, 46, 462T) that the so-called " rapic acid " formerly reported to be characteristic of rape oil actually consists .of ordinary oleic acid with, at most, very small amounts *(ca.* 1%) of its isomerides. Bureš and Sedlář report the isolation of a phytosterol, *raphanisterol,* m.p. 136°, $C_{27}H_{54}OH$, from the unsaponifiable matter of hedge-mustard seed oil (Almanah Kong. SIQV. Apot. 3rd Congr., 'ttelgrade-Zagreb-Spalato, 1934, 221 (1935); Amer. Chem. Abstr. 1937, 108).

Owing to the similarity of the two oils, the detection of hedge-mustard seed oil in rape-seed oil is extremely difficult. According to Valenta, the most characteristic test (applicable when fairly large quantities of hedge-mustard seed oil are present) is' the appearance of a green coloration when the oil'is partially saponified with alcoholic potash, and the concentrated filtered soap solution is decomposed with excess of hydrochloric acid.

E. L.

"HEDONAL" jsec-Amyl carbawiate,

$$C_3H_7OHMeOCONH_2,$$

m.p. 74°, b.p. 215° (G.P. 120865). Has been used to a small extent as a hypnotic.

HEDYOTINE. Hcdyotinc was isolated by Dcy and Lakshminarayanan from *Hedyoti* auricupiria* (Kam. ltubiarca») (Arch. l'harm. 1933, **271,** 485). This plant grows wild in the wet lands of the Western Ghats, throughout the length of the Indian Peninsula from the Konkan to Cape Comorin, extending to Ceylon. The inhabitants of South Kanara use it specially for intestinal troubles and dysentery. For further details, see Chopra, " Indigenous Drugs of India," Calcutta, 1933, p. 323.

Hedyotine, $C_{16}H_{28}O_3N$,, is a yellow amorphous, very unstable base, decomposing rapidly when dried in a desiccator. Only the wilts wrro obtained in pure form, they crystallise easily and arc but **slightly** soluble 'in H_2O.

Ci6^{H}22°3^{N}2-HCI, m.p. 245° (sintering at 227°), dissolves in 400. parts of H_2O at room temperature, is easily soluble in MeOH and EtOH; *nitrate,* m.p. 252° (sintering at 238°); *picrate,* m.p. 265°.

The chemical structure of Jiedyotine has not yet been elucidated.

Schl.

•" *HEGONON"* A preparation from albumose and ammoniacal silver salts in which the ftetal appears mainly in the colloidal condition (Gjaldbaek, Dansk Tidsskr. Farm. 1929, 3, 133). It is of value for its antigonococcal action (Pharm. Zentr. 1931, 72, 362 f Mandl, Wien. kMn. Woch. 1932,45,918).

HELENIEN. The lipochrome of *Helenium autumnale* is helenien, $C_{72}H_{116}O_4$. It separates in dark red needles from ethyl alcohol, m.p. 92°, and exhibits absorption maxima at 5110, 4780 and 4660A. (in carbon disulphide). It is the dipalmitate of lutein. Helenien also occurs in *Cheiranthus, Arnica montana, Heliopsis,* etc. (Kuhn and Winterstein, Naturwiss. 1930, 18, 418, 754; Kuhn, Winterstein and Lederer, Z. physiol. Chem. 1931, 197, 150; Winterstein, Angew. Chem. 1934, 47, 315.)

F. S. S.

HELEN IN (v. Vol. I, 1756).

HELIANTHIC ACID. An acid isolated from sunflower seeds (Ludwig and Kromayer, Arch. Pharm. 1859, [ii], 99, 11) and later identified with chlorogenic acid, $C_{ie}H_{18}O_9$ *(q.v.)* (Gorter, Arch. Pharm. 1909, 247, 436).

" *HELICON "(v.* Vol.1, 5174).

HELIIMCONE COLOURS *(v.* Vol. I, 232c).

~~HELINUS OVATUS. (Fam.~~ Rham> naceae.) A climbing shrub indigenous to South Africa. It was examined chemically by Goodson (J.C.S. 1920,117,140) who isolated from the leaves aconitic acid, quercitol, a saponin and scyllitol.

HELIODOR *(v.* Vol. I, 6856).

"HEUO" **DYESTUFFS and PIGMENTS(J;.VOHV,236M>).**

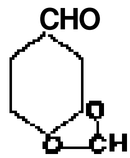
HELIO FAST YELLOW (v. Vol. I, 233a).

~~HELIOTROPE (*v.* Vol. II, 25a, 517e).~~

HELIOTROPE PERFUME. The common heliotrope, *Heliotropium europseum* (Fam. Boragin®) is a. native of the south ar*d west of Europe, and its flowers are used for the preparation of perfumes, but owing *\o* the discovery synthetic heliotropin (piperonal) the'natural perfume finds a very limited employment. The plant is known in this country as "cherry pie." Several members of the *Composite* are known as heliotrope on the Continent. Most gf the artificial^ heliotrope perfumes contain modifiers of the geraniol type, the basic ingredients being heliotropin, with a little vanillin, coumarin and dimethylhydroquinone.

E. J. p

HELIOTROPIN. This valuable syntheti^ perfume, also known as piperonal, *i»* a crystalline compound having a powerful odour of heliotrope. It occurs naturally in various planU. but It does not pay to extract it, as it can be prepared artificially at a much lower cost. It was originally prepared from the base piperine, from pepper berries. This is today merely a matter of historical interest. Heliotropin is the mcthylene ether of protocatechuic aldehyde of the following constitution:



It crystallises in needles, m.p. 37°; forms two oximes, m.p. 112° and 146° respectively, and a semicarbazone, m.p. 146°.

In commerce it is prepared from safrol, which is isomerised to isosafrol by boiling with caustic alkali. Five parts of such isosafrol are oxidised by a solution of 35 parts of potassium dichromate, 38 parts of sulphuric acid and 80 parts of water. The reaction product is steam distilled, the distillate extracted with ether, and the heliotropin so obtained is purified in the usual manner.

Heliotropin should be stored in a cool dark place, as otherwise it is liable to decomposition. It is used in many perfumes, and blends well with cftumarin, vanillin or with lemon, bergamot and neroli oils.

HELIUM. Sym. He. At. no. 2. At. wt. 4-003 (c/. Baxter, Honigschmid and Lebeau, Eighth Report of Committee on atomic weights, International Union of Chemistry, Ber. 1938, 71 [A], 93. Bainbridge and Jordan (Rev. Mod. Physics, 1937, 9, 370) have obtained the value 4-00389, and Aston <Nature, 193C, 137, 357, 613) the value 400391; both these values were both these values obtained by mass-spectrographic methods, and they are referred to the physical Bcale, in which ^{16}O=16-00000. After applying the correction factor, 1-00027, for conversion to the chemical scale (naturally occurring oxygen=16-00000), the mean value becomes 4-00285, with a probable error of about 1 unit in the fourth place). Isotopes: natural helium probably contains the single atomic species <He; Bleakney, Harnwell, Lozier, Smith and Smyth (Phys. Rev. 1934, [ii], 46, 81) find that ordinary helium contains less than 1:10^{5} and 1:10« of ^{3}He and Me, respectively.

Helium is a gaseous element which is the of lightest member of the group of rare, or " inert " gases discovered late,m the^last century by Rayleigh and Ramsay, and which now forms Group 0 in the Periodic Ctantotran of the elements. Helium is the .^^{h}*«* »". ^ " ^ with the exception of hydrogen, and its most striking property is its complete chemical inertness,

HISTORY.

HeKumwasdisc0Vered epectnwcopicaUy in the sun nearly 30;gu. before ite p^nçe m the earth was M.> « i Uunng tne soiai_ eci^e of AugVst 18, 1868, a bright yeUow line observed » t o * r t m o f 2 ^ * romosphere; this was generally t. o be the D doublet of sodium, but Janssen (Compt. rend. 1868, 67, 838) showed that it did not coincide with the sodium lines. On October 20 of the same year, Lockyer observed the new line in the spectrum of a solar protuberance, but regarded it as a new hydrogen line (Proc. Roy. Soc 1869, 17, 91, 131, 288; Phil. Mag. 1869, Liv], **38,** 66). Later, however, Lockyer recognised that the yellow line (which was called D_3 on account of its association with the sodium lines, and had a measured wave-length of 5,876 A.) was due to a new element, which he named *Jielium,* from the greek *ŷXios,* the sun; Lockyer also attributed other unassigned lines in the solar spectrum, at 5,016, 4,922 and 6,678 A., to helium (Proc. Roy. Soc. 1870,**18,** 354). Young (Amer. J. Sci. 1872, [iii], 4, 356) also assigned a line at 4,472 A. to the new element. Helium lines were soon discovered in the spectra of hot stars by Secchi (Compt. rend. 1869, **68,** 237, 359). A general account of the discovery of helium in the sun is given by Lockyer (Nature, 1896, 53, 319).

In 1881 Palmieri (Rend. Accad. Sci. Fis. Mat. Napoli, 1881, **20,** 233; Gazzetta, 1882,**12,** 556) claimed to have observed the D_3 line in the spectrum of a Bunsen flame into which certain volcanic products from Vesuvius had been introduced, but the observation is almost certainly incorrect as helium lines cannot be excited by such means. Later Hillebrand (Bull U.S. Geol. Survey, 1891, 78, 43; Amer. J. Sci. 1890, [iii], **40,** 384; 1892, [iii], **42,** 390) obtained an inert gas on treating certain uranium minerals with sulphuric acid, or on fusing them with sodium carbonate; the gas was not studied fully, but it was thought from its spectrum to be nitrogen, although the existence in the spectrum of unidentified lines was duly noted. Ramsay, doubting the production of gaseous nitrogen *in* the sulphuric acid reaction, suspected that the gas might have been argon, and undertook a more detailed examination of the gas from cleveite. He found an inert residue which would not combine with oxygen on long sparking; its spectrum was examined by Ramsay, and by Crookes, who recognised the bright yellow D_3 line of helium, in addition to argon lines (i/. Proc. Roy. Soc. 1895, 58, 65, 67, 81; Chem. News, 1895, 71, 151). The occurrence of helium in gases from uranium minerals was discovered independently a few days later by Langlet, at Upsala (c/. Cleve, Compt. rend. 1895, **120,** 834). Further research showed that the cleveite gas consisted of much -helium, with traces of argon and some hydrogen, carbon dioxide and nitrogen; the last three gases were removed by sparking with oxygen over potassium hydroxide solution. The density of helium was found to be not greater than 2*13, and the ratio of its specific heats (1*65) showed that helium resembles argon in being monatomic; the atomic weight was thus stated to be not more than 4*26 (Ramsay, Collie and Travers, J.C.S. 1895, 67, 684). The D_3 line in the spectrum of terrestrial helium was afterwards found to be a doublet (Runge, Nature, 1895, 52, 128), and its identity with solar " helium " was doubted, but the solar D_3 line was also found to be double (Lockyer and Hale, *ibid.,* p. 327; Proc. Roy. Soc. 1896, 59, 4) and the identity of the elements was thus established. A number of workers have doubted the elementary nature of helium on account of the complexity of its spectrum, but all attempts to separate the gas into two or more constituents have failed (*see* Ramsay and Travers, *ibid,* 1898, **62,** 316).

Helium was first detected in the atmosphere by Kayser (Chen^ News, 1895, *72,* 89), who observed its lines in the spectrum of crude argon preparations obtained from air. The production of helium during disintegration of radio-active elements, which explains its presence in uranium minerals, was discovered by Soddy in 1903.

For an account and bibliography of the early investigations on helium, *see* Ramsay, Ann. China. 1898, [vii], **18,** 433, and Travers, "JKie Discovery of the Rare Gases," London, 1928.

OCCURRENCE.

In the 8*n, Stars and Nebulae.—Helium **has** been detected spectroscopically in the chromosphere of the sun, in which it also occurs in an ionised form, and in protuberances and sunspots (c/. Pringsheim, " Vorlesungen tiber die Physik der Sonne," Leipzig. 1910). Helium is also present in nebulae, the.planetary " mist," fixed stars, and *novae,* or stars of recent origin. The occurrence of helium is related to the temperature of the star (Lockyer, Proc. Roy. Soc. 1897, **61,** 148). The spectra of *novae* contain helium absorption lines displaced towards the violet, showing that the gas is in radial movement towards the observer and away from the stars (Eddington, " Expanding Universe," 1933, p.- 11). Helium is present to the extent of 0-23-36 x $10^{\wedge e}$ c.c. per g. in certai.i specimens of meteoric iron, from which it is liberated by dissolution in acid (Paneth *et ol.,* Z. Elektrochem, 1928, **34,** 645, 648; Z. physikal. Chem. 1931, **152,** 127). The rôle of helium in the evolution of the universe and development of stars of various types is discussed by Saha (Phil. Mae. 1920, [vi], **40,** 472; 1921, [vi], **41,** 267, 809; Proc. *Roy.* Soc. 1921, A, 99, 135; Z. Physik, 1921, 6, 40).

In the Earth's Atmosphere.—Numerous **workers** have shown the existence of small amounts of helium in the atmosphere, of which it forms about 0-0005% by volume, or 000007% by weight (Claude, Compt. rend. 1909, **148,** 1454; Watson, 'J.C.S. 1910, 97, 810). It has been claimed that the helium content of air should increase in the upper layers of the atmosphere; Paneth and Glückauf (Nature, 1935, **136,** 717) have found that the helium content is constant up to an altitude of about 18 km., but is increased by 8% at 21 km. According to one theory^ the atmosphere should consist almost entirely of hydrogen and helium at altitudes greater than about 100 km., the content of helium falling with increasing height (Jeans, "Dynamical Theory of Gases," Cambridge, 1925). Convincing evidence in favour of such theories appears to be lacking.

In Volcanic Oases, Hot Spring Gases, etc.— Small percentages of helium are of frequent occurrence in gases of volcanic origin. The proportion of helium and the yield of gas vary between very wide limits in different regions, and rich helium sources are usually localised. A number of hot springs yielding gases rich in helium are grouped round a line drawn through the French towns of Moulina, Dijon and Vesoul, Details of some of the more prolific French springs are tabulated below; the figures are taken from Mottreu and Lepape, Compt, rend. 1012, 155, 167; *see also* Moureu, J.C.S. 1923, 123, 1913. •

Location and name \M spring*	Percentage or [illegible] In gas.	Yield ID litres-per / m i	
		Total gas. *	Helium,
Santenay (C6te d'Or):			
Source Lithium	lii-lti	51,000	5,182
Source Carnot .	9- 97	179,-^0	17,845
Source Fontaine-SalSe. . .	8-40	^_,	—
Maizieres (C6te d'Or):			
Source Romaine	5-9,2	18,250	1,080
Griay (Sa6ne-et-Loire):			
Source d'Ys.	2-18	—	—
Bourbon Lancy (Saone - et - Loire) t			
Source du Lyrnbe	1-84	347,500	10,074
Ncris (Allier):			
Source Cisar .	0-97	3,504,000	33,090
La Bourboule (Puy » de - D6me):			
Source Choussy	•001	30,484,800	3,04$

The helium content of 8-10% recorded at Santenay are very exceptional. Many other French springs liberate helium-bearing gas, but the helium contents fluctuate considerably. The neighbouring European countries also possess springs yielding helium, bttt the quantities are generally much smaller. The King's Well, Bath, England, gives a gaa containing about 015% of helium, but the annual yield is small. A few German spring gaaes *(e.g.* from Baden-Baden and Wildbaaj contain about 1% of helium (c/. Sievelting and Lautenschlager, Physikal. Z. 1912,13,1043). According to Von An*;erer and Funk <Z. physikal. Chem. 1933, B, 20, 368) a spring at Diirkheim is the only German source which yields a gaa comparable in helium content with American natural gas, *i.e.* containing 1-2% of helium. The famous *soffioni* of Tuac%ny contain Bdme helium *(e.g.* 00155% of helium in gas from Larderello). Gases containing 0-002-0-0146% are obtained from natural sources in Iceland. New Zealand natural gases almost always contain some helium (Farr and Rogers, New Zealand J. &d Tech. 1929, 10, 300). Details of many other sources are given by Moureu, J.C.S. 1923, **123,** 1905, and in Abegg's '" Handbuch der tinorganischen Chemie," Vol.IV, Section 3_r Fart I (" Die Edelgase").

Xt ia generally **accepted** that naturally occurring helium has been produced by radioactive disintegration, but the quantities available over small areas indicate that the supplies are being drawn from gas which has accumulated **during** past ages, and not from continuous radioactive sources. Prolific helium sources occur where local conditions have favoured the accumulation of the gas in underlying strata. It is estimated that the earth's cruBt contains radioactive material equivalent to about 2-4 x 10^{M} g. of uranium, which would produce approximately 2 x 10^{T} cu. m. of helium per year. If this estimate is correct considerable quantities of helium have been lost from the earth during geological time, possibly by diffusion into space. Interesting regularities in the composition of helium-bearing gages have been noted; the helium content of hot-spring gases is usually small if they contain a large proportion of carbon dioxide. Lepape (Compt. rend. 1935, 200, 163, 336) has observed that gaaes rich in helium are associated with springs yielding larger quantities of lithium Raits, and that sources very rich in helium also yield rubidium and caesium salts; it is suggested that the helium has resulted from the radioactive decomposition of demerit 87, the alkali-metal which still remains to be isolated.

In ? Deposits Associated with Hydrocarbons; Natural Gas.—Gases from mineral springs contain a very largo proportion of nitrogen, or, less frequently, carbon dioxide. The " natnraj gas " occurring in the United States and elsewhere is of a different type, and contains large amounts of methane, ethane and other hydrocarbons. The natural-gas, sources are " dry " wells, and the deposits are usually associated with petroleum. The presAice of helium in American natural gas was discovered by Cady and McFarland (J. Amer. Chem. Soc. 1907, 29, 1523; *see also* hid. Kng. Chem. 1938, 30, 845), who found helium contents of up to 1-48% in specimens of gas from various localities. The natural gas wells in the United States now form **thanrincnMd** commercial source of helium. The helium-rich wells occur chiefly in the States of Kansas, Oklahoma and Texas, with less important regions in Ohio, Montana and California, Typical analyses of natural gas are given in the table on Hhe next page; the figures are due to Moore {J. Franklin Inst. 1921, **191,** Mil; Ind. Eng. Chem. 1926,18, 198) *{see oho* C*dy and McFarland, *I.e.).*

The amount of helium liberated from United States gas wells has been estimated at 18 million cu.m. per year (Moore, *I.e.)*; the total quantity available is assessed at some thousand million cu.m. As remarked above, such large supplies can only be due to accumulation of helium under favourable geological conditions during past ages.. Although the helium vellrf are located in oil-bearing region a, it is noteworthy that " mixed " sources of helium and oil are rare, the helium wells being completely dry. In the famous Fetcolia field, which has supplied lsrge quantities of helium for commercial undertakings, the gas originates in strata 500 metres below the surface, but oil is obtained at a depth of only 100 metres.

Natural gaues containing about 0-3% of helium occur in Alberta and Ontario, Canada;

Field.	Locution.	**i'•imposition** *ofgai,* *%.*					
		N,.	**CH«.**	**CjH^etc.**	**Of**	**co$_{t}$.**	H«.
Rogers.	Cliautauqua, Kansas.	**43-68**	54-20	000	**u-s:i**	000	**1-38**
Petrolta.	Clay, Texas,	**31-li**	56-85	10-33	0-54	0-25	(MM
Pearson,	Oaage. Oklahoma.	**39-M**	59-33	000	0-45	0-00	H)03
Augusta.	Butler, Kansas.	1108	74-74	12-92	057	019	0-60
Big Bell.	Montgomery, Kansas.	21-49	7223	5-10	0 09	(MM	0-41
Gleen Mary.	Scott, Tennessee.	3-22	.ill Mi	•31-73	0 65	018	0-36
Pavilion.	Uvnesee, New York,	2-66	87-96	8-68	0-49	000	03J
Breckenridge.	Stephens, Texas.	**18-80**	76-48	19-68	012	000	0-21
Beaver Creek.	Floyd, Kentucky,	**n-:|7**	77-55	2113	0 66	016	0-13
Lanco Creok.	Niobrara, Wyoming.	**0-92**	6906	29-19	063	0-20	trace

the deposit* are probably related geographically to those in Montana, U.S. Natural gas sources yielding helium also occur in certain parts of Europe: the most prolific is at **Netmgam**me, *oust* Hamburg, where a gas containing **0*016-** 0-025% of helium is liberated, corresponding to 25,000 cu.m. of the latter gas per year (dteako, Z. anorg. Chem. 1913, 82, 249). A rich source (0-095%; 20,000 cu.m. per year) is recorded at Vaux-en-Bugey, France, and a relatively high percentage of helium is given for a well at Leaquin, near Lille (IMK4%; 1,359 cu. in. per year) *{ef.* Moureu, J.C.S. 1923,123, 1905). Clay (Proc. K. Akad. Wetenach. Amsterdam, 1925, 28, 529} records that petroleum gases from Indian sources contain 0*006-0 0033% of helium.

The ratio of helium to nitrogen in (ire-damp ia often much greater than the corresponding ratio for air, and fire-damp has been found to Contain as much as 0-05% of helium. The yearly losa of helium into the atmosphere from underground workings must bo considerable, an large volumes of gas are discharged.

In Mintrals and Racks.—Minerals which contain appreciable quantities of helium generally contain thorium or uranium, from which the helium has been produced by radioactive changes. Strutt (Proc. Roy. Soc. 1908, A, 80, 572), using very delicate moans of detection, has shown that traces of helium occur in a very wide variety of minerals. The gas occurs in solid solution or in minute cavities in the mineral, and is not chemically combined. The highest helium contents have been found in specimens -.1 ihorianite and uraninite (of which cleveite and pitchblende are particular varieties), these contain up to 0-19% {10-5 c.c. per g.) and 013-015% (7-2-8-1 etc. per g.; cleveite), respectively *(cj.* tiievcrts and Beqgncr, Bcr. 1912$_{t}$ 46, 2576 ; Uunstan and Blake, Proc. Roy. Soc 1905, A, 76, 253; Ramsay, Ann. Chim. 1898, [vii], 13^433; Abegg, *op.* cti.pp. 55-67). Monazitc, a mineral available in relatively large quantities, often contains about 1 c.c. of helium per g., and haa been used as a secondary commercial source of the gas. The quantity of helium obtained from a mineral of known uranium or thorium content haa been used to estimate the geological age of the mineral, as a given mass of uranium or thorium produces a fixed volume of helium per year by radioactive disintegration. The ages obtained by* this method vary from 100,000 years for more recent strata to 600 million years for rocks of the lower pre-Cambrian period (Lawson, Naturwias. 1917, 5, 429, 452). The ages obtained by the helium method are less than those derived from determinations on lead iuotopes, suggesting that partial loss of the helium has occurred.

PREPARATION.

In the Laboratory.—Helium may no obtained from the minerals named %bove by heating with dilute sulphuric acid, fusion with alkali, alkali hydrogen sulphate, pyrosulphate or dichromate, or by heating the mineral in a vacuum. The last-named process is the simplest, but & tarn* perature of 1,000-1,200° ia necessary if the maximum yield of helium is to bo obtained ; about 50% of the gas available in the mineral is evolved on heating to a red heat in a hard-glass tube (Wood, Proc. ttoy. **Soc.** 1910, A, 84, 70). A larger but still not quantitative yield is given *by* the fusion process, which is comparatively rapid: a hard-glass tube about a metre long is charged v^th successive layers of magnesium carbonate (10 cm.), a mixture *at* 3 parts by weight of finely pondered cleveite and 2 parts of potassium pyrosulphate (Travera used equal weights of the powdered mineral and potassium hydrogen sulphate), kept in position with an asbestos plug, copper oxide, powdered mag. neuium and pbuapltorun pentoxide. When the tube is*heatcd in a suitable furnace the magnesium carbonate produces a stream of carbon dioxide, in which the helium is carried off and collected over potassium hydroxide solution *(cf* **Longlet,** *Z.* nnorg. Chera. 1895, 10, 289). Tho fusion method often gives trouble in practice owing to frothing and breakage of the tube The most convenient method is to decompose the mineral completely with -sulphuric acid Ewers (Ann. Phya. 1905, [iv], 17, 797) gives the following details of the extraction process - 150 g. of finely powdered cleveite are mixed to a paste with water in a 500 c.c. flask. Air in the flask is displaced with a current of carbon dioxide, and 225 c.c. of concentrated sulphuric acid are added through a dropping funnel. The helium evolved is removed by a slow stream of carbon dioxide, and collected over potassium hydroxide solution. Cleveite is a fairly cheap laboratory source' of helium, as 1 kg. of the mineral should yield up to 8 litres of the gas. A much commoner mineral which contains workable quantities of helium is monazite,Jarge supplies of which are used in the extraction of cerium, thorium and rare-earth metals; monazite affords up to a litre of helium per kilogram, and the gas is extracted by heating to 1,000°. The Auer-Gesellschaft have marketed crude (75%) helium obtained by this method as a by-product of gas-mantle manufacture.

Minerals liberate helium slowly in a vacuum at room temperature, and a small proportion is evolved on powdering the mineral; Gray (Proc. Roy. So*. 1909, A, 82, 301) recovered 28% of the available helium in thorianite by powdering to a particle diameter of 3/x., but a further reduction in size gave no additional yield.

Helium may also be isolated from the rare-gas mixture obtained from atmospheric nitrogen by passing it over heated magnesium (Ramsay and Travers, *ibid.* 1899, 64, 183) or a heated mixture of magnesium and quicklime (Maquenne, Compt. rend. 1895, **121,** 1147), but the process is very laborious and the yield is at most 1 litre of helium from 200,000 litres of air. The residues obtained commercially from the fractional distillation of liquid air are, however, a practical source of helium *(see below).* Mineral springs have also been made to yield small quantities of helium for laboratory use; Ramsay obtained it from King's Well, Bath (Proc. Roy. Soc. 189$ 59, 198).

The purification of the crude helium obtained by any of the above methods is conveniently effected by fractional adsorption; as the other inert gases with which helium is associated are also inert chemically, no chemical purification method is applicable. The crude gas is introduced into an evacuated tube containing adsorbent charcoal, which is cooled in liquid air; all the inert gases except helium and neon then condense, and the helium-neon mixture can be pumped off. The vapour pressure of neon is so much less than that of helium at liquid air temperatures that a systematic repetition of the process gives fairly pure helium (Ramsay, *ibid.* 1905, A, 76, 111; Watson, J.C.S. 1910, 97, 812). The adsorption process can be rendered continuous (Edwards and Elworthy, Trans. Roy. Soc. Canada, 1919, 13, III, 47). According to Peters (Z. physikal. Chem. 1937, *A** **180,** 41), the adsorptive separation of neon and helium on charcoal can be completed by cooling to -225°. Fused quartz at 1,000-1,200° is permeable to helium, and if a heated quartz tube is surrounded with the impure gas, pure helium can be pumped from the interior of the tube. The conditions necessary for a sharp separation appear to be somewhat critical; Watson *(l.c.)* records that the process is not successful with all kinds of fused quartz. Paneth and Peters *[ibid.* 1928, B, 1, 253) have effected a complete separation of helium from neon by a similar process of diffusion through hot glass; they also record that palladium is permeable to hydrogen but not to helium, affording a simple method of separation for these two gases.

On the Commercial Scale.—The principal commercial source of helium to-day is the plant set up by the United States Government at Amarillo, Texas, for the extraction of helium from natural gas. The use of helium on a commercial scale, and for airships, has only been possible since the vast resources of the American natural-gas wells have been utilised. The natural gas used at Amarillo is collected at a pressure of 700 lb. per sq. in. on the neighbouring Cliff side field; it contains about 1*75% of helium. Traces of carbon dioxide are first removed by treating the gas with sodium hydroxide solution in large towers; this process is important as carbon dioxide solidifies and chokes up the liquefaction apparatus if it is allowed to remain in the gas. The natural gas is then cooled to —185° under 300 lb. pressure, when all the constituent gases liquefy except helium and some nitrogen, which are pumped away; the liquid residue is allowed to vaporise and cool the incoming natural gas, and is then sold as a by-product for heating purposes. The crude gas containing about 50% of helium is purified by a similar liquefaction process under 2,500 lb. pressure, which gives 98% pure helium; this second, high pressure stage is carried out separately from the main bulk of natural gas in order to avoid loss of helium in the liquefied residues, in which it is appreciably soluble. The purified helium is charged directly into cylinders at a pressure of 2,000 lb. per sq. in. The operating costs of the process in 1938 totalled $12 per 1,000 cu. ft., or $9 if allowance is made for the sale of by-product gas; it is stated that the costs could be reduced to S0 by intensive production. The production of helium in the U.S.A. is now a Government monopoly. For further details, *see* Seibel, Ind. Eng. Chem. 1938, 30, 848.

Attempts to produce helium from natural gas on a commercial scale have also been made at Calgary, Alberta, using a process of cooling similar to that described above with a final purification by adsorption of impurities on charcoal (McLennan, J.C.S. 1920, **117,** 923; Edwards and Elworthy, Proc. Roy. Soc. Canada, 1919,13, III, 47 ; Lang, *ibid.* 1923,**17,** III, 181; McLennan and Shrum, *ibid.* 1922, 16, III, 181; 1923, **17,** III, 21). The distribution and production of helium in Canada are discussed by Rosewarne and Offord, Canada Dept. Mines Publ. 1932, No. 727, 42. Attempts were also made during the War of 1914-18 to obtain supplies of helium from the *soffioni* in Tuscany (Porlezza, Giorn. Chim. ind. appl. 1920, 2, G38, 087).

The separation of appreciable quantities of helium from air is difficult, as the content by volume is only about 1 part in 200,000. Owing to their low boiling points helium, neon and hydrogen are the last constituents of the atmosphere to condense on cooling. Dewar (Proc. Roy. Inst. 1903,**17,** 223) has obtained a gas containing 50% of helium and neon by a condensation process working at normal pressures, using liquid hydrogen; this is impracticable on the commercial scale. Claude (Compt. rend. 1908,**147,**

024) obtained a similar mixture, containing about 50% of helium and neon with 50% of nitrogen, as an mu-ondcnsable residue from a liquid-air plant. Regular supplies of this crude gas win be obtained from liquid-air rectification plants, which are a valuable source of the rare gases; a-Claude plant produces some 20 litres of helium and neojn per 1,000 cu.ro. of air liquefied, small losses occurring through the solubility of helium in liquid nitrogen and oxygen. After removal oi t he nitrogen the heliura-neon mixture contains about 25% of the former gas. The separation of helium and neon is particularly difficult on a large scale; for further details of the methods used, which have been described briefly above, *see* Ramsay and Travers, I'hil. Trans. 1001, A, **197,** 47; Crommelin. Comm. Leiden, No. 102c (iy23); Rec. trav. cbim. 1923, 42, 814; Meissner, Naturwiss. 1925, 13, 695. Natural gas is free from neon, so that pure helium can ho obtained from this source without the difficult separation from neon, which is inevitable if the gases are obtained from the atmosphere.

PHYSICAL PROPERTIES OF HELIUM.

Helium is a colourless gas with a *demity* of 0-17340 g. per litre at N.T.P., or 008023 g. per litre at 0°C. and 380 mm. (Baxter and Starkweather, Proc. Nat. Acad. Set 1920, 12, 20), giving *& gram-molecular volume* of 22-410 litres at N.T.P., in agreement with the results of other investigators. The *molecular weight* derived from the density data is 4-000, but as the gas is monatomic the accepted atomic weight gives the value 4003. *Isotherms* of*helium have been plotted by Onnes *et al.* at temperatures between -270° and 20° (Comm. Leiden, Nos. **164** (1923), 105c, 170a, 1706 (1924), and 176fc (1925); Abegg, op. **eft.** p. 376), Holborn and Otto (-258° to 400°) (Z. Physik, 1025, 33, 1 ; 1926, _88, 350), Wiebe, Gaddy and Heins (-70° to "200°, with pressures up to 1,000 atm.) (J. Amer. Chem^Sor. 1931,53, 1721), and by other workers over smaller temperature ranges. Onnes repreaents'fhe iBOtherms by an equation of the type:

$$pv=A+\frac{B}{v}+\frac{C}{v^2}+\frac{D}{v^4}+\frac{E}{v^6}+\frac{F}{v^8}$$

where the " virial coefficients " A-F are const;mt at each temperature; in practice only A, B and C need be considered, the remaining terms being negligible. Values of these constants are given below :

Temp., °C.	*A.*	BxlO^3.	CxlO*.
0-00	0-99970	0-512	0-12
20-00	1-0J273	0-534	013
10035	I-3C0C7	.0073	016

(*p* is in atmospheres, and)' in multiples of the sp»-<-inc volume at N.T.P.). An equation of state used by Holborn and Otto, and Wiebo, Gaddy and Hcins is of the type :

$$pv=A'+B'p+C'p^2+D'p^3+E'p^4$$

The latter authors give the following values of A', JJ' and C, expressing *pv* in Amagat units, *i.e.* values of the ratio *pvjp$_9$v$_a$,* where *p$_0$* and t'$_o$ are the pressure and volume at N.T.P. :

Temp., "('•.	A'.	B' x 10*.	C> ID^8.
-70	0-7438	5-322	4-332
-35	0-8721	5-29(3	4-33(i
0	1-00059	5-217	3-876
50	1 18480	51043	3-5308
100	1-3004	5-0442	3-4889.
200	1-73284	4-7795	2-2518

As before, *D'* and E' are negligible. Jaeyna, Derewjankin, Obnorsky and Parfentiev (Bull. Acad. Polonais£, 1934, A, 379) state that the following equation represents the behaviour *of helium at —150° to 500° with considerable accuracy:

$$pv=RT-ap\{10T-T_0(1-11e^{bp/KT})\},$$

the constants having the following* values; *a,* -1085 x 10-" ; *b,* **-6*86** X 10"* j T$_o$, 273-22°; K, 211-82; the units are metres and kilograms. The *fundamental coefficient of the normal helium Uiermomeler,* which determines the change of pressure of a quantity of helium on varying the temperature at constant volume, is 0-0036607 (Kcesom, van der Horst and Taconia, Physica, 1JW4,1. 324).

The *viscosity coejficimt* of helium at 20° is HH1 x I0-* (Trautz and Binkele. Ann. Physik, 1930, [v], 5, 5(il; values are given for temperatures up to 200°). The variation of viscosity with temperature is given by :

$$\eta_1/\eta_2=(T_1/T_2)^{0{\cdot}66},$$

Vhere η_1 and η_2 art- the viscosities at the absolute temperatures *T$_1$* and T$_2$. Data for lower temperatures are given by van Itterbeek and Keesom (Physica, 1938, 6, 257). The viscosity of helium is independent of pressure except at pressures below abou£ 2 mm.

According to Scheel and Heuse (Ann. Physik, 1913, (iv], 40, **473)** the *specific heat* of helium at constant pressure is 5040 g.-cal. per g.-mol. at 18°, and 4-980 at -180°; the ratio of the specific heats *(y)* is calculated to be 1-6G0, confirming that the gas is monatomic. Keesom and van fcterbeek find that the *velocity of sound* in helium gas at —1S2-9^a is 5591 metres per see., giving y=l-6ftl at this temperature (Proc. K. Ak«d. Wetenseh. Amsterdam, 1930, 33, 440; 1931, M, 204). The *thermal conductivity* of helium at 0^D is 0-0003365 g.-cal. per sq. cm. per sec. per °C. (Eucken,.Physikal. *Z.* 1913, 14, 324).; this value is for normal pressures, at which*the variation of heat conductivity with pressure is negligible.

The *refractive index* of helium for the wavelength of the green mercury line (A 5461 A.) hi 1-00003489 (Cuthbertson and Cuthbertson, Prou. Roy. Soc. 1932, A, 135, 40; dispersion data are also given).

Helium is diamagnetie; its *volume susceptibility* is -0-780 xlO-^{10} at N.T.P. (Hector, Physical Rev. 1924, [ii], 24, **418).**

The *dielectric constant* of helium at N.T.P. is 10O0O68 (Hocliheim, Verh. deut. physikal. Ges. 1908, Lii], 10, 446).

The arc *spectrum* of helium contains two series of lines, the " orthohelium" and " parahelium " series; the discharge in a Gcisslcr tube with a. gas pressure of 3-5 mm. is orange-yellow in colour, and the orthohelium lines predominate. If the pressure is reduced or the discharge intensified the colour becomes greenish, the' change corresponding with intensification of the paraholium lines; the wave-lengths of the principal lines in both series are given below {the wavelengths are in Angstrom units; the ortho- and para-helium series are denoted by 0 and P, respectively).

3888-64 0
39G4-7:; I^1
4026-19 0
4120-81 0
4387!):i I^1
1171-48 0
471315 O
4921-93 P
5015-68 P
5875-63 O
6678-15 P
7065-20 «
7281-35 I'

(Kayser, " Tabelle der Hauptlinien der Elemente,*' Berlin, 1026). A strong condensed discharge gives the so-calfed " spark " spectrum of helium (c/. Lyman. Nature, 1924. **113,** 785; Astrophys. J. J924, 60, 1).

Reference has been made above to the *diffusion* of helium through quartz glass at high temperatures. The results of numerous studies of the diffusion of helium through solids are somewhat inconclusive. The rate of diffusion through fused quartz at temperatures between —7u° and 562° ia approximately proportional to the pressure, a$d inversely proportional to the thickness of the quartz diaphragm (Braaten and Clark, J. Amer, Cheffn. Soc. 193.% 57, 2714^ Lord Rayleigh (Nature, 1935, 135, 30, 993; Proc. Roy. Soc. 1936, A, 156, 350) records **that** helium nasaes freely through celluloid, gelatin and " *cellophane* " at room temperature; the gas is said to pass between constituent crystals of the solid. Single crystals of quartz and other substances are impermeable or only slightly permeable to helium. Lor4 Rayleigh supports the view that the transmission of helium through vitreous quartz, boron trioxide, etc., is due to crcepage of the gas molecules along sub-microscopic channels in the structure; addition of alkali to the glass closes the channeta at room temperature and prevents diffusion of the. gas. Taylor and Rast conclude, however, that diffusion of helium through Pyrex 'glass is governed by chemical factors {J. Chem. Physics, 1938,6,612).

The Ostwald coefficients for the *solubility* of helium in water are as follows :

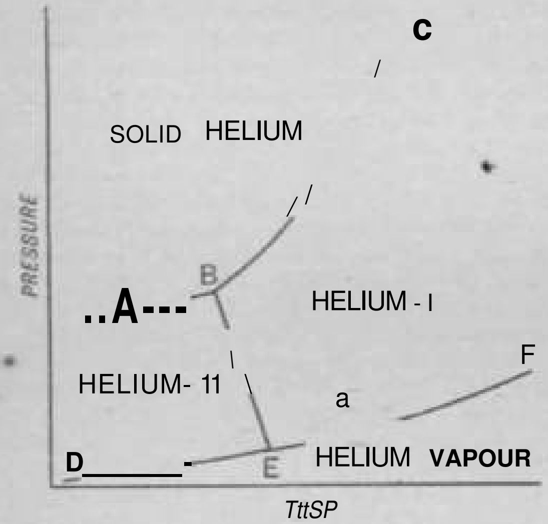
Temperature	0°	10^s	20°	30°C.
Ostwald coeff.	000955	00093	0-0091	00090

(The corresponding Bunsen coefficients are 0-00955, 0-00895, 0-0085 and 0-0081, respectively) (c/. Cady, Elsey and Berger, J. Amur. Chem. Soc. 1922, 44, 1456", and a correction by Valentiner, Z. Physik, 1930, 61. 563). Wiebe and Gaddy (J. Amcr. Chem. Soc. 1935, 57, 847) have determined the solubility in water at 0-75°,' with gaa pressures up to 1,000 atmospheres.

Critical Constants of Helium; Liquefaction of Helium.—The critical temperature of helium is —268-0° *(5-V* abs.), and the critical pressure is 2-3 atmospheres. At normal temperatures the Joule-Thompson effect **for** helium (for measurements, *see* Roebuck and Osterbci-g, Physical Rev. 1933, [ii], 43, (ill) in opposite in sign to that for most gases, and helium is heated on expansion through a jet or porous plug; the usual methods of cooling used in gas liquefiers *(cf.* LIQUEFACTION OF GASES) cannot be applied for this reason. In addition, the critical temperature is extremely low, so that helium cannot be liquefied by application of pressure at any readily available temperature. In 1908 Onncs found that the Joule-Thompson effect for helium was reversed by cooling the gaa in solid hydrogen, and was able- to use the effect to produce further cooling, and eventually Liquefaction of the helium (Coinpt. rend. **1908,** 147, 421 ; Proc. K. Akad. Wetensch, Amsterdam, 1909,11, 08). An apparatus for the continuous production of liquid helium is described by Onnes (Versl. Akad. Amsterdam, **1920,** 35, 862; Proc. K. Akad. Wetensch. Amsterdam, 1926, 29, 1176). Cooling is effected on tlir cascade principle, temperatures of—85°, -150°, —183° and —253° being reiuhcd by evaporation of liquefied methyl chloride, ethylene, oxygen and hydrogen, respectively, in successive cycles, **Tho** helium is compressed to 30 atm, pressure, cooled to -253°, and expanded through a jet; tlii.s process, proceeding continuously, ultimately causes liquefaction of the helium. For descriptions of other liquid-helium **plants,** see Linde*munn mid Kcekiy, Nature, 1933, 131, 191, and Kapitza, Proc. Roy. Soc. 1934, A, 147, 189. Kapitza's apparatus does not require liquid hydrogen for its operation. Prc-cooling with liquid nitrogen is found to suffice, further cooling of the helium to about 10° abs. being produced by a small expansion engine incorporated in the apparatus; the final liquefaction depends on the Joule-Thompson effect. The apparatus prodaces liquid helium 1{ hours after starting, and the output is 2 litres per hour, with a **Hqmd** nitrogen consumption of 1£ litres per litre of liquid helium.

The *boiling point* of liquid helium under 760 mm. pressure is 4-216° abs. (Schmidt and Keesom, Physica, 1937, 4, 9G3). Data for the *vapour pressure* over the range 0-760 mm! are given by the same authors *(ibid. IM7,* 4, 971). The *density* of liquid helium at the normal boiling-point is 0-122 g. per c.c, giving a *molecular volume* of 31-9 c.c, Tho *compressibility,* 7 to 8 x $10^{\sim a}$ sq. cm. per kg., is the highest of any known liquid (Kecsom and Ctusius, Proc. K Akad. Wetensch, Amsterdam, 1332, 36, **820).** The *latent heat of vaporisation* has a broad maximum in thS neighbourhood of 3° (approx. 5-6 g.-cal. per g.}, and falls rapidly at higher temperatures (Dana and Onnjjs, *ibid.* 1926, 29, 1051;" Van Laar, *ibid,* 1920, 29, 1017).

Liquid helium is one of the most remarkable substances known to ehemists; it exists in **two** distinct forms, known as helium-land hdium-ll. The relationships between these two liquid **fonna** and the vapour and solid are illustrated iliagrammatically in the curve below, which is not to scale. Liquid helium exists as helium-I at normal pressures; the liquid, which can be kept for short periods in a good Dewar vessel, is almost invisible, but the surface has a similar appearance to a sheet of mica by reflected light. Slow boiling produces a stream of bubbles of helium vapour rising through the liquid. If the pressure over the liquid is reduced to a point in the curve DE immediate transformation to helinm-II takes place; tho only visible evidence of a change is the sudden cessation of the stream of bubbles as the point E is passed. The point E, commonly known as the A-point, is the triple point at which helium-I, helium-II and the vapour coexist in equilibrium ; it corresponds with *n,* temperature of 2-18H° abs. and a vapour pressure of 3-83 cm. (Schmidt and Keesom, **Phyufca,** 1937, 4, 971). The line EB (tho " A-line ") represents the variation of the A-point



with ch&atm of pressure. The A-point corresponds with a sharp maximum in the specific heat otlifjuicl helium (Keesom and Clusjua, Proe. X. **Akad,** Wctcnseh. Amsterdam, 1932, 35, 307), but there is apparently no latent heat associated with the transition between the two forms. Tin: density of the liquid at various pressures reaches a maximum value along the A-line (**Keesom** and Keesom, Physiea, 1933-34,1, 128). The viscosity falls rapidly bclnw the A-point, ami tfie viscosity of helium. 11 at low temperatures is remarkably low *(e.g.* 1 -24 micropoises at 1-304" ahs.; water at 20° has a viscosity of about 10,000 micropoiscs) (IT/. Keesora and llaewood, Physica, 1938, 5, 737). The thermal **conductivity** of liquid helium also shows a remarkable change at the A-point; it rises from 6x1O-^{B} g.-cal. per sq. cm. per see. per °C. at 3-3* abs. (helium-I) to K0 (same units) at 1-4-1-75^{0} abs. (helium-II). Helium-II is by far thg best conductor of heat yet discovered. Hclium-Il also has remarkable capillary properties ; it forms a film about 5 x 10~^{B} em. tfeick on Lwiiy solid with which it comes **into** contact, and Uie liquid is **tnuu&md** through this film to the lowest **available level** (Daunt and Mondelssohn, Nature. 1938, **141,** 911; **142,** 475). No discontinuity occurs iu the surface tension of liquid helium at tho A-point (Allen and Misener, Proe. Camb. Phil. Soc. 1938, **34,** 299), and the molecular refractions of the two liquid forms are equal (Johns and Wilhelm, Canad. J. Rea. 1938, A, 16, 131). Debye-Scherrer Jf-ray diagrams of helium-I and ,-II have been obtained by Keesom and Taconis (Physica, 1938, 5, 270), who consider that the latter has a partly ordered lattice structure based on a face-centred cubic arrangement, but with half the atoms missing, leaving channels in the structure. The* degree of order in the structure of helium.II ig thus less than that in the solid, but greater than that in helium-I.

The portions DE and EF of the CURVES represent the vapour pressures of helium-II and -I, respectively. These, vapour pressures (p, in cm.) are given by the following equations:

Helium-I:

$\log_{10}p$=1-217-3-024/T+2-208 logftT.

Helium-II:

$\log_{10}p$=2-035-3-859/T+0-922$\log_{10}$T.

(Keesom *et al.,* Pro*e. K. Akad. Wetensch. Amsterdam, 1929, **32,** 864, 1314). The point B represents the triple point for *solid helium,* helium-I, and helium-II, at 1-753^{D} abs. and 29-91 atra. pressure. Solid helium is obtained only by compression of one of the liquid forms; the solid, liquid and vapour cannot coexist in equilibrium. Solidification of helium is accompanied by little change in appearance, and is detected experimentally by the freezing up of a mechanical stirrcr. Even at the absolute zero of temperature, solid-helium would not be stable at pressures less than abfiut 25 atm. (Keesom, Physica. 1934, 1, 128, 161; Kaischew and Simon, Nature, **1034, 133.** 400; Simon, ***ibid,*** 1934, **133,** 529). The density of solid helium **in** equilibrium with liquid helium-I is 0-23 at 4-0° and 0-22 at 3-6° abs,; the heat of fusion is G-75 g.-cal. per g.-atom at 4-0°, and 5-1 g.-cal. at 3-4° abs. (Kaischew and Simon, *I.e.).* The melting-point curve,BC, over the range 12-42° aba., is given by the equation :

$$\log_{10}(p+17)=1{\cdot}5544\log_{10}T+1{\cdot}236\,;$$

p is expressed in kg. per sq. cm. (Simon, Ruheroann and" Edwards, Z. phyaikal. Chem. 1929, H, 2. 340; 6, 62). According fit Keeaom and Taconis (Proc, K. Aliad. Wetensch. Amsterdam, 1938, 4f, 95), solid helium at 1-45° abs. and 37 atra. pressure has a hexagonal close-packed KlriK'ture ; there are two atoms in the unit cell, 3-57 A. apart, and the spacing* of the {100} and {101} planes are 3-07 and 2-75 A., respectively.

For gtneral accounts of the physics of aolid and liquid helium, *see* Satterly, Rev. Mod. Physics, 1936,8,347; Keesom, Natuurwetensch. Tijds. 1029, **11,** 65; and Burton, Smith and Wilhelm, " Phenomena at the Temperature of Liquid Helium," New York, 1940.

CHEMICAL PROPERTIES OF HELIUM.

There is little evidence for the existence of well, defined stoicheiometric compounds of helium, although a number of aolid substances of indefinite composition containing helium have been obtained, generally under the action of an electric discharge. Intense electron bombardment of helium in the neighbourhood of a tungsten filament gives a black substance which Boomer (Proc. Roy. Soc. 1925, A, 109, 198; Nature, 1925, 115, 16) considered to be a tungsten helide WHe$_2$. Boomer also found indications of the existence 6T compounds with mercury, iodine, phosphorus and sulphur. Damianovitch (c/. a review covering the question of the formation of helium compounds, Bull. Soc. chim. 1938, [v], 5, 1085, 1092, 1106) has also obtained a supposed compound of helium and platinum. There is no evidence for the formation of hydrates, or o? compounds with boron trifluoride similar to those given by argon.

HELIUM AND RADIOACTIVITY.

The a-rays produced in radioactive processes consist of the nuclei of helium acorns, which become, neutral helium atoms after regaining two electrons apiece. One gram of radium in equilibrium with its disintegration products yields 167 cu. mm. of helium per year. The production of helium in* the disintegration of radioactive elements has been confirmed experimentally in a number of cases (Abegg, *op. cit.* p. 173). The helium produced in the " artificial" nuclear reaction

^B+Jn -» jHe+jLi

has also been collected and determined by Paneth, Glückauf and Loleit (Proc. Roy. Soc. 1936, A, 157, 412).

Attempts have been made to obtain the helium isofSbpes ^{3}He and ^{6}He by artificial disintegration methods. Evidence has been obtained for the production of ^{3}He from deuterium in a mass-spectrograph (Bleakney, Harnwell, Lozier, Smith and Smyth, Physical Rev. 1934, [ii], 46, 81) and Joliot and Zlotowski (Comptf. rend. 1938, 206, 1256) state that 'He is formed with protons during a-particle bombardment of paraffin wax (jHe+jH -*gHe+}H). For a general discussion of the question, *see* Lord Rutherford, Nature, 1937,'140, 303.

DETECTION AND DETERMINATION OF HELIUM.

Helium is invariably detected by its characteristic arc spectrum *(see* above), giveft by a discharge through the gas in a Geissler tube. This method has been refined by Paneth and Peters (Z. physikal. Chem. 1928, 134, 353) to permit detection of 10''^{10} c.c. of the gas; the lines at 5875-63 and 5015-68 A. are the last to disappear from the spectrum when the quantity of helium present in the discharge is reduced.

The determination of helium in gas riixtures, in the absence of other inert gases, is carried out by volume measurement after removing all other gases by adsorption on charcoal, as in McLennan's apparatus for the determination of helium in natural gases (J.C.S. 1920, 117, 943), or by chemical means *(see,* for instance, Moureu, J. Chim. phys. 1913,11, 63). If other rare gases are present the determination is more difficult, but gases other than helium and neon can be removed by fractional adsorption (Moureu, *I.e.)* and the helium-neon mixture analysed by the method of Paneth and Urry (Mikrochem., Emich Festschrift, 1930, 233), which employs a hot-wire manometer in a Wheatstone bridge circuit. This method can be used with gas pressures as low as 6 x 10~^{6} mm. A similar method can be used for the determination of 7 x 10~^{9} to 10~^{4} c.c. of pure helium, with an error of about 1% for the larger of these volumes. Schröer (Z. anal. Chem. 1937, 111, 161) and Germann, Gagos and Neilson (Ind. Eng. Chem. [Anal.], 1934, 6, 215) have described methods for the determination of helium in gas mixtures.

USES OF HELIUM.

Large quantities of helium have been used for filling balloons and dirigibles; helium has 92% of the lifting power of hydrogen, and has the overwhelming advantage of complete non-inflammability. In addition, the loss of gas by diffusion through the envelope is smaller with helium than with hydrogen. Up to 26% of hydrogen may be mixed with the helium without producing an inflammable mixture (Satterly and Burton, Trans. Roy. Soc. Canada, 1919,13, III, 211; Ledig, J. Ind. Eng. Chem. 1920,12, 1098).

Increasing amounts of helium are now being used for medical purposes. It is of great value in certain types of respiratory obstruction, as a mixture containing 79% of helium and 21% of oxygen (corresponding with air in composition) is much easier to breathe than air, minimising muscular effort (Sykes and Lawrence, Brit. Med. J. 1938, ii, 448). Substitution of helium for the nitrogen in the air supply to divers reduces their liability to " divers^{1} bends," a complaint caused by separation of nitrogen from the blood on reduction of pressure. " Decompression " of cases of " bends " is much more rapidly effected with helium and oxygen than with air (End, Amer. J. Physiol. 1937,120, 712). Helium has also been used for pneumothorax fillings (Klin. Woch. 1938,17, 1153).

In the laboratory liquid helium is extensively used in low temperature physics. Temperatures less than 1° abs. can be reached by evaporation of the liquid under reduced pressure. Thcv helium vapour-pressure thermometer is also useful in the same field. The helium gas thermometer is the basis of the International helium scale of temperature.

Owing to the simplicity of the helium molecule, helium has been made the subject of numerous studies in molecular and atomic physics, which are outside the scope of this article; reference should be made to the Indexes of one of the Abstract Journals. A full account of the work done on the chemistry of helium up to 1927 is included in Abegg's " Handbuch der anorganiqehen Chemie," Vol. IV, Section 3, Parti, "Die Edelgase."

A J E. ^Y

" *HELLA"* **BUSKLIGHT** *(v.* Vol.'V,'486d)."

HELLANDITE. Silicate of yttrium, erbium, calcium, aluminium and manganese crystallised in the monoclinic system. One analysis showed Y$_2$O$_8$19-29, Er$_2$O$_2$15-43, Ce$_2$O$_3$101%. The crystals are prismatic in habit, and when fresh are nut-brown in colour with a resinous lustre on the conchoidal fracture. Sp.gr. 3-70; hardness 5J. The mineral is readily soluble in hydrochloric acid with evolution of chlorine, and it is fusible in the Bunsen flame. Usually, however, it is much altered to a yellow or white earthy material which is optically isotropic and contains much water. The crystals are found singly, in association with tourmaline, apatite, thorite, orthite, etc., embedded in the granite pegmatite-veins which are quarried for felspar in the neighbourhood of Kragerö in the south of Norway.

L. J. S.

HELLEBOREIN, HELLEBORIN, HELLEBRIN *(v.* Vol. II, 3876, c).

HELLEBORUS. In ancient Greek medicine *èXXepopvy* was a drug prescribed for mania. The Black Hellebore of Theophrastus (" Enquiry into Plants," trans. A. Hort, London, 1916, II, 265) has been identified by Thiselton-**Dyer as *HeUeborus cyclophyllus* Boiss., and the** Greeks' White Hellebore was considered by the same authority to have been *Veratrum album* L. The Romans (Celsus, c. A.D. 10) administered *V. album* under the name Helleborus. The confusion of *H.* species (Fam. Ranunculaceae) and *V.* species (Fam. Liliaceae) continued in later centuries *(cf.* Gerard's " Herball," 1597) until the present day. Thus Green Hellebore, *//. viridis;* Stinking Hellebore, *H. fœtidus;* and Black Hellebore, *H. niger,* have been traditional remedies in England, but none of these drugs is included in the British Pharmacopoeia, 1932. In the United States, however, Green Hellebore, a native swamp plant, *V. viride,* is official in U.S. Pharmacopoeia XI; White Hellebore is *V. album,* a closely related substitute imported from Europe but not officially recognised. The risk of confusing true Hellebores with Veratrum species is pointed out in the literature *(e.g.* Henry, " Plant Alkaloids," 3rd ed., 1939, p. 629; "Extra Pharmacopoeia," 1941, I, p. 364; B.P.C. 1934, 505).

H. niger, Christmas Rose *(v.* Vol. II, 1). For the active cardiac glycosides recently isolated, *see* Vol. II, 3876. The drug is the root and Rhizome. The powdered root is irritant and sternutatory; given internally it is strongly cathartic, and toxic, over doses have had fatal results. *H. niger* does not contain alkaloids (Keller and Schöbel, Arch. Pharm. 1927, 265, 1238). For further references, *see* J. L. L. van Rijn, " Die Glykoside," 2nd ed., Berlin, 1931, pp. 128, 132, 133; " U.S. Dispensatory," 22nd ed., 1937, p. 1406.

Helleborus viridis, Green Hellebore, Fam. Ranunculaceae, is found as a rare wild flower in England and was a traditional remedy for dropsy (Sowerby, "English Botany," 1873, Vol. I, p. 56). A continental variety contained the glycosides previously found in *H. niger* and in addition four alkaloids: *celliamine,*

$C_{11}H$[illegible]O[illegible]N,

m.p. 127-131°; *sprintillamine,* $C_{88}H_{45}O_4N$, m.p. 228-229°; *sprintilline,* $C_{26}H_{41}O_3N$, m.p. 141-142°, which are cardiac alkaloids, and *alkaloid V,* $C_{25}H_{43}O_6N$, m.p. 267-268° (Keller and Schöbel, *I.e.; ibid.* 1928, **266,** 545). The three named alkaloids are pharmacologically similar and resemble cevadine, aconitine and delphinine (Franzen, Arch. exp. Path. Pharm. 1931, **159,** 183). For a comparison of the potency of six Helleborus species, *see* Tschirch, " Handb. d. Pharmakognosie," 2nd ed., Vol. II. Berger discussed characteristics and tests for the black and green species (Scientia Pharm. 1939, 10, 83). The rhizomes of these species cannot be distinguished unless the radical leaves are still attached (Wallis and Saunders, Pharm. J. 1924, **113,** 90, 133).

H. fœtidus (Sowerby, *op. cit.),* formerly e. reputed antithelmintic. *H. orientalia* has been analysed by Sonntag and Kunlmann (Apoth.-Ztg. 1937, 52, 227 j *see also* papers in Pharm. Ztg. 1937, 82).

White Hellebore.— *Veratrum album* (Fam. Liliaceae). The drug is the dried rhizome and root of a European alpine plant; it is not official in the British Pharmacopoeia or in U.S. Pharmacopoeia XI, and is classed in Part 1 of the (British) Poisons List. *V. album* was formerly prescribed as a cardiac depressant. Its toxicity is best determined by a bio-assay,' *e.g.* on *Daphnia magna* (Viehoever and Cohen, Amer. J. Pharm. 1939, **111,** 86). The powdered drug has been used as a parasiticide. In appearance and properties *V. album* so closely resembles *V. viride* that some authors considered the drugs to be equivalent. The alkaloids of *V. album* have been studied by Wright and Luff (J.C.S. 1879, 35, 405) and by Salzberger 'Arch. Pharm. 1890, 228, 462) and recently Poethke *(ibid.* 1937, 275, 357, 571; 1938, **276,** 170; Amer. Chem. Abstr. 1939, 33, 807) has revised the existing data and described some new alkaloids. Those now known include *jervine,* $C_{2e}H_{37}O_3N$, m.p. 243°; *rubijervine,* $C_{26}H_{43}O_2N$, *n.p. 239°; ***pseudojervine,* $C_{33}H_{49}O_8N$, m.p. 304°; *proto-vfratrine,*** $C_{40}H_{f13}O_{14}N$, Sa.p. 255°; and *germerine,* $C_{36}H_{57}O_nIM$, m.p. 193°. These are crystalline, and protoveratrine is highly toxic; ***see also* Henry, *op. cit.,* p. 629.**

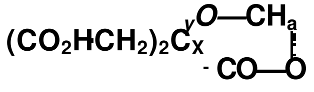
Green Hellebore, American Hellebore.— *Veratrum viride* (Fam. Liliaceae), *cf.* White Hellebore above. The drug is official in the U.S. Pharmacopoeia XI, but not in the British Pharmacopoeia; it is classed in Part 1 of the (British) Poisons List. It has been prescribed as a powerful cardiac sedative. For its standardisation, *see V. album.* It has been largely used in dilute aqueous suspension for destroying insect larvo in garbage, but its toxic properties render it dangerous for spraying vegetables. The alkaloidal consent resembles that of *V. album* but has not been so closely studied; the presence of cevadine has been reported in *V. viride* (Wright, J.C.S. 1879, 85, 422; *cf.* T. Sollman, " Pharmacology," 5th ed., Philadelphia, 1936).

J. N. G.

HELLHOFFITE *(v.* Vol. IV, 545d).

HELMINTHOSPORIIM *(v.* Vol. V, 65a).

***"HELMITOL," "formamol."* Trade name for** a compound prepared from hexamethylenetetramine by the action of anhydromethylene citrio acid,



obtained by the interaction of formaldehyde or chloromethyl alcohol and citric acid * (G.P.

129255, 150949). It is valued as a urinary antiseptic and is used in the treatment of rheumatism.

HELVITE (*v.* Vol. Ill, 547a).

HEMELLITHENOL. 3:4:5-Trimethylphenol, m.p. 81°. (Jacobsen, Ber. 1886,19,2518).

HEMICELLULOSES. The cell-walls of many plants contain polysaccharides other than ce'lnlose; certain of which have been described by the general name of " hemicellulose." The term waS suggested by E. Schulze in 1892 to embrace certain polysaccharides which he obtained from plant materials by extraction with dilute alkali. Since that time the came has been gixen to polysaccharides of the cell-wall which are soluble in alkali and hydrolysed readily by dilute acid. It is obvious that by this definition a large number of carbohydrates with no significant constitutional relationsjiip will fo included, and in practice the term is retained, only because of its convenience for referring in general to the complex mixture of polysaccharides obtained when plant material is extracted with alkali. Homogeneous products isolated from such a mixture are usually named from the C_6 or C_5 sugar they yield on hydrolysis, *e.g.* xylan from esparto gross, mannan from the ivory-nut. For convenience, these substances are described under CARBOHYDRATES, Vol. II, 287a, 303c.

The difficult task of preparing pure homogeneous specimens from hemicellulose material has been accomplished in comparatively few cases. Most workers partly purify their products by fractional precipitation (*e.g.* by acidification of the alkaline extract, and by the addition of alcohol) or by forming an insolubfy copper complex (Heuser, J. pr. Chem. 1922, [ii], 104, 261), but this process rarely yields pure products. Separation may sometimes be effected by methylation (*see* Hampton, Haworth and Hirst, J.C.S., 1929, 1739).

A brief note on the hemicelluloses isolated from the chief sources follows.

Wood.—The hemicellulogp from American white eak gives on hydrolysis d-xylose, *I*-arabinose, d-mannose and d-galactose (O'Dwyer, Biochem. J. 1923, 17, 503). English oak has also been examined by O'Dwyer (*ibid.* 1939, 33, 713; 1940, 34, 149). Two main fractions of the hemicellulose have been obtained; A, by acidification of the alkaline extract, and B, by addition of alcohol to the filtrate from this operation. " Hemicellulose A" from both the sapwood andtheheartwood contains xylose and a methyl uronic acid, but that from the sapwood contains also some 10% of glucose. " Hemicellulose B " from both sources contains xylose and * uronic acid, and that from sapwood contains glucose in addition.

Boxwood yields a product from which xylose and a uronic acid have been isolated (Preece, *ibid.*, 1931, 25, 1304). From larch wood (*Larix occidental*) an " e-galactan " has been obtained, which has been separated into a galactan and an araban (Peterson, Barry, Unkauf and Wise, J. Araer. Chem. Soc. 1940,62,2361; Hirst, Jones and Campbell, Nature, 1941,147, &5). The molecular weights of several polysaccharides from wood have been calculated by Husemann from osmotic pressure measurements (Naturwiss. 1939, 27, 595).

Straw.—From oat and rye straw hemicelluloses have been obtained which on hydrolysis yield o*-xvlose, Z-arabinose and d-galactose (Norman, Biochem. J. 1929, 23, 1353). Those from wheat straw and lucerne hay yield chiefly o*-xylose and /-arabinose (Weihe and Phillips, J. Agric. Res. 1940,60,781; Phillips and Davis, *ibid.* 1940, 60, 775).

Seeds.—*d-Xyloae,* Z-arabinose, cf-glucose and uronic acids have been found on hydrolysis of the hemicellulose from wheat bran (Norris and Preece, Biochem. J. 1930, 24, 60), and maize cobs give somewhat similar products (Preece, *ibid.* 1930,24,973; Angell and Norris, *ibid.* 1936, 30, 2155). From the shell of the ivory-nut (*Phytelephos mocrocarpa*) mannans have been isolated (Patterson, J.C.S. 1923, 1139; Klages, Annalen, 1934, 509, 159). From the peanut (*Arachis hypogsea*) a galactan and an araban have been obtained, and it appears that the structure of the latter is similar to that of the araban present in apple pomace (Hirst and Jones, J.C.S. 1938, 496; 1939, 454).

For a discussion of the many problems in this field, *see* A. G. Norman, " The Biochemistry of Cellulose, the Polyuronides, Lignin, etc," Oxford University Press, 1937. For experimental details of the methods used in these investigations and a description of the isolation of many hemicelluloses, *see* Dorée, " The Methods of Cellulose Chemistry," Chapman and Hall, 1933.

G. T. Y.

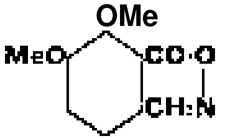
HEMIMELLITENE (*v.* Vol. Ill, 457a).

HEMIMORPmTE (or Electric Calamine). Hydrous silicate of zinc, $Zn_2H_2SiO_5$, crystallising in the orthorhombic system, and an important ore of zinc. The water is expelled only at a red heat, and the formula may be written as an acid salt or as a basic metasilicate, Zn«$(OH)_2SiO_3$, or as a basic diorthosilicate, $H_2Zn_2(ZnOH)_2(SiO_4)_2$. An important chemical character, of help in recognising the mineral, is the fact that it readily gelatinises with acids. Crystals are not uncommon, but are usually small; they are often grouped in fan-like aggregates, at the edges of which the perfect prismatic cleavage with pearly lustre may often be seen. When doubly terminated, they show a characteristic hemimorphic development, different kinds of faces being present at the two ends of the vertical axis. Connected with this polarity is the strong pyroelectric character of the crystals. The mineral also forms mamillated and stalactitic masses; or it may be massive and cavernous and cellular, being then often mixed with clayey matter or smithsonite. The colour ranges from white to yellow and brown, and is sometimes bright blue or green. Sp.gr. 3*45; hardness 4J-5. Hemimorphite usually occurs in association with zinc carbonate (smithsonite) and zinc-blende and ores of lead, often *;s veins and beds in limestone strata. Fine large crystals are found at Santa Eulalia, Chihuahua, Mexico; and the mineral has been mined as an ore at several localities, *e.g.* Cumberland, Altenberg in Rhenish Prussia, Sardinia, Santander in Spain, Hungary, Northern

Rhodesia, United States, British Columbia, etc. The ambiguous namo calamine *(q.v.)* is often applied to this mineral species.

L. J. S.

HEMIPINIC ACID, $C_{10}H_{10}O_6$ (3:4-dimethoxyphthalic acid, 3:4-dimethoxybenzene-l:2-dicarboxylic acid) is a product of oxidation of many alkaloids, *e.g.* narcotine (Wöhler, Annalen, 1844, 50, 17), berberine (Schmidt, Ber. 1883, 16, 2589). It may be prepared by warming 3:4-dimethoxy-2-methylbenzoic acid with alkaline permanganate (Perkin, J.C.S. 1916,109, 921), or by heating Liebermann's opianic acid oxime anhydride (Ber. 1886, 19, 2278),



with potassium hydroxide, acidifying and extracting with ether (Goldschmidt, Monatsh. 1888, 9, 376). The melting-point varies with the rate of heating, 177° (Perkin, J.C.S. 1889, 55, 73, 85), 186-188° (Rabe and McMillian, Annalen, 1910, 377, 239, 241). It crystallises with $2H_?O$ usually, but. also with 1 mnl. and *21* mol. of water.

Slightly soluble in cold water, but more so than opianic acid, from which it may be separated by means of its calcium salt (Rodionow and Abletzowa, Chem. Zentr. 1935, II, 685). Soluble in alcohol but sparingly soluble in ether. Heat of combustion 102-46 g.-cal. (Leroy, Compt. rend. 1900, 130, 510), K=Mx1O-^{3} at 25° (Kirpal, Monatsh. 1897, 18,- 462). The aqueous solution gives an orange-yellow precipitate with ferric chloride solution. Lead acetate gives a gelatinous precipitate soluble in excess of the reagent and reprecipitated as a dense powder on heating.

On heating at 180° for 1 hour the *anhydride* is formed (Beckett and Wright, J.C.S. 1876, 29, 173, 282). The anhydride is also obtained by the action of 4 mol. phosphorus pentachloride on the *dvcd* acid at 140° for 2 hours in sealed tubes (Freund and Horst, Ber. 1894, 27, 333). The anhydride, m.p. 166-167°, reacts with resorcinol forming dimethoxyfluorescein (Friedl, Weizmann and Wyler, J.C.S. 1907, 91, 1584).

Gentle nitration gives *6-nitrohemipinic acid,* m.p. 154-155°, and *6-nitro-2:3-diniethoxybenzoic acid,* m.p. 189° (Wegscheider and von Rušnov, Monatsh. 1908, 29, 546; Wegscheider and Klemenc, *ibid.* 1910, 31, 740), while fuming nitric acid at 60° gives, amongst other products, *5:6-dinitro-2:3~dimethoxybenzoic acid,* m.p. 196-197° (Wegscheider and Klemenc, *I.e.).*

Heating with concentrated sulphuric acid gives 1:2:5:6-tetrahydroxyanthraquinone (Liebermann and Chojnacki, Annalen, 1872, 162, 327).

*5-CMorohemipinic acid,** m.p. 168-169°, is obtained from the acid and potassium hypocfylorite in caustic potash solution. 5:6-*Dichlorohemipinic acid,* m.p. 130°, is obtained by the direct chlorination of an alkaline solution of the acid (Faitis, Wrann and Kiihas, Annalen, 1932,497,88).

For *6-amino; 6-hydroxy-, (t-chloro-* and *6-iodohemipinic acids, see* Griine, Ber. 1886, 19. 2302; Faltis and Kloibcr, Monatsh. 1929, 53/54, 620.

The acid forms many esters, both mono- and di-esters. The 2-monomethyl ester exists in two modifications; the labile form crystallises from water with 1 H_2O, m.p. 96-98°, anhydrous 121-122°; the stable form v ith 1 H_2O crystallises from ether, m.p. 98-102°, water-free crystals 138° (Wegscheider, Monatsh. 1897,18, 418, 589, 629).

Hemipinic anhydride condenses with o-cresol in the presence of $AICI_3$ to give 3:4-dimethoxy-2:2-4i(4-hydroxy-3-methylphenyl) phthalide and 3:4 - dimethoxy- 2-(2-hydroxy-3-methylbenzoyl)-benzoic acid (Jacobson and Adams, J. Amer. Chem. Soc. 1925, 47, 283).

m-Hemipini'o Acid (4:5-dimethoxybenzene-l:2-dicarboxylic acid).—Obtained by the deg;adational oxidation of alkaloids such as papaverine (Goldschmiedt. Monatsh. 1885, 6, 380) or corydalin (Dobbie and Marsden, J.C.S. 1897,71, 664), also*) by oxidation of brazilin trimethyl ether (Gilbody, Perkin and Gates, *ibid.* 1901, 79,1405) and of emetin (Windaus and Hermanns, Ber. 1914, 47, 1471; *cf.* Spath and Leithe, *ibid.* 1927.60, [B], 688)

The acid may be, prepared by the alkaline oxidation of 4:5-dimethoxy-2-methylbenzoic acid with potassium permanganate (Luff, Perkin and Robinson, J.C.S. 1910, 99, 1136), or by condensation of 3:4-dimethoxybenzoic acid with' chloral and sulphuric acid followed by reduction to 3:4-dimethoxy-6-ft8-dichloroethyl-benzoic acid, and oxidation to m-hemipinic acid with alkaline permanganate (Meldrum and Parikh, Chem. Zentr. 1935, II, 213). It may also be prepared by the oxidation of 5:6-dimethoxy-1-hydrindone with nitrictacid (Perkin and Robinson, J.C.S. 1907, 91, 1083).

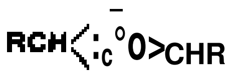
, m-Hemipinic acid crystallises with 1 and 2 mol. of water, and also in the anhydrous form ; m.p. (gradual heating) 174-175°, (more rapid heating) 179-182°; yields the *anhydride,* m.p 175°, on heating above 190°. The acid is much less soluble in water than the isomeric acid and gives a cinnabar-orange precipitate with ferric chloride and a white precipitate with silver nitrate. Nitric acid gives dinitroveratrol, and 4:5-dihydroxyphthalic acid is obtained by hydrolysis with hydriodic acid (Rossin, Monatsh. 1891, 12, 493). The acid may be identified by means of its *ethylimide,* m.p. 229-230°, and by the anhydride.

woHeVnipinic acid (3:4-dimethoxybenzene-l:5-dicarboxylic add), has been isolated from lignins (Freudenberg, Janson, Knopf, Haag and Meister, Ber. 1936, 69, 1415).

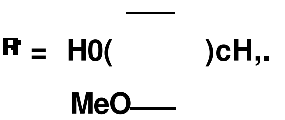
HEMISINE. Syn. for Adrenaline *(q.v.).*

HEMLOCK *{v.* Vol. Ill,324c).

HEMLOCK SPRUCE RESIN. The main constifiient of the resin, *e.g.* from *Picea exceha* and from the Japanese hemlock (Kawamura, Bull. Imp. Forestry Exp. Stat. Tokyo, 1932, No. 31, 73) is *tsugaresinol,* m.p. 235-237°, C,,$H_{i0}O_6$. Its structure is given as:'



where



HEMP (*v.* Vol. V, 162c-163c).

HEMPSEED OIL. The seeds of the hemp plant, *Cannabis saliva* L., contain about 30% of oil, of which the bulk can be removed by expression. Hemp is cultivated in most warm and temperate lands, either for the sake of the fibre or as a source of oil. The chief producers of the oil, which is mainly consumed locally, although the expressed hempseed cake appears in international trade, are China (Mancharia), Russia, France and Italy; the Russian production of 530,000 to 956,000 tons per annum over the years 1925-30 equalling that of linseed oil. The annual French production" of oil has been estimated at over 10,000 tons, whilst a similar amount has been forecast for Germany. The cultivation of hemp has also been undertaken of late years in the United States, where appreciation of the oil as a raw material for the paint and varnish industry has been steadily growing.

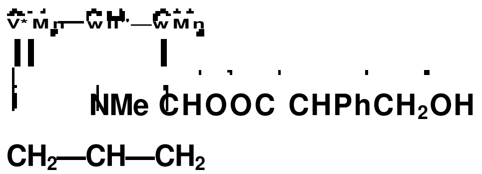
Freshly expressed hempseed oil is light green to greenish-yellow in colour, becoming brownish-yellow on keeping, and is readily refined. The chemical and physical characteristics of the oil fall within the following ranges : d* 0-925-0-933; saponification value 188-194; iodine value 140-170 (usually between 150 and 166); m.p. of fatty acids 17-21°C. Sprinkmeyer and Diedrichs (Z. Unters. Nahr.-u. Genussm. 1912,23,679) obtained 8*8% of ether-insoluble bromides by brominating the *oil* itself; Eibner (*cf.* Eibner and Wibelitz, Chem. Umschau, 1924, 31, 123) obtained only 2% of ether-insoluble bromides from the *fatty acids* of hemp oil, but Heiduschka and Zwergffl (Pharm. Zentralh. 1936, 77, 551) and Kaufmann and Juschkevitsch (Z. angew. Chem. 1930,43,90: examination of an expressed Russian oil) find 17-8% and 20-5% of insoluble (fatty acid) hexabromides, respectively.

From 4-5 to 9-5% of saturated acids has been isolated from the oil by various observers, but the composition of the remaining unsaturated acids is uncertain. Kaufmann and Juschkevitsch, using the thiocyanometric method, compute the composition of the fatty acids (iodine value 174-5) from an oil of iodine value 167 to be: saturated acids 10%,[1] oleic acid 12%, linoleic acid 53% and linolenic acid 25% (*cf.* Schestakoff and Kuptschinsky, Z. dcut. Oel-u. Fett-Ind. 1922, 42, 741). It is likely that the proportions of the unsaturated acids, and especially of linolenic acid, may vary with the climate of source or locality of the seed. Hempseed oil may be classed as a semi-drying oil, and is used, especially on the Continent, in the manufacture of green soft soap, and of boiled oils for the paint and varnish industry {*cf.* V. S. Kiselev and Charov, Maslob. Shir. Delo. 1929, No. 11, 24; Chim. et Ind. 1930, 23, 1461; Kansas City Prod. Club, Oil, Paint and Drug Rep. 1935, **128,** No. 22, 64). In Asiatic countries the oil is extensively consumed as an edible oil, some 60-65% of the total Russian production being thus used [*see* report by Tilgner and Schillak, Polish Agric. and Forest Ann. 1938, 44, No. 2/3, 437 (Amer. Chem. Abstr. 1938, 32, 8613) on the suitability of refined hempseed oil for the canning of fish] although the presence of traces of toxic or narcotic substances in the oil has occasionally been reported (*cf.* Kaufmann and Juschkevitsch, *l.e.;* T. Y. Lo, Natl. Peiping Univ. Coll. Agric, Nutrit. Bull. B. 1935, (2), 22, 57). In the United States the use of hempseed oil in the paint industry is extending, and it has also been strongly recommended as a grinding oil for paint pigments (H. Friedman, Amer. Paint. J. 1936, 20, January 13, 48). Its employment as a cosmetic oil has been suggested.

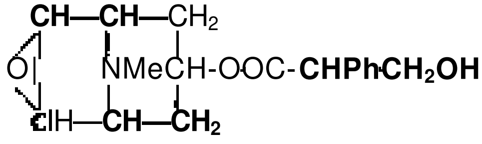
The expressed hempseed cake may be used in limited amounts as a feeding-stuff for cattle, although it is liable to contain traces of a narcotic principle (Lemcke, Seifens.-Ztg. 1907, 34, 1229); in France and Belgium the cake is used as manure.

E. L.

HENBANE, *Hyoscyamus niger* Linn. (Solanacesc), is a biennial herb, a native of Europe, North Africa and North and West Asia, and cultivated in England and elsewhere. The lower leaves vary in length up to 25 cm. and are ovate-lanceolate whilst the upper leaves are shorter, sessile and ovate-oblong: their margins are coarsely dentate and both surfaces are covered with long, soft hairs. The flowers, crowded together, arise in the axiles of large, hairy bracts, are large, funnel-shaped and dull yellow with purple veinings. The fruit is a capsule. The seeds may be separated by sieving into two fractions according to size; the smaller produce annual plants whilst the larger give rise to biennials (Holmes, Pharm. J. 1921, **106,** 249). The whole plant emits a strong, characteristic odour and possesses a bitter, acrid taste. The dried leaves and flowering tops are official in the British Pharmacopoeia, 1932, under the name of Hyoscyamus and are required to contain not less than 0-05% of the total alkaloids, calculated as *hyoscyamine,* and to comply with certain pharmacognostical standards. A liquid extract (0.045-0.055% total alkaloids), a dry extract (0-27-0-33% total alkaloids) and a tincture (0-0045-0-0055% total alkaloids) are the official preparations. Henbane contains the alkaloid hyoscyamine, the Zawo-isomer of atropine (tropyltropeine),



and smaller amounts of *hyoscine,* the 2-tropyl ester of scopinc,



together with volatile bases similar to those in belladonna leaf. The roots contain a greater proportion of alkaloids than the aerial parts of the plant. Methods of estimation of the alkaloidal content are described in the British (1932)

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[1] *I.e.* 0-5% on the oil determined by Bertram's method.

arid U.S.A. (XI) Pharmacopoeias. Critical reviews of available methods have been published by Caines and Evers (Pharm. J. 1926,117, 179; Caines, Quart. J. Pharm. 1930, 3, 344), Exler (Pharm. Weekbl. 1928, 65,1152), and Evans and Goodrich (J. Amer. Pharm. Assoc. 1933, 22,824). For pharmacological methods of assay, *see* Nolle, Arch. exp. Path. Pharm. 1929, 143, 184; Jendrassik and Will, *ibid.* 1930, **153,** 94; Fernandez, *ibid.* 1928, **127,** 197, 204; Pulewka, *ibid.* 1932, **167,** 96; Keil and Kluge, *ibid.* 1934, 174, 493; Trabucchi, Atti. Soc. med. chir. Padova, 1935, 13, 172.

W. H. L.

.HENDECOIC ACIDS (UNDECOIC ACIDS), $C_UH_{22}O_2$.

(1) w-Undecylic Acid, CH-CCHJJVCOOH, is obtained by the reduction of undecylenic acid by hydrogen and colloidal palladium (Levcne and West, J. Biol. Chem. 1914, 18, 464) or with hydrogen iodide and red phosphorus (Krafft,Ber. 1878. 11, 2219). Also by the oxidation of methyl undecyl ketone with chromic acid (Krafft, *ibid.* 1929, 12, 1667). It may be obtained by heating a-chloro- or a-brorao-myristic acid to 350° with alkali, and by the oxidation of 6:7-dihydroxvstearic acid with alkaline permanganate (Green and Hilditch, J.C.S. 1937, 764); m.p. 29-30°; b.p. 164°/15 mm., 179°/28 mm., 228°/160 mm.

Amide, m.p. 96-97°; *2-benzimldazole* derivative, m.p. 114-114-5° (Pool, Harwood and Ralston, J. Amer. Chem. Soc. 1937, 59, 178). *Acid chloride,* b.p. 123°/11 mm. (Ford-Moore and Phillips, Rec. trav. chim. 1934, [iv], 53, 15, 847). Evidence for enantioiyopism is given by the transition temperature 12-5-20° observed by Garner and Randall (J.C.S. 1924, **125,** 887) and by the different heats of crystallisation of the two forms, and the X-ray examination (de Boer, Chem. Zentr. 1927, I, 1410).

The *zinc* and *magnesium* salts find some use in cosmetics *{ibid.* 1934, II, 1215; 1936, II, 884) The *triglyceride* has also been prepared (Verkade$_x$ '/an der Lee and Meerburg,- Rec. trav. chim. 1932, 51, 13). The ethyl ester condenses with benzene in the presence of aluminium chloride to give ethyl phenylundecylate and diethyl phenyldiundecylate (Baranger, F.P. 679041; Chem. Zentr. 1930, II, 307).

(2) Methyldibutylacetic Acid,

$(CH_3CH_2CH_2CH_2)_aC(CH_3)COOH$.

Prepared by the oxidation of a-methyl-aa-dibuty lace tone with 60% nitric acid (Meerwein, Annalen, 1919,419, 148); b.p. 158-159°/18 mm. It is also obtained with other products in the oxidation of I'sotributylene. A white crystalline solid, m.p. 66-70°*, soluble in alcohol and ether, insoluble in water.-

(3) Ethylpelargonic Acid.—Prepared from 3-ipdononane and sodiomalonic ester (Bagard, Bull. Soc. chim. 1907, [iv], 1, 359) or from acnanthylmalonic ester and ethyl brtmiide (Bowden and Adkins, J. Amer. Chem. Soc. 1934, 56, 689); b.p. 117-11875-6 mm.

(4) An acid, $C_nH_{22}O_2$, is obtained by blowing air through melted paraffin for some days at 130-135° (Bergmann,Z. angew. Chem. 1918, 31, 69); m.p. 53-7°, easily soluble in ether and light petroleum, but difficultly so in alcohol.

HENDECENOIC ACID, $C_nH_{20}O_2$, an acid obtained from alkaline extracts of petroleum distillates, b.p. 250-270° (Hell and Medinger, Ber. 1874, 7, 1217 ; 187J, 10, 451). It has also been termed *pelrohumic acid.* Another hendecenoic acid is obtained by oxidising non-hydroxylated drying oils (U.S.P. 2020998). After suiphonation, or sulphonation of products of its condensation with aromatic hydrocarbons, it may be used as a substitute for Turkey Red oil.

HENEQUEN *(v.* Vol. V, 166a).

HENNA (Al-henneh, Al-henna, or All-Ken n a). The dried leaf of a small shrub indigenous in Egypt and the Levant, also known **as Egyptian privet, *Lawsonia alba, L. inermis*** and certain other species of *L.* An aqueous infusion of the leaves has long been used in the East as a prophylactic against certain skin diseases; the root is alleged to be a specific against leprosy, the flowers yield a perfume and the fruit is used as an emmenagogue. The plant is cultivated mainly, for the leaves; these are dried and powdered for use as the dye henna, which as a stain for the hair, or for colouring the finger nails and soles of the feet, has been known from the earliest times. Lai and Dutt (J. Indian Chem. Soc. 1933,10,575) describe the uses of the plant in India for a diversity of ailments.

The colouring matter of henna has been investigated by Lai and Dutt *(I.e.),* by Tommasi (Gazzetta, 1920, 50, i, 263) and by Cox (Analyst, 1938, 63, 397). The leaves contain no tannin or starch but gallic acid and *lawsone,* which has Veen shown to be identical with 2-hydroxy-l:4-naphthaquinone, m.p. 192° *;acetyl* derivative, **m.p. 128°, *monoxime,* m.p. 180°; *2-A-dinitro-*** *phenylhydrazone,* m.p. 225°. Lawsone is an acid dyestuff which dyes wool or silk a bright orange colour from an acid bath. Other colours can be obtained by use of a mordant (c/. Tommasi, *I.e.).* Air-dried henna leaves contain about 1-1-4% of 2-hydpoxynaphthaquinone which may be determined quantitatively by reduction to trihydroxynaphthalene and titration in an atmosphere of carbon dioxide as described by Cox *(l.c).* Processes have been patented for the extraction'bf lawsone from hennaJB.P. 236557, 1924). For the composition of henna hair-dyes and compounded hennas, *see* HAIR DYES (HUMAN) (this Vol., p. 170c). *See also* ALKANET and ALKANNA.

HE**PAR** SICC. Liver extract, used in the treatment of anaemia; it produces a rise in the red blood cell count and relieves the symptoms. There are more then 50 proprietary preparations The active principle against pernicious an«mia, la ^ nS 1 ^ ^ ^ 1 1 1 and West, J, Biol- <*«»! 7w-?i . 48 I 9)'appears to contain 2 substances (Wills *et al.,* Lancet, 1937, i, 311; Extra Pharmacopoeia, 1941, 566). The Minister of Health (Pharm. J. 1941, i, 24, 71) has decided that liver extracts may not be administered to persons suffering from pernicious antemia otherwise than by injection. This decision was extended to other megalocytic antemias in **"L *Tn* ^Xtf a «(Rcgulftti°n of Use Amendment Order,' 1941."**

HEPARIN. The anticoagulant substance prepared from liver and used in blood transfusion. A formula proposed is

$$C_{2a}H_{29}O_{12}(OSO_3H)_5(CO_2H)_2(NH.COCH_3),$$

Extra Pharm. 1941, 575 (*v.* ¥ol. II, 23d, 24c).

HEPTALDEHYDE, $CH_3[CH_2]_5$-CHO, ajso known commercially as *cenanthol,* b.p. 153-155°, $d^{16{\cdot}5}$ 0-825, n£° 1-415, is a synthetic^perfume with a heavy, persistent fruity effect. It should never be used in greater amount in the finished product than 0-1% or it will destroy entirely the perfume value. 5t gives a very pleasant note to most floral bouquets.

E. J. P.

HEPTOIC ACIDS, $C_7H_{14}O_2$.

(1) n-Heptoic, Acid, CEnanthylic Acid,

$$CH_3[CH_2]_5\text{-}COOH.$$

Formed by the oxidation of heptaldehyde (Organic Syntheses, 1936, 16, 39) and by the action of anhydrous potassium hydroxide at 220-230° on ?i-heptyl alcohol, ^he yield being nearly theoretical (Guerbet, Compt. rend. 1911, 153, 1489; Bull. Soc. chim. 1908, [iv], 2, 168). Also formed by the oxidation of castor oil and of oleic acid (Schorlemmer, Annalen, 1872, 161, 279; Tripier, Bull. Soc. chim. 1894, [iii], 11, 99).

An oily liquid, b.p. 222-224°; 118-119°/17 mm. Density 0-92217 (Bilterys and Gisseleire, Chem. Zentr. 1936,1, 3999). *Acid chloride,* b.p. 74-75°/l-9 gun. (Ford-Moore and Phillips, Rec. trav. chim. 1934, [iv], 53,15). *Amide,* m.p. 94-95° (Asano, Chem. Zep.tr. 1922,1,1227). It may be identified as its phenazine salt, m.p. 95-96"" (Pollard, Adelson and Bain, J. Amer. Chem. Soc. 1934, 56, 1759); for its 2-benzimidazole, m.p. 137-5-138°, *see* Pool, Harwood and Ralston, J. Amer. Chem. Soc. 1937, 59, 178.

The acid is important in perfumery and an account of its preparation from castor oil has been published, " Das Ricinusöl als wichtiges Rohprodukt für die Darstellung synthetischer Riechstoffe," Riechstoffindustrie, 1927; *see also* Riv. ital. essenze profumi, 1930, 12, 58. The zinc and magnesium salts have been used in cosmetics (F.P. 45471, Pat. Add.).

(2) woHepfoic Acid (a-methylhexoic acid), CH_3-$[CH_2]_3$-CHMe-COOI I. — Obtained by boiling hexyl cyanide with alcoholit potash (0. Hecht, Annalen, 1881, 209, 309) or bythe reduction of fructose carboxylic acid (Kiliani, Ber. 1885, 18, 3071). An oily, rancid-smelling liquid, b.p. 209-6°, d^{21} 0-9138. Completely miscible with alcohol, ether, chlorofotm and carbon disulphide. Slightly soluble in water.

(3) woAmylacetiq Acid,

$$CHMe_2\text{-}[CHJ_3\text{-}COOH.$$

Prepared by the action of sodium and *iso*-amyl iodide upon ethyl acetate (Frankland and Duppa, Annalen, 1866, 138, 338) or by the distillation of taoamylmalonic acid (Paul and Hoffmann, Ber. 1890, 23, 1498), b.p. 216° (Levene and Allen, J. Biol. Chem. 1916, 27, 442), <*" 0-9155 (Wallach, Annalen, 1915, 408, 190).

(4) Methyldiethylacetic Acid (aa-methylethylbutyric acid), C M e E t_2-C.OO H.—Obtained by prolonged heating of methyldiethylmethyl cyanide with strong hydrochloric acid (E. Schdanoff, *ibid.* 1877, 185, 120), b.p. 207-208°/753 mm. Nearly insoluble in water.

(5) j8-Methylcapronic Acid,

$$CH_3\text{-}[CH_2]_2CHMe\text{-}CH_2COOH.$$

Prepared from malonic ester and sec-amyl alcohol (Dewael and Weckering, Bull. Soc. chim. Belg. 1924, 33, 495); b.p. 212-213°/755 mm. This acid is identical with the methylhexoic acid prepared by G. Ciamician and P. Silber (Atti. R. Accad Lincei. 1908, [v], 17, 1, 185; Ber. 1908, 41, 1077; 1913, 46, 3080) from 1-methylhexan-3-one.

(6) Methyl/sopropylpropionic Acid (]8y-dimethylvaleric acid),

$$CH_3(C_3H_7)CHCH_2\text{-}COOH.$$

Obtained by heating sodium iwvalerato with sodium ethoxide in a stream of carbon monoxide (Geuther. Frölich and Looss, Annalen, 1880,202, 321); b.p. 220°.

(7) Ethylpropylacetic Acid (a-ethylvalerlc acid),^CHEtP^{a}COOH.—Obtained by hydrolysing ethyl ethylpropylacetate with alkali (H. Kiliani, Ber. 1886, 19, 227), b.p. 209-2°. The acid and its salts have been used as vulcanisation regulators (U.S.P. 1997760).

(8) Ethylisopropylacetic Acid (ay-dimethyl valeric acid), CHEtpf-COOH.—It has been reported (G.P. 441272; Chem. Zentr. 1927. I, 2137) to havetbeen obtained from methyl alcohol, carbon monoxide and hydrogen, by heating under pressure and treating the resulting oil with alkali. It may be prepared by the standard malonic ester synthesis (M. W. Burrows and W. H. Bentley, J.C.S. 1895, 67, 511); b.p. 204-205?.

HEPTYL ALCOHOL. This alcohol, $C_7H_{16}O$, and its esters are sometimes used in perfumery, and the series of esters from the formate to the valerianate have been prepared and put on the market. Their value in synthetic perfumery is mostly of a " text-book " nature, and they are not of any real importance to the perfume industry.

P. T. P.

n-HEPTYLSUCCIIMIC ACID,

$$C_7H_{15}CH(COOH)CH_aCOOH.$$

Formed by the reduction of n-hexyl-itaconic, -citraconic or -mesaconic acid with sodium amalgam (Fittig and Hoeffken, Annalen, 1899, 304, 337); m.p. 90-91°. Soluble in water and chloroform, difficultly soluble-in benzene.

*-*HERATOL"(v.* yd. I, 75a).

"HEROIN." Acetomorphine. Diacetylmorphine, used as a sedative.

HERBACETIN, HERBACITRIN- *(v.* Vol. III, 407a).

HEVICYNITE *(V.* Vol. IV, 279d).

HERDERITE (Þ. Vol. I, 685a).

" HERMITE FLUID," (v. Vol. IV, *20d).*

HERRING OIL (v. Vol. V, 2280^s).

" HERTOLAN'!(». Vol. II, 264c).

HER2ENBERGITE. Tin sulphide, SnS, as black, flaky orthorhombic crystals, closely resembling *franckeite {q.v.)* and *teallite* (and to some extent also graphite) in,appearance. As a natural mineral it was first recognised from the Maria Teresa mine, Huari, Bolivia, by R. Hcrzenberg in 1932 and named by him *kolbeckine.* This name being preoccupied, it was later renamed herzenbergite and proved to be identical with artificial SnS. The mineral has also been found in small amount in the Stiepelmann mine near Arandis in South-West Africa (P. Ramdohr, Z. Krist. 1935, 92, 186; W. Hofmann, *ibid.* 1935, 92, 161). Crystals of the same kind are formed during tin smelting when the ore contains sulphides. These were at first described as an orthorhombic modification of tin (" fl-tin"), but afterwards proved to be SnS (L. J. Spencer, Min. Mag. 1921,19,113).

L. J. S.

HESPERITINIC ACID (*v.* Vol. V, 61a).

HESSITE or TELLURIC SILVER. Silver telluride, Ag_2Te, crystallised in the cubic system and isomorphous with *argentite [q.v.).* The silver (Ag 63-3%) is often partly replaced isomorphously by gold, forming a passage to *petzite.* The colour is lead-grey, and the material somewhat sectile; sp.gr. 8-3-8-9^1, hardness 2J-3. The best crystals, though much distorted, are from Botes in Transylvania, and massive material was formerly obtained in some quantity in the Slavodinsk mine in the Altai Mountains, Siberia. The mineral has also been found in California, Colorado and Utah.

L. J. S.

HESSONITE v. GARNET.

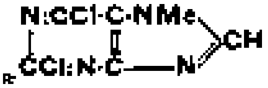
HETEROXANTHINE,' 7-methylxanthine, 2:6-dioxy-7-methyIpurine,

$$\begin{array}{l}\text{NHCOCNMe}\\ \qquad\qquad\qquad\quad\text{CH}\\ \text{CONHC——N}\end{array}$$

occurs together with xanthine and paraxanthine as a constituent of normal human urine (Salomon, J*er. 1885, 18, 3406; Virchow's Archiv. 1891, 125, 554; Wada, Acta Schol. Med. Univ. Imp. Kioto, 1930,13,187); 10,000 litres yielded 22-2 g. of the mixed bases, of which 11-36 g. was heteroxanthine (Salomon and Krüger, Z. physiol. Chem. 1898, 24, 364); it occurs also with xanthine in the urine of the dog (Salomon, *ibid,* 1887,11, 410). Heteroxanthine appears to be a product of the metabolism of theobromine and caffeine, for when these alkaloids are administered to rabbits, dogs or men, heteroxanthine appears in the urine (Boridzynski and Gottlieb, Ber. 1895, 28, 1113). According to Albanese (Gazzottn, 1895, 25, ii, 298) heteroxanthine is an intermediate product in the degradation that caffeine undergoes in the organism, the methyl groups being successively removed until xanthine is obtained, which is then converted into urea and ammonia. Heteroxahthine acts as a powerful diuretic on dogs and rabbits wh^n injected hypodermicqlly in small doses; larger doses are toxic, an injection of 1 g. killed a dog weighing 8 kg. in 10 days (Albanese, *I.e.; cf.* Kruger and Salomon, Z. physiol. Chem. 1895, 21, 169; Schmiedeberg, Ber. 1901,84, 2556).

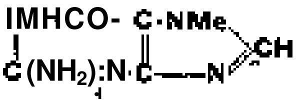
The isolation of heteroxanthine from yeast (1-2 g. from 40 kg. dried brewer's yeast) has been described by Wiardi and Jansen (Rec. trav. chim. 1934, 53, 205). The yeast was extracted with water containing 0-1% benzoic acid. The bases were adsorbed on fuller's earth, extracted with barium hydioxide solution, precipitated with sodium silicotungstate and then purified by precipitating twice with silver nitrate in iV/IQO HNO_3. The heteroxanthine was recrystallised from *N/2* hydrochloric acid.

The synthesis of heteroxanthine from theobromine (*v.* Vol. II, 197c) has been effected by Fischer (Ber. 4897, 30, 2400). When 2:6-dichloro-7-methylpurine,



$$\begin{array}{l}\text{N:CCl·C·NMe}\\ \qquad\qquad\qquad\quad\text{CH}\\ \text{CCl:N·C——N}\end{array}$$

obtained by the action of phosphoryl chloride on theobromine, is heated at 120-125° with hydrochloric acid (sp. gr. 1*19), it is converted into the hydrochloride of heteroxanthine. When 2:6-dichloro-7-methylpuripe is heated with allyl alcohol and sodium, it yields 2:6-diallyloxy-7-methylpurine, m.p. 111-112°, which may be reduced catalytically to heteroxanthine (Bergmann and Heimhold, J.C.S. 1935, 1365). Another synthesis was carried out by Sarasin and Wegmann (Helv. Chim. Acta, 1924, 7, 713); the nitrate of 5-chloro-l-methylglyoxaline, when treated with concentrated sulphuric acid, is converted to 5-chloro-4-nitro-l-methylglyoxaline, m.p. 147-148°, which, on heating with potassium cyanide and a little iodide in alcoholic solution, gives 4-nitro-5-cyano-l-methylglyo'xal^ne, m.p. 141-142°. Hy&rolysis of this nitrile gives the amide, m.p. 257-258° (decomp.), and then reduction yields the amide of 4-amino-l-methylglyoxalinecarboxylic acid (m.p. 184-185°, hydrochloride, m.p. 214-215°). This amino amide reacts with ethyl carbonate at 160 170° to give heteroxanthine. Kruger and Salomon (Z. physio]. Chem. 1898, 26, 389) also obtained it by the action of nitrous acid on epiguanine (7-methylguanine, 2-amino-6-oxy-7-methylpurine),



$$\begin{array}{l}\text{IMHCO- C·NMe}\\ \qquad\qquad\qquad\qquad\text{CH}\\ \text{C(NH}_2\text{):N·C——N}\end{array}$$

and as Fischer *{I.e.)* has synthesised epiguanine, this method is also synthetical.

Heteroxanthine is a crystalline powder; when heated gradually it melts and decomposes at 341-342°, when heated rapidly it darkens at 360° ami melts and decomposes at 380°. It dissolves in 142 parts of boiling water (Fischer *I c)* or in 7,575 parts of alcohol at 17°, or in 2,250 parts at the boiling-point (Bondzynski and Gottlieb, Ber. 1895, 28, 1113). Heteroxanthine possesses both acidic and basic properties, the basic *(k_b)* and acidic (*$_a$) dissociation constants being 11.82x10-" and 4019x10-" respectively (Wood, J.C.S. 1906, 89, 1840). For the dissociation constants in water and 90% alcohol at 18°, *see* Ogston (J.C.S. 1935, 1376); and for the ultra-violet absorption spectrum, *see* Gulland and Holiday (Nature, 1933, 132, 782) and

Gulland, Holiday and Macrae (J.C.S. 1934, 1639).

Heteroxanthine forms salts with acids which are readily dissociated in water; the *hydrochloride* crystallises in tufts of transparent crystals, and yields a micro-crystalline* *platinichloride;* the *sulphate,* $C_6HJO_2N_4\text{-}H_2SO_4$, is decomposed by water. Heteroxanthine forms a characteristic *sodium* derivative,

$$C_6H_6O_2N_4Na,5H_2O,$$

crystallising in plates or prisms, melting at about 300°, readily soluble in water, sparingly so in sodium hydroxide; the *potassium* derivative has similar properties and a higher melting-point (Salomon, Ber. 1885,18, 3406; Virchow's Archiv. 1891, **125,** 554). Heteroxanthine yields a crystalline precipitate with mercuric chloride, and forms a crystalline derivative with silver nitrate. It is also precipitated by copper acetate, pjiosphotungstic acid or lead acetate in the presence of ammonia (Salomon, *I.e.).* It is differentiated from hypoxanthine, xanthine and guanine by the sparing solubility of its sodium derivative in sodium hydroxide; it differs from paraxanthine in its solubility and in not yielding a precipitate with picric acid in the presence of hydrochloric acid.

When a solution of heteroxanthine containing chlorine-water and nitric acid is evaporated, the residue develops a red colour with ammonia, becoming blue on addition of sodium hydroxide. On oxidation with potassium permanganate in concentrated sulphuric acid, heteroxanthine yields three of its four nitrogen atoms as ammonia or iftea, and the fourth as methylamine (Jolles, Ber. 1900, 33, 2J20, 2126).

By electrolytic reduction in sulphuric acid solution, heteroxanthine yields 2-oxy-7-methyl-1:6-dihydropurine (Tafel and Weinschenk, *ibid.* 1900, 33, 3374).

HETEROGENEOUS REACTIONS.

Heterogeneous reactions, by definition, take place at phase boundaries or involve transport of matter across the boundaries. The possible phase boundaries are:

gas-solid; liquid-solid; gas-liquid; liquid-liquid; solid-solid.

Reactions at each of these phase boundaries will be briefly reviewed in turn. The phenomena covered by the term " heterogeneous reaction " include many processes discussed elsewhere in this dictionary *(v.* DIFFUSION, Vol. I11, 6046; CRYSTALLISATION, Vol. I11, 445d; CATALYSIS IN INDUSTRIAL CHEMISTRY, Vol. II, 422d; HARDENED OR HYDROOENATED OILS, this Vol., p. 1776; ABSORPTION, Vol. I, 66; and ADSORPTION. Vol. I, 147d). The present article will therefore describe the underlying principles and modern examples of certain processes, but for reasons of space will deal primarily with reactions usually regarded as chemical.

A. REACTIONS AT THE GAS-SOLID INTERFACE.

(i) Systematic Classification of the Kinetics of Heterogeneous Reactions.—A reaction at an interface may be controlled by any one of the steps:

(a) Transport of reactants to the interface.
(6) Adsorption of the gases,
(c) Reaction on the surface.
\d) Desorption of the products,
(e) Transport of the liberated products away from the surface.

(a) and (e) are normally diffusion processes. (6) and *(d)* may be chemical or physical in nature, while *(c)* is the essentially chemical process. In the majority of reactions at gas-solid interfaces (c) governs the reaction velocity. First, however, the less usual steps will be considered.

***Diffusion as a Rate-Determining Step.*—Diffusion** is of primary importance in many reactions at liquid-solid interfaces (p. 2156). It may also control reaction rates at the gas-solid interface when the solid is present as a porous mass. Diffusion to and from the important internal surfaces is then slow enough to govern the rate of reaction. This has been observed during coal or coke combustion under special conditions (Tu, Davis and Hottel, Ind. Eng. Chem. 1934,26, 749; *see also* p. 215a) and in the activated adsorption of hydrogen by charcoal at high temperatures (Barrer, Proc. Roy. Soc. 1935, *A?* **149,** 256). As a rule, however, it is a supernumerary phenomenon in heterogeneous gas reactions.

Sorption and Desorption as Rate-Determining Steps.—At high temperatures on certain surfaces, for example, charcoal, the ortho-para conversion of hydrogen may occur by activated adsorption of hydrogen (p. 2146, *d),* followed by desorption (A. Farkas, " Orthohydrogen, Parahydrogen and Heavy Hydrogen," Cambridge University Press, 1935, p. 89).

O-H.+ 2C (solid) **->2CH** (surface)
->2C (solid) +*p-H%*

The overall reaction rate is controlled in this case by the sorption and desorption velocities. The same mechanism has been proposer} for exchange reactions between hydrogen and deuterium. An alternative suggestion, however, is that the ortho-para hydrogen conversion occurs by exchange between gaseous molecules or molecule? sorbed by Van der Waals forces and the chemisorbed layer:

$$D_t+H\text{-}S\rightarrow HD+D\text{-}S$$

where 8 denotes an atom of the surface.

Desorption of nitrogen is probably rate-controlling in the decomposition of **IMH,** by iron (Taylor and Jungers, J. Amer. Chem. Soc. 1935, 57, 660); and chemisorption of nitrogen by iron may be the slowest process in the technically important synthesis of ammonia using iron catalysts. *Hinshelwood (" Kinetics of Chemical Change," Oxford University Press, 1940, p. 207) then gives as a general reactioi? equation :

$$\text{Rate}=k_2\theta[B]=\frac{k_1k_2[A][B]}{k_1[A]+k_2[B]} \quad . \quad . \quad (1)$$

where A is the reactant undergoing slow adsorp* tion (N_t) with a velocity constant k_v A is removed by reaction with B (H_3), the velocity constant for this process being £,. $ denotes the fraction of the total available surface covered by A. If, as in ammonia synthesis, A",<^fc$_a$ the rate equation reduces to

$$\text{Eate}=i_1[A] \quad . \quad . \quad . \quad . \quad (2)$$

Chemical Head ion as a Rate-Determining Step. •—The number of adsorbed atoms or moJcculea of reactants and resultants controls the reaction rate Rnd thus quantitative aspects of adsorption equilibrium must be reviewed.

Langmuir (J. Amer. Chem. Soc. 1916, 38, 2268) deduced a simple isotherm for an immobile monolayer by equating the velocities of adsorption and dcsorption at equilibrium ;

$$\text{Velocity of adsorption} = k_x p(1-\theta) \quad . \quad . \quad (3)$$
$$\text{Velocity of desorption} = k_a\theta, \quad . \quad . \quad . \quad .$$

iv hen ft'

$$\theta=\frac{ap}{1+ap} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where it,, k_2 are constants, and a=r*; and where /Co

TABLE I.—UKIMOLECULAR PROCESSES.

No.	Conditions.	Rate equation.	Examples.
1.	Single reactant weakly adsorbed.	$-\frac{dx}{dt}=k\theta=kap$	N_2O on gold.[1] HI on Pt.[2] PH_3 on porcelain[3] and glass[4]. H_2Se on Se,[5] AsH_3 on glass.[6] HCO-H vapour on glass, Pt, Rh, TiO_2.[7]
2.	Single reactant moderately adsorbed.	$-\frac{dx}{dt}=k\theta=\frac{kap}{1+ap}$ $\frac{d}{}\ kp^n$ (*n* denotes an exponent less than one.)	SbH_3 on Sb.[8, 9]
S.	Single reactant strongly adsorbed.	dx	HI on gold.[10] NH_3 on W (at moderate or low temperatures).[11] NH_3 on MGandOs.[1*]
4.	Single reactant weakly adsorbed, resultant moderately adsorbed.	$-\frac{dx}{dt}=k\theta=\frac{kap_1}{1+bp_2}$	N_2O on Pt (retarded by O_2).[18]
5.	Single reactant weakly adsorbed, resultant P strongly adsorbed.	$-\frac{dx}{dt}=k\theta=\frac{kap_1}{bp_x}$	NH_3 on Pt wire at 1.OOO'o.[1*] (retarded by H_2).
8.	Reactant and resultant both strongly adsorbed.	$-\frac{dx}{dt}=k\theta=\frac{kap_1}{ap_1+bp_2}$	Dehydrogenation of alcohol in presence of H_2O, CH_3COCH_3 or benzene, as increasingly effective poisons.[18]
7.	Single reactant weakly adsorbed, two resultants strongly adsorbed.	$-\frac{dx}{dt}=k\theta=\frac{kap_1}{bp_2+ap_3}$	NH_3 on Pt in pressure range 0-0-1 mm. (Retardation by N_2 and H_2)."

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[1] Hliishelwood ami Prk-lmrd, Proc. Roy. Soc. 1925, A, 108.211.
[2] Blndhelwood anil Uurk, J.C.3. 1025, 127, 2896.
[3] Tnuils and Hbamiarkar, Z. anorg. Chem. 1919, **106,** 05.
[4] **Hlnshehraod** und Toplcy, J.C.S. 1924, **1S5,** 3t)S.
[5] Bodenatctn, Z. physical, them. 1899,29, 429.
[6] Van't Hoff, " Btudeade dynamlque chimlque," Amsterdam, 1884, p. &3.
[7] Hlnshelwood and Topley, J.C.S. 1923,123, 101*.
[8] JEiii-helivood. *op. cit.* p. 191.
[9] Stock and Umlcnslcin, Tier. 1907,40, 570; Stock, Qomolka and Heynemann, *Und..* D. 532.
[10] Hfiwhelwooii and Pritliard, J C.S. 1025,127, IS52.
[11] Hinshclwootl and Burk, J.C.8. 1025,*12T,* 1**186.**
[12] Biirk, Proc. Nat. *Acad.* **ScL** 11)27,13,07 ; Kunaman, J. Amer. Chem. Soc, 1028,50, 2100 • Arnold and Burk, J. Amer. Chem. Soc. 1032,54, 23.
[13] Hinshelwood and Prk-hnra, J.C.S., 192.1,127, 327.
[14]
[15] Schwab and Schmidt, Z. physikal Chem. 1929, B, 3, 337.

t* Schwab and Schmidt, Z. physikal. Chem. 1029, B, 3, 337.

TABLE II.—BIMOLECULAR PROCESSES.

No.	Conditions.	Rate equation.	Examples.
1.	Two reactants weakly adsorbed.	$-\frac{dx}{dt}=k\theta_1\theta_2$ $=k(ap_1)(bp_2)$	H_2 and C_2H_4 on weakly active Cu.[1] C_2H_4 and Br_2 on glass.[3]
2.	Two reactants, one weakly, one moderately adsorbed.	$-\frac{dx}{dt}=k\theta_1\theta_2$ $=k\frac{(ap_1)(bp_2)}{(1+bp_2)}$	Water gas reaction $H_2+CO_2 \rightleftharpoons CO+H_2O$ at 1,000°C. on Pt (retardation by CO_2).»
3.	Two reactants, one weakly, one strongly adsorbed.	$-\frac{dx}{dt}=k\theta_1\theta_2$ $=k\frac{ap_1}{bp_2}$	Oxidation of H_2 on Pt below 700°c. (retardation by H_2).* Oxidation of CO on Pt below 700°C. (retardation by CO). Oxidation of CO on quartz.* H_2 and C_2H_4 on active Cu between 0° and 20°C.«
4.	Two reactants, but only one kinetically active.	$-\frac{dx}{dt}=k\theta_1\theta_2$ $=kp_1$ or kp_2 according as the pressure of 1 or 2 is much the greater.	Reaction of CO and O_2 on Pt above 700°C. Surface probably saturated with component in excess. Reaction occurs when the other component bombards this surface.*
5.	Two reactants one product strongly sorbed.	$-\frac{dx}{dt}=k\theta_1\theta_2$ $=\frac{k(ap_1)(bp_2)}{cp_3}$ $-\frac{dx}{dt}=k\theta^2$ $=\frac{k(ap_1)^2}{cp_3}$ when 1 and 2 are of the same kind.	— Decomposition of NO on **Pt-Rh** (retardation by O_2).[7]
6.	Two reactants, one strongly sorbed, and the other moderately sorbed on remaining part of the surface.	$-\frac{dx}{dt}=k\theta_1\theta_2$ $=\frac{k(ap_1)}{(1+bp_3)}$ $\simeq\frac{k(ap_1)}{(bp_3)^n}$ $(n<1)$	Oxidation of SO_2 to SO_3 on Pt. O_2 is strongly sorbed and SO_3 retards the reaction.*

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[1] Pease, J. Amer. Chem. Soc. 1023,45, ! 10B : Oraast, Nuovo Cim. 1010, [vi], **11,** U7.

[2] IStcwnrt IUHJ KiLlutitl, **J. Amer. tilicii). 3oc, 11)2.1,46, 1014.**

[3] **Hinshelwood** and Pritchard, J.C.S. 11)25,127, 800.

* Langmuir, Trans. Faraday Soc. 192Z, 17, **021.**

[5] Bodenstein and Ohlmer, Z. physikal. Chem. 11)05, 53, 100.

[6] l'r;Lirt? t C

[7] **UachnW&nd** *d.* **B. Taylor, J.** Phys. Chem. 1020,33, 447.

* lkidcnstc!nnuil.l iiLk,Z. **physikal. Chem.** 11)07,60, 1.

B denotes the fraction of the whole surface covered by the monolayer. This simple isotherm expresses well the θ—p relations of many sorption systems (*see,* however, p. 2116). The isotherm was deduced for a homogeneous surface and many of the deviations from it are due to the presence of capillaries and cracks in the surface, and to the presence of other adsorbed impurities. The isotherm was originally deduced for an immobile monolayer but equations of similar form are obtained for mobile monolayers (Volmer, Z. physikal. **Chem. 1926, 115,** 253) and the adsorption isotherm may be accurately determined using statistical mechanics (Fowler and Guggenheim, " Statistical Thermodynamics," Cambridge University Press, 1M9, pp. 426 *et seq.).*

The Langmuir isotherm is thus a convenient basis for the classification of heterogeneous processes. For example, a unimolecular reaction may occur in an adsorbed film. Then, at low pressures:

$$-\frac{dx}{dt} = k\theta = kap$$

since $\theta = \frac{ap}{1+ap}$ and for small p, $ap \ll 1$.

At intermediate pressures $-\frac{dx}{dt} = k\theta = \frac{kap}{1+ap}$

while at high pressures

$$-\frac{dx}{dt} = k, \text{ since for large } p, \; ap \gg 1.$$

When two gases exerting equilibrium pressures p_1 and p_2 respectively are simultaneously adsorbed, the isotherms may be expressed by

$$\theta_1 = \frac{ap_1}{1+ap_1+bp_2} \quad . \; . \; . \; . \quad (6)$$

$$\theta_2 = \frac{bp_2}{1+ap_1+bp_2} \quad . \; . \; . \; . \quad (7)$$

where θ_1, θ_2 are the fractions of the surface covered by each component and a and b are constants. One of these gases may be a reactant, one a resultant, or both may be reactants. Similar isotherms obtain when more than two gases are competing for the surface. Should the resultant cover the whole surface the reactant is almost completely displaced and the resultant then poisons or retards the reaction. If the subscript 2 refers to this resultant

$$bp_2 \gg ap_1 \text{ or } 1 \text{ and so } \theta_1 = \frac{ap_1}{bp_2}$$

Thus in a unimolecular process

$$-\frac{dx}{dt} = k\theta_1 = \frac{kap_1}{bp_2}$$

Many such possibilities can arise and a systematic classification of heterogeneous reactions in terms of Langmuir's isotherm has been made. In Tables I and II are summarised different reaction equations, the conditions giving rise to them and examples of heterogeneous processes obeying them. Reactions of a higher order than bimolecular are rare but are amenable to the treatments of Tables I and II.

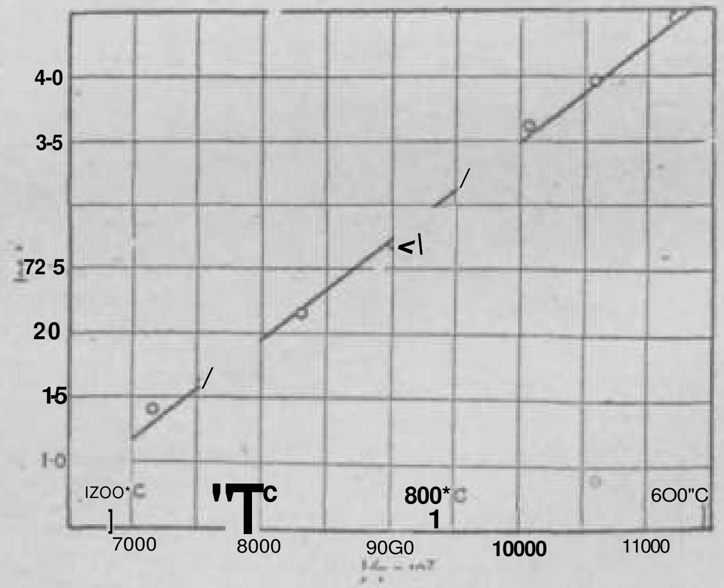

FIG. 1. INFLUENCE OF TEMPERATURE UPON THE HETEROGENEOUS DECOMPOSITION OF N_2O ON A PLATINUM WIRE. t is the Time Required for Half Decomposition $\left(\propto \frac{1}{k}\right)$.

(ii) The Order of Heterogeneous Reactions.—The data of Tables I and II show that the real order of a heterogeneous reaction may have little or no relation to the form of the equation governing the kinetics. The latter are controlled by adsorption equilibria. The apparent order and the true order of a reaction are the same only when the amount of each reactant adsorbed is proportional to its equilibrium pressure.

(iii) The Activation Energy of Heterogeneous Reactions—The velocity constant k of a heterogeneous reaction usually obeys the equation

$$\ln k = -\frac{E_a}{RT} + \text{constant} \quad . \; . \; . \quad (8)$$

where k is the velocity constant, and E_a denotes the apparent energy of activation. This is illustrated in Fig. 1 for a typical instance.

The adsorption equilibria, however, alter with temperature, and therefore the term E_a may include the heat of adsorption, ΔH, or a function of ΔH, for each reactant and resultant, according to an expression analogous to the Clapeyron equation.[1]

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[1] This expression takes the form

$$\left(\frac{\partial \theta}{\partial T}\right)_p = -\frac{\Delta H}{RT^2}$$

where θ denotes the fraction of the surface covered at constant pressure p, and ΔH is the heat of adsorption.

Simple examples have been worked out (H. S. Taylor, "Treatise on Physical Chemistry," MacmiUan & Co., 2nd ed., 1931, Vol. II, pp. 1081 *et 8eq.)* and the relations between the true and apparent activation energies *Et* and E_a, respectively, are summarised belo^w.

Surface Saturated with Reactant at Both Temperatures.—The reaction is of apparent zero order at both temperatures; the surface population of reactant molecules does not* alter and tfie heat of adsorption is not involved in E_0. Therefore

$$E_t=E_a.$$

3.y. decomposition of HI on Au (Table I, ref. 10) f?,,=#i=25,000 g.-cal. per g.-mol. ; decomposition of NH_3 on W (Table I, ref. 11) $\#_{f1}$=:^=42,000 g.-cal. per g.-mol. *n*

Process Unimolecular and Reactant Weakly *Adsorbed.*—The surface population decreases with increasing temperature if sorption occurs exothermically and $E_a=Et+AH_v$ Here AH_X denotes the heat of adsorption and following thermodynamic convention is to be given a *negative* sign for an exothermal sorption. If AH_X is appreciable, E_a may be small. *E.g.* decomposition of HI on Pt wire (Table I, ref. 2) E_a—14,000 g.-cal. per g.-mol.

***Process Unimolecular, Reactant Weakly Adsorbed and Resultant Strongly Adsorbed.—In* this** case $E_a=Et+AH_1—AH_2$ where the subscript I refers to reactant and 2 to resultant. When the resultant is strongly adsorbed, AH_2 is large and therefore E_a may become very great. *E.g.* decomposition of NH_3 on Pt (Table I, ref. 14) $E_a \simeq 140{,}000$ g.-cal. per g.-mol. The reaction is inhibited by hydrogen and AH_2 for the adsorption of hydrogen on platinum may be as large as —100,000 g.-cal. per g.-mol.

***Bimolecular Process with Two Reactants Weakly Adsorbed.*—Then** $E_a=E_t+AH_t+AH_2$ where the subscripts refer now to the two reactants. *E.g.* $C_8H_4+H_2 \xrightarrow{} C_2H_{f1}$ (Table II, ref. 1). The copper must Be weakly active and the temperature above 200°c. Then $E_a \simeq$ 10,000 g.-cal. per g.-mol.

***Bimolecular Process, One Reactant Weakly and one Strongly Adsorbed.*—The relation now is** $E_a=Et+AIli—AH_2$ where the subscript 2 refers to the strongly adsorbed reactant,

e.0. C_2H4+ Hj-^CaH,, (Table II, ref. 6). The reaction is now confined to low temperatures on active copper. Since E_a, *AH* and AH_2 under these conditions are 10,000, -11,000 and -16,000 g.-cal. per g.-mol. respectively,*$t* must bv $\simeq 5{,}000$ g.-cal. per g.-mol.

(iv) In homogeneity of surfaces .—Inhomogeneity of surfaces may show itself in several ways. Thus it may modify the adsorption isotherms uritil the Langmuir treatment of adsorption no longer applies and the heat of Borption varies with 0, the fraction of the surface covered *(e.g.* Barrer, Proc. Roy. Soc. 1937, A, **161,**476; Garner and Kingman, Trans. Faraday Soc. 1931, 27, 322). The true activation energy may also vary with *0* (Barrer, Proc. Roy. Soc. 193f), A, **149,** 253; J.C.S. 1936, 1256) and. furthermore, there may be areas of the surface upon which one reaction occurs and other areas where a second reaction takes place, both reactions involving the same reactants "(Taylor, Proc. Roy. Soc. 1925, A, **108,**105; Hinshelwood, *op. cit.* p. 225).

This last phenomenon may be considered further. Frequently the effect of a surface in promoting a reaction is destroyed by minute traces of some poison (c/. Table VIII). The active fraction of a surface may thus be very small. Moreover, catalysts may be poisoned with respect to one reaction while remaining active in promoting others. Carbon disulphide in suitable amount inhibits the hydrogenation of $C_{f1}H_5COCH_3$ but does not prevent reduction of *cyclohexene,* piperonal and nitrobenzene, all on the surface of platinum black (Vavon and Husson, Compt. rend. 1922,**175,** 277). Perhaps these results are to be explained in terms of selective sorption in which the affinity for the platinum increases in the order:

C_eH_6-CO-CH_3<CS_a<piperonal,cycfohexeneor nitrobenzene.

Other examples of this behaviour have been installed by Hinshelwood *(op. cit.* p. 227) and by Yoshikawa (Bull. Inst. Phys. Chem. Res. Japan, 1934,**18,**1042).

Another view, the adlineation theory of active centres, is due to Schwab and Pietsch (Z. physikal. Chem. 1928, B, 1,385; *ibid.* 1929, B, 2, 262; Z. Elektrochem, 1929, 85, 573; Schwab, " Die Katalyse, vom Standpunkt der chemischen Kinetik," J. Springer, Berlin, 1931); according to this tfeory the centres are crystal grain boundaries. Reaction would then occur primarily along a network of lines intersecting the surface of any natural crystal and following the grain boundaries.

Considerable evidence has been accumulated by Maxted and co-workers (Maxted and Lewis, J.C.S. 1933, 502; Maxted and Stone, *ibid.* 1934, 26, 672; Maxted and Moon, *ibid.* 1935, 393, 1190; 1936, 635) which appears to contradict the concept of active centres. These data indicate the catalyst surface to be energetically homogeneous for certain reactions, such as the decomposition of H_8O_2 by platinum.

The inhomogeneity of surfaces leads to kinetic consequences of interest. Some reactions have to be interpreted as though there were a multiple adsorbing surface on different zones of which the reactants are independently adsorbed. The kinetics in Table III have been analysed from this standpoint, although certain of the mechanisms are open to alternative interpretations *(e.g.* No. 2, Table III, and No. 4, Table II). On the present view, in order to have a reaction, the independent adsorbing sites must be mixed up among one another so that the reactants are in juxtaposition, or else surface diffusion must be possible with reaction at the boundaries* of the t^o-dimensional phases.

(v) Comparison between Homogeneous and Heterogeneous Reactions.—Certain reactions occur by both homogeneous and heterogeneous mechanisms. Instances where the true energies of activation have been determined for

TABLE III.—Two SURFACES—BIMOLEOHLAB REACTIONS.

No,	Conditions.	Sorption lao therms.	Kuictics.	Examples.
1.	Reactnnt 1 weakly, rcartfint *2* moderately adsorbed, each independently of the other.	t>,=aj>, on surface 1, "*t-l + bPt* on surface 2.	dx = ——— 1 + A/E	Oxidation of CO on quartz. Oxygen is weakly adsorbed.[1]
2.	Reactant 1 weakly, reoctant 2 strongly adsorbed, each iiyiUpcndently of the other.	*B^api* on surface 1. *0*$_{t}$— 1 on surface 2,	dx	**Oxidation** of CO on porcelain, Au, Ni, Cu, NiO, CuO."
3,	Reaetants 1 and 2 strongly and independently adsorbed.	0j = l on surface 1. fl, = I Oil surface 2.		Hj+CjH^=CjH. on Ca-tCaHj.a [1]
4.	Reactants 1 and 2 moderately and independently adsorbed.	A ○ P l on surface 1. A — 6 p * on surfa.ee 2.	= ——— U+«Pi)O + &/>i) at Atap,)"^)" where n, m<1.	1-f^+COa-CO+H-O on W.* H$_{£}$+NjO = N$_{s}$+H$_{2}$O on "Au.» aHj+O^SHjjO on porcelain.'

both mechanisms are given in Table IV, These data show that the homogeneous process takcp place with the larger activation energy. Th« function of the solid has been to replace the homogeneous mechanism, in whieh activation energy ia accumulated by a collision process, by an alternative reaction path involving a much smaller activation t nergy. *Thti is the typical property of* ***a*** *catalyst.* The relationships may be summarised in the potential energy diagram of Fig. 2.

By mint; the transition-state method it is possible to determine the relative -velocities of a heterogeneous reaction and the same homogeneous reaction under otherwise identical conditions {Glasstone, Laidler and Evrine *ot cit.,* p. 389}. Then

No. of molecules reacted hetorogeneouBly
No. of tuolectiles reacted homogeneously

per unit time per cm.* *3M*
per-unit time per c.c, ~ ^{w} RT

where $AE=E_{ham}$~E^ in g.-eal. per g.-mol. transformed. Thus for the reactions to be comparable iu velocity it would be necessary to have a surface *of* 10" cm.* or else *eXT* would **have** to be ~ io», *U.* E_{ko}^>E_{h}^ At 500°K, with **a** surface of 1 cm.^{a} and a volume of 1 c.c. d* would need to be 27,000 g.-cal. per g.-mol

TABLE IV.—COMPARISON OF ENERGIES OF ACTIVATION FOR HOMOGENEOUS **AND** HKTGROGENEOUS RBACTIONB.[1]

Tlwrmal dcconiposition of	Approximate activation etiergy for heterogeneous reaction (g,-cal,/g.-muU.	Activation eneray for lldEllOjfCltBOUS reaction fB.-cfl)./g.-i)iol.).
HI . . .	2r>,000 0B Au* 14,0(10 on Pt^{s}	44,000
N$_{t}$O . .	20,000 on Au * 32,fiOO on Pt *	68,600
NH$_{S}$ . .	42,040 on W • 32,«MJ to 4*2,000 on Mo^{7} 47,dOO on Oi^{e}	>80,000
CH$_{4}$ . .	55,000 to 60,000 on Pt»	> 80.000

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[1] Dcnton *and* Wllllutnn, J. Physical Cliein. 1020,30, 1487.

* *Bone* mid Andrew, Proc. Hoy. Soc. 1025, A, 109, 450 ; *ibid.* 1S2C, A, **110.** 18 Bone and Forshaw, Profl. Hoy. Hoc, 1027. A, 114, 1B9.

[a] **FMH** and **Stewart,** J. Amur. Chcm. Soc. 1025,47, 27C3,

* **Blnshetwwd** and Friclinrd, J-.C.8. 1925,**127,**1640.

[1] IHnshelwpocI mill Hutchtnsou, J.C.S.]i)2fl, 129, 1550, i

* Bodcnstein, Z. phyiilkal. Cln>in. 18D9, 29, 005.

[1] Glasstmic, Laldlcr and Eyring, "Theory of Bate Processes," WcGruw-Hill Ilouk Co., 1041, p. 390

*• Ufiislielwood and **FrMuud,** J.C.S. 1925,127 15.")'

[3] Ulosbelwood and Burk, J.C.S. 1Q25,**127,** 28[H(,

* Hiii»lii"lwood QUII I'ricltard, Proc. Koy. So% 1825 A, 10o, 211.

Hlnsliclwood and Prtehiird, J.C.R. lftiZy, 127 327

• liarrcr, Trans. Kururl.iy So*:. l(>3(i, 32, 400

[v] Knimniati, J. Amcr. Chtm. Soc. 1028,50, 2100

Arnold SIIKI Iturk, J. Antcr. (Jh«ni. Soc. 10112,54 23.

Schwab and Pictsoh.Z, physikal. Chem. 1026,121, \m.

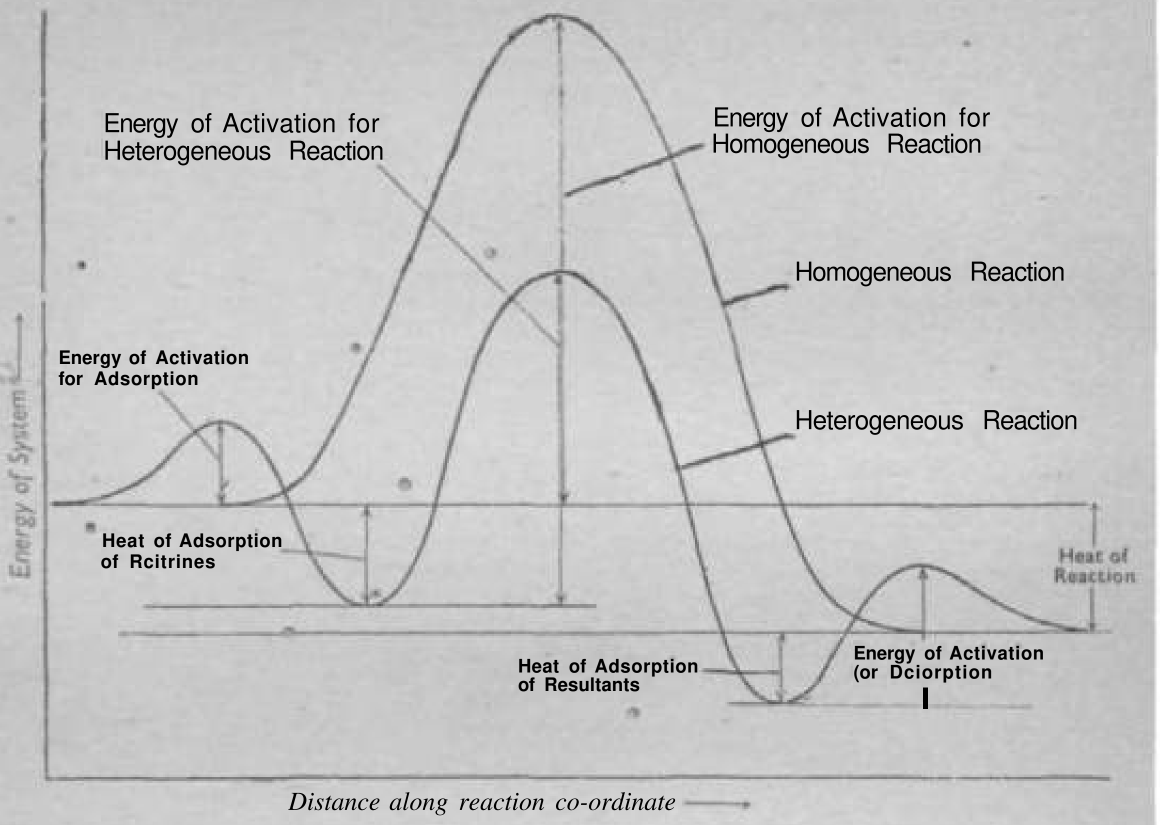

FIG. 2.—DIAGRAMMATIC COMPARISON OF ENERGY RELATIONS OF THE SAME REACTION OCCURRING BY HOMOGENEOUS AND HETEROGENEOUS MECHANISMS.

to obtain equality inmates. Such values of AE are similar to (fnom.—i'het.) in Table IV.

(vi) The Absolute Velocity of Heterogeneous Reactions.—The calculation of absolute reaction velocities is essentially similar for heterogeneous and homogeneous reactions. For a **unimolecular** surface reaction, one may write:

$$R+S \rightleftharpoons (R\text{-}S)^* \rightarrow \text{Products}$$

where R denotes the reactant and S the site on which it is adsorbed. The star denotes that the reactant has received the activation energy needed for reaction (i.e. it is in the activated or transition state). The expression for **the** reaction velocity according to the calculations of Eyring (J. Chem. Physics, 1935, 3, 107), Evans and Polanyi (Trans. Faraday Soc. 1935, 31, 875) and others (Glasstone, Laidler and Eyring, *op. cit.*, Chapters I and IV] is

$$\text{Rate}=C_g C_s \frac{kT}{h} \frac{f^*}{F_g f_s} e^{-\frac{E}{RT}} \quad . \quad . \quad . \quad (9)$$

where C_g = the concentration of reactant molecules in the gas phase.

C_s = the number of sites available for adsorption per unit area.

k = the Boltzmann constant.

h = Planck's constant.

f^* = the partition function of the transition state complex, excluding the partition function for the co-ordinate in which decomposition occurs.

f_s = the partition function of the adsorption sites.

F_g = the partition function for unit volume of the gas.

E = the energy required to produce the activated state.

The partition functions can be evaluated for certain simple systems, and since E, C_s and C_g may be measured, the reaction rates may be calculated. Table V compares some observed and calculated reaction velocities. The procedure has equal success in calculating the velocity of oxidation of nitric oxide on glass, a bimolecular reaction.

TABLE V.—OBSERVED AND CALCULATED VELOCITY CONSTANTS OF UNIMOLECULAR SURFACE REACTIONS.[1]

Decomposition of	Surface.	T°K.	Specific reaction rate (sec.⁻¹) Calc.	Obs.
PH_3	Glass	684	2·2 x 10-*	4·7 x 10-?
HI	Pt		1·2 x 10-»	1·0 x 10-'
N_2O	Au		3·4 x 10-*	12·3 x 10"

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[1] From data of Glasstone, Laidler and Eyring, *op. cit.*, Table XLI.

(vii) Heterogeneous Reactions involving Isotopic Molecules.—When the heavy hydrogen isotope was obtained in chemically useful quantities by progressive electrolysis of acidulated water (Washburn and Urey, Proc. Nat.

Acad. Sci. 1932, 18, 496; Lewis and MacDonald, J. Chem. Physics, 1933, 1. 341) the attention of chemists was directed to reactions involving isotopes and isotopic molecules. It then became apparent that *isotopes do not behave identically in chemical reactions* (Table XII). The differences are greater the more the mass ratio differs from unity, and is most marked with the isotopes of hydrogen. Some approximate mass ratios are:

$$\frac{D}{H}=2{\cdot}00;\quad \frac{^{18}O}{^{16}O}=1{\cdot}125;\quad \frac{^{7}Li}{^{6}Li}=1{\cdot}17;$$

$$\frac{^{13}C}{^{12}C}=1{\cdot}08;\quad \frac{^{15}N}{^{14}N}=1{\cdot}07.$$

As the atomic weight rises the isotopic mass ratio approaches unity. This means that the chemical differences between $^{ai)T}$Pb and ^{M}«Pb, for instance, will be too small to be detected.

Three factors contribute to differences in heterogeneous reaction velocity in isotopic systems:

(i) Differences in gas kinetic velocities, leading to different rates of bombardment of a surface, and contributing to differences in adsorption equilibrium.

(ii) Differences in zero-point energy. The lighter isotopic molecule has the higher *zero-point* energy, and is assisted in gaining the necessary activation energy by the amount of this energy. Therefore, other things being equal, the light isotopic molecule reacts more quickly than the heavy isotopic molecule (*e.g.* H_2 and D_2).

(iii) The tunnel effect. Quantum mechanics predicts that an atom may under certain conditions pass over an energy barrier from an initial to a final chemical configuration without acquiring the necessary activation energy. Light and heavy hydrogen are the only isotopes of mass small enough for this effect to be detected; but the phenomenon has not yet been observed in any heterogeneous or homogeneous isotopic reactions.

In Table VI are collected some differences in apparent energy of activation for heterogeneous reactions. The light isotopic molecule always reacts more rapidly, as the theory would predict. Moreover, the observed values of J B are of the magnitudes calculated, (Eyring and Sherman, J. Chem. Physics, 1033, 1. 345). On p. 219rf arc considered some other processes involving isotopes.

TABLE VI.—DIFFERENCES IN APPARENT ENERGY OF ACTIVATION FOR HETEROGENEOUS REACTIONS[1] INVOLVING ISOTOPIC MOLECULES.

Reaction.	*E* (apparent) g.-cul. per K.-mol.	in g.-cxl. per g.-mol.
H_1+2$C_{K>}$iid -* 2CH surface Dj+ 20,011,1 ->2CD surface	15,700	700*
2NH_s^>Nj+3H, 2ND,^» N,+ 3Dj	42,400	800, 790 [3] 830, 900
2PH_3-^2P+3H_a 2PD_3-^2P+3D_S	32,200	510. 550 [3]
12H_aO+Al$_4$C,-v4Al(OH)$_a$+3CH$_l$ 12D$_{l!}$O+Al$_<$C$_3$^4Al(OD)$_3$+3CD,	14,200	750*
CH$_4$-f 3C$_o$iid -*4CH surface CD$_4$4 3C$_w$iid ->4CD surface	>26,700	780*
H,H-CUO^CU+HJO D$_a$4-CuO -*-Cu+D$_a$O		,400"
Hydrogenation of atyrol (Pd-BaSO$_4$ catalyst)		540 •
H$_3$-D$_t$+O$_a$i^H,O-D$_3$O		750 [7]
Hg-D$_t$+N$_t$O^i. H$_t$O-D$_t$O+N,		720 [7]
rVD$_t$+C$_t$H$_4$!% C$_t$H$_t$-C$_{\%}$H$_t$D$_t$		700 [7]

[1] Data from Barrer, " Diffusion in and through Solids," Cambridge University Press, 19*1, p. 188
[2] Barrer, Trans. Faraday Soc, 1938, 32, 482.
[3] Harrer, *ibid.,?.* 490.
[4] Barrer, *ibid.,-p.* 486.
[5] Melville and Htdenl, Pro.. Roy. Soc. 1830, A, 153, 89.
[6] Cremer and Polanyi, 2. physikal. Chem. 1932, B, 19, 4*3.
[7] Melville, J.C.S, 1934, 1243.

(viii) Activated Adsorption and Chemisorption as Heterogeneous Reactions.—When oxygen is sorbed by charcoal at moderate temperatures, the process is chemical and the oxygen cannot be recovered by evacuation and further heating, only oxides of carbon being evolved. The process is an example of irreversible chemisorption. In other cases, however, the sorbed gas may be recovered at a higher temperature and under vacuum, yet the sorption occurs slowly and is chemical in nature (*e.g.* H_2 by charcoal, graphite and diamond, at high temperatures (Barrer, Proc. Roy. Soc. 1935, A, 149, 231; Trans. Faraday Soc. 1936, 82, 482; J.C.S. 1936,1256}). For chemical adsorption, occurring reversibly and requiring an activation energy, the term *activated adsorption* has been proposed (Taylor, J. Amer. Chem. Soc. 1931, 63, 578; Barrer, *op. cit.,* p. 232).

The combustion of carbon has-been studied extensively (reviewed by Mayers, Chem. Rev. 1934, 14, 31; *also* Faraday Society Disi;r«aion on " Chemical Reactions involving Solids," Pait He. Trans. Faraday Soc. 1938, 84, 1011); in furnace beds (Tu, Davis and Hottel, Ind. Eng. Chem. 1934, 26, 749); urMer low pressure conditions with small quantities of charcoal {Cassel, J. Amer. Chem. Soc. 1936, 58, 1309), graphite or diamond (Barrer, J.C.S. 1936, 1261); and using graphite filaments (Lang amir, J. Amer. Chem, Soc. 1915, 37, 1?54. Meyer, Z. physikal. Chem. 1932, E, 17, 385). The kinetics have been observed under these various conditions with static and flowing gas atmospheres. Combustion may be governed at low temperatures by irreversible desorption rates of a chemically-held layer of oxygen. At high temperatures the rate of chemical reaction between oxygen and carbon can be the deciding factor, and at the most elevated temperatures, or in furnace beds at lower temperatures, the rate of inter-diffusion of gaseous reactants and resultants is the slowest process.

Activated adsorption has been studied in a number of instances. The chemical uptake of hydrogen by the various forms of carbon must be regarded as the first step in hydrogenation. To induce further reaction, however, catalysts and high pressures are necessary. Among the first activated adsorptions to be studied were reactions involving oxides (Cr_2O_3, ZnO-Cr_2O_3) (Taylor, J. Amer. Chem. Soc. 1931, 53, 578), but it is not certain to what extent these are reversible and therefore how far they are irreversible chemisorptions and how far activated adsorptions. To this class belong the following systems:

H_2-D_2-Cr_2O_3[1]
H_2-ZnO-Cr_2O_3[2]
O_2-$CuCr_2O_4$,-$ZnCr_2O_4$,-$CoCr_2O_4$,-$NiCr_2O_4$, and -BCO[3]
H_2-MoO_3-SiO_2[4]

B. REACTIONS INVOLVING THE SOLID-LIQUID INTERFACE.

The solid-liquid interface is the seat of numerous technical reactions. The velocity of these reactions may be governed by the chemical processes at the interface, but equally often by diffusion of reactants or resultants to and from the interface. If chemical processes are slower, the reaction velocity is governed by considerations of the same kind as given on pp. 203,209, in systematising the kinetics of gas-solid reactions. There is the additional complication that a solvent medium is usually present, and that reactants and resultants compete for the surface with solvent molecules, and with other solutes. These may substantially modify the surface populations of the reactants. Moreover, diffusion in liquid media is much slower than in gases and therefore reaction kinetics in such systems are more often those of diffusion than in gas-solid reactions.

(i) Diffusion as a Rate-controlling Process.—Down any concentration gradient the rate of diffusion may be defined by

$$P=-D\frac{\delta c}{\delta x} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where *P* denotes the quantity of solute diffused per unit time, *D* is the diffusion constant, and $\frac{\delta c}{\delta x}$ is the concentration gradient. The diffusion constant may be related to the mobility *S* {defined as the steady velocity of the particle moving through the solution under unit force) by the relation

$$D=\frac{RT}{N}B \quad . \quad . \quad . \quad . \quad . \quad (11)$$

The value of *B* for spherical particles large compared with the molecules of solvent is given by

$$B=\frac{1}{6\pi\eta r} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where *r* denotes the particle radius and IJ the viscosity of the medium. The law is not necessarily valid when the dimensions of solute and solvent molecules are similar, although it is frequently applied to such solutions. If it is assumed that the liquid solvent behaves as though it were quasi-crystalline[1] the diffusion constant may be evaluated by methods used for diffusion in solids (summarised by Barrer, *op. cit.,* Table 76) and is given by

$$D=\frac{\nu d^2}{6}\left(\frac{E}{RT}\right)^{f-1}\frac{1}{(f-1)!}e^{-\frac{E}{RT}} \quad . \quad (13)$$

where *v* is the vibration frequency of the solute atom in one quasi-equilibrium position, *E* is the energy of activation needed for it to jump to another such position distant *d* from it, and *f* denotes the number of degrees of freedom among which the activation energy may be distributed.

Noyes and Whitney (Z. physikal. Chem. 1897, 23, 689) first used diffusion theory to interpret their experimental work upon the solution rates of benzoic acid and lead chloride. Cylinders of these solids were rotated in water and the concentration of solute was determined as a function of time. They assumed that the water just in contact with the solid was saturated with solute, and that the concentration diminished linearly over a small distance S until it was substantially the concentration in the bulk of the stirred

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[1] Taylor and Diamond, J. Amer. Chem. Soc. 1934, «, 1821; KohlechUtter, *I.* physikal. Chem. 1934, 170, 300.

[2] Pace and Taylor, J. Chem. Physics, 1034, 2, 578.

[3] Fnzer tnd Heard, J. Physical Chem. 1938, 42, 665,

[4] Urlffltli and Hill, Proc. Roy. Soc., 1036, A, 148, 196 ; HolUogs, Griffith and Bruce, *ibid.,* p. 18ft.

[1] There Is considerable evidence in favour of this view, especially for associated liquids near their freezing PflttBh

solution. Then the simple diffusion theory gives {Nernst, *ibid* 1904, 47, 52):

$$\text{Rate of solution} = \frac{DA}{V}\,\frac{(C_s-C)}{\delta} \quad . \quad (14)$$

Where A denotes the area of the solid, C_s and C are the saturation concentration of solute and its concentration in the stirred solution, respectively, and V denotes the volume of the solution. Integrating

$$\text{E B A - K} \quad \ldots\ldots \quad (15)$$
$$c_s - c$$

where $k=\frac{AD}{\delta}$ and * denotes the time. From the measured values of k and D, S varies in typical cases from 2<V to 50/* (Brunner, *ibid,* 1904, 47, 56). Evidence supporting the diffusion layer theory has since been obtained *by* various workers for chemical as well as physical processes (Van Name and Edgar, *ibid.* 1910, 73, 97; Van Name and Bosworth, Amer. J. Sci. 1911, 32, 207; Van Name and Hill, ***ibid.*** 1913, 36, 543). It should be emphasised that the form of the relationship does not depend upon the conception of a diffusion layer of definite thickness 8. Equations of similar form can be derived without its use. Further, the velocity of solution or reaction may depend upon the crystal face exposed and can be altered by addition of other solutes. The surfaces exposed soon become eroded and this may modify the value of A, and cause trends in k, although the factor this introduced was much less than the roughness factor of the surface (for a discussion of the literature, *see* Taylor, " Treatise on Physical Chemistry," Macmillan & Co., 1931, Vol. II, p. 1028).

Certain characteristics of reactions controlled by diffusion have emerged :

(1) The reaction rate varies with the rate of stirring *(r)* of the solvent:
Reaction velocity=AT"
where $n < 1$.

(2) Factors altering the viscosity y of the medium alter D, and so $k=\frac{AD}{K\delta}$.

(3) Temperature strongly influences the viscosity.

The viscosity decreases and so the diffusion constant increases as the temperature rises, thus giving a positive temperature coefficient to the reaction velocity. The temperature coefficient of diffusion is usually much smaller than the temperature coefficient of a chemical reaction and therefore the reaction rate is less sensitive to temperature in a diffusion-controlled process. In water the temperature coefficients of D for various simple electrolytes[1] at room temperatures range from 1·19 to 1·^8 per 10° rise *(e.g.* Oholm. *'I.* physikal. Chem. 1904, 50, 309; *ibid.* 1910, 70, 378; **Modi** K, Vetenskapsakad. Noi»l-Inst. 1912, 2, Noa. 23, 24, 26). As the size of the solute molecules or ions increases, **however,** so does the temperature coefficient of diffusion. Nevertheless, these temperature coefficients are below those for chemical reactions which are usually not less than 2 per 10°c. rise at room temperature. A useful criterion of a reaction limited by diffusion is therefore a temperature coefficient not above 1·5 per 10°c. rise. The same reaction may begin under certain conditions as one controlled by diffusion, and change, under other conditions, to one controlled by chemical reaction. Thus when certain metals were dissolved in HCl the temperature coefficients altered with concentration in a typical instance as follows (Guldberg and Waage, Ostwald's Klassiker, No. 104, 52):

Normality of HCl	1·3	2·0	2·6	4	8
$\frac{\text{Rate at } 18°\text{c.}}{\text{Rate at } 0°\text{c.}}$	1·58	1·68	1·70	2·44	3·23

Again, on platinum black the decomposition of H_2O_2 has a temperature coefficient of 1·28 per 10°c. rise. On colloidal platinum, by contrast, the temperature coefficient becomes " chemical" in magnitude *(2·2* per 10°c.) (*cf.* W. *M.* McC. Lewis, "A System of Physical Chemistry," Longmans, Green & Co., 1923, Vol. I, pp. 458 *et seq.).* This appears to be a general difference between massive and colloidal catalysts which has not yet been satisfactorily explained. It is possible that Brownian movement removes the colloidal particle from its atmosphere of resultants, thus continually exposing it to fresh supplies of reactants independently of diffusion.

According to the diffusion theory, the reaction rate follows a pseudo first-order rate equation. Typical reactions of this kind, where equilibria are established in presence of massive platinum as catalyst, are :

$$\text{Co(CN);'}^{w}\text{+H+ s± Co(CN),'''+iH,i}$$
$$Ti^{+++}+H^+ \rightleftharpoons Ti^{++++}+\tfrac{1}{2}H_2\ ^{2}$$
$$Cr^{++}+H^+ \rightleftharpoons Cr^{+++}+\tfrac{1}{2}H_2\ ^{3}$$
$$H_2O+2Co^{++}+\tfrac{1}{2}O_2 \rightleftharpoons 2Co^{+++}+2OH'\ ^{1}$$

Reaction proceeds to completion in other instances, such as:

Reactions of metals (Zn, Cd, Hg, Cu, Ag) with I_2 in KI solution.[9]
Reaction of **Hg** with Br;.[6]
Solution of MgO in benzoic, acetic and hydrochloric acid solutions.[8]
Solution of $CaCO_3$ in hydrochloric acid.[8]
Solution of benzoin acid, $PbCl_2$, CH_3CO_2Ag, in water.[8]

(ii) Chemical Reaction as a Rate-controlling Process.—Most reactions in solution occurring at the surfaces of inorganic or organic colloids have the high temperature coefficients appropriate to chemical processes. Some systems in which diffusion should govern the rate of reaction are not, in fact, so controlled. The solution of Al, Cd, and Sn in hydrochloric acid may occur at rates independent of the diffusion

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[1] For an electrolyte $D = \frac{2UV}{U+V}RT$ where U and V are the mobilities of cation and anion, respectively.

[*] Maachot and Hmo«, Bcr. 1000 33, 1742.

I^tit'liu wd Foenrter, Z. phyaikaLChem. JOOS, 62, 129; Dnnliam, (tirf. NU0, 72, 041.

[1] Jablwynskl, *ibid.* **190s,** M, 748.

[*] Obcrcr, Dtss., **Zurich,** 1W)3.

[8] Van Name and Edgar, Z. physlktii. **Chem,** 1(110, 73.

[Ui-•] *Of,* Taylor, *op. tit.* Vol. II., p. 1032; Bruouor, Z. physikai. Cboiu. 1904, 47, 56.

process and with chemical temperature coellicients (Centnerszwer, Z. physikal. Chem. 1?2tt, 141, *297). Formic acid solutions decompose at the surface of rhodium with a temperature coefficient of 2 (Blackadder, Z. phystkal. Chem. 1012, 81, 385) and also palladium sponge decomposes aqueous Na_aHPO_a with the typical chemical temperature coefficient of 2 per 10°o. rise ai room temperature (Sieverts and Peters, Z. phyaikal. Chem. 1916, 91, 199).

To interpret the kinetics one may employ the Langmuir isotherm as indicated on p. 208a and p. 208c.

$$\frac{x}{m}=\frac{kac}{1+ac}$$

where $\frac{x}{m}$ denotes the amount of a solute adsorbed per unit mass of catalyst, *k* and a are constants and c is the bulk phase concentration of Rotate, If there is competition for the surface by two molecular species one may write for each (*ff*, p. 210a)

$$\frac{x_1}{m}=\frac{k_1ac_1}{1+ac_1+bc_2}$$

$$\frac{x_2}{m}=\frac{k_2bc_2}{1+ac_1+bc_2}$$

The interpretation of reaction kinetics is not as complete as at this gaa-eolid interface (Tables J, II and III), but typical kinetics are summarised in Table VII. It is possible to offer alternative suggestions such as No. 2, Table III, and No. 4, Table II, to ejqilain why x_2 is independent of a:, in No. 5, Table VII. Reactions at the liquid-

TABLE VII.—REACTION KINETICS AT THE LIQUID-SOLID INTERFACE.

No.	Conditions.	Itnte equation.	Examples,
1.	Single reactant weakly adsorbed.	$-\frac{dc}{dt}=k'x$ $=kc$ (*x* denotes amount adsorbed, *c* denotes concentration of reaetant in eolation).	Hydrolysis of lactose and sucrose by enzymes at small sugar concentrations.[1] Decomposition of H_aO_2 on colloidal metals.* Decomposition of H,Oj by hffltnase.[3]
2.	Single reactant strongly adsorbed.	$-\frac{dc}{dt}$ $=k$ (surface saturated).	Tlydrolysia of sugars bj' *eaxytoee* at high sugar concentrations.[1] Decomposition of. $H_aO_?$ by aofhe colloidal or finely divided oxides in alkaline media.[2]
3.	Single reactant moderately adsorlied.	$-\frac{dc}{dt}=k'x$ $=\frac{kac}{1+ac}$ $\simeq Kc^n$ $(n<1)$	Decomposition of formic acid solutions on Rh.*
4.	Two reactauts, one strongly adsorbed, the reaction governed by diffusion of the other.	$-\frac{dc}{dt}=k'c_1x_2$ (since surface saturated with component 2).	$Tl^{+++}+H^{+}\rightleftharpoons Tl^{++++}+\frac{1}{2}H_2$ catalysed by Pt black in Loth directions (H_2 strongly adsorbed).' Catalytic hydrugenations (if many compounds containing etliylonic double bonds (liquid organic molecule itrongli adBorbed).[8]
5.	Two reactant*, one mni<\-erately adsorl^d, the other present in great excess.	$-\frac{dc}{dt}=k'x_1x_2$ $=\frac{kac_1}{1}$ if x_2 does not alter <l •ring the course of reaction, *Le.* c_a substantially constant.	$NaH_2PO_2+H_2O$ $\rightarrow NaH_2PO_3+H_2$[7] (palladium bln.k as catalyst).

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[1] Armst ng, Proc. oy. S c. 1904, 73, 508.

[2] Hm%Tnd Von B?rnrck, Z. physikal. Chem, 1800,31, *M** Bmllg and Ik.dn, («A **1*01,37,** 1.

[3] 8ent«r,»W. 1906,51,678,

[4] Blackadderi *ibid.* I'Jli, 81, M5.

[5]

[6] ffa^/andHlmH..Pnr Roy. fjoc lull) A 96,137; 1920^,98,27; 1021, A, 100,240.

[7] Blevcrte ftud Inters, 2. vhjRlkal. Cticin. 1010, 91, 109.

solid interface are susceptible to poisons in the same way as those at the gas-solid interface For instance, the catalytic hydrogenation of hydrocyanic acid to methylamine at the surface of platinised platinum is almost inhibited by excess of cyanide ion (Barrer, Thesis, University of New Zealand, 1931). Again, the decoraposition of hydrogen peroxide is strongly poisoned by minimal quantities of several reagents (Table VIII).

TABLE VIII.—POISONIHO OF H_2O_2 DECO MFOSITION.[1]

Reaction on:	Poison used.	Quantity of poison to reduce rate to half the unpolsoncdrate
Colloidal Pt sols containing io-^{6} g.-atoms of Pt per litre.	HCN	5xlO-*N
	ICN	7x ICHN
	•a	7xlO~^{8}N
	$HgCl_2$	2-5xlO-*N
Blood catalase .	HCN	1x10~^{8}N
	"a	2 *x* 10-^{6}y
	H_aS	1 x'0-*h
	HgClj	5X10-'N

[1] *Cf.* W. C. McC. Levin, •• A System of Physical Chemistry/' Longmans, Green & Co., 1Q25, Vol. I. p. 456.

The poisoning action is often to be explained, just as in gas-solid reactions, by a strong preferential adsorption of the pq'aon at the catalytic surface. That powerful adsorption of hydrocyanic acid occurs on platinum is further indicated by the observation that its catalytic reduction to met hy la mine is of apparent zero order with respect to HCN, i.e. the catalytic surface is maintained saturated with HCN.

(iii) Base-Exchange Reactions.—An important series of liquid-solid reactions involves base exchange. Base exchangers include synthetic gel zeolites, natural zeolites, clays, greensand, organic substances such as humic acids, proteins, wood and coal products and basic and acidic synthetic resins. For some purposes at least the resins bid fair to displace the inorganic base exchangers, for they may be prepared in forms stable to acids and alkalis, resistant to heat, of high base exchange capacity, and rapid in action (H. Myers, Eastes, and F. Myers, Ind. Eng. Chem. 1941, 33, 097). Processes involving base-ex changers include water-softening, total deminoralistng of water, purification of sugar juices, and the recovery of small amounts of valuable solutes, from electroplating wastes, of alkaloids and utnino acids, or of cuprammonium from rayon-spinning waste liquors. Exchangers have also been used in analysis, separation of isotopes (*see* Table XIII), as solid buffers for p_R control in the fermentation industries, mid in the preparation of NaNOj from $Ca(NO_a\}_2$ and sea-water. Many new applications will follow further technical development of the **BdbJMt.** (For a brief summary, *see* Walton, J. Franklin Inst. 1941, 232, 306.)

In technology the exchange process is usually carried out in flow systems. The solution containing reactants enters one end of a column of exchanger and flows out at the other, depleted of reactants. When exhausted the exchanger is regenerated by reversing the rôles of the cations involved in the first stage. It is unfortunate that the kinetic studies on these processes are at best semi-quantitative. Reaction may be confined to the surface layer, or diffusion into the gel or crystal may cause the exchanging cation to displace entirely the cation initially in the solid. The kinetics are then governed by ditfusion within the solid and the equation - -

Amount of exchange=AV^

would appty to a first -approximation. It is improbable that complete base-ex change occurs in many systems unless a far longer period is allowed for equilibrium to be established than is economically expedient. For most purposes, however, reaction on exchangers of practical importance is soon negligibly slow and it is then observed empirically that *, after a sufficient time (has elapBed, $\left(\frac{c_1}{-}\right)$ $=fc\left(\frac{c}{-J}\right)^p$ where *k* and the exponent *p* are constants and e, and c_a are the concentrations of the exchanging species in both Bolid and liquid phases. The law of mass action would predict for simple equilibrium that *p* = \. Table IX, which gives values of *k* and *p* for a few **typical** systems, shows that *p* usually differs considerably from unity. One explanation may be *hat true equilibrium is not normally established.

Further qualitative observations have been mmle on crystalline minerals. Those showing

TABLE IX.—CONSTANTS IN THE EQUATION

$$\left(\frac{c_1}{c_2}\right)_{solid}=k\left(\frac{c_1}{c_2}\right)_{solution}$$

The subscript 2 refers to the cation originally in the zeolite and 1 to the added ion.

Reaction system (X denote* the zeolite s\ibatr»te).	*p*.	*k*.	Concentration of added Ion
NH_4X (fusion product^ Na^+ .	0-67	0-36	—
NH_4X (fusion product)+K+ .	0-72	1 0	—
Li-beneonite+NH/ .	0-80	1-25	—
K-bentonite+ NH_4^+ .	1·1	0·5	—
NaX (gel product) + $Ca+^+$	0-63	0-67	0-25N
NaX (gel product) + Ba^{++}	0-56	1-78	0-25N
<-green aand+$Ca+^+$.	0-6	0·6	I00N
Ba-casein-f Na^+ .	0-7	0'0045	—
2a-casein+Ba^{++} .	0-75	1-2	—
3a-casfiin+$Ca^{+"f'}$.	0-45	0-6	—

[1] Other types of equation have also been prosoMd S«, for example, Wlefnw, J.8.CJ. 1931?W, Ml^

base-exchangers can be grouped into three categories : fibrous structures, plate-like or micaceous structures and three-dimensional networks. The more open the network the more rapid is the base exchange, whilst the theory of diffusion requires, and experiment shows, that the rate of exchange is usually increased by increasing the state of subdivision of the particles {*cf.* Zocb, Chcm. Erde, 1915, i, 1-55). Two typical classifications of base exchange *capacity,* to some extent Linfused with base exchange *velocity* in certain cases *(cf.* Table IX), are given in Tables X and XL

TABLE X.—CLASSIFICATION OF MINEBALS AS BASE-EXCHANGERS.[1]

High base-exchanges.	**Moderate base-es change.**	**Low or nog legible base-exchange**
Montraorlt-lonite **Eeidellltcfft),** **Hatloysite *(b).*** **spvurat leo-litvafn, *h, e).***	**Several oo-lites (a, *b,* r).** **Micas (6).** **Chlorite* (6).** **Aluminous amphiboles *(a).*** **Aluminous pyroxenes *(a),*** **Leucitc («).**	**PyrOphyliSU' (6).** **KiioltLiiU'(6).** **N on-a luminous ampttibolen *(a).*** **Kon-aluminous pyroxeties (a).** **Apophyllite (ft).**

[1] **Br&mmall and Leech, Scl. J. Roy. Coll. Sci. 1938, B, 43 ; Gdrlraann, Trans. Third Intcrnat. Cong. Soil Set. 1030,3,07.**
(n) Fibrous structures,
***ib)* Laminar structures.**
(ej Three-dimensional networks.

TABLE XI.—CLASSIFICATION oy MINERAL EXCHANGERS.[1]

Mineral.	**Volume per O atom.**	Cation exchange.
Garnet *(c)*	15*4ou. A.	None
Muscovite (6) (a mica) ,	**19-2**	Slight
Orthoclase (<•) (a fel-	23	Slight
Nosean (c)	23-1	Fair
Ultramarine (c) . . .	231	Very good
Apophyllite (6) . . .	**26-8**	San-
Natrolite(a)	280	Very good
Glauconite	28	Excellent

[1] **Walton, J. Frauklln InBt. 1841,232, 305.**
(») Fibrous structures.
***(b)* Laminar structures.**
***(e)* Three- dimensional networks.**

Table X shows that the kind of crystal structure does not govern the velocity and extent of base-exchange, save indirectly by conditioning the openness of the lattice. The latter is the vital factor and Table XI attempts to indicate a measure of the openness by giving the atomic volume available per oxygen atom in the lattices of some base-exchanging minerals. The method gives correctly the qualitative order of ease of base-ex change. Base-exchange experiments with crystalline minerals such as zeolites must be continued for periods of days or months to reach completion, and approach to this state is asymptotic. (For *a* survey of base exchange data, *see* Doelter, " Handbuch der Mineralchemie," Bd. II. 1 Halfle, 1914, p. 93; Bd. II, iii. 1921, pp. 1-416.) If the solute does not decompose at high temperatures, the hydrothermal method of digesting the zeolite at 100-200°c. with the salt **solution** in a sealed system causes acceleration of the reaction. (A summary of Lemberg's and Thugutt's extensive researches using this method is given by JSi-hneiderhohn, Jahrb. Min. Beil.-Bd. 1914, 40, 163. Base-exchange in ultramarines is discussed by Jaeger, Trans. Faraday Soc. 1929, 25, 320.) At still higher temperatures the zeolite may be heated with a fusible or volatile salt {*t.g.* NH_tCI) with further acceleration of reaction in some instances. (Method largely developed by Clarke and Stoiger, in a series of papers from 1899-1905, *e.g.* Clarke, Z. anorg. Chem. 1905, 46, 197.)

C. REACTIONS INVOLVING THE GAS-LIQUID INTERFACE.

Processes involving the gas-liquid or vapour-lifjiiid interface may be either physical or chemical. Physical reactions of solution and evolution of vapours from liquids are fundamentally important in industry, for they control rates of approach to the steady state in distillation, or solvent extraction processes. The industrial still may be idealised as a column containing a number of perforated plates. These hold up a small amount of liquid continually washed by ascending vapours. The latter in their turn partly condense and run back from plate to plate. Eventually by this process of washing and condensation a steady state is reached with volatile components predominating at the top of the still and the less volatile components at the bottom. This steady state is established quite slowly, and the more slowly the larger the total holdup of vapour and liquid along the height of the column, so that a good still is designed to minimise this hold-up. For practical purposes the still with total reflux is converted into one with a definite forward flow, by withdrawing liquid or vapour slowly from the top of the still. The separation obtained depends upon the number of " theoretical plates " {*see above)* which the still may be said to contain. In theory the separation may be made as complete as desired by increasing the number of plates, but in practice this will reduce the rate of [establishing the steady-state separation of components in the top and bottom of the column.

Chemical reactions at the gas-liquid interface may be exchange processes in counter-current systems basically not unlike the still described above, or they may be changes confined primarily to the gas-liquid phase boundary. These types of chemical change will now be discussed.

(i) Exchange Reactions.—Such reactions have become important recently in separating isotopic mixtures, largely in the hands of I'rcy and his co-workers (summarised by **Drey,** Kep. on Prog. Phys. 1939, 6, 48). Isotopes have slightly different chemical reactivities, as noted on p. 213d. Equilibria, in which gas and liquid isotopic mixtures participate give {Table XII) equilibrium constants which differ slightly from unity. The separation factors have proved sufficient however, to separate isotopes effectively by use of two-phase counter-current methods, either non-regenerative or regenerative in type. The method, "with modifications, has succeeded, or partially succeeded, in the instances given in Table XIII.

TABLE XII.—ISOTOPJC EQUILIBRIA.[1]

Reaction.	Equilibrium constants:		
	273-1°K.	238- 1°K.	600°R.
, giBQ , H 18Q _j. *is^O* 4- H "O	1034	1028	1003
1Q18Q f-H 1SQ__i tC IS O +H 'f'O	1064	1054	lul-t
iiflO5-j-H, lfi O—^ *k* 1!i O +H '^O	**HiiM**	**1-020**	1003
"CO+ "CO —' ia CO-l '^CO	1-098	1-086	1029
* 8S CL+H"Clr a i"Ct1,+ H 3B CI . . . . - .	1004	1003	100015
$\frac{1}{2}{}^{79}Br_2 + H^{81}Br \rightleftharpoons \frac{1}{2}{}^{81}Br_2 + H^{79}Br$	1-0005	10004	**0-99097**
i» N J- 1Eh NO —^4 J *N ^"NO	1016	1015	i-0077
9 LiH+ ? Ll ^ T LiH+ a Li . . . . •	1-028	1025	1-008

[1] Urey and Grelff, J. Atner, Cheni. Soc. 19^5,57 ..

TABLE XIII.

Phases,	Method.	Isotopes partially separated.
Liquid-Solid. . .	Saline solutions were percolated **through columns** uf **Na** zeolite. The procedure was that of **(thro**matograpliic analysis. Total redux **was** not obtained[1]	^{7}Li concentrated in leading sample of LiCI Kdlution, ^{8}Li concentrated in zeolite. ^N concentrated in leading sample of **NH,,C!** olution. ^{3B}**K oonoentruted** in leading sample of KC1 solution.
Liquid-Liquid . .	Exchange rmution proceeded betwi-i n Li amalgam and LiCI in anhydrous CH_3OH. Amalgam dropped **through** column of al-**DohouoLiCl** 18 metres long. At the bottom the Li in the Li nmalgatn was converted to LiCI in **alcohol** mid led into base of column. System arranged to give total reflux.[2]	'Li **conoootmtod in the** amalgam, •Li in LiCI.
Gas-Liquid . . .	Ammonium salt solution in water flowed down through a fractionating column. NH_3 gtts was liberated at the bottom by **boiling** with NaOH. **and** the NH_3 passed upward through **column.** System arrungi • to give total reflux.[3]	$\frac{^{15}N}{^{14}N}$ = 2·5% instead of 0-38%, usinji $(NH_4)_4SO$, its ammonium salt. ^{10}N concentrated in liottoin of coiuinn.
Gas-Liquid . . .	vHCN gas was fed into the bottom of the column. At the top it was absorbed in NaOH and **thfl** NaCN passed *linwn* the column. Total re H u wobt a ined. *	Cori-entmtion of ^{13}C in gaa phase attopofcolumn. Couoentration of ^{ia}C in liquid phase at bottom of column.

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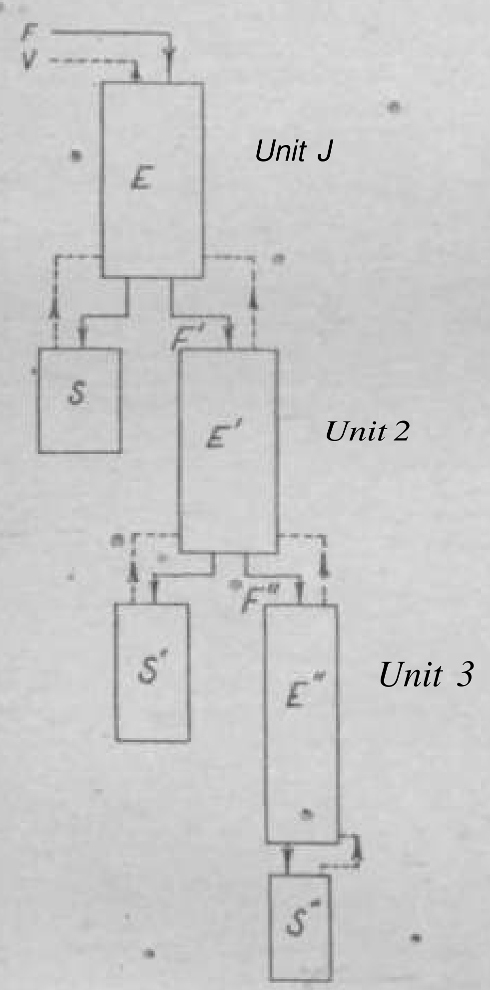
[1] T. Taylor and Urey, J. Cliem. Hiyakfl, 1U38,6, MS.

[1] UwU and MacOnaald, J. Amer. Chem. Sac. I1U0, 68, 2511).

* Urey, Hulfmatin, Thodc nml *fax,* J. Chem. Physics, 1937, 6, 850,

* Roberts, Thmle and Urey, J. Chum. Physics, 1030, 7, 137; Uroy, Mills, Rebuts, Thode *ud Hufl in ii in i. *ibid.,* p. 138.

In the systems of Table XIII used for partial separation of nitrogen isotopes, carbon isotopes and lithium isotopes by total reflux, a very long time would be needed for the steady-state separations to be established. This militates against large separations in ^reasonable times. However, the casuade system of Fig. 3 will produce a high concentration of ^{16}N in a relatively short interval. In the original system three separation units were employed. Ab F, atnmoniflm nitrate entered unit 1. which was analogous in principle to the column described in Table XIII for the separation of ^{U}N and ^{1S}N, In this unit the isotopic abundance ratio **was**



Fio. 3.—THBEE-UKIT CASCAL»K SYSTEM
FOR SEPARATION OF NITROOEM ISOTOPES.[1]

altered seven-fold. Six-sevenths of the hW was diverted from E to S, where boiling with **NaOH** served to **liberate** ammonia which **in** turn passed upwards through E and out at V. It was **then** converted to N**H$_4$NO,** and returned to £ at F. The remaining sixth entered the second unit at F" where the **tsotopk** ratio was altered nine-fold. About eight-ninths of the total solution was passed to S' where **boiling** NaOH solution liberated ammonia **which** was returned **through** E' and E. The remaining one-ninth was passed into the third unit E" where the abundance ratio was altered a further •If ven-fold. *All* this fraction was fed into S" where boiling NaOH solution again liberated ammonia which was fed back into unit 3 and passed up through the whole system. Each jnit consisted of glass columns of suitable leighU varying from 24 m. (1st unit) to 75 m. (3rd unit) and packed with Berl saddles or Fonsko lu'lices, all of glass. A maximum con-cciitrfttion of 72-8% ^{1S}N was obtained and the net transport of ^{15}N from ordinary nitrogen to samples ranging from 0-57 to 70-6% ^{1S}N was 0-75 g. per day. (Thode, Gorham and Urey, *i.* f liein. Physics. 1938, 6, 296; Thode and Urey, *ibid.* 1939,7,94.)

The cascade method has also succeeded in **producing** concentrations as high as 22% of ^{13}C at the rate of 0-1 g. per day. (Urey, Kep. on **Eroa. Phyfc 1989,** 6, **62).** The exchange reaction used was *[cf.* Table XIII):

$$H^{12}CN(gas) + {}^{13}CN'(aq.) \rightleftharpoons H^{13}CN(gas) + {}^{12}CN'(aq.)$$

Finally, the reaction

$${}^{34}SO_2(gas) + H^{32}SO_3'(aq.) \rightleftharpoons {}^{32}SO_2(gas) + H^{34}SO_3'(aq.)$$

has served partly to resolve sulphur isotopes (Thmlc, **Qorham** and Urey, J. Chem. **Pfaytlcs,** 1938, 6, •>{*<>; Stewart and Cohen, *ibid.* 1940, 8, 904).

(ii) Reactions confined to the Interface.—iJonic reactions occur only or primarily at & liquid-vapour interface. The reaction between hydrogen and sulphur is **belioYdd** to proceed in part in this way (Norrish and Hideal, J.C.S. 1922, 123, 696; *itfd.* 1923, 123, 1689). The decomposition of methanol occurred AS readily on liquid zinc as on zinc just below the melting-point (Steacio and Elkin, Proc. Roy. Soc. 1933, A, **142,** 467 ; Canad. J. Res. 1934,11, 47). The chief interest, however, centres upon reactions of a solute with insoluble monolayer films situated at the interface.

Oleic and ct's-petrosoh'c acids form insoluble monolayer films which are attacked at the double bond by dilute acid permanganate (Hughes and Rideal, Proc. Roy. Soc. 1933, A, 140, 253). The reaction occurs more easily when the films are dilute, since then the molecule lies flat on the surface and the double bond is accessible to chemical attack. When the molecule is oriented vertically by compression of the monolayer, the double bond is not readily accessible and reaction is slow. Reactions of hydrolysis have also been observed, both of simple esters and of y-hvdroxy-stearo-lactono, on alkaline substrates *(e.g.* Alexander and Schuhnan, *ibid.* 1937, A, **161,** 115). At constant surface pressure and alkali concentrations the latter reaction was of the first order with respect to the lactone and had **a** mmilur energy of activation (12,500 g.-cal. per g.-mol.) to the bulk phase reaction.

Auto-oxidation of j3-ehuo»teimn and its mal«ic anhydride addition compound has been studied (Geo u.fid Rideal, *Ond.* 1935, A, 158, lltf; Gea. p. 129) and it was found that the oxidation velocity decreased at higher film compression, jiifct us with oleic acid. Some film reactions are of obvious biological importance. Thus tannins combine with a protein monolayer *(cf-* Adam

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[1] After Urey, lUp. on Proa. Phy». 1039,6, 01.

"Physics and Chemistry of Surfaces," Oxford University Press, 1938, p. 97), and snake venoms attack lecithin by removing a long chain fatty acid group (Hughes, Biochem. J. 1935, 29, 437). A very striking phenomenon is the influence of the most minute traces of metallic cations upon the nature of surface films and upon reactions involving the films (Harkins and Myers, Nature, 1937, **139,** 367). The results available are fragmentary, but it appears that certain cations may influence the photolysis of stearic anilide films (Rideal and Mitchell, Proc. Roy. Soc. 1937, A, **159,** 206) and reactions of a a-hydroxystearic acid, stearic anilide and proteins (Harkins and Myers, Nature, 1937, **139,** 367; Rideal, Mitchell and Schulman, *ibid.* 1937, **139,** 625). It may be presumed that the cations are adsorbed under the monolayer, altering its physical state or chemical reactivity in ways not yet understood.

Films exposed to the action of solutes may be collected and subjected to qualitative chemical examination Nitrocellulose films exposed to sodium hydroxide solution and scraped off the surface by a glass rod were thus proved to have been denitrated (Adam, Trans. Faraday Soc. 1933, 29, 96). Langmuir and Schaefer (J. Amer. Chem. Soc. 1936, 58, 284) found that dilute **$Ca(OH)_2$** and **$Ba(OH)_2$** reacted with monolayers of fatty acid to give calcium and barium soaps if the p_a was sufficiently high. Other reactions at the gas-liquid interface are adequately reviewed by Adam ("Physics and Chemistry of Surfaces," Oxford University Press, 1938, pp. 95 *et seq.).*

D. REACTIONS INVOLVING THE LIQUID-LIQUID INTERFACE.

Few quantitative studies have been made of reaction rates in liquid two-phase media, although such systems are of the greatest importance in applied chemistry. The two liquids may be interdispersed as droplets, yielding emulsions, or they may be in the form of quiescent layers. Solvent extraction, soap-making, nitration and sulphonation are examples of large-scale processes where the velocity is of paramount importance. In these systems, the reaction zone often extends beyond the interface because the two liquids may be mutually soluble or the reactants may be distributed between them. The reactants may interact appreciably in one medium only, or both media may be active.

(i) The Velocity of Establishing Distribution Equilibria.—Studies on the rate of establishment of distribution equilibrium have led to seemingly contradictory conclusions. On the one hand, Berthelot and Jungfleisch (Ann. Chim. Phys. 1872, [iv], 26, 396, 408) found that the distribution equilibrium of iodine and bromine between water and carbon disulphide required several hours to be established; while on the other hand Nernst (Z. physikal. Chem. 1891, 8, 119) remarked upon the rapidity and certainty with which equilibrium was reached. Big differences may be due, however, to the extent of mixing and mechanical agitation. A solute introduced into one quiescent liquid layer requires many days to distribute itself uniformly and at equilibrium between the first layer and a second quiescent liquid layer.

(ii) Reaction Occurring in One Liquid Phase Only.—The simplest of liquid-liquid reactions are those confined either to the interface, or to one or other of the media. Löwenherz (*ibid.* 1894, **15,** 389) interpreted the hydrolysis of an ester partly miscible in water and present in excess as saponification occurring in the aqueous phase only. The rate of hydrolysis is increased by adding acid catalysts. The reaction rate is then

$$-\frac{dx}{dt} = k\,C_{\text{ester}}\,C_{\text{acid}}$$

By stirring, the equilibrium solubility of ester in water is maintained and so Cecter and Cadd both remain constant. Thus the rate of hydrolysis is constant. Using alkali as catalyst the reaction equation is approximately, under otherwise identical conditions,

$$-\frac{dx}{dt} = k\,C_{\text{alkali}}$$

The velocity equations of soap and fatty acid manufacture are subject of these equations.

The studies have been extended to the hydrolysis of an ester distributed between two liquid phases, aqueous acid solution (where reaction occurred) and benzene (Goldschmidt and Messerschmitt, *ibid.* 1899, **31,** 235). If it is assumed that the distribution equilibrium is maintained during the reaction, the reaction equation is:

$$-\frac{dx}{dt} = k\frac{V_1 a}{V_2 + V_1 a}(a - x)$$

where V_1 denotes the volume of the aqueous layer and V_2 that of the benzene layer; *a* is the absolute amount of ester and *z* is the amount hydrolysed at time *t*; *k* is the velocity constant and a is the distribution constant $= \frac{C\text{ (in water)}}{C\text{ (in benzene)}}$.

Integration gives

$$k = \frac{1}{t}\,\frac{V_2 + V_1 a}{V_1 a}\ln\frac{a}{a - x}$$

an equation admirably obeyed when ethyl acetate, distributed between water and benzene, was hydrolysed by water 1·0305N with respect to **HCl;** and when allowance was made for the fact that an esterification-hydrolysis equilibrium is set up. The analogous reaction using aqueous alkali and benzene obeys the law

$$k = \frac{1}{t}\,\frac{a+1}{a}\,\frac{x}{a(a-x)}$$

when V_1 and V_2 are made equal, and the concentration of alkali and ester are equal; but the reaction follows the equation

$$k = \frac{1}{t}\,\frac{a+1}{a}\,\frac{1}{(a-b)}\ln\frac{b(a-x)}{a(b-x)}$$

when the initial concentrations *a* and *b* are different.

Hydrolysis of a fat by a Twitchell reagent may occur at the interface itself. The hydrophilic autphonlc acid group dissolves in water; the hydrophobic hydrocarbon groups dissolve in the oil. The reagent therefore is adsorbed at tho interface, lowering the surface tension and assisting emulsification as well as bringing oil and water into more intimate contact through the adsorption layer. In Table XIV are given the hydrolytic cleavage efficiencies of 1% sulphonic acid solutions on neutral cotton seed oil heated in a current of steam.

TABLE XIV,—REACTION RATES WITH DIFFERENT TWITCHELL REAOENTS.[1]

Sul phonic-Btearo Aromatic compound of	Relative amounts of hydrolysis after					
	lire.	hra.	I** hre.	hrs_A	til Itr-.	30 hra.
Naphtha leno	140-7	190-7	201--1	211-4	—	—
Anthracene .	E-6	21-8	70'3	170-7	180-5	100-7
Phcnanthrenn .	467	1257	177-7	1S3-U	l'.ll 1	E01-1

[1] After Lewkowitsch, "Chemical Technology of Oils, Fata and Wanes," Oth ed., 19^1, Vol. I, p. 90.

E. REACTIONS AT THE SOUD-SOIXD INTERFACE.

Adequate discussion of reactions involving the Bolid-solid interface is impossible in this article. The processes of precipitation-hardening, photography, diffusion in solid media and across phase-boundaries, reactions in certain explosives, and of tarnishing and oxidation of metallic surfaces, and the dissociation of hydrates may be taken as typical of the chemistry of solid two-phase systems (surveyed in Discussion on "Chemical Reactions involving Solid*," Trans. Faraday Soc. 1938,34, pp. 821-984).

(i) Reactions of a Gas at the Solid-Solid Interface.—A common reaction of this type is found in hydrate and ammoniate formation, and in dissociation of carbonates ;

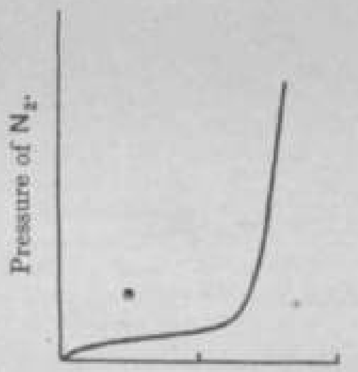
$$Na_2CO_3.10H_2O \rightarrow Na_2CO_3 + 10H_2O$$
$$Na_2SO_4.10H_2O \rightarrow Na_2SO_4 + 10H_2O$$
$$CaCO_3 \rightarrow CaO + CO_2$$

Such reactions do not occur save at the interface between the two solid phases, and it is frequentlj' necessary to scratch or *break the crystal before the reaction becomes appreciable. The reaction rate is then autoeatalytic, being divided into a slow initiation of reactive centres (the induction period), a spreading of reaction at rapidly growing interfaces, and finally, an exhaustion of the supply of material. Fig. 4 shows a typical curve for the decomposition of azjdes {Garner, Trans. Faraday Soc. 1938, 84, 885; Gamer and Maggs, Proc. Roy. Soc. 1939, A, **172,** 299; Wiscbin, *ibid.*, p. 314):

$$2KN_3 \rightarrow 2K + 3N_2$$
$$2NaN_3 \rightarrow 2Na + 3N_2$$
$$PbN_6 \rightarrow Pb + 3N_2$$

Quantitative studies of azide decomposition have shown that metallic nuclei form on the surface and interior of the crystal, and gradually increase in number. The dimensions of each reaction-nucleus also increase steadily; in barium azide the radius r increased at a constant rate for any given nucleus:

The constant *A* was an exponential function of temperature; $A = A_o e^{-\frac{23.000}{RT}}$. The number n of nuclei increased according to the expression *n—Bfi.* To interpret the azide reactions, Mott {*ibid.* 1939, A, **172,** 325) assumed that nitrogen driven off from the surface releases interstitial atoms of alkali which diffuse into the crystal. These, when their concentration is high enough, aggregate into metallic nuclei. The nuclei then act independently aa reaction centres. Aggregation of a similar kind may occur in Bilver halide crystals during the photographic process. The light liberates numbers of silver-atoms (and equivalent chlorine atoms) in proportion to its intensity. Some of the chlorine atoms diffuse away and react with gelatin. The interstitial silver remains, in a pattern of density reproducing the original image, as atomic centres from which reduction spreads during the developing of the visible picture from the latent image. This reaction is, however, complicated by other factors which are not considered here. {*See* Discussion on "Chemical Reactions involving Solids," Ft. 11A, Trans. Faraday Soc. 1938, 34. 883).



FIQ. 4.—INCREASE OF NITROGEN PRESSURE AS A FUNCTION OF TIME IN THE DECOMPOSITION OF AZIDSS.*

Typical autocatalytic reactions in which the reaction curve resembles that of Fig. 4, although, of course, the atomic and molecular mechanisms may differ inter *at,* are given below :

$$CuO + H_2 \rightarrow Cu + H_2O\ ^1$$
$$CuO + CO \rightarrow CO_2 + Cu\ ^2$$
$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2\ ^3$$
$$Ag_2O \rightarrow 2Ag + \tfrac{1}{2}O_2\ ^4$$
$$2AgMnO_4 \rightarrow Ag_2O + 2MnO_2 + 1\tfrac{1}{2}O_2\ ^5$$

• After Mott, Hpp. on l'roa. Phys. 1030, 6, 201. *

[1] Pease aud Taylor, J. Amer. Ohem. Sou. 1D21, 43, 2170.

• JOIJM and Taylor, J. Phyiilcal Chcm. 1&23,27, 623,

a Lcscoeiir, Aim. **Chlm.** Phyr 1892, Jvl), 26, 430.

* KciuUill and Fuclis, J. Amer. Chem. Soc, 11)21,43, 2017.

* SieverU rfhd Thcbcrnth, *I.* phyilksl. Chctn. 122, **100,** 463.

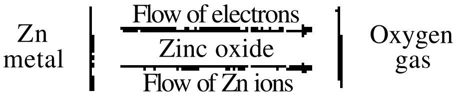
In some cases the deliberate creation of interfaces causes an acceleration in the reaction (Hulett and G. Taylor, J. Physical Chem. 1913, 17, 567). Thus, at 500°c. mercuric oxide gives oxygen and mercury. Because the mercury is a vapour at this temperature, the new interface is not developed and the equilibrium

$$Hg + \tfrac{1}{2}O_2 \rightleftharpoons HgO$$

is only very slowly established. But if iron oxide, manganese dioxide or platinum is added, equilibrium is at once set up. Similar observations were made when silver oxide, mercuric oxide and barium peroxide were decomposed in the presence of other oxides.

(ii) Tarnishing Reactions.—The oxidation of metals causes the formation of a skin of oxide which sometimes remains compact and coherent. A new phase is thus created and reaction can continue either at the gas-solid interface by transport of metal atoms or ions through oxide or at the solid-solid interface by a similar transport of oxygen atoms or ions. (For a survey, *see* Wagner, Trans Faraday Soc. 1938, 34, 851; Mott, Rep. on Prog. Phys. 1939, 6, 186.) There thus occur simultaneous diffusion and reaction, either of which may limit the rate of growth of the oxide film. Sometimes the film continues to grow steadily (**ZnO** on Zn) and sometimes oxidation virtually ceases when the film is not a great many atomic layers in thickness (**Al_2O_3** on Al). (v. Vol. III, 3686).

Zinc oxide can take up a stoicheiometric excess of zinc. Oxidation of this metal therefore occurs by diffusion of excess zinc from the metal through the zinc oxide to the external surface, where, it reacts with oxygen and forms more oxide. Zinc diffuses slowly, as ions, and electrical neutrality is maintained by an equivalent flow of electrons:



Oxidation of this kind obeys approximately the so-called parabolic diffusion law, $x^2=kt$ as required by the laws of diffusion (Wagner and Grünewald, Z. physikal. Chem. 1938, B, 40, 455. Vernon, Akenyd and Stroud, J. Inst. Metals, 1939, 65, 301, noted departures from the parabolic diffusion law).

Cuprous oxide is formed on metallic copper by another variation of the diffusion process (cf. Wilkins and Rideal, Proc. Roy. Soc. 1930, A, **128,** 394). Cuprous oxide is capable of taking up a stoicheiometric excess of oxygen (*cf.* Wagner, Trans. Faraday Soc. 1938, 34, 854). The process involves formation of equal numbers of holes at certain Cu^+ ion lattice sites and Cu^{++} ions' at others. The lattice is not otherwise disturbed and the crystal may then be regarded as a solid solution of cupric oxide in cuprous oxide. The holes diffuse from the oxide-oxygen interface to the metal-oxide interface, and are there filled by Cu^+ ions from the metal, the electron liberated passing into the oxide lattice and converting an equivalent number of Cu^{++} ions into Cu^+ ions. The mixed oxide near the oxygen-oxide interface is thus richer in cupric oxide than parts of the film adjacent to the metal.

Sometimes coherent films may be formed which do not grow in thickness beyond a certain value. Thus in the system **$Al/Al_2O_3/O_2$** the thickness of the **Al_2O_3,** if it remains coherent, does not exceed about 10^{-6} cm. An explanation has been given (Mott, *ibid.* 1939, 35, 1175) in terms of the quantum-mechanical effect known as tunnelling (p. 214c). The tunnelling particle is here the electron, and it has been shown that though the electron might penetrate an oxide layer 5×10^{-6} cm. thick (producing on the external surface of the oxide oxygen ions equivalent to the Al^{+++} ions which diffuse through the oxide from the metal), these electrons cannot be transmitted through appreciably thicker layers. Layer growth therefore quickly ceases.

F. REFERENCES TO TYPES OF HETEROGENEOUS REACTIONS NOT DESCRIBED ABOVE.

I. Precipitation-hardening in metals: Taylor and Mott (Rep. on Prog. Phys. 1939, 6, 205); R. Becker (Ann. Physik. 1938, [v], 32, 128). II. Development of the photographic image: R. Gurney and N. Mott (Proc. Roy. Soc. 1938, A, **169,** 151; various papers in the Faraday Society Discussion on " Chemical Reactions involving Solids" (Trans. Faraday Soc. 1938, 34, pp. 821-984). III. Quantitative aspects of crystallisation, of melts, and from aqueous solutions: Taylor's "Treatise on Physical Chemistry," 2nd ed., Vol. II, pp. 1033 *et seq.* (Macmillan & Co.). IV. Quantitative aspects of diffusion in solids: Barrer, " Diffusion in and through Solids " (Cambridge Univ. Press, 1941).

R. M. B.

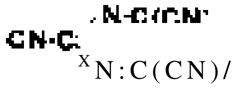
" *HETOCRESOL"* The cinnamoyl ester of tti-cresol used as a non-irritant dusting powder in the treatment of tuberculosis.

HEWETTITE. A hydrated vanadate of calcium, **$CaO\cdot3V_2O_6,9H_2O$,** crystallised in the orthorhombic system. It forms mahogany-red, earthy masses, composed of minute silky needles, and occurs somewhat abundantly as an oxidation product of patronite at Minasragra, near Cerro de Pasco in Peru. The mineral fuses readily to a dark-red liquid, and is slightly soluble in water. Sp.gr. 2-55.

Meiahewettite is identical with hewettite in composition and in crystallising in the orthorhombic system, but it differs somewhat in its optical characters and behaviour during dehydration. It is found as a dark-red, powdery impregnation in sandstone at Paradox Valley in Colorado, and over a wide area in eastern Utah.

L. J. S.

HEXACYANOGEN,



$$CN\cdot C \begin{matrix} \diagup N{-}C(CN)\diagdown \\ \diagdown N{:}C(CN)\diagup \end{matrix}$$

is produced by dehydrating the triamide of cyanuric acid at 210-250° with phosphorus pentoxide (Ott, Ber. 1919, 52, [B], 661) Mp 119°, b.p. 262°/771 mm./ 1 1 * W mm. It is decomposed by water and alcohols but withstands the action of dry hydrogen chloride.

n-HEXADECANEDICARBOXYLIC ACID, COjjH-tCH^e-COaH, is prepared by what is essentially the method of Crum-Brown and Walker (Annalen, 1891,261,125), *i.e.* by electrolysis of potassium ethyl sebacate followed by hydrolysis of the resulting ethyl hexadecanedicarboxylate (A. Franke and O. Liebermann, Monatsh. 1923, 43, 589). It has also been obtained by indirect reduction of clupahodonic acid (Y. Inoue and H. Kato, PTOC. Imp. Acad. Tokyo, 1934,10, 463).

Hexadecanedicarboxylic acid has m.p. 124°. For absorption spectrum, *see* Ramart-Lucas and F. Salmon-Legagneur (Compt. &nd. 1929, 189, 915); for crystallography, W. A. Caspari (J.C.S. 1928, 3235); for X-ray measurements, A. Normand, J. Ross and £. Henderson (J.C.S. 1926, 2632); and for dipole moment, C. Smyth and W. Walls (J. Amer. Chem. Soc* 1931, 53, 527).

This afid has achieved some technical importance by reason of its conversion into *cydo*-heptadecanone by heating its salts of rare earths (Swiss P. 122510-3; L. Ruzicka and co-workers, Helv. Chim. Acta, 1926, 9, 230, 389). W. Carothers and J. Hill (J. Amer. Chem. Soc. 1933, 55, 5043) have utilised the thallium salts (the first product of heat treatment being a linear polymer) and have also obtained polymeric cyclic esters on heating the acid with trimethylene glycol *(ibid.* 1932, 54, 1559). The suitability of several derivatives of hexadecanedicarboxylic acid for this ring-closure has also been examined (P. Pfeiffer and E. Lübbe, J. pr. Chem. 1933% [ii], 136, 321; P. Chuit and J. Hausser, Helv. Chim. Acta, 1929, 12, 850; c/. *also* S. Landa and A. Kfejvan, Coll. Czech. Chem. Comm. 1931,3,367).

HEXAHYDRITE *(v.* **Vol. IV, 3216).**

HEXAHYDROXYBENZENE is obtained by acidifying potassium carbonyl (Lerch, Annalen, 1862,124,22); by reducing tetrahydroxybenzoquinone (Maquenne, Bull. Soc. chim. 1887, [ii], 48, 64; *cf.* G.P. 368741); and by oxidising inositol with nitJic acid (Gelormini and Artz, J. Amer. Chem. Soc. 1930, 52, 2483). It forms needles which darken without melting on heating and is a strong reducing agent. Esters are prepared by fusing it *m* with the anhydride and*Na salt of the appropriate acid (Backer and Van der Baar, Rec. trav. chim. 1937, 56, 1161).

HEXALDEHYDE *(n-Caproaldehyde).* This aldehyde, C_5H_nCHO, is used in perfumery, and has a fruity odour, by which special effects can be achieved in most floral perfumes. It has b.p. 131°/760 mm., 28°/12 mm.; d^{30} 0-6337.

n. y p.

" ***HEXALIN*** " *(v.* Vol. I, 147<Z).

" HEXAMECOLL." A preparation of guaiacol and hexamethylenetetramine, used as a disinfectant dusting powder.

HEXAMETHYLENETETRAMINE *(v.* **FORMALDEHYDE, Vol. V, 3206).**

HEXAMETHYLENETRIPEROXIDIAMINE *(v.* **Vol. IV, 543A).**

" *HEXAMINE* " *(v.* **Vol. I, 326a).**

CYCLOHEXANE (Hexahydrobenzene; hexamethylene), C_eH_{12}.—A hydrocarbon occurring naturally in the petroleum oil of Rumania, Galicia and the Caucasus. It is produced by the catalytic hydrogenation of benzene with a nickel or noble metal catalyst (Sabatier and Senderens, Compt. rend. 1901, 132, 210; Ipatiew, J. Russ. Phys. Chem. Soc. 1907, 39, 681-693; Amer. Chem. Abstr. 1907, 1, 2878; Skita and Meyer, Ber. 1912,45, 3593).

Pure cyctohexane has m.p. 6-4°C., b.p. 81°$_f$ d^{20} 0-7791, and n£° 1-425. The commercial product has a melting-point of about +3° which indicates a fairly high degree of purity. It is the beat known solvent for 'both paraffin wax and rubber, and is also a valuable solvent for recrystallising purposes, being less toxic than the corresponding unsaturated hydrocarbons *cyclo*-hexene and benzene, A summary of observations on the toxicity of these three hydrocarbons is given in E. Browning, " Toxicity of Industrial Organic Solvents," issued by the Medical Research Council (Industrial Health Research Board), 1937, pp. 118-122. For properties and uses of the commercial solvent, *see* T. H. Durrans, " Solvents," 4th ed., London, 1935.

J. W. B.

HEXANITRODIPHENYLAMINE (Hexyl)(Vol.IV,489a).

HEXANITRODIPHENYL SULPHIDE (Picryl sulphide) (Vol. IV, 484c).

HEXANITRODIPHENYLSULPHONE (Vol. IV, 484d).

. HEXANITROMANNITOL (Vol. IV, 5004).

HEXANITROSULPHOBENZIDE (Vol. IV, 484d).

CYCLOHEXANOL (Hexahydrophenol),

C_tH_u-OH.

This isocyclic alcohol is produced by the catalytic hydrogenation of phenol in either the gaseous or the liquid phase. Conditions for this hydrogenation have been described in various publications and patents (Sabatier and Senderens, Compt. rend. 1903, 137, 1025; Ipatiew, Ber. 1907, 40, 1286; Brochet, Compt. rend. 1922,175, 583).

Common to these processes is the need for somewhat raised temperatures although the reaction itself is highly exothermic. Phenol is more readily hydrogenated than its homologues, and this seems to be only partly explained by the greater purity of the crystalline substance. A nickel catalyst is the one most commonly employed. Pure cyctohexanol is a crystalline solid, m.p. ca. 25°, b.p. 161-5°, d^{20} 0-947 and fig- 1-4654. CycZohexanol is stated to exist in two allotropic modifications (Nagctnov, Amer. Chem. Abstr. 1928, 22, 4485). Data as regards the melting-point are therefore somewhat uncertain.

Commercial cycZohexanol has a high degree of purity* containing only a small proportion (under 0*5%) of cyctohexanone. It has been marketed under various trade names, *e.g.* *" Anol,"* *" Hexalin,"* as well as under its chemical name.

Cyclohex&nol and its derivatives have obtained considerable importance as technical chemicals. The alcohol itself is a good solvent for dyes, waxes and shellac, and has found use in the manufacture of polishes, spirit varnishes and inks as well as in the textile industry. The esters, acetate, phthalate, etc., have found considerable use as solvents and plasticisers.

Methylcyclohexanol, $C_6H_{10}MeOH$. While four structurally isomeric methylcyclohexanols exist, interest is mainly centred in the three derivatives of the corresponding *ortho-*, *meta-* and *para-* cresols, *i.e.* the *hexahydrocresols*. These are obtained from the cresols by catalytic hydrogenation in the presence of a nickel catalyst under varying conditions according to the process used. Common to all is the use of a somewhat raised temperature. The 1:2-, 1:3- and 1:4-methylcyclohexanols show small differences in boiling-point and other physical characteristics (1:2- b.p. 167-168°, $d^{15\cdot5}$ 0·933; 1:3- b.p. 175-176°, $d^{15\cdot5}$ 0·924; 1:4- b.p. 173-174°, $d^{15\cdot5}$ 0·924). Stereoisomeric forms of m-methylcyclohexanol are known.

The methylcyclohexanol of commerce (also known under various trade names such as *"Sextol," "Methylanol," "Methylhexalin"*) is a mixture of the above three isomers in various proportions, and may also contain small quantities of cyclohexanol, and usually contains a very small percentage of the corresponding **ketones.** A typical commercial product has the following approximate composition: o-methylcyclohexanol 30%; m-methylcyclohexanol 35%; p-methylcyclohexanol 35%, and has b.p. 168-175°, d«-5 ₀.^5.

Methylcyclohexanol has become a solvent of considerable commercial importance. This is due not only to its solvent power for fats, oils and dyes, but also to its outstanding ability to reduce surface tension and to stabilise emulsions. These properties have led to an extensive use of this solvent in the textile industry, for the preparation of textile- laundry- and dry-cleaning soaps, and for textile dyeing and printing.

The esters, acetate, phthalate, a tea rate, etc., are used extensively as solvents and plasticisers in various branches of industry (v. Durrans, "Solvents," 4th ed., 1935).

J. W. B.

HEXATRIENE (**Vol.** II, 151a).

" HEXANON " (Vol. I, 38<M).

HEXOGEN (**Vol.** *III, 533d).*

HEXOKINASE (Vol. V, 24c, 35c).

HEXOPHAN (Bayer Products). 2-(4'-hydroxyphenyl) **quinoline-4:3'-dicarboxylic** acid, used in the treatment of gout (Pharm. J. **1925,** 114. **-02).** *"Lytopham"* is **2-phenylquinoline-**4:3'-dicarboxylic acid ((!udze&t and Kcip, Ther. d. Gegenw. **1821, Sft 127),**

HEXURONIC ACID (*v.* Vol. I, 502a).

HEXYL (v. Vol. IV, 480a).

n-HEXYL ALCOHOL, C_6H_{13}-OH. This alcohol and its esters have been used as synthetic perfumes. They are, however, of little importance.

E. J. P.

HIBBENITE *v.* HOPEITE.

HIDDENITE. A transparent, emerald-green variety of the mineral spodumene, $LiAlSi_2O_6$, used as a gem-stone. It is found **with** emerald in North Carolina, and has been popularly, but erroneously, known as " lithia-emerald."

L. J. S.

" *HIDUMINIUM* " (*v.* **Vol.** I, **253b).**

HIERATITE (*v.* Vol. V, 606).

HIGHGATE RESIN. Copalin, a fossil resin resembling copal found in the blue clay of Highgate Hill.

HIGH PRESSURE REACTIONS. *The Influence of Pressure upon Chemical Reactions* ***in*** *the Liquid Phase.*—In considering the effect of pressure upon the course and rate of a **chemical** reaction in the liquid phase it is necessary to take into account its influence upon certain of the physical properties of the medium. Thus, for example, any change in the specific volume, viscosity, specific heat or the melting- and boiling-points of the reactants may exert an appreciable influence upon the velocity. It is also well known that solvents may interfere with the mechanism of a reaction, and in a number of instances a correlation has been observed between the effect of the solvent and such properties as refractive index, dielectric constant and cohesion (Moelwyn-Hughes, " Kinetics of Reactions in Solution," The Clarendon Press, 1933, p. 51). Although such **relationships** are quite **specific,** it is clear that any factor, such as pressure, tending to bring about a change in one or more of them will exert an influence upon reaction velocity. There is also evidence that pressure may give rise to an induced or increased polarity of the reactant molecules, and it has been suggested that some of the potential energy gained by a system as the result of isothermal compression may, in certain circumstances, become available as part of the activation energy necessary for reaction to take place (Fawcett and **Gibson,** J.C.S., 1934, 380).

Two important properties which require consideration are compressibility and thermal dilatation. The volume change when a liquid is subjected to hydrostatic **pressure** is determined by changes in molecular configuration, by the closer packing of individual molecules and, to some extent, by the deformation or compression of the molecules **themselves.**

The thermal dilatation of liquids, in general, decreases with increasing pressure up to about 4,000 **atm.,** after which **the** pressure effect **becomes** irregular and, in some instances, changes in sign, the dilatation increasing over a range of several thousand atmospheres and then again decreasing.

It will be seen from the data in Table I that both in respect of the compressibility and the dilatation, there is a tendency for most liquids at high pressures to lose the individual differences which usually characterise them; thus, the ratio of **the** dilatation of ether to that of amyl alcohol at low pressures is 1·5 whilst at [illegible] has fallen to 1·03; furthermore, the effect of pressure in decreasing the compressibility is [illegible] than its effect in decreasing the dilatation.

The ***Collision Number*** *in the Liquid Phase.*—[illegible] molecules in a liquid differ in some important respects from those in a gas.

TABLE I.—CHANGES OF COMPRESSIBILITY AND THERMAL EXPANSION PRODUCED BY PRESSURE (Bridgman, Proc. Amer. Acad. 1913, 49, 1).

Liquid.	Compressibility K.			Dilatation δ.		
	$\frac{K_1}{K_{12,000}}$	$\frac{K_{8,000}}{K_{12,000}}$	$K_{12,000}$	$\frac{\delta_1}{\delta_{12,000}}$	$\frac{\delta_{8,000}}{\delta_{12,000}}$	$\delta_{12,000} \times 10^4$
Methyl alcohol	18·4	2·20	7·4	4·29	1·23	2·98
Ethyl alcohol	13·7	2·02	8·1	4·50	1·30	2·08
n-Propyl alcohol	16·8	1·04	7·0	4·80	1·33	2·37
isoButyl alcohol	18·6	1·08	8·8	4·16	1·17	2·75
isoAmyl alcohol	14·1	1·88	7·1	4·40	1·30	2·40
Ethyl ether	—	1·62	9·6	—	1·32	2·48
Acetone	—	1·85	8·7	—	1·35	2·88
Carbon disulphide	13·8	1·82	8·7	5·47	1·31	2·02
Phosphorus trichloride	14·2	1·81	8·4	4·84	1·31	2·78
Ethyl chloride	—	1·78	9·0	—	1·37	2·87
Ethyl bromide	14·9	1·87	8·2	—	1·33	2·00
Ethyl iodide	14·9	1·89	8·1	4·86	1·22	2·48

In a liquid containing, for example, two reacting species A and B in solution, each reactant molecule will be surrounded by a cage of solvent molecules and collision can only occur by a process of diffusion during which one molecule penetrates into the cage occupied by another. Once having become "co-ordinated" in this way the 2 molecules may make a large number of collisions before separating. In a gas a collision is a unique event and a second collision between any two specific molecules hardly ever occurs immediately.

The number of binary collisions in a gas is given by the equation:

$$Z = n_1 n_2 \sigma^2_{1,2}\left\{8\pi RT\left(\frac{1}{M_1}+\frac{1}{M_2}\right)\right\}^{\frac{1}{2}} \quad (1)$$

where n_1 and n_2 are the number of molecules per c.c. of molecular weight M_1 and M_2, respectively, and $\sigma_{1,2}$ is the average molecular radius. The corresponding number for a liquid under similar conditions would be about 10 times greater and would increase with pressure approximately as the viscosity. Reaction occurs as the result of collisions between molecules having energies equal to or in excess of a certain critical value E. The number of such collisions is obtained by multiplying (1) by $e^{\frac{-E}{RT}}$. The majority of liquid phase reactions are bimolecular and the rate of change is given by

$$\frac{dn}{dt} = C \cdot n_1 n_2 \sigma^2_{1,2}\left\{8\pi RT\left(\frac{1}{M_1}+\frac{1}{M_2}\right)\right\}^{\frac{1}{2}} e^{\frac{-E}{RT}} \quad (2)$$

where C is the ratio of the collision number in the liquid phase to that in the gaseous phase.

From (2) the bimolecular velocity constant k, expressed in litres per g. mol. per sec. can be evaluated. Thus, if N is the Avogadro number

$$k = \frac{dn}{dt} \cdot \frac{1}{n_1 n_2} \cdot \frac{N}{1,000} \quad (3)$$

By combining (2) and (3)

$$k = \frac{N}{1,000} \cdot C \cdot \sigma^2_{1,2}\left\{8\pi RT\left(\frac{1}{M_1}+\frac{1}{M_2}\right)\right\}^{\frac{1}{2}} e^{\frac{-E}{RT}} \quad (4)$$

and, differentiating with respect to temperature,

$$\frac{d\ln k}{dT} = \frac{E + \frac{1}{2}RT}{RT^2} \quad (5)$$

A similar result may be obtained from the Arrhenius equation

$$k = BZe^{\frac{-E_a}{RT}} \quad (6)$$

In this equation Z denotes the number of encounters between reacting molecules under specified conditions, E_a is the "critical increment of energy" and B is a factor representing the probability that a collision involving the requisite energy will lead to reaction.

On differentiating (6) with respect to temperature

$$\frac{d\ln k}{dT} = \frac{E_a}{RT^2} \quad (7)$$

From (5) and (7)

$$E = E_a - \frac{1}{2}RT \quad (8)$$

The difference between E and E_a is usually unimportant except where T is high or E is small.

The velocity constants and critical increments of a large number of bimolecular reactions in solution have been measured at atmospheric pressure and about 40% of them are found to have normal velocities in accordance with (1); in such cases the calculated collision frequency varies little from reaction to reaction, an average value being about 2·8 × 10^{11}, and the probability factor does not differ much from unity. Of the remaining reactions the greater part are "slow" in the sense that their velocities are from 10 to 100,000 times slower than the calculated values and B is less than unity, whilst a few, on the same basis, may be classified as "fast," B being greater than unity. All three types of reaction show positive responses to pressure.

Whilst the cause of such abnormal rates is not known with certainty there are a number of factors which might be responsible. Thus, in the case of "slow" reactions the endothermic formation of a complex prior to the reaction proper, deactivation by molecules of the solvent, or special conditions of orientation or of internal phase of the reacting molecules at the moment of impact would account for the apparent slowness of the reaction. "Fast" reactions might be due to the exothermic formation of a complex prior to reaction, the distribution of the energy of activation among a number of internal degrees of freedom of the reactant molecules, the occurrence of a chain reaction, or activation by some external source of energy (Moelwyn-Hughes, *op. cit.*), If it be assumed that, prior to reaction, two molecules posseading the requisite activation energy must come together and form a pre-activated complex, then reaction will occur when the life period *8* of the complex is equal, to or greater than the time (required for the completion of the internal motions of the molecules necessary to bring the atoms to appropriate distances, and with suitable relative velocities for new bonds to be formed. If the collision complex is stable, *6* will be large and the factor B of equation (6) will be constant and independent *ofE;* on the other hand, when, (ia appreciably greater than 0, a correlation should be observable between BZ and *E*. Since the life of the complex in terminated, either by separation of its constituents by deactivation in a collision, or by cheuu'cal transformation, the effect of hydrostatic- pressure would be, presumably, to increase its stability (Fairclough and Hinahelwood, J.C-S. 1937, 538). In this connection recent work has shown that whilst pressure accelerates both " normal " and " slow " reactions its effect upon the latter class is far greater than upon the former; in " slow " reactions moreover both B and *E* are found to vary with pressure in a regular manner.

As a typical example of a normal reaction the interaction of sodium ethoxide and ethyl iodide in alcohol solution may be considered {Gibson, Faweett and t'crris, Proc. Roy. Soc. 1935, A, **150,** 223). The reaction

$$C.H,\text{-}ONa+C_2H_BI \rightarrow C,H_S\text{-}O\text{-}C_2H_S+NaI$$

is bi molecular and the velocity constants are found to vary with the initial concentration of the sodium ethoxide but mlt with that of the ethyl iodide. In Table II the constants for 0-1 normal solutions at temperatures between 15° and 30°C. and over the pressure range 1-5,000 kg./cm.^{E} are given.

TABLE II.—Tire VELOCITY CONSTANTS FOE THIC IJTTERACTION OF SODIUM ETHOXIDE AND ETKYI. IODIDE IS ALCOHOL SOLUTION AT VAHIOCS PBKSSURES.

Temperature, °C.	Pressure, kg.;cm.*.	$K_1 \times 10^3$.	K (obs.) $\times 10^3$.	**K (cole.) XJO^8.**
		g. nial./lltrc/mli**into.**		
14-85	1	—	2-30	2-27
19-95	1	—	4-19	4-26
25-0	I	—	7-73	7-79
300	1	—	13-60	13-90
14-85	2,980	4-25	3-65	3-57
19-95	2,980	7-59	663	6-72
250	2/.>80	14-40	12-40	12-30
KM)	2,980	25-20.	21-60	2200
150	5,000	6-6	46	4-65
•200	5,000	10-3	8-4	8-48
25-1	5,000	19-4	15-9	15-80
301	5,000	84-2	281	27-50

The constants *K*, in column 3 of the table are uncorrected for the changes in concentration due to the thermal expansion and compressibility of the solvent; in column 4, *K* (obs.) are the corrected values.

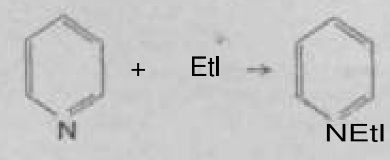
It will be seen that whilst the velocity increases with pressure the effect is not very marked and at 5.000 kg./cm.^{2} the rate is only about double that at atmospheric **pressure.** From the experimentally determined constants the values of BZ and *E* (equation 6) are found to be:'[1]

Pressure, kg./cm.-.	BZxlO^{13}.	d *B,* g.-cal.
1	1-28	20,740
3,000.	2-23	20,800
5,000.	1-32	20,34V

The values of *K* calculated from these constants are given in.'-column 5 of Table II. The changes in BZ and *E* with pressure are not. in tins instance, of sufficient magnitude to enable any distinction to be made as to their relative importance in determining the observed acceleration of the reaction.

Somewhat similar results, are found for the hydrolysis of sodium monochloroacetate by sodium hydroxide in aqueous solution. The reaction ia biraotaeular and " normal " and its velocity increases with pressure, the value at 12,000 kg./cm,^{3} being about 6-5 times the value at atmospheric pressure.

The above reactions may now bo compared with a typical " alow " reaction, namely that between pyridine and ethyl iodide in acetone solution



The rate of this reaction at 3,000 kg./cm.^{1} is 7-2 times, and at 8,500 kg./cm.^{2} is 47-5 times as great as that at atmospheric pressure. The variations of tt.e constants of the Arrbenius equation with pressure are as follows:

Pressiiri-, kg./cm.^{1}.	BZxio^7.	A', R.-cal.
1	2-13	14,390
2,975.	.71 *	15,350
5,000.	.1970	15,510
8,500.	.2,4<*0-0	16,380

Both constants show a marked increase with pressure.

In the foregoing examples the reaction rates have Ueen measured in dilute solution and are, therefore, influenced to some extent by changes in the physical properties of tho solvent with pressure.

An interesting example in which the pure reactants and products only are concerned ia that of the esterification of acetic acid by a series of alcohols (F'ong, Sapiro, Linstcad and Newitt, J.C.S. 193S, 784). Measurements have been made of the rates of eaterification at a numl>er of pressures from atmospheric to 4,000 atm. and the **corresponding** velocity constants have been **dftttminod.** The valueb of tho constants of the Arrheuiua equation for the reactions are given below :

VALUES OF THE CONSTANTS OF THE ARRHE.VIUS EQUATION FOB THE RATE *OV* ESTERIFICATION OF ACETIC ACID WITH A SESIKS OF ALCOHOLS, •

Alcohol.	Pressure, **lillll.**	*B*, g.-cal.	A or BZ.
Ethyl	1	13,770	4-58 x 10^{s}
	2,000	13.790	2-40 x 10^{3}
	3,000	13*830	6-10 x 10^{8}
	4,000	1&980	1-61 X 10*
n-Propyl . . .	1	13,550	4-10 x$1O^{3}$
	2,000	13,910	2-98 x 10^{s}
	3,000	14,190	8-87 x 10^{8}
	3,750	14,740*	3-33x10*
n-Butyl . . .	1	13,720	5-69 x$1O^{a}$
*	2,000	14,580	700 x$1O^{8}$
	3,000	14,950	244 x 10*
	3,750	15,190	5-72 x 10*
troPropyl .	\	16,890	3-20 x 10^{s}
	2.000	19,400	2-15 x 10*
	3,000	20,660	2-60 x 10'
	3,750	22,220	4-38 x 10^{s}
uoButyl .	1	16,480	4-84 X 10*
	2,000	17,850	1-30x10«
	3,000	18,240	3-35 x 10^{8}
	3,750	18,7KM	1-16 x!0^{T}
sec. -Butyl	]	**17,460**	2-50x10*
	2,000	19.790	3-53 x 10«
	3,000	21,010	4-90 x *W*
I	3,750	21,7-0	2-22 x 10^{B}

Both E and BZ increase with pressure, the effect being greatest with t«opropyl and sec.-butyl alcohols; there is also, in all eases, a functional relationship between the two constants, straight lineB being obtained by plotting values of *E* against log BZ,

UnimoUctdar Decompositions.—It would be expected from the Le Chattier-Bra un principle of mobile equilibrium that increase of pressure would exert a retarding effect upon the rate of a unimolecular reaction, and such is,found to be the ease. Phenyl ben zylmethy Lilly la mmoniuin bromide decomposes at & measurable rate in chloroform solution at temperatures between 25 and 45^{g}C. The reaction is reversible and to determine the velocity constant of the decomposition it is necessary to measure the equilibrium constants a at the various temperatures employed. The results for a 00975 normal solution are summarised in Table III (Williams, Perrin and Gibson, Proc. Roy. Soc. 1936, A, 154, 084).

TABLE III.—DECOMPOSITION or PHENYL-**BENZYLMETHYLALLYLAMMONIUM BaOMIDI** IN CHLOBOFOBM SOLUTION.

(Strength of solution <~0-097f> normal.)

Temperature, "C.	Pressure, *kg*, /cm.^{1}.	**a**	*K* (oba.) **xlO*.**	***K* (wile.)** x$1O^{4}$.	***aK*** **xlO*.**
			g. me	L/litw/mJ	**mite.**
250	*1*	**7-97**	3-23	**318**	**0-2&S**
29-95	**1**	**51**	**7-4**	71	0377
84-03	**1**	**2-21**	**J5-8**	**IK-SB**	**0-350**
1M	**1**	**1-44**	**3£-3**	**347**	**O-49S**
44-9 i	**1**	0*64	**74-5**	**730**	**0-478**
25-0	**2,980**	78 •*	**B-Ifl**	**2-24**	**1-83**
29-I)">	**2,080**	**340**	**51**	**49**	**1-74**
34-95	**2,980**	**18-8**	**10-7**	**109**	**1-80**
40'0	**2,0SO**	**106**	**22-9**	**23-4**	**2-43**
44-U	**2,980**	7-37	**47-8**	**48-9**	**351**

Polymerisations by Prusure.-^As an example of the effect of pressure upon this class of reaction the behaviour of a.-metfaylstyrcno may be given. Under normal conditions the trimeride is the highest polymer obtained either by heat alone, or with addition of Florida earth or boron trichloride; on the other hand, at 5,000 ntma. and 100°C, a mixture of high polymers with a mean molecular weight of 5,600 is obtained. The effects of temperature and time upon the yields obtained at different pressures are aa follows:

POLYMERISATION OF a-METHYLsTYHRNK (Sapiro, Linatead and Newitt, J.C.S. 1937, 1784).

'IVmpcr- **ntiiirp °fl**	Pressure, at in.	Time, hours.	Yield, per cent.			Mean molecular weight of high polymers.
			Monomer.	Low polymers.	High polymers.	
100	6,000	1	98-99	—	—	—
		14	**82-6**	3-4	C4'0	—
		90	Id	—	85	6,400-5,800
no	3,500	95	23	12	65	2,600
120	2,000	**Bl**	68-3	27-2	4-5	1,600
		260	**48*0**	48-7	5-3	—
125.	4,000	96	46-4	27-7	* 260	1,050
	10,000	47	210		790	1.170
150	4,000	48	18-1	81-9 (M.W.~37O.)	none	—

Another example of **prnmra py**merisation has been worked out in detail (iiuint>rick, Sapiro and Newitt, J.C.S. 193tt, 17til). When *cyclo-*pentadietie in the pure liquid phase is subjected to high hydrostatic pressure, reaction is found *%o* proceed in three distinct Btagea, depending upon the temperature and pressure, viz. (1) dimerisn.t,ion to dicye/opentadiene only, (2) association to higher polymers amongst which the trimer and tetramer have been identified, and (3) a violent disruptive reaction producing methane and a highly carbonised residue.

The bimolecular velocity constants of the dimerisation reaction have been measured over the temperature range 0-40°C. up to a pressure of 5,000 atm. The values of the ratio *KpjK-i* tabulated below show an increase with temperature, particularly in the higher pressure ranges.

THE INFLUENCE OF TEMPERATURE UPON.THE RATIO *KpjK^* FOB VARIOUS PRESSURE RANGES.

Temp., °C.	Values of $J(_r!K_1$ for the pressure range (atm.):				
	1-500.	1-2,000.	1-3,000,	1-4,000.	1-5.000.
0°	1-53	**5-48**	12'3	23-7*	44-2
20'	1-6fi	7'65	15-5	33-3	—
30°	I'8(1	7'74	I8-S	—.	—
«0°	2-or.	8-75	—	—	—

As with most other liquid phase reactions which have been investigated at high pressures the values of BZ and *B* of the Arrhenius equation increase with pressure. The term BZ is made up of the collision number Z and a probability factor B both of which may vary with pressure. If the collision number be assumed to remain constant at 10^{14}, i.e. about 10^s times.greater than the gas collision number, then it is found that for a pressure increase of 5,000 atm, the probability of interaction between two *cyclo*-pentadiene molecules with the requisite energy *E* is in creased by more than 10^s times. Thi3 result is not improbable ; the viscosity of the medium ja increased by a factor of at least 10 at the higher pressure, and the tendency towards orientation of the molecules, always evident in the liquid phuse, is thereby increased. If such orientation brings pairs of molecules into the correct relative position for interaction, the probability factor will show a corresponding increase.

The activation energy term *E* is composite and made up of energy contributions arising from changes in the physical properties of the medium and from variations of the rate of diffusion of the reactant molecules. Since BZ also contains terms which depend upon such changes some simple relationship between them ja to be expeclw]. In nearly all cases it is found that on plotting Jog BZ against *&* ^{a} straight line is obtained. It baa also been shown by Newitt and Waasermann (J.C.& 1940, 735) that the pantnutters *E* and BZ calculated for constant volume conditiona ;in: Independent of pressure.

a*n. N.

HIGH TEMPERATURE CARBONISATION (*r.* \VI. V, **3074, 4.10,** «1).

H11ROGANE.—" Hiirogane " ia the name given to a blooil-red coloured metallic coating obtained on copper by treatment with an aqueous solution of copper sulphate and verdigris, or on copper alloys by heating with a paste containing a cupric salt, borax and a little water. The colour may be due to a mixture of cuprous and cupric oxides (*cf.* Miyazawa, J. Chem. Intl. TokyO, 1917, 20, 1102; J.S.C.I. 1918, 37, 21U).

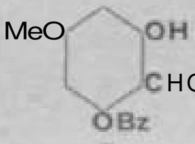
HILGARDITE. Hydrated chloroborate of calcium, $Ca_{fi}(B_{fl}O_{11})_sCl_4,4H_2O$, aa colourless triangular plates with monoclinic-domatic symmetry. It is found amongst the sandy residue accumulating at the bottom of the brine well in the Choctaw salt dome in Louisiana. Dimorphous with this, antl with the crystals tnte.r-grown in parallel position, ia *jMrakflgardite* with triclinic-pedial symmetry (C. S. Hurlbut and E. E. Taylor, Amer. Min. 1937. 22, 1052: 1938 23, 7G5, 89SN.

L. J. ft

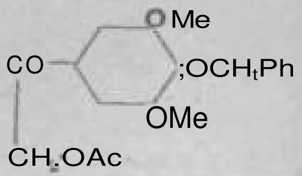
HINK'S TEST (*v.* Vol. II, 167a), ,

HIPPOCASTANIN (*v.* Vol. 111,276).

HIRSUTIOIN is the .anthocyanidin obtained by arid-hydrolysis of hirsutin (*q.v.,)$_t$* a colouring matter of the petals of *Primula hirsute.* Karrer and Widmer {Helv. Chim. Acta, 1927, 10, 758) recognised it as the 5:3':5'- or 7:3':5'-trimethyl ether of delphinidin (*q.v.)* from analytical data, colour reactions and the formation of syringic acid when hiroutone (*set* HntSOTnr) was hydrolysed by means of alkali. The correctness of the second alternative was established by synthesis (Bradley, Robinson and Schwarzenbaeh, J.C.S. 1930, 7EJ4). 4-O-Methyl-i'-O-benzoylphloroglucinaldehyde (I) and &i-acetoxy - 4 - benzyloxy - 3:5 - dimethoxyacetophenono (II) condensed by means of dry HCl in ethyl acetate solution gave a benzoylfited salt, from which (III), identical with hirsittidin chloride, was obtained by de-acylation.



I.



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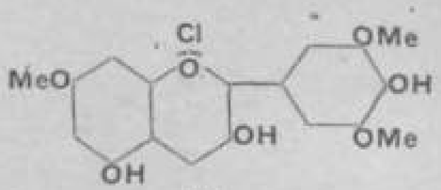


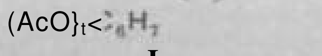
III.

The *chloride.,* $C_{18}H_nO_TCl$, crystalJises from aqueous HCl in the form of **short,** dark red, [jointed prisms. It dissolves in hot water ;o a pale red solution with a violet tinge, jut this rapidly becomes colourless on boiling Wring to formation of the *pseudo-base*; on Hiding acid the colour is restored. Even in hot)-5% HCt the salt is only **roaringly** soluble *At* a reddish solution, and A *oola* ia(orated soluiou in 4% HCl is pink. A freshly prepared solution in methyl alcohol is violet-red, and this becomes pure blue on the addition of solid sodium acetate or sodium carbonate solution. If the solution is kept for some time previous to* the test a greenish-blue colour is obtained". The chloride **dissolves** in 01iV aqueous sodium hydroxide forming a purple-Blue solution which rapidly becomes crimson-blue (dichroic) and then fades to emerald green. The cooled solution in hot 0-25% HC1 apparently contains much *pseudo-base* since excess of sodium carbonate gives a brownish-green solution changing to olive-green. Unlike cyanidin and delphinidin (</.(>.), both of which reduce **FchUng'a** solution in the cold, hirsutidin is affected only on heating. It gives no colour reaction with ferric chloride.

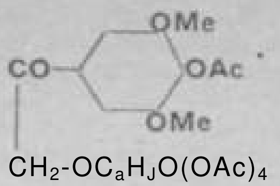
\V. B.

HIRSUTIN. A study of the colouring matters of *Primula* has shown that She petals of *P. viscoea* owe their hueto malvin, which is also present ifi the blue wild mallow *(Alah-usylvestrin),* **that P.** *iiitcgnfolia* contains malvin and an anthocyanin with a smaller methoxyl-contint. whilst *P. Itirsutn* **contains hirautin,** n. **methyl** ether of malvin (Kurrer"[1] and VVidmer, Helv. Chim. Acta, 1!t^7, 10, 758}. Hirsutin *chloride* crystallises **readily** and **separates** from hot 1% HC1 on adding 5% **methyl-alcoholic** HC1 **in** the form of deep brownish-violet **felted needles of the** ***UirahydraU,*** $C_{30}H_{37}O_{17}CI,4H_2O$ (dried En **a** desiccator over **Btuphurio acid},** m,p, 150-153° (decomposing after sintering at about 145°). The anthocyanin is sparingly soluble oven in very dilute HCI to a violet-red solution which is bluer than tiiat of **cyanifl (?.w.).** In alcohol the colour is a **deeper** blue. **Whan** sodium acetate or sodium carbonate **wadded** to an acid solution the violet *colour-bast* (IV) separates-; hirsntift is unique amongst natural anthoeyanius in that the colour-base does not dissolve in alkalis to form a blue alkafi suit. Hinmtin is **hydrolysed** on heating with 20% HCI to **hirsofcidin** (1 **mol.)** *(q.v.)* and glucose (2 mol.)- It is oxidised by 15% hydrogen peroxide to *himutone,* CaQH^O^, a •colourless, highly crystalline ketone which dissolves easily in hot water b*t sparingly in cold. Hirsmtone is very easily hydrolysed by means of aqueous sodium **hydroxide with** formation of syringic; acid (3:5-di-O-niethylgallic acid).

The constitution of hirsutin has bfen established by K. Hobinson and co-workers (J.C.S. 1930, 793) who showed tint hirautidin ia the 7:3'J:5'-trimethyl ether of delphinidin. Bobinson and Todd *(ibid.* **1932,** 2293} showed that the sugar component is present in the form of two glucose **nnita** attached to positions 3 and 5, they synthesised hi is u tin by condensing 2-O-tetra-aeetyl-*fl*-gluecwidyl-4-O-methyl^hloro-glueinaklehyde (1) with w-O-<t'tra-aeetyl-/J-glucosidoxy-4-acetoxy-:i:5-dinicthoxyacetophenone (II) **to** a ilavytium sail which was then **deaoetylated to hinatin (III).**



I.



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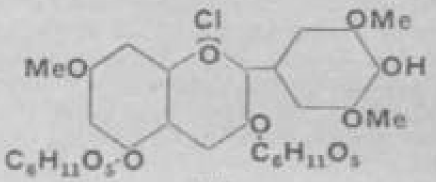
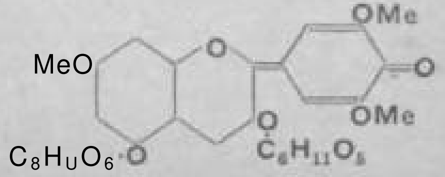


III.



IV.

I'mils hir.sutidin-3-0-glueoside and **binratidin** S-jS-liwrtoskle differ in properties from **hJrsutm.** The 3:5-dig!ucoside structure **relates himrtin to** pelargonin, cyanin, paonin, delphiu and malvin.

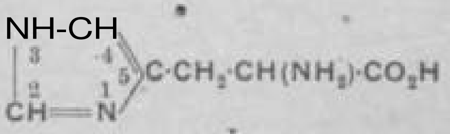
W. B.

HIRUDIN (». Vol. II, 24c).

HISPIDOGENIN (o. Vol. II, 385d).

HISTAMINE(i>. **Vol.IV,33W).**

HISTIDINE, *ijlyoxalint-a-alaninc,j}-i>ninil' zotyl-a-aminopropionic acid,*



I.

was Jiscovered by Kossel (Z. physiul. Chem. *lH'M,* 22, 170) among the products of hydrolysis of the protamiue sturine, which contain 12-9% histidine (Kossel, *ibid.* 1900, 31, 207). It ia an important constituent of many animal and vegetable proteins and according to Bo one (Med. **BulL** Tniv. Cincinnati, 1931, 6, **103)** it iMtiipies a terminal position, since 5-20% of the histidine content can be isolated in an optically active state after mild alkaline hydrolysis of hemoglobin, edestin, casein **sad** XVitte'tt peptone. HbtidJne occurs in histones (basic proteins) (Lawroff, Z. physiol. Chein. 1809, 28, 383; Abderhakien and Kona, *ibid.* 1904, +1, 278; Kossel and Staudt, ***ibid,*** 1926, **159,** 172); in gelatin and egg albumin (Sirums, ,1. (Jen. Physiol. 1928, **11. 6*3)**j **in crystalline** insulin (2-57%) (Jensen, Wintersteiner and Du Vigneaud, J. Pharm. Exp. Ther. 1W2«, **32,** 387); in horse haemoglobin (7-64%) (Vickcry and Leavenworth, J. Biol. Cbem. 1928, 79, 377);«in crystftliiiK: nwluiuiuglobin {7-5-7-6%) (Abderluildcn* Fleisehmann and Irion, Fermcntforach. 1929, 10, 44(3); in the antipeptone obtained by **pancreatic digestion** <>*f* fibrin (Kutecher, *Z.* physiQL Chem. 1898, **25,** 195); and haa been isolated from other proteins (Hedin, *ibid.* 1896,

22,191); from red blood corpuscles (15 g. of the hydrochloride from 500 c.c. of blood corpuscle pante) (Jones, J. Biol. Chem. 1918, **33,** 429; Hanke and Koessler, *ibid.* 1920, 43, 521; Chemnitius, Pharm. Zentralk. 1928, 69, 471); from fresh fish (Suzuki, J. Agri. Tokyo, 1912, 51, 1); from fish sperm (Yamagawa, Mikawa and Tomiyama, J. Imp. Fish Inst. Tokyo, 1926, 22, No. 2,30; Biol. Abstr. 1927,2,975); from *Octopus octopodia* (Morizawa, Acta Schol. Med. Univ. Imp. Kioto, 1927, 9, 299); from diphtheria bacillus (Tamura, Z. physiol. Chem. 1914, 89, 295); from newly hatched chicks (0·05%) (Yoshimura, J. Chem. Soc. Japan, 1936,**57,**318); from the yolk, white, embryo and shell membrane of hen eggs (Calvery, J. Biol. Chem. 1932, 95, 297); and from human hair (0-5%) (Vickery and Leavenworth, *ibid.* 1929, **83,** 523). Histidine occurs in human pregnancy urine and its presence has been suggested as a test for this condition (Foldes, Biochem. Z. 1936, **283,** 199; 1936, **285,** 294, 296; *cf.* Kapeller-Adler, *ibid.* 1936, **285,** 123; Armstrong and Walker, Biochem. J. 1932,26,143; Kapeller-Adler and Haas, Biochem. Z. 1935, **280,** 232; Renton, S. African Med. J. 1935,9,441; Bod6, Amer. Chem. Abstr. 1935,29,1865), but this suggestion has met with severe criticism (Louros, Klin. Woch. 1934, **13,** 1156; Gertler, Endokrinologie, 1936, **17,** 45; Bosman, S. African Med. J. 1935, 9, 514; Hecksteden, Deut. Z. ges. gerichl. Med. 1935, **24,** 253), especially since it occurs in normal urine (Wada, Acta Schol. Med. Univ. Imp. Kioto, 1930,**13,** 187; Pellizzari, Boll. Soc. Ital. Biol. sperim. 1934, 9, 517). Histidine occurs also in the products of hydrolysis of vegetable proteins, notably in the seeds and seedlings of ***Picea excelsa* Linn., *Pinus sylvestris* Linn., *Cucurbita pepo* Linn., *Lupinus luteus* Linn,** and *Pisum sativum* Linn.; in the case of the conifer seeds 300 g. of dry protein yield 3 g. of histidine hydrochloride (Schulze and Winterstein, Z. physiol. Chem. 1899,**28,**459,465; 1901, **83,** 547). It is present in *Secale cornutum* (Frankel and Rainer, Biochem. Z. 1911, **74,** 167); in some of the lower fungi (Sullivan, Science, 1913, **38,** 678; Reed, J. Biol. Chem. 1914, 19, 260); in soya bean (0-62 g. as dichloride from 5 kg.; Sasaki, J. Agric. Chem. Soc. Japan, 1932, 8, 417) and various species of beans and peas (Kiesel, Belozerskii and Skvorzov, Zhurnal exptl. Biol. Med. 1927, 4, 538; Amer. Chem. Abstr. 1928, **22,** 603; Jodidi, J. Amer. Chem. Soc. 1935, **57,** 1142); in potatoes (Yoshimura, Biochem. Z. 1934, **274,** 408); and in extracts of ergot (Trabucchi, Boll. Soc. Ital. Biol. sperim. 1934, 9, 501). It is also found in soils (Schreiner and Shorey, J. Biol. Chem. 1910, 8, 381; Skinner, Bied. Zentr. 1913, 42, 213, from Pioc. 8th Int. Cong. Appl. Chem. 1912; Lathrop, Chem. Zen£r. 1917, II, 560).

The preparation of histidine usually involves its isolation from the products of protein hydrolysis, and methods by which this is effected can be seen from the following examples. Vickery and Leavenworth (J. Biol. Chem. 1928, **78,** 627), and also Mendel and Vickery (Carnegie Inst. Washington Yearbook, 1929, **28,** 367) hydrolyse haemoglobin and then precipitate the silver-histidine compound at p_u 7*0 or 7*4. After removal of the silver, the histidine is separated from most of the accompanying amino-acids by precipitation with mercuric sulphate (Hopkin's reagent) and recovered by treatment with hydrogen sulphide. The histidine is crystallised at the isoelectric point a/id further purified by-crystallisation of the dihydrochloride. The base may be conveniently recovered by neutralisation to p_R 7*2 with magnesium oxide, advantage being taken of the solubility of magnesium chloride in ^alcohol. Smorodincev described the hydrolysis of ox blood with concentrated hydrochloric acid. The excess acid was evaporated, the solution was made slightly alkaline, boiled to drive off ammonia and precipitated with mercuric chloride; the precipitate was dissolved in hydrochloric acid and reprecipitated with mercuric chloride and sodium carbonate, then decomposed with hydrogen sulphide and filtered. Evaporation of the filtrate gave tho histidine hydruchloride (43 g. from 1 kg. of dry blood) (Biochem. Z. 1930, **222,** 425). The mercuric chloride method is more direct, less costly and gives a better yield than the silver oxide method (Abderhalden *et al.* Amer. Chem. Abstr. 1929, **23,** 2994). In the treatment according to Kapfhammer and Spdrer (Z. physiol. Chem. 1928, **173,** 245) of protein hydrolysates, arginine is first removed as the flavianate and the filtrate is treated with Reinecke's acid,

$$[(SCN)_4Cr(NH_8)_8]H.$$

The precipitate contains histidine, hydroxyproline, and proline, and is decomposed by suspending in methyl alcohol and treating with copper sulphate which precipitates the Reinecke ccid. Excess copper is removed with hydrogen sulphide and sulphuric acid with baryta; addition of picrolonic acid now precipitates histidine which can be recovered as the dihydrochloride (12-2 g. from 250 g. haemoglobin) by decomposing the precipitate with concentrated hydrochloric acid, filtering and evaporating. The hydroxyproline and proline can be separated with cadmium chloride which precipitates the latter. For the separation of histidine from hydrolysed blood corpuscle paste by Foster and Schmidt's method of electrical transport (J. Amer. Chera. Soc. 1926,48,1709), *see* Cox, King and Berg, J. Biol. Chem. 1929, 31, 755. Since cystine is precipitrted by silver oxide at p_n 6 it may occur in the crude histidine fractions from proteins; its copper salt, however, is very insoluble and these fractions may be freed from cystine by boiling with copper hydroxide, cooling and filtering (Vickery and Leavenworth, *ibid.* 1929, 83, 523). For the separation of histidine from histamine and choline by electrodialyji's, and also the recovery of the base from the dipicrate, platinichloride, etc., by this method, *see* Gebauer-Fiilnegg and Kendall, Ber. 1931, 64 [B], 1067. Quantitative separation of histidine from arginine may be obtained by adding an excess of a soluble silver salt and adjusting the p_R value to 7-0 by careful addition of barium hydroxide solution. A second precipitation as the silver compound gives histidine free from arginine. The latter is precipitated as the silver salt at p_H 10-11. The histidine is conveniently recovered from the precipitate by decomposition with hydrochloric acid {Vickery and Leavenworth, J. Biol. Chem. 1927, 72, 403; 75, 115; *see also* Rosedale, Bioehem. J. 1929, 23,161). According to Bnssit {Bull. Soc. Chim. biol. J034, 16. 727), Hopkin's mercuric sulphate reagent does not give Quantitative separation from arginine. Separation of hiatidine from tyrosine may be effected by means of a reagent containing mercuric chloride, sodium **acgtste** and sodium chloride, tyrosine remaining in solution (Lang, Z. physioL Chem. 1933, 222, 3).

The constitution of histidine as *a-a>»ino-β-glyoxalint-b-propionic acid,* has^ecn established by the work of Frankel, Pauly, Knoop and Wiridaus, and of Pyman. Frankel (Monatsh. 1003, 24, 229) showed that histidine contains a *carboxyl-group,* since it displaces carbon dioxide from silver and copper carbonates, and an amtno-group because on treatment with hypobromite»or nitrous acid one nitrogen atom is removed and a hydroxyl group introduced. Frankel therefore represented lu'sttdinc by the partly expanded formula

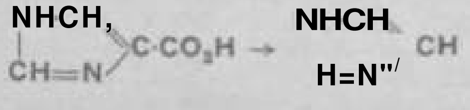
$$NH_2\text{-}C_5H_6N_2CO_2H,$$

and gave the name *kislinc* to the complex —CjHgNjj—, and *hydroxydtaminohistidinc* or *hydrojnjhi.itinecarbozylic acid* to the compound, HO-CsHgNjCOjH, obtained from bistidine by the action of nitrous acid. Pauly (Z. physiol. Cbem. 1U04, 42, 513) contirmed the presence of the car boxy] group in histidine by preparing the methyl eater, and proved that the histine complex —$C_6H_eN_a$—contains an *imino* group, because histidlne yields a dinaphthalenesulphonyl derivative, and forms a red dye **with** diazobenzenesulphonii: chloride. These considerations, and the stability of the compound, led Pauly to conclude that the complex *ftiatine* contains an iminazolc (glyoxaline) ring, and thai, histidine lias the constitution I.

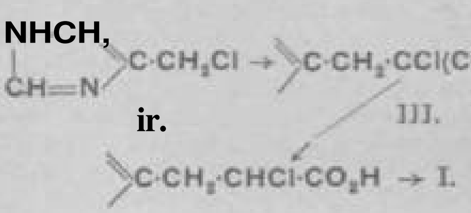
This conclusion has been confirmed by Knoop and Windaus (Beitr. chem. Physiol. Path. 1905, 7, 144), who obtained *ghfozaline-H-propionic add [\minazolyl.ft-pTOpionic acid),*

by reducing Frankel's hydr ixyhistinecarboxylic acid, and showed that it was identicar'with the synthetic product prepared by the action of formaldehyde and ammonia on Wolff's glyoxylpropionic aeid (Annalen, 1890, 260, 71)). *Cf.* Frankel (Beitr. ohem. Phyaiol. Path. 1907, 19, 116).

Knoop *{ibid.* 1907, 10, 111) also showed that by the successive oxidation of hydro xyhistinecarboxylic acid, glyoxaline-6-carboxylic acid is obtairied which, when heated at 2811°, IOSCB carbon dioxide and yields glyoxaline,



The complete synthesis of histidine is described by Pyman (J.C.S. 1911, **99,** 1380). S-Chloromethylglyoxalino (II), obtained from diaminoaetone *(ibid.* 668), condenses , with ethyl sodiochloromalonate to form the compound HI, This ester on hydrolysis is converted into *dl-a-r,hloro-l$-glyozalin£'5-propumic acid* (IV), which reacts with ammonia to form dJ-bistidine (I),



IV.

Pyman *[ibid.* 1916, **109,** 186) also synthesised *ill*-histidine from benzoyt-f/Mjistidine (see ***below]*** by boiling this for 4 hours with 20% aqueous hydrochloric acid.

Histidine gives the biuret reaction (Herzog, Z. physiol. Chein. 1903, 37, 248). Jt also gives ilie Weidel pyriinidinc **reaction** (Frankel, *I.e.).* With diazobcnzcnesulphonic chloriik- in the presence of sodium carbonute, histidine gives a dark cherry-red coloration, becoming orange on the addition of an **acid (Pauly,** Z. **phyaioL** ('hem. 19U1, 42, S08; 1915,94,427). This is a very sensitive test for iminazole derivatives, and amongst the products of protein hydrolysis only histidine and tyrosine give this reaction. It may be used to detect histidine in the presence of tyrosine after addition of benzoyl chloride (Inouye, *ibid.* 1913,88, 79) or after a preliminary separation with mercuric chloride (Lang, Lc). If the coloured solution obtained by Pauly's reaction is reduced, *e.g.* with zinc dust and hydrochloric acid, and then made strongly alkaline with ammonia, the presence of histidine is indicated by the formation of a bright golden-yellow colour (Totnni, Bioehem. J. 1915, 9, 385). Histidine develops a yellow colour with bromine water; this disappears on warming but after a time a pale red colour appears, which afterwards deepens to a wine-red. The reaction is sensitive to concentrations of 1:1,000 but is vitiated by too large excess of bromine water (Knoop, Beitr. cbem. Physiol. Path. 1908,11, 356). For testing urine, the reaction is best conducted in faintly acid solution (Armstrong and Walker Bioehem, .1. 1032. 26,143); for further improvements, *sec* Hunter, Amer. Chem. Abetr, 1923,17, 574; *cf. ibid.* 193fi, SO, 7804. Bromination of hU>tidine in 33% acetic acid gives a black substance which dissolves in concentrated ammonia with a purple-red, and in ammonium carbonate with a strong blue-violet coloration, tin* intensity of which is proportional to the concentration of histidine. This reaction is sensitive to 1:50,000 and is **•pacific,** hut histamino gives a weak golden-yellow and methylhiatidine a very pale reddish-violet colour (Kapeller-Adler, Bioehem. .Z. 1933, 264, 131).

-Coltjri metric methods of estimating histidine based on Pauly's and Kfinilkr-Adler's reactions have been devised. Thus diazotiscd **sulphanfljc** acid is used by Weiss and Sobolev (Bioehem. Z. 1913, 58, 119) in the presence of sodium carbonate and comparison is made with an identtcally treated standard histidine solution. *See also* Loeper, Lesure and Thomas, Bull. Soc. Chim. biol. 1934, **16,** 1385. Suzuki and Kaishio (Bull. Agric. Che in. Soc. Japan, 1927, 3, 33) use sodium hydroxide as the alkali and compare the golden-yellow colour with JV/lOO potassium dichromate. The microdetermination by Pauly's reaction using a photometer with a filter (S53) is described by Lang (Z. physiol. Chem. 1933, 222, 3). The reaction is inhibited by glycine, aspartic acid and uric acid, but this may be overcome by adding larger quantities of the reagent. Urea does not interfere (Meshkova, *ibid.* 1936, **240,** 199). Diazotised *p*-nitraniline has been suggested as a reagent for the determination of histidine in blood (Barac, Compt. rend. Soc. Biol. 1935, **118,** 198; 1935, **119,** 545). Kapeller-Adler's method cannot be applied to the direct determination of histidine in urine owing to the inhibition by phosphates, etc., and so a preliminary separation, *e.g.* with Hopkin's reagent (Biochem. Z. 1933, **264,** 131) or with magnesium chloride in alkaline solution (Iojo, Diagnostica tec. lab. (Napoli) Riv. mensile, 193(5, 7, 8) is necessary. For the use of the step-photometer in this method, *see* Kapeller-Adler, Biochem. Z. 1934, **271,** 206. Folin's method for the determination of umino-aci'ds in blood gives low values owing to incomplete precipitation of the proteins by tungstic-sulphuric acids. Phosphotungstic acid or, better, trichloroaceticacid gives much smaller errors (Re and Potick, Rev. soc. argentina Biol. 1929, 5, 725; Compt. rend. Soc. Biol. 1930, **103,** 1283; *see also* Wechsler, Z. physiol. Chem. 1911, **73,** 141). A modification of the Van Slyke method in which the histidine is estimated colorimetrically is described by Cavett (J. Biol. Chem. 1932, **45,** 335); other modifications are due to Russo (Boll. Soc. Ital. Biol. sperim. 1927, 2, 174) and Davies (Biochem. J. 1927, **21,** 815, 1920). For a modification of Hanke and Koessler's method (Amer. Chem. Abstr. 1920, **14,** 3687) of determining histidine, *see* Jorpes (Biochem. J. 1932, **26,** 1507); and for its estimation in small quantities of protein by precipitation with mercuric sulphate after alkaline hydrolysis, *see* Rosedale and Da Silva *(ibid.* 1932, **26,** 369); and by bromination after hydrolysis, *see* Thrun and Trowbridge (J. Biol. Chem. 1918, **34,** 343). For a microchemical method, *see* Kober and Sugiura, J. Amer. Chem. Soc. 1913, **35,** 1546; and Van Slyke, J. Biol. Chem. 1915, **23,** 411, *cf. ibid.* 1911,9,185; 10,29; 1912,12,279. Histidine can also be determined volumetrically by titration with titanium trichloride of the dye formed in the Pauly reaction (Lautenschlager, Z. physiol. Chem. 1918, **102,** 226).

c?/-Histidine is obtained by raceinisation of the naturally occurring /-form, for example by heating under pressure (Abelerhalden and Weil, *ibid.* 1912, **77,** 435), or with 20% hydrochloric acid at 160° (Frankel, Beitr. chem. Physiol. Path 1906, 8, 160); it crystallises in quadrilateral plates and decomposes at 283° (corr.) (Pyman, J.C.S. 1911, **99,** 1397). dJ-Histidine can be resolved by the fractional crystallisation of its salts with d-tartaric acid into the *d-* and *l*-isoiners, and the Z-histidine so obtained is identical with the naturally occurring compound. Partial resolution can be obtained by means of yeast, the c/-isomer remaining unattacked (Abderhalden and Weil, Z. physiol. Chem. 1912,**77,**435; Ehrlich, Biochem. Z. 1914, **63,** 379). The spontaneous resolution of histidine hydrochloride has been described by Duschinsky (Chem.^and Ind. 1934,**53,**10). Thus, a hot mixture of pure *I-* and (/Miistidine hydrochlorides with 1*5 parts of water, when cooled rapidly to 20° and quickly filtered, gives the *I*-salt; addition of alcohol and ether to the mother liquor and further cooling to 0° yields almost pure (//-salt, while concentration of the filtrate and rapid cooling to 20° gives almost pure (/-salt, **dl-*Histidine monohydrochloride,***

$$\mathbf{C_6H_9O_2N_3\text{-}HCl,2H_2O,}$$

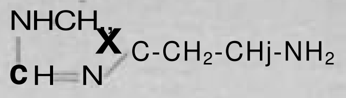
has m.p. 117-119° (corr.); the *sesquihydro* chloride,* $(C_6H_BO_2N_3)_2$-3HCI,H_2O, has m.p. 168-170° (corr.); the *dihydrochloridt,* m.p. 235-236°(corr.); *thepicrate,*$C_{12}H_{12}O_BN_6$,H_2O, decomposes at 180-181° (corr.); the *dipicrate,* $C_{18}H_{15}O_{16}N_9$,$2H_2O$, decomposes at 190° (corr.) (Pyman, J.C.S. 1911/99, 339; *cf.* 1916, **109,** 196).

(/-Histidine crystallises in monoclinic plates forming elongated hexagons; it decomposes at 287-288° (corr.), and has $[a]_D$ +39-3°. d-***Histidine-d-hydrogen tartrate* is sparingly soluble,** decomposes at 234° (corr.) and has $[a]_D$ +13-3° (Pyman, *ibid.* 1911, **99,** 1937; 1916, **109,** 197); ***d-histidine hydrochloride* crystallises with 1 H_2O** (Duschinsky, *I.e.).*

I-Histidine is soluble in water, sparingly soluble in alcohol and insoluble in ether (Kossel, & physiol. Chem. 1896, **22,** 184); it crystallises from water in anhydrous needles or plates, m.p. 287° (corr.), n_a 1-520, *np* indeterminable, n_y 1-610 (Frankel, Monatsh. 1903, **24,** 229; Keenan, J. Biol. Chem. 1929, **83,** 137f; for photomicrographs of the crystals from water and 50% alcohol, *see* Vickery and Leavenworth, *ibid.* 1928, 7C, 701. In aqueous solution it has a sweet taste (Pyman, J.C.S. 1911, **99,** 1397), is feebly alkaline (Hedin, Z. physiol. Chem. 1896, **22,** 191) and is optically active, $[aft^0$ -39-74° (Kossel and Kutscher, *ibid.* 1899, **28,** 382; Duschinsky, *I.e.;* c/.$_M$Pyman, I.e.). The isoelectric point occurs at p_H 7-64; the dissociation- constants at 25° (expressed as logarithms, p_K) are 1-77 (CO_2H), 6.0 (iminazole), 9-0 (NH_2) (Schmidt, Appleman and Kirk, J. Biol. Chem. 1929, **85,177;** Levy, *ibid.* 1935, **109,** 361; Birch and Harris, Biochem. J. 1930, **24,**564 • and Amer. Chem. Abstr. 1932,**26,**485). For the ultra-violet absorption spectrum offZ-histidine and comparison with that of histamine, *see* Ellinger, Biochem. Z. 1929, **215,** 279; Becker, Arch. ges. Physiol. (Pfluger's), 1-931,**228,** 751; Hicks and Holden, Austral. J. Exp. Biol. 1932, **10,** 49, and in the long-range ultra-violet, Ellinger, Biochem. Z. 1932, **248,** 437; for the infra-red absorption betweeii,A=0-8/x and A=8/A, *see* Heintz, Compt. rend. 1935, **201,** 1478. Irradiation of histidine with ultra-violet light causes decomposition in a number of ways. Thus, under conditions favouring oxidation, elimination of ammonia appears t<J be the main reaction and may account for 90% of the histidine decomposed (Lieben and Urban, Biochem. Z. 1931, 239, 250); the residue of the molecule becomes iminazolylacetaldehyde {Szendrō, Arch. ges. Physiol. (PHiiger's), 1931, 228, 743). In the absence of oxygen, deearboxyiatiou to histamine takes place and has been demonstrated by isolation and characterisation of the base (7 mg. from 1 g.) (Holt/., Klin. Woeh. 1933, 12, 1(113; Arch. exp. Path. Pharm. 1934, **175,** 97) **and** by pharmacological tests (Bourdillon, (jaddinn and Jenkins, Proc. Koy. Soc. 1930, B, 106, 388). For this reaction light of wave-length shorter than 2,650A. is much more active than the longer wave-lengths, also the effect is slight in acid **iohitioo** but very intense in alkaline (Lieben, Biochem. Z. 1927, **184,** 453; Bourdillon *et at.. I.e.).* Histidine (and other amiiso-acids) is adsorbed from aqueous solution un activated carbon, » very marked maximum being shown at the isoelectric point (Phelps and Peters, Proc. Roy. Soc. 1929, A, **1S4,** 554 ; Ito, .1. Agric. Chem. Soc. Japan, 1030,12,204).

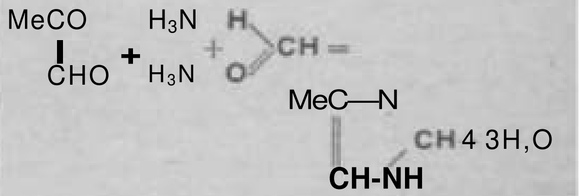
When hist]dine is administered as a food, or by intravenous injection, very little (0-4 g. out of 10 *g.)* is recoverable as such from the urine; the creatinine (Abderhaklcn and Buadze, Z. physiol. **Chem.** 1931, 200, 87), urea and ammonia in the urine are largely increased but the increase of uMimioin is very plight **(Abderbalden,** Einbeck and Sehmid, ***ibid.*** 1909, 62, 322 ; 1910, 68, 395 j Abderhalden, *ibid,* 1911, **74,** 481; Abdcrhalden and Weil, ***ibid,*** 1912, 77, 435; Kowalewsky, Biochem. 2.^1909, 23, 1). Both <- and f-forms an.- utilised in the animal organism, but tiled-form ia rather less efficient ^n promoting the growth of rats on a histulincdefieient diet (Cox anS Berg, J. Biol. Chem. 1934, **107,** 497). The *d*-form can be obtained from the urine of rabbits fed on rf/-histidinc. Histidine markedly increases, the glyeogeii mobilisation effect of adrenaline (Taniuchi, Folia pharmacol, japon. 1330, 10, No. 164), and also reduces the coagulation time of blood (Bjjrger, Klin. Woeh. 1930, 15, **660).** It appears to be the precursor of the erythema-causing irritant which is formed in the human skin during exposure to ultra-violet light (Fran ken burger and Zimmer**toann,** Naturwiss. 1933, 21, 116}. It»has been found of use si .the treatment of gastric and duodenal ulcers (Weiss and Aron, Compt. rend. Soc. Biol. 1933, **112,** 1530; Eada, Amer. J. Digest. Dis. Nutr 1935, 2, 426); and in **oon**junction with tryptophan, in the treatment of **hay-fever** (U-normand, Presse med. 1933, 41, 1141}. For the catabolism of hiatidine in the animal organism, *see* Dakin and Walkman, •T. **Sid** Chem. 1912, 10, 499, and an the forerunner of purine bodies in animal metabolism, *see* Ackroyd and Hopkins (Bioehem, J. 191C 10,551).-

I-Histidine administered subcutaneously to rabbits is excreted as urocanic acid (iminazolylae.rylic acid). The fungus, **Outturn** facfis, **convert** i it into the saturated iminazolylpropionic acic (Kiyokawa, Z. physiol. Chem. 1933, **214,** 38). When **histtdina** undergoes anaerobic hurteria cleavage by the action of putrefying **paoonaa** it is converted **almost** cuiaiitittitivdy by the loss of.carbon dioxide into *R-fi-aJninoelhylylyozaline* (β'-iininazolylethylaniine, *hi8lamine,)f*

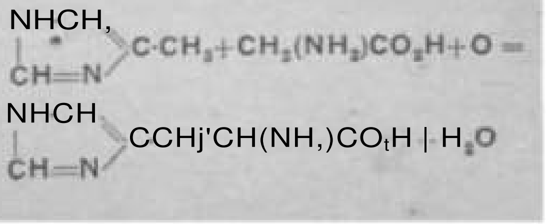


minazoUjl-H^ropiwuc acid (v. p. 2336), being the alii! t (*ee Ackerinann, Z. physiol, Chem. 1910, 65, .'i04). The 5-j3-aminoethylglyoxaline thus obtained *is* identical with the base prepared **synthetically by Wisdom** and Vogt (Ber. 1907, 40. .'ill!)I) from ethyl iminazoJylpropionate or by 1'ynuui (J.C.S. **1911,** 99, 6(58) from diarumoicetone, and is also identical with the ergot mse *ki&tamine* isolated by Barger and Dale (Phil. Trans. 1910, 2592) which is also present in Popielski's *vasodilalin* (Barger and Dale. J. Phvaiol. 1911, 41, 499); **«fi** Mellanby and **Twort** (J. Physiol. 1912, 45,53) who isolated a bacillus of the colon group which splits off **carbon dioxide** from histidino and converts it to histamine. *Bacillus coli communia* transforms histidine into histamine to the extent of 50% in the presence of glycerol or dextrose and potassium nitrate or ammonium chloride {Koessler find Hanke, J. Biol. Chem. 1919, 39. 539 ; 1920,43, 529, 543). Raistrick {Biochem. J. **1917, fl, 71** j 1919,13, 440), found that bacteria of the Coit-typhus group convert histidine into urocanic acid in certain media. {-Histidine is converted to the extent of 11% into *d*-0-iminazo**lyllactic** acid by the prolonged action of *Proteus vulgaris* in a protein-free nutrient medium (Hirai, Acta Schol. Med. Kioto, 1919, 3,49).

A possible explanation of the formation of histidine in the plant economy is afforded by the work of Knoop*and Windaus* {Beitr. chem. Physiol. Path. 1905,6, 292; Ber. 1906,39,3886; 1907, **40,** 799) on the synthetic formation of iminazole derivatives from sugars and ammonia. These authors find that when a solution of glucose containing zinc hydroxide dissolved in ammonia is exposed to sunlight at the ordinary temperature for some weeks, it is converted to the extent of 10% into *5-methyliminaitAe.* **li** is probable that methylglyoxal and formaldehyde are produced as intermediate products and then react with the ammonia according to the **eqaatkn**



//Man nose, (/-fructose, *d* -sorhose, I-arabinose or I-xylose also yield mcthvliminazole when similarly treated. The authors suggest tha* histidinu may be fortned naturally by the con* densation of metl 13' 1 iminazole with glycine, and simultaneous oxidation: *



Enzymes from the liver of various **aniroah** cause decomposition of histidine with elimination of ammonjn (KRiiffmann an<l Miskiwitzer, Biochem. Z. 1930, 226, 325; 1931, 234, 101); the'eame type of decomposition is induced by .boiling with hone black (Lieben and Benek, *ibid.* **1635,** 280, 88). Electrolytic oxidation of histidme l«uls to the formation of carbon dioxide, ammonia and malonic acid, probably th rough the intermediate formation of aspartie acid (Takuyuma and Ocda, J. Chem. Soc. Japan, 1934, 55, 649; Bull. Chem. Soc. Japan, 1934, 9, 535). Oxidation with sodium hypochlorite or hydrogen peroxide or permanganates causes liberation of carbon dioxide and ammonia **(Hexzog,** Z. physiol. Chem. 1903, 37, 248; **Kaiyagina,** Arch. Sei. biol. U.S.S.K. 1935, 37, 372 (in German, 370); Lieben and Bauminger, Biochem. Z. 1933, 261, 387). Oxidation with dichromate and sulphuric acid yields ace tie and hydrocyanic acids (Frankel, Beilr, chem. Physiol. I'ath. 1906, 8, 159). Sodium hypochlorite (I moi,) converts hisiidinc monohydiochloride into imiiiHy.ulvl-5-acelaIdehvite (Langheld, Ber. 1909, 42, 2373; Chem. Zentr. **1910,** II, 1104). For the rate of reaction with formaldehyde in 0-1 A'-nod iu in hydroxide at 37°, *see* Holden and Freeman, Austral. J. Exp. Biol. 1931, 8, 189. When warmed with acetic anhydride in pyridinc, carbon dioxide {1 niol.) is liberated and the product, *when* evaporated With 10% hydrochloric acid, gives colourless prisms, m.p. 205-206", of 4-in3inazolyl-3-amino-butan-2-one d ihyd rochloride,

$$\begin{matrix}\text{NH-CH,} & \\ | & \rangle\text{C·CH}_2\text{·CH(NH}_2\text{)·CO·CH}_3\text{2HCI} \\ \text{CH=N} & \end{matrix}$$

(Dakin and Went, J. Biol. Chem. 1928, 78. 74 C).

/-lli.stidine forms stable salts with acids and their solutions arc dextrorotatory,

Monohydrochloride, CgH_BOj,N_3HCI,HjO, forms large colourless rhombic crystals, *a:b:c* =0-7965:1:1-7110. has $[a]_D$ +1-74°, m.p. 80°, and loses water at 140° (Koasel, Z. physiol. Chem. 1890, 22, 176 j Hedin, *ibid.* p. 191 ; Bauer, *ibid.* pp. 182, 285 ; Kossei andKutscher, ***ibid.*** 1899,28, 382; Frankel, Monatsh. 1903, 24, 229). It is fairly soluble in water, insoluble iu alcohol and ether (Herzog, Z. physiol. Chem. J89U, 22, 193). The *dihydrochloride,* $C_sH_9O_aN_3$-2HCI, forma rhombic tables, a:&:c=0-70537:l:l-77516. isomorphous with the monohydrochlorido (Kosael and Kutscher, *I.e.*; Sehwantke, ***ibid.*** 1699, 28, 38fl; 1800, 29, **492)** j it has m.p. l»0° (245°, **Koaael** and KuUeher, I.e.) and $[aft^0$ +7-6° (Abderhslden and Einbeck, ***ibid.*** 1909, 62, 330)-

Histidine Cadnr'um Chloride,

$$C_{(}H,O,N_a\text{-HCI-CdCl}_a$$

niflts and decomposes at 270-275°, is very soluble in water but almost iti.su]nIik- in hot or cold **methyl** or ethvt **alcohol** (Sehonc/t, *ihid.* **1904,** 43, **73:** *cf.* **Kutwher,** Chem. Zentr. **1908, 1,** 404). **Histidine** gives a **complex** copper salt, CutCflH^OjNjjj (Kober and **Soginra,** J. Jliol. **Chem.** 1913, 13, 5), and a compound with **Iron,** $Fe(C_6$•<$_sO_sN_9)_|$(G.1$^>$. 206522).

Histidine Phosphot u ?igatate,

$$\{C_6H_eO_2N_3)_3\text{-}2H_3PO_4\text{-}24WO_3,$$

crystallises without water of crystallisation (Wechsler, Z. physiol. Chem. 191], 73, 140). The *nitrate,* $C_{f1}H_BO_3N_32HNO_s$, crystallises in prisms **from** waLr, m.p. 149-152° {Frankel, **Uonatah.** 1903, 24, 243). The ***reineekate,***

$$C_6H_9O_2N_3\text{·}2C_4H_7N_6S_4Cr,4H_2O,$$

is precipitated from a solution made,,acid to Congo Ked. Its solubility, 0-2948-0-3(^44 g. in 100 c.c. is greater than that of the carnosine compound andi.it cart bo used for their separation **(Smwodineev,** Biochem. Z. 1930, 222, 425). The *manopicrolonate,* $C_8H_sO_aN_aC_{10}H_gO'_5N_<$, crystallises in j'ellow needles (Kossei and **Prmgle,** Z. physiol. Chem. 1905, 49, 319 ; Weiss, ***ibid.*** 52, 113; *Bvigl, ibid.* 1910, 64, 337, 339; Stcudel, *ibid.* 1905, **44,** 157); 1 part is soluble in 150 **parts** of water; the *dipicrdanale* if orange. The *di-xa-brontopicrolonate* decomposes at 216—218° (Zimmerman/} *and* Cuthberfson, *ibid.* 1932, 205, 38), The *dipierato,* C^H^O^N^HjO, **has** m.p. Sii^6 (corr.) ^Pyman, J.C.S. 1911, 99, **343)**j the pentahydratc, $C_{18}H_{1s}O_{1f1}N_9,5H_2O$, has m.p. 80° (Hugounenq and Florence, Bull. Soc. **Cfcm.** biol. 1919, 1, 102). The di-2:4-*dhiitroA-naphtfiol.l.sulphonaie* separates in yellow needles containing jH_aO and decomposing at 251-254°, depending on the rate of heating. The fret; base or its salts can be recovered by decomposing the compound with dilute acid and extracting the reagent with butyl alcohol (Vickery, J. Biol Chem. 1927, 71, 303). **The** *2:ii~diiodo-l-p}i£twl'i-8ulphonate* (sozoiodolate) decomposes at 2fJ7-LU.S]>ml **1*938** g. dissolve in iOO g. of water at 16° (Ackermann, Z. physiol. **Chem,** 1934, 225, 46). The *rufianate* (quinizarin-**2-Bulphpoate)** is sparingly soluble in water but the base can easily be liberated with baryta (Zimmcrmann, ***tind.*** 1930,188, 180).

1-//ialidiiie-il-hi/dftM/en Tartrale,

$$C,H_eO_aN,\text{-}C_4H,O,,$$

is easily soluble it_t water, crystallises in largo well-defined prisms, and decomposes at 172-173° (corr.) and has $[a]_D$ +16-3°. ***l-Hittidim-U hydrogen tartratc*** is sparingly soluble in cold **water,** crystallises in (.-lusters of prisms and decomposes at 234° (corr.), and ifas $[a]_o$ -12-1° (Pyman, **J.C.S.** 1911,99, 1397, 1400).

The histidme silver compound *in* formed as an amorphous **precipitate** which, at 100°, has the composition $Agj,C_eH,O»N_3,H_EO$; it is soluble in ammonia (Hudin, Z. physiol. Chem. 1896, 22, 194).

DERIVATIVES.

Uistidine Methyl Ester liydrochloride,

$$C_5H_sN_3\text{-}CO_sMe,2HCI,$$

forms flat rhombic prisms, m.p. 196° (decomp.); the free ester is an oil (Pauty, ***ibid.*** 1904,42, 508; Fischer and Cone, Annnlen. 1908, 363, 108). *Histidi?uanhdidCHOMJ* 14 . 6 orms glittering prisms, m.p. 34<;° (Fischer and .Suzuki. **SitzungBber.** K. Altai). **VViss. Beriin,** 1904, 1333; *cf,* AbOvrhaldvn and Ooidel, l'VinifntforHch. 1931, **12,** 518); the f-anhydride has m.p, .

328°- in a closed evacuated tube, crystallises with 2£Hj,O, and has [a]Jg -66-24° in normal hydrochloric acid solution; the ifl-anhydride also has in.p. 328°, and is obtained by heating the ethyl ester of histidine at 100° (Pauly, *'A-* physiol. Chem, 1910,64, 75) ;,the;»mi(e decomposes at 255° (corr.); the *hydrochhride,* at 320°. ***Ghtorohistidinecarboxyiio*** *acid {a-chloro-^-iminazolyipropionic acid)* forma thick prisms, m.p. 191° (decomp,), the corresponding raccmic compound decomposes at 201° (corr.) (Pyman, J.C.S. 1911, 99, 1394), the *ozalale* of the *ethyl ester* has m.p. 161° **(WittdftUB** and Vogjj, Beitr. ohem. PhyrioL Path. 1908, 11, 406). *N-Carbol)enzyl-oxy* ***lKiidi*** *ne,*

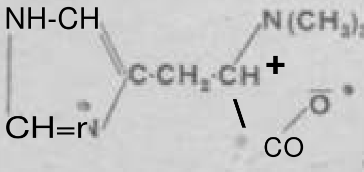
$$C_3H_3N_ECH_2\text{-}CH(CO_1H)NHCOOCH_2C_eH_5$$

has m.p. 209° (Bergmann and Zervas, Bcr. 1932,65 FB], 1192). ***NzH'-hutufat&dmttphonic*** *acid* ig obtained in the form of potassium salts by the action of N-pyridiniumsulphonic **acid** and potassium carbonate on histidinc **at** -l-llt (Baumgarton, MarEprnff and Daminann, Z. phyaiol. Chem. 1932, 209, 145).

dl-i'Methylhistidine is formed during the hydrolysis of anserine *{q.v.)* with ba^'ta; it decomposes at 248—252° with fnaming and the nitrate decomposes at $144\text{-}141S^0$ (Linneweh, Keil and Hoppo-Seyk-r. <*h,,i,* 1829, 183, 11). /-3-MHliylhistidine is obtained if the hydrolysis of anserine *is* carried out with 20% sulphuric acid; jt crystallises with $1H_SO$, m.p. 248-249°, $[a]\},^8$ —25-98°; nitrate, m.p. 21fi°; picrolonate, m.p. 246°, sintering at 240° (Linneweh and Linneweh, *ibid.* 1930, **f89,** 80).

Direct methyluiion of histidine affects the glyoxaline ring. Under certain conditions the« may be obtained *pentamethylhistidint* which forms a stable chloride and a sparingly **soiubb** aurichloride, $C_nH_MO_aN_3Au_2Cl_{f1}$, m.p. 220°, but which does not respond to the diazo-reaction (Engelaud and Kutsclier, Chem. Zentr. 1913, I, 28).

Triimth-ylhialidine {henynhic}, the *betaine* corresponding to hietidine, *



occurs in fungi, *e.g.* in *Boletus edulis* (Winter-atetner and Reuter, Z. physiol. Chem. 1913, 86, 234), it ia not known in the free state, but has been isolated as the auricbloride,

$$C_9H_{17}O_2N_3Au_2Cl_6,$$

m.p. 183° (decomp.) (Engeland and Kutscher, *l.c,* Zentr. Physiol. 1912,26,569). Bargcr.md Ewins (Biochem. J. 1913, 7,204) proved the identity of specimens obtained from various Bources. The *picrate* has m.p. 201-202°, the *dipicrate,* m.p, 213-2J4" and the *pkrolonate,* m.p. 229-230°. *See aim* Barger and Ewins, J.C.S. 1911, 99, 2340; Kiing, Z. physiol. Chem. 1914, 91, 249.

Formyl-l-histidine is formed when histidine ifl heated with anhydrous formic add (Fischer and Cone, Annalcn, 1908, 363, 116); it crystallises in needles from **methyl** alcohol, in.ji. 203° (decomp,), is very easily soluble in water, and jives a deep red colour with diazotised sulphanilie acid. *BevzoylA-Iiislidimi,* obtained by the Schotten-Baumann method, forms colourless crystals $+1H_2O$, m.p. 249° (decomp.) (Pauly, *l.c;* Frankel, *I.e.;* Gerngross, Z. physiol. Chem. 1920,108,54); it is insoluble in water and organic solvents but easily soluM-' in alkalis. In a solution faintly alkaline, with sodium hydroxide, it smoothly takes up 2 atoms of iodine on the carbon atoms of the iminazole ring (Strauss and Maschmann, Ber. 1935, 68 [B], 1108; Pauly, Ber. 1910, 43, 2243). *BemoyUM-* ***histidine*** (from a-benzoylamino-^-iminazolyl-aci'vlic acid on reduction with sodium amalgam in aqueous suspension), has m.p. 248° (corr. decomp.); it cryatalliBes in hanl, glistening prisms with $1 H_E6$, which is lost at 115°. The *hydrc•ihloride* crystallises from water jn bard, glistening prisms, m.p. 232° (corr., foaming). The *pi crate* crystallises in bunches of yellow feathery needles, m.p. 226° (eorr.) (Pyman, I .< US. I i'lft, 109, H>5). Bcnzoylation of histidme methyl eater yields a trihenzoyl derivative,

$$CH(NHBz){:}C(NHBz)CH_2\cdot CH(NHBz)CO_2Me$$

m.p. 2iy° (m>t sharp), which does not give the red colour with diazotised aulphanilic acid; on heating, the iminazole ring closes again and the product gives the characteristic colour reaction (Kossel and Edtbaehcr, Z. physiol. Chem. 1915, 93, 390; *cf.* Inouye, *I.e.,* who points out that in order to obtain the colour reaction excess o benzoyl chloride must not bo present). The *azlactone* of *be7izoy"lhisUdine* is obtained from benzoylhistidine and hydrazinc hydrate and has m.p. 215° (Kiiater and Jrion, ***ibid.*** 1929, **184,** 225). *\)-Nilrobenz6ylhititidine* has m.p. 251-252° (Pauly). *a-PhthalyUustidinr* informed by fusing hIBtidine with jihthalic anhydride at 180-200°; it has m.p. 188°, picrate, m.p. 251"; the methyl ester has m.p. 187° and its hydrochloride m.p. '238-240°; the ethyl ester has m.p. 195°. *da'BrominsohtToyllhixtidirte methyl eater,*

$$C_4H_9\cdot CHBr\cdot CO\cdot NH\cdot CH(C_4H_5N_2)CO_2Me,$$

d-a-bromo'tsohcxoyl-l-hiatidine, $C|jjH_{1g}O_3N_3Br,$ has m.p. 118° (corr.); ***l-lcucyl-l-hiatidine,*** $C_4H_9CH(NH_S)\text{-}CO\cdot NH\text{-}CH(C_4H_BN_8)CO_2H$, crystallises in plates or prisms containing water -which is lost at 100°/I5-20 mm., and has m.p. 178° (corr. decomp.); the copper salt forma deep violet crystals; *glycylA-histidine* melts at 130-155"; *diroianyl-l-histidiu-:* **crystaJttei** with 1 H,O (Abderhalden and Geidcl, *I.e.);]-histidyl*\\-*hi#tidi?ie* forms a lemon-yellow piorate,

$$C_{12}H_{16}O_3N_6\cdot 2C_6H_3O_7N_3,$$

which crystallises ftom water in prisms; on heating *in vocuo* at 80° it becomes orange-yellow and has m.p. 105-175° (Fischer and Suzuki, *I.e.).*

M. A. W.

H I&TOZYME („. Vol.IV, 315«).

H1TTORF TRANSPORT (OR TRANSFERENCE) NUMBER. When an electric **entreat** ***i**** **paitsd** through a solution of an electrolyte, equivalent quantities of each ion are discharged at the electrodes, as required by

Faraday's law. The current, however, is not usually carried equally by the two ions, since the ions move at different speeds. This gives rise to an unequal change in quantity of electrolyte round each electrode. The los^ of slectrolyte round each electrode is proportional to the speed of the ion .moving away from the electrode. The transport (or transference.) number of an ion gives the fraction of the total current carried by that ion.

If u and n are the mobilities of the cation and anion respectively (i.e. their velocities in cm. per sec. for a potential gradient of 1 volt per cm.) the transport numbers of the cation, *ric,* and of the anion, n_a, are TI*= $\frac{u}{(u+v)}$, and $n_a=\frac{v}{(u+v)}$. Alternative symbols are $/_+$ and J_.

Since $n_c+7i_a=l$, it is necessary to know only one of these in order to calculate the other, and very often the anion transport number is called simply the " transport number," and denoted by *n.*

Unlike the mobilities of the separate ions, the transport number varies from salt to salt, *e.g.* the transport number of the Cl' ion is different for KCI and NaCI. It is clear that by measuring the quantity of electrolyte present round un electrode before and after electrolysis, the transport number; *n,* can be calculated.

There are various types of apparatus in use *{see* H. S. Taylor, "Physical Chemistry," Macmillan, 1930, Vol. I, p. 680; A. Findlay, 'Practical Physical Chemistry,*[1] 7th ed., Longmans Green, 1935, p. 18(i). Fig. 1 is a diagram of the apparatus used by Nernst and Loeb (Z. physikal. Chcni. 1888, 2, 948). All types of apparatus utilise the same principles, which are as follows:

A quantity of cWtrieity, measured by a coulonieter in series with the apparatus. \> passed through a solution of an electrolyte of known concentration. The solutions (unolyte and catholyte) round the electrodes are separated to prevent mixing, convection and heating of the solution being minimised by using a weak current (0'01-0-02 amp.) for two hours or more. At the end of this time, the liquid in the anode or cathode oomp&rtment is withdrawn and analysed. The liquid between the anode and cathode is also withdrawn and analysed, and should not have changed in composition. Any chaiigo indicates that mixing has occurred.

It is advisable, where possible, to prevent the evolution of gas bubbles. A soluble ano<l<. <//, Cu in $CuSO_4$, Agin $AgNO_3$, is thus often used, but in the calculation of transport numbers account must be taken of the metal dissolved from the anode.

In the case of the alkali halogenides, gases ar/jevolved at both electrodes. The evolution of hydrogen can be avoided by using a merenro cathode covered with a solution of zinc chloride or copper nitrate. If a cadmium anode is used for the electrolysis of sodium chloride solution. cadmium chloride is formed at the anode, and the Cd" ions migrate to the cathode. However, they move much more slowly than the Na* ion*, and do not catch up with the latter. At the cathode, all the Cl' ions have migrated away, and are replaced by OH' ions from the water, and as these are fast ions, there is mixing. Hydrogen is evolved, but as it rises from the cathode in the upper part of the apparatus, mixing does not occur in the bulk of the solution.

In his original work Hittorf (Ann. Phyaik, 1858, 103, 1) employed mombranea to separate the anolyte and catholyte. It was found by Bi-iis that such membranes may influence the speed of the ions, and they are no longer used.

Hittorf *(I.e.),* Lenz (Ann. Physik Beibl. 1883, 7, 399) and Jaim (Z. physikal. Chem. 1901, 37, 073) used a ground glass stopper to separate *be anolyte and catholyte after the experiment. Weiske (Ann. Physik, 1858,103,406) and Rieger used a wide-bore stopcock for this purpose. Noyes *(I.* physikal. Chem. 1901, 36, G3) «evised an apparatus so that the liquids round the electrodes could be kept neutral during electrolysis by constantly adding acid or alkali. In Findiay's apparatus (A, Findlay, *op. ciL$_f$* Fig. 8i) the electrodes are in two bulbs joined by a U-tube, thus decreasing the resistance and minimising heating and convection currents. The caliuildtion for an experiment using the Nernst and Loeb apparatus shown in Fig. 1, which is typical of all types of measurements, is as follows:

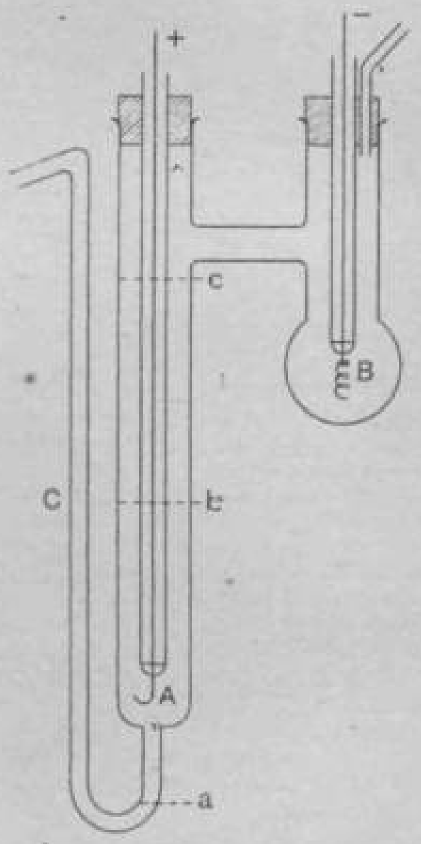


FIG. I.

The anode A *h a.* thick silver wire Mated Into a glau tube which is piared in the loiiKt-r arm of the vessel. During the axperfnii m the amount of nohito around the anode Increases, and the heavier layer of solution lonn i i in a cathode of silver foil or wire. The apparatus is placed in a thermostat and the experinioiita carried out as described above (Nenut and

Locb, I.e.). At the end of the experiment the liquid bfitwppn a-b 1H fore-ed out of the side ami Cant I analysed. The liquid in the mMdl« compartment b-c is also withdrawn and analysed. The total decomposition is obtained from the iveiiiht or silver deposited In the silver coulomctcr in series with file apparatus.

In an experiment I R. of Che silver nitrate solution contained 0-001136 R. AS and *0-9982* g. H^O. In electrolysis with *a.* diver omlonidtet in series, 00322 g. Ag WHS deposited in the coutometer and an equal weight therefore dissolved from the anode In t.hc transport apparatna. After the experiment the anode *li(\\M* contained 0-03055 g. Ag associated with 20-03 g. HjO. Jn tlie original solution thin weight of water was asaoetaUfl with 0-02280 R, Ag, hence 0-05955- 0-02280 = 001675 g. Ag have bCLn added to the anode liquid. The Ion by migration fs thus 0-0322-Q-010:&=04)1545 g. Ag, and the transport number of Ag is $\frac{0{\cdot}01545}{0{\cdot}0322}$ -0-470. That of NO_3 Is 1-0-479-0-521.

The Hittorf method is satisfactory if the experiment is carefully carried out, but in the case of very dilute solutions a so]veilt correction is necessary for conducting impurities in the solvent, which carry part of the total current. If K_0 and « are the conduct)vities of the solvent and solution, respectively.

$$n_{\text{true}} = n_{\text{observed}}\left(1+\frac{\kappa_0}{\kappa}\right).$$

When determining transport numbers, the possibility of complex ton formation must be borne in mind. Cadmium iodide shows a transport number greater than unity in concentrated solutions, because the comples ion Cdl_4" is formed, and cadmium is carried to, instead of from, the anode.

The modern theory of electrolytes indicates that the transport number is not *a,* true con* stant, but depends on concentration. The values given below are thus extrnpoln'ed to infinite dilution *[ef.* Dole, J. Physical Chcm. 1931, 35. 3617; Glnsstone, "Electrochemistry of Solutions," Metlnien, 1887, p. Mitt).

CATION TRANSPORT NUMBERS AT 18° o.

Electrolyte.	Concentration in gram.-equivalent a per lit re.						
	0005	0-01	0-02	frOS	**0-1**	0-2	0-5
Lithium chloride .	—	0 332	0-328	0-320	**0-313**	**0-304**	
Sodium chloride .	0-397	0-397	0-39(5	0-393	**0-390**	iKtsf,	
Potassium chloride	0-496	**0-498**	0-490	0-49(5	"495	I) I!M	
Cadmium iodide .	0-445	**0444**	0-442	0-396	**0-296**	**0-127**	
Hydrochloric acid .	0-832	0-833	0-833	**0-834**	0-835	**0-837**	0-838
Copper sulphate .	—	—	**0-876**	**0-875**	0-373	**0-38]**	**0-327**
Potassiu mjiy d roxid e	—	—	—	—	0-265	**0-SM**	**0-262**
Barium chloride .	—	—	—	0-425	^•421	**(H09**	**0-392**

J. R. P.

H.M.T.D. **(B.VOLIV.6436).**

HOCHOFEN CEMENT {». Vol. TI, 145ft).

HOFMANN DEGRADATION *(v.* Vol. 11, 375a).

HOFMEISTER or **LYOTROPIC SERIES** (t>. Vol. **III,** 286d).

HOFSASS BURNER (V Vol. V, 247a).

HOLARRHENINE, **HOLARRHIMINE.** HOLARRHINE *(>:* Vol. **III,** 322c, 323d, *d).*

HOLLANDITE, A manganese o«e of essentially the aamtT'com position as psilomelftne, but occurring in a crystal Used c -ndition, usually as fibrous masses and sometimes as tetragonal crystals. It is a mnnganate with the geseral formula $mR_a''MnO_6+»R/''(MnO_6)_3$, where R" is Mn, Ba, K_2, H_a, (Fe, Ca, Mg, Na_2, Co, Ni, Cu), and R'" is Mn, Fe, (Al). The extreme values shown in four analyses are: M.IOJ 66-6S-7MKS, MnO 5-12-14-20, Fe_2O_3 4-43-10-.'56, BaO 2 06-17-59, K_aO 0-3-31, H_BO 0-1 10%. The colour is greyish-black, and the lustre su bimetallic; sp.gr. 4-70-4-95; hardness 4-6. The mineral occurs abundantly in the manganese ore deposits at several plates in Contra! India, and is largely exported from the mines at Sitapar and lUlagbnt., Closely allied minerals, perhaps identical with hoilandite, are Hit- crystalline manganates *romanec-hiie* (containing less iron and more water) fron Romaneche,Krance,andcor«7!«'/i'r(withhighlead and low barium contents) from Arizona. (L. L. F•"ermor, The Mfinganesc Ore Deposits of **India,** Mem. Geol. Survey Indi«, **1909*** 37; Ke<. Geol. Survey India, 1917, 48, 103.)

L. J. S.

HOLMES STILL *(v.* Vol. I, **W6o).**

HOLMIUM. Ho. At. no. 67. At. wt. 163.5, This element, which belongs to the vftrium group of the rare earth metals, was discovered spectroseopically by Cleve in 1879 in the terbia of C. *U.* Mosander or erbiw of N. J. Berlin. Many years elapsed, however, before Holmberg *(Z.* anorg. Chem. 1911, 71, 22(1) wan able to obtain sufficiently pure specimens of holmium salts to establish definitely the individuality of the element. From 2U kilos of euxenite he first separated the yttrium earths and then fractionally crystallised the jw-nitrobenzenesulphonates; the head fraotfanu 0OBtaining Y, Ho, Dy, Tb, Gd_f Eu and Sm were converted intn tb<- niii.iii;, hisnmtli nitrate added, and crystallisation continued to remove gadolinium. The oxalstew were now fractionated, the most soluble fractions lieing further treated as nitrates. Final purification was by parti&Wprecipitntton with aniline.

Dripgs and Hopkins (J. Amer. Chem. Soc. J925, 47, 363) found that the most persistent impurity in Imlniiiim wan erbium which could bo removed by i-rystallisation of the bromates. In this way it was possible to obtain fractions contaminated inly with yttrium, an impurity which could be eliminated fairly readily by partial decomposition of the nitrates; the course of the separation was followed by determining the magnetic susceptibility. Atomic weight determinations from the purest fractions of holmium chloride gave Ho=103-47.

Physical Properties.—According to Aston (Proc. Roy. Soc. 1934, A, 146, 46) holmium is a 'single element possessing only one isotope ^{186}Ho, the mass-spei-trum atomic weight beinj 164-91, a figure considerably higher than the best atomic weight determined chemically, Bartlett, Jr. (Physical R«v. **1934,** [ii], 46, 847) *has* shown on theoretical grounds that the isotope $^{\text{fi!}}$»**Ho nhould bo st.nhlo and. possibly, it still** awaits detection.

The atomic magnetic moment of the holmium ton is probably 13689±006. The reduction potential and the potential of metal formation ore, respectively, — l-7tK> and — 1-885.

Spectra.—The most prominent lines in the arc and spark spectra are: 33990, 3425-4, 3428-1, *3453-1,* 34560, 34620, 3474-3, 3484-8, 3494-8, 3515-6, 3598-8, 3662-3, 37482, 3757-3, 3889-0, 38910, 4045-4, 4103-8, 4254-4 (King, Physical Rev. 1929, [ii], 33, 540; Aatrophys. J. 1930, 72, 221).

Absorption spectra have been studied by Holoiberg *(I.e.),* Ynteraa (J. Amer. Chem, Soc. 1023, 45, 907), Prandtl and Schemer *(Z.* anorg. Chem. 19.14, 220, 107) and Gobrocht (Physikal. Z. 1930, 37, 549).

Compounds.—Numerous salts of holtnium have been niado but, like those of many other rare earths, descriptions of them are meagre.

Holmium Sesquioxide frlolmia), Ho_s0_3.—Obtained as a yellow solid by igniting the hydroxide, nitrate, oxalate or sulphate; it dissolves in acids to form yellow-coloured holmium wilts. For its magnetic properties, *see* Cabrera (Compt. rend. 1937, 205, 400), Trombe (Ann. Physique, UOT, fxi], 7, 385) and Velayos (Anal. Fis. Quim. 193/i, 33, 297).

^Holmium Chloride, $HoCI_3$.—Ltght-yellow crystalline solid, ra.p. 718°C, formed by heating the hydrated salt in a current of hydrogen ohloride at 350°.

A similar method is employed for the preparation of the *bromide,* except that ammonium bromide is mixed with the hydrated salt and is then removed either by heating to 600°, or at 350° *in vacua.* It melts at 914°.

The *iodide* is also a light-yellow solid, m.p. l.OlOi 10°, and is obtained by passing hydrogen iodide over the anhydrous chloride at 600° (Jantsch *et aL, Z.* anorg. Chem. 1932, 207, 353).

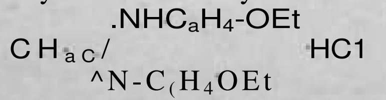
Holmium Sulphate Octahydrate,

$$Ho_2(SO_4)_3,8H_2O,$$

has been made and its magnetic properties have been closely studied.

G. R. 1>.

"*HOLOCAINE."* syn. "*Phenocam"* di-(p-ethoxyplieriyOacetaniidine hydrochloridi.



$$CH_{ac}\begin{matrix}\diagup \text{.NHC}_aH_4\text{-OEt} \\ \diagdown \text{N-C}_(H_4OEt\end{matrix}\quad HC1$$

finds application as & local anaesthetic in ophthalmic surgery, but its more general use ia restricted by its toxicity (G.P. 798(38, 80568).

HOLOKLASTIT *(v.* Vol. IV, 464a).

"*HOMATROPINE,"* tropine mandelio ester, CsHj-NO-CO-CHtOHJ-CaHs, is prepared by prolonged heating of tropine mandelate with dilute hydrocnloric acid; the hydrochloride so produced is usually converted into the hydrobromide. It is used as a mydriatic which is less toxic than atropine; the mydriatic activity is still more marked when used with e^hedrine (Pak and Tang, Proc. Soc. Exp. Biol. Med. 1930, 27, 887). Identification of homatropine: Ekkert, Pharm. Zeatralk. 1930,71,180; Celsi, Anal. Farm. Bioqudu. 1930, 1, 140. Microchemiatrjy: KoftW and Mtiller, Mikrothem. 1937, 22, 43.

HOMOCATECHOL, homopyrocatechol, 3:4-dihydroxytoluene, m.p. 65°, b.p. 251-252°; *creo#ol is* t'te- 3-methyl ether, m.p. 5-5°, b.p. 221-222°, <« Mil.

HOMOCHELIDONINE (e. Vol. HI, 627d).

HOMOCOL {•« Vol. I1l, 5156).

HOMOEUONYSTEROL {tr. Vol. IV, 400c).

HOMOGENEOUS CATALYSIS.

SYNOPSIS OF THE SDBJECT.

(a) Introduction (p. 24<W).
(b) Catalysis and the clasaical dissociation theory (p. 241fl.
(c) Sn.lt effecta tn catfllj-sed reactions (p. 213A),
(rf) Modern views on ncids and bases *(p. 247a).*
<c) General acid-base cutulysi^ (p. 2406).
<J) The use of catalytic measurements for determining hydrogen- and hydroxyl-ion concentrations **(p. 251i>>.**
(*g*)i Relations betweea catalytic power (ind acid-base strength (p. 2S3ef).
(h) The mechanism of acid-base catalysis (p. 255ft).
(i) Other types of positive catalysis in solution (p. 2584).
(k) Negative catalysis in solution (p. 280c).

(a) INTBODUGTIOK.

The term *catalysis* in its modern sense was introduced by Berzclhis in 183C to describe a number of chemical phenomena in which one of the substances apparently responsible for the reaction (the catalyst) remains unchanged. The phenomena which he considered would now be divided into two classes, *heterogeneous catalysis* and *homogeneous catalysis,* according to whether '•he catalyst is present as a separate phase, or constitutes part of i homogeneous system. Of the two, heterogeneous catalysis has probably been the subject of more investigation, largely because of its practical importance in gas reactions *(v.* CATALYSIS IN INDUSTRIAL CHEMISTRY). On the other hand, homogeneous catalysis in solution has been closely connected with the development of the modern theory of solutions, and is involved in many organic reactions of practical importance, notably esterifieation and hydrolytic reactions.

It has long been realised that the function of catalysts (both heterogeneous and homogeneous) is to modify the velocity of a reaction, without affecting the position of the equilibrium which 13 finally reached. In the case of homogeneous catalysis the relation between the amount of catalyst present and the reaction velocity usually has a simple form. For example, if a reaction A -*• B is taking place under the effect of a catalyst X, then its progress with time *t* will usually be governed by the equation

$$-\frac{d[A]}{dt}=k_x[X][A] \quad . \quad . \quad . \quad . \quad (1)$$

where the square brackets denote concentrations. For a given reaction the constant k_x depends upon the nature of the catalyst X, and on the temperature and the nature of the solvent: it is known as the *catalytic constant* and serves as a measure of the effectiveness of the catalyst under the given conditions.

Since [X] remains constant throughout the change, the course of a single reaction will be kinetically of the first order with a velocity constant fc=fc$_x$[X]: the catalysed reaction is thus of the same kinetic order as the uncatalysed reaction A -*- B. On the other hand Oquation (1) is identical with that for a bimolecular reaction between X and A, except that the concentration of X remains constant during the reaction: *i.e.* instead of

$$A+X \rightarrow B+Y$$

where X is transformed into Y, we have

A + X - ^ B + X

where X ultimately emerges unchanged from the reaction. *kx* has in fact the dimensions of a bimolecular velocity constant, and the above reaction must be pictured (in spite of its first order kinetics) as depending on bimolecular collisions between A and X. Exactly similar considerations apply to reactions of higher order. For example, if the reaction A + B - * C + D is catalysed by X the kinetic equation will be

$$-\frac{d[A]}{dt}=-\frac{d[B]}{dt}=k_x[X][A][B] \quad . \quad . \quad (2)$$

and the reaction will follow a second order course with a velocity constant Jfcx[X].

In the case of reversible reactions the law that the position of equilibrium js unaffected by a catalyst imposes some restrictions on the catalytic constants. For example, if the reaction A ^ B is catalysed by X the velocities in the two directions are given by

$$-\frac{d[A]}{dt}=k'_x[X][A],\ -\frac{d[B]}{dt}=k''_x[X][B] \quad . \quad (3)$$

At equilibrium the velocities in the two directions must be equal, giving Tr^=r?: hence LAJ *x the ratio $\frac{k'_x}{k''_x}$ must be independent qf the nature of X, though of course the separate values of *k'* and *k''* will depend upon X. Moreover, if thp reaction proceeds under the same conditions of solvent and temperature in the absence of a catalyst, then the ratio of the uncatalysed velocity coefficients $\frac{k'}{k''}$ must also have the same value. These relations have been verified in a few cases, and can be regarded as firmly established on account of their thermodynamic basis. It should, however, be noted that they will only remain valid provided that the concentration of the catalyst is not too high. A very large catalyst concentration will produce an appreciable change in the nature of the solvent medium, and may thus affect the position of equilibrium like any other change of solvent.

The types of reaction which are subject to homogeneous catalysis are very diverse, and no enumeration or classification will be attempted. On the other hand, most of the catalysts on which information is available fall into a few well-defined classes, as follows:—

(i) *Catalysis by Acids and Bases.*—This is by far the most extensive field in homogeneous catalysis, and a large part of this article will be devoted to various aspects of acid-base catalysis.

(ii) *Catalysis by Ions other than Acid or Basic Ions.*—There are a number of isolated instances of catalysis by metallic ions and halide ions, usually depending upon possibilities of alternate oxidation and reduction of the catalyst. These will be described in section *(i).*

(iii) *Catalysis of Organic Reactions by Inorganic Halogenides.—This* class of reaction, typified by the Friedel-Crafts reaction, is often carried out under heterogeneous conditions, but appears to be essentially homogeneous in character. A brief account is given in section (»').

(iv) *Catalysis by Enzymes.*—This may formally be treated as a type of homogeneous catalysis in solution, but the laws governing it are much more complex than for ordinary chemical catalysis (v. ENZYMES; FERMENTATION, ALCOHOLIC; HYDROLYSIS).

(v) *Negative Catalysis.*—This occurs both in gas reactions and in solution, and is a characteristic of chain reactions. Its occurrence in solution is dealt with in section *(j).*

(b) CATALYSIS AND THE CLASSICAL DISSOCIATION THEORY.

The early study of catalysis by acids and bases was closely connected with the development of the *electrolytic dissociation theory* towards the end of the nineteenth century, and this theory gained a good deal of support from measurements of reaction velocity. Thus both Ostwald and Arrhenius carried out such measurements, particularly on the *hydrolysis of esters* and the *inversion of cane sugar,* both of which are catalysed by acids. It was found that the catalytic power of a solution of an acid was directly proportional .to its electrolytic conductivity for a large range of concentrations. This was interpreted by supposing that the hydrogen ion in solution was the only effective catalyst present, and that the hydrogen ion concentration was measured by the electrolytic conductivity.[1] Although according to modern views some qualifications must be attached to these statements (especially for certain other reactions), they still constitute a valuable working basis in many cases. Table I shows the figures given by Ostwald (J. pr. Chem. 1884, [ii],

---

[1] TheTast statement is not strictly true even according to the simple dissociation theory, since that part of the conductivity depending on the anlon will vary from one acid to another. However, owing to the very high mobility of the hydrogen Ion little error is made in assuming that the conductivities of solutions of different acids arc proportional to their hydrogen Ion concentrations.

30, 93). All the data refer to [illegible] aqueous solutions of the acids, and the numbers represent relative values of their conductivity and of their catalytic effects in the hydrolysis of methyl acetate and the inversion of cane sugar, the value for hydrochloric acid being taken arbitrarily as 100 in each case.

TABLE I.—RELATIVE CONDUCTIVITIES AND CATALYTIC EFFECTS OF DIFFERENT ACIDS.

Acid.	Conductivity.	k (ester).	k (sugar).
HCl	100	100	100
HBr	101	98	111
HNO_3	99·6	92	100
H_2SO_4	65·1	73·9	73·2
CCl_3COOH	62·3	68·2	75·4
$CHCl_2\cdot COOH$	25·3	23·0	27·1
$COOH\cdot COOH$	19·7	17·6	18·6
$CH_2Cl\cdot COOH$	[illegible]	4·30	4·84
HCOOH	1·68	1·31	1·53
$CH_3CH(OH)CO_2H$	1·04	0·90	1·07
$CH_3\cdot COOH$	0·424	0·345	0·400
$CH_3\cdot CH(CH_3)COOH$	0·311	0·208	0·335

Similar conditions obtain in alcoholic solutions, though data are here less numerous. Table II (Goldschmidt, Ber. 1895, 28, 3218, and later papers) shows the parallelism between conductivity and catalytic effect for the esterification of formic acid in ethyl alcohol solution. The ethyl alcohol serves both as solvent and as reactant, and the hydrogen ions are provided by an added catalyst acid, formic acid being too weak to have any appreciable catalysing effect. The concentration of the catalysing acid was 0·1 N. throughout.

TABLE II.—CATALYTIC EFFECT OF ACIDS IN THE ESTERIFICATION OF FORMIC ACID IN ETHYL ALCOHOL.

Catalysing acid.	Relative conductivity.	Relative velocity constant.
Hydrogen chloride	100	100
Picric	10·4	10·3
Trichloroacetic	1·00	[illegible]
Trichloro butyric	0·35	0·30
Dichloroacetic	0·22	0·18

An exactly analogous interpretation can be applied to catalysis by bases, *i.e.* the catalytic effect of a basic solution depends upon its hydroxyl ion concentration, which can be determined from its conductivity. Experimental data are, however, much less extensive than in the case of acid catalysis. Most of the early work was done on the hydrolysis of esters in presence of alkali, which cannot, strictly speaking, be classed as a catalytic reaction since hydroxyl ions are used up during the reaction, *e.g.*

$$CH_3COOC_2H_5+OH^- \rightarrow CH_3COO^-+C_2H_5\cdot OH$$

It was found that in dilute solutions of sodium, potassium and calcium hydroxides (which may be regarded as completely dissociated) the rate of hydrolysis is proportional to the normality of the alkali and is independent of the nature of the catalysed reaction: further, solutions of the weak base ammonia give rise to much smaller velocities. Similar results have been obtained later with the reversible conversion of acetone into diacetone alcohol according to the equation

$$2CH_3\cdot CO\cdot CH_3 \rightleftharpoons (CH_3)_2C(OH)CH_2\cdot COCH_3,$$

which is catalysed by solutions of strong and weak bases.

It is possible on the basis of the classical dissociation theory to make some general statements on the variation of reaction velocity with hydrogen ion concentration or with p_H

$$(-\log_{10}[H^+]).$$

These statements apply strictly only to catalysis by dilute solutions of strong acids and bases, but for many reactions they serve also to give a general description of the behaviour in presence of weak electrolytes. Many reactions are catalysed both by acids and by bases, and the most general equation for the observed velocity constant it is

$$k=k_0+(k_{H^+})[H^+]+(k_{OH^-})[OH^-] \quad . \quad (4)$$

where k_{H^+} is the catalytic constant of the hydrogen ion, k_{OH^-} the catalytic constant of the hydroxyl ion, and k_0 the velocity constant of the so-called "spontaneous" reaction.[1]

The relative importance of the three terms in equation (4) varies very much under different conditions and for different reactions (*cf. e.g.* Skrabal, Z. Elektrochem. 1927, 33, 322). The application of the law of mass action to the dissociation of water gives $[OH^-][H^+]=K_w$, the ionic product of water, and insertion of this in equation (4) gives

$$k=k_0+(k_{H^+})[H^+]+\frac{(k_{OH^-})K_w}{[H^+]}$$
$$=k_0+\frac{(k_{H^+})K_w}{[OH^-]}+(k_{OH^-})[OH^-] \quad . \quad . \quad (5)$$

Since $K_w \cong 10^{-14}$, $[H^+]$ and $[OH^-]$ vary by a factor of about 10^{12} in passing from 0·1N. hydrochloric acid to 0·1N. sodium hydroxide, so that unless k_{H^+} and k_{OH^-} differ by a factor of more than about 10^9 there will be two ranges of p_H easily accessible to experiment in which one of the last two terms in equation (5) can be neglected. In these ranges the velocity is a linear function of $[H^+]$ and $[OH^-]$ respectively and the values of the corresponding catalytic constants k_{H^+} and k_{OH^-} can easily be separately determined from the experiment. Between these two ranges the reaction velocity will pass through a minimum value of

$$k_{\min}=k_0+2\sqrt{\{K_w(k_{H^+})(k_{OH^-})\}} \quad . \quad . \quad (6)$$

---

[1] It will be seen later that the term "spontaneous" is really a misnomer, since the observed velocity is actually due to catalysis by the solvent molecules. However, the term is in very general use and will be retained.

at a hydrogen ion concentration given by

$$[H^+]_{min} = \sqrt{\frac{K_w k_{OH^-}}{k_{H^+}}} \quad . \quad . \quad . \quad (7)$$

If £OH-=A;$_H$+ *^^{e} minimum velocity will be at the neutral point, while tfie two possibilities *kon->h$_a$+* and &OH-<£H+ correspond to, a minimum velocity respectively on the acid and on the alkaline side of the neutral point.

Under some conditions (A;$_o$ not too small, (^H+)(fOH-) not too large) the second term in equation (6) is negligible compared with the first, and the velocity at the minimum point is enual to the spontaneous velocity fc$_0$. Moreover, reference to equation (5) shows that under the same conditions there will be an appreciable range of *p*^ values over which the two last terms of this equation contribute very little to the velocity. Under these conditions the spontaneous velocity k_0 is directly observable as the measured velocity in this p_H range. When this is not the case the value of k_0 must be obtained either from tjie observed minimum velocity by using equation (6), or by extrapolating the linear parts of the *k—[H+]* or *k*—[OH-] plots to zero concentration of [H$^+$] or [OH-]. Finally, many reactions are of course known in which one or more of the constants k_0, k_a+ and &OH- is zero, or at least so small that it cannot be detected.

The following list gives the different possible types of behaviour, with a few of the better known examples of each type:

(1) Catalysis by both acids and bases, spontaneous reaction directly observable. Example—the mutarotation oi glucose.

(2) Catalysis by both acids and bases, spontaneous reaction detectable but not directly observable. Example—the halogenation of acetone.

(3) Catalysis by both acids and bases, spontaneous reaction not detectable. Examples—the hydrolysis of amides and y-lactones.

(4) Catalysis by acids «only, spontaneous reaction directly observable. Examples—the hydrolysis of alkyl orthoacetates and orthocarbonates.

(5) Catalysis by bases only, spontaneous reaction directly observable. Examples—the hydrolysis of /}-lactones, the decomposition of nitramide, the halogenation of nitro-parafiins.

(6) Catalysis by acids only, no spontaneous reaction detectable. Examples—the inversion of sugars, the hydrolysis of diazoacetic ester and of acetals.

(7) Catalysis by bases only, no spontaneous reaction detectable. Examples—the tlepolymerisation of diacetone alcohol, the decomposition of nitrosotriacetonamine.

(c) SALT EFFECTS IN CATALYSED REACTIONS.

Although the classical theory gave a good general account of the experimental data, a number of discrepancies remained, of which the following are the most important:

(i) The reaction velocity is not exactly a linear function of the hydrogen or hydroxyl ion concentration as calculated from the conductivity. In particular, in catalysis by solutions of strong acids an increase" of acid concentration invariably causes the velocity to increase more rapidly than the conductivity.

(ii) The reaction velocity is often affected considerably by the addition of neutral salts, *i.e.* salts which are neither acidic nor basic and which have no ion in common with the catalyst. This discrepancy is particularly marked in solutions containing weak electrolytes.

(iii) The addition of a salt having an ion in common with the catalyst does not usually depress the velocity as much as would be expected from the simple law of mass action.

Subsequent work on the theory of acid-base catalysis has been largely devoted to clearing up these discrepancies, and the following are the chief modifications and additional assumptions which have been introduced into the classical theory:

(1) The ionic concentrations of strong electrolyte solutions are not proportional to their conductivities.

(2) The simple law of mass action does not apply exactly to ionic equilibria.

(3) The reaction velocity in ionic systems is not exactly a linear function of the concentrations of the reactants, but also depends on other properties of the solution, *e.g.* the concentrations of other ions present.

(4) Hydrogen and hydroxyl ions are not the only catalysing species.

Of these, (1), (2) and (3) are closely connected with modern electrolytic theory, and are treated in this section under the general description of " salt effects." *((14* is the fundamental assumption of the theory of general acid-base catalysis, and forms the subject of the two following sections.

According to modern views (based partly on theoretical considerations and partly on experimental evidence) those electrolytes commonly classed as " strong " are, practically speaking, 100% dissociated even at concentrations where their conductivity ratios are considerably less than unity. The decrease of conductivity is attributed to electrostatic forces between the ions, and not to incomplete dissociation. This **hypothesis of *complete dissociation of strong*** *electrolytes* often introduces a considerable simplification into the treatment of catalytic data. This is illustrated by the data in Tables III and IV (p. 244) (c/. Dawsoh and Lowson, J.C.S. 1928, 2140; LaMer and Miller, J. Amer. Chem. Soc. 1935, 57, 2074; Koclichen, Z. physikal. Chem. 1900, 33, 129). The experiments of Koclichen were carried out at 25-2°, and his velocity constants have been reduced by 1-3% to make them comparable with those'at 25°.

It will be seen thai the catalytic constant $\frac{k}{c}$ remains constant over a large range of concentrations provided that the catalyst is assumed to be* completely dissociated, although the conductivity ratio $\frac{\Lambda}{\Lambda_0}$ varies by 13-16% over the Bame concentration range. (The last column contains the activity coefficient/of the catalyst, **and** will be discussed later.) It should not be

TABLE III.—HYDBOLYSIS OF ETHYL ACETATE AT 25°, CATALYST HC1.

jt=nrat-order velocity constant, min.-^{1}.

c(HCI).	$\frac{£}{c'}$	$\frac{A}{Ao*}$	/(HCI).
00002	6*49	0-999	0-993
00005	6-50	0-998	0-984
0-0010	650	0-997	0-965
00020	6-49	0-990	0-957
00100	fl-54	0-984	0-924
00200	**6-45**	0-973	0-892
00400	**6-50**	0-952	0-860
01000	648	0-903	0-814
0-2000	6-57	0-895	0-783
0-5000	6-76	0-865	0'762

TABLE IV.—DECOMPOSITION OF DIAOETONB ALCOHOL AT 25°, CATALYST NaOH.

=first it-order velocity constant, mm.$^{-i}$

Author,	*a* (NaOH).	$\frac{A}{e*}$	$\frac{A}{Ao}$	/{NiOH).
(U	000471	2-20	0-970	0936
(1)	000942	232	0-956	0904
(1)	0-0188	2-29	0-901	0865
(2)	0-0205	2-22	0-897	0-860
(2)	00292	2-23	0885	0-838
(1)	00471	2-32	0-867	0-810
(2)	00518	2-24	0-861	0-804
(2)	0·0616	2-22	0-854	0-793
(2)	00710	2-22	0-848	0-782
(2)	0-0864	2·19	0-843	0'770
(1)	00942	2-28	0-840	0-706
(2)	0-1045	2-21	0-838	0-760

(1) Koeliehcn. **(2; La Merand Miller.**

assumed that the reaction velocity ia always exactly proportional to the concentration of the catalyst ion, since deviations from such proportionality will be discussed a little later under the heading of primary salt effects. However, the velocity ia always more nearly proportional to the concentration than to the conductivity. The position is similar in non-aqueous solvents, in fact the direct proportionality between catalyst concentration and reaction velocity found by Goldsdimidt *tt al. (ibid.* 1912, 81, SO; 1920, 94, 233) for eaterification reactions in mcthyl and ethyl alcohols, constituted some of the most convincing eviden/ie for complete dissociation in these solvents (c/. Bjerrum, Fysisk Tidsskr. 1916, 15, 59; Z. Elek<rochem. 1918, 24, 321).

TChe most important deviations from the classical laws of catalysis occur when weak electrolytes are present, and these are now attributwMo the *secondary mil effect* (Brdrtsted, J.C.S. 1921, 119, 574; Bronated m?d Pedersen, *Z.* pheyeikal. Ohem. 1924, 108, 185}. The term " secondary " refers to the fact that these effects are not primarily concerned with the reaction itself, but with the ionic equilibria present. According to modern electrolyte theory these equilibria, and hence the concentrations of the catalysing ions, are affected to a considerable extent by the total ionic concentration of the solution. This is expressed in terms- of *activity coefficients; e.g.* for the dissociation of a weak acid HA according to the equation HA ^ H^{+}+ A~ the simple mass action expression must be replaced by

$$\frac{[H+]fA\sim]}{[HA]}\frac{(f_{H^+})(f_{A^-})}{/HA}=K. \qquad (8)$$

where *K* ia the true or thermodynamic dissociation constant (depending only on the temperature and the solvent) and the *f* s are activity coefficients. The " classical " concentration dissociation constant K_e is that given by

$$K_c=\frac{[H+IA-]}{[HA]}\frac{fa}{(VKA-)} \qquad (9)$$

The activity coefficients are all equal to unity at very low ionic concentrations, but as the concentration of ions increases /n+ and *f*\~ both decrease. Hence in fairly dilute solutions an increase of ionic concentration increases K_c, the degree of dissociation, and the velocity of any reaction catalysed by hydrogen ions. In more concentrated solutions a change in the reverse direction often takes place.

Apart from measurements of reaction velocity or theoretical considerations, there is abundant evidence from indicator and electrometric measurements for the increased dissociation caused by tho addition of salt. Table V gives topical data obtained from electromotric measurements, which illustrate the magnitude of the effect (I.ars*>on and Adcll, *ibid.* 1931, 156, 352).

TABLS V.—CONCENTRATION DISSOCIATION COWSTAST OF AOBTIC ACID IN SALT SOLUTIONS.

I8"o. ii=9alt molality.

M.	10^{s} Ji_{c}.	
	tti KCl.	in $SrCl_r$
0 ,	1-74	1-74
001	1-80	—
005	2·19	—
01	2-P9	309
02	2-fl5	3-47
on	3-17	4-07
f-o	295	437
20	2·19	3-89

It is important to note that the ions formed by the dissociation of the weak electrolyte ui'll contribute to these inUjrionie effects injust the same way as the ions of an added salt. This factor is not important in a solution made directly by dissolving a weak electrolyte. Bin in these cases the ionic concentration is small. However, in a buffer solution, niu-h as awtic arid plus sodium acetate, tho acetate ions must be taken into account in calculating the total salt concentration in spite of the fact that they also take part in the dissociation equilibrium. In consequence of this fact the hydrogen ion concentration of a buffer mixture does not remain quite constant when the solution *is* diluted, as would be predicted by the classical law of mass action : for example, $[H^+]$ in

$$0\text{-}10N.CH_3\cdot COOH+0\text{-}10N.CH_3\cdot COONa$$

is greater than in

$$0\text{-}02N.CH_3\cdot COOH+0\text{-}02N.CH_3COONa$$

on account of the higher ionic concentration in the former solution.

The secondary salt effect is still more prominent in non-aqueous solutions, since on account of the lower dielectric constant the electrostatic forces are much greater than in water. In these solutions the ions formed by the weak electrolyte itself may produce a considerable effect, so that large deviations may occur even in unbuffered solutions of weak electrolytes without any salt additions. Typical data are given in the following table, containing data for the concentration dissociation constant of picric acid in ethyl alcohol measured by a colorimetric method (Grose and Goldstern, Monatsh. 1930, 56, 316). It will be seen that although the ionic concentration never exceeds 0-005N. the classical dissociation constant varies by a factor of more than 3.

TABLE *Vi.*—DISSOCIATION OF PICBIO AOID IN ETHYL ALCOHOL AT 20°C.

c_1	c_2	c_i	10* *K*.
0	0	0	1-84 (oxtra-nolatcd)
1-022 X1O-3	0	907 x 10-*	104
1-873X1CT*	0	1.71 x 10''6	Mill
4080x1O-	0	3-48 x 10~»	E-09
l'280x](T*	0	8-97x10-*	2-13
2870 X 10''*	0	1· ×10-	2-i>8
1 087 X10-*	0	4-18x10-''*	2-&S
2-337X10-*	3-27x10-*	4-75 x 10 *	2-1)6
1-705X10-3	0	5-81x10''*	•11U
2-S30X10-4	4-10x10-*	6-30 x lOr*	2-76
2-857x10^	0	7-84 x 10-*	301
2-914 x 10-*	10I0X10-*	I-20xlO-»	3:(J
7-041X1O-*	0	1 35 x 10 :i	3-24
2&!3 x 10''*	iflsxio-3	1-84 x 10-»	3-92
1-453 X *	4-111 xl(H>	4-21 x 10-3	6-21

c_1 = concentration of picric acid.
c_2=concentration of added salt (lithium chloride),
c_i = total ionic concentration,

The bearing of secondary salt effects on catalysed reactions was first realised by Bronsted, and most of the experimental work on this subject comes from his laboratory (*e.g.* Bronsted and Teeter, J. Physical Chem. 1924, 28, 579; Bronsted and King, J. Amer. **Chem,** Soc. 1925, 47, 2523; Kilpatrick, *ibid.* 1926, 48, 2091; Bronsted and Wynne-Jones, Trans. Faraday Soc. **1929,** 25, 59). Table VII (Bronsted and Teeter, *l.c.)* illustrates the effect of adding a neutral salt to a weak acid. The third column shows the values of $[H^+]$ calculated from the kinetic data, using the catalytic constant obtained from dilute solutions of strong acids. The last column contains the corresponding calculated dissociation constants, which may be compared with those in Table V.

TABLE VII.—DECOMPOSITION OF DIAZQACETIO ESTEB ts 005M. ACETIC ACID AT 15*.

fc=first-order velocity constant, min.^{-1}.

$[KNO_3]$.	10*.	tO*$[H^+]$.	10»K«.
0	12-71	9-52	1-85
0005	13-10	9-77	1-95
001	13-45	1007	2-07
0-02	13-70	10-27	2·15
0-05	14·19	10-62	2-30
0-10	14-58	10-90	2-44

The secondary salt effect in buffer solutions is illustrated by Table VIII, which gives data for the acid-catalysed hydrolysis of ethylacetal (Bronsted and Wynne-Jones, *l.c.).* Although the buffer ratio is constant throughout there is a steady rise in velocity in the first five experiments, due to the increase of salt concentration and the resulting increase in the dissociation constant of formic acid. On the other hand, the last four experiments, in which the total salt concentration has been kept constant by the addition of the requisite amounts of sodium chloride, show an almost constant velocity. This device of adding a neutral salt to keep the total salt concentration constant is frequently used to eliminate the secondary salt effect and thus to simplify the interpretation of experimental results. It can, however, only be applied successfully in fairly dilute solutions, since above a salt concentration of 0-1~0-2N. (in aqueous solutions) individual differences between the effects of different salts begin to become serious.

TABLE VIII.—HYDROLYSIS OF ACETAL IS FORMATE BUFFERS AT 20".

Formic acid: formate=2-96 throughout.
k=first-order velocity constant, min.^{-1}.

[Furnilc acid].	[Formate]-	[N»CI],	tonic strength.	10»*.
0-0898	O-0I0O	—	0-0 U	12-5
00592	00200	—	0020	13·4
01480	0-0500	—	0050	15·1
0-2220	00750	—	0075	16-4
0-2960	0-1000	—	0-100	17-8
01776	00000	00400	0100	17-6
00987	00333	0-0667	0-100	J7-7
00222	00075	0-0925	0100	18-2

The interionic attraction theory of electrolytes leads to a theoretical expression for the activity coefficients in equations (8) and (9), thus providing a theoretical basis for the secondary salt effect and making it possible to predict its sign and approximate magnitude.

The *Debi/e-HUckel limiting law* for the activity coefficient/; of an ion of charge 2/ is

$$-\log_{10} f_i = A z_i^2 \sqrt{\mu} \quad . \quad . \quad . \quad (10)$$

x, the tonic *strength,* is defined by

$$\mu = \tfrac{1}{2}\Sigma m_i z_i^2 = \tfrac{1}{2}\Sigma c_i z_i \quad . \quad . \quad . \quad (11)$$

where *vt;* ftnd c; arc respectively tho mobility and equivalent concentration of an ion of species i, and the summation is made over all the ions present in tho solution, including the ion whoso activity coefficient is required. The constant *A* ta given by the theory in terras of the temperature and properties of the solvent: for aqueous solutions at ordinary temperatures it is approximately equal to 0-5. In order to apply the theory to the dissociation of a weak electrolyte the values of the activity coefficients must be substituted in equation (9), giving

$$\log_{10} ir_e = \log_M Jr + 24vV \quad \bullet \quad \bullet \quad (12)$$

This equation predicts that the concentration dissociation constant will increase with increasing ionic strength, as illustrated in Tables V-VIII. However, both theory and practice indicate that equation *(\0)* (and hencf other equations derived from it) will only be valid for extremely dilute solutions, say up to about ^=0-01 in water, and for most work on catalysis it will therefore only serve as a rough guide to the magnitude of the effect. It does, however, predict one notable feature of the secondary salt effect, namely that if the reaction velocity is plotted against *ft* (or the concentration of added salt) the resulting curve is strongly concave to the concentration axis.

The above considerations apply to solutions in which the hydrogen ion concentration ia determined by an equilibrium of the type. HA^i' H^+ +A~. Other types of equilibrium are possible: *e.g.* in a solution of an ammonium salt we have NH_4+ ^ NH_3+H^+, and in a solution of ft disnlphate HSO^-^ SO_4~+H+. The effect of salt concentration can be predicted iHtalitatively by again using equations (9) and (10), taking into account tho different charges on the Bpeciea present. It is found that in the former case the hydrogen ion concentration should be unaffected by salt concentration, while in the latter case it should be increased. These predictions are borne out by the experimental results. The position is similar in reactions which are catalysed by the hydroxyl ion. In solutions of ammonia or an amine the relevant equilibrium is NH_3+H_aO^NH€++OH-, and the hydroxyl ion concentration ia increased by addition of salt. On the other hand, in a buffer solution containing secondary and tertiary phosphate the equilibrium is

$$PO_4^{\equiv} + H_2O \rightleftharpoons HPO_4^{=} + OH^-$$

amt theory predicts a *decrease* of hydroxyl ion concentration on the addition of salt, w/iich is in fact the observed effect (Bronsted and King, J. Amer. Chem Soc. 1925, 47, 2523).

Catalysis in solution may bo also subject to the *primary salt efftct,* though this is normally of less importance than the secondary effect. As the name "primary" implies, this effect operates directly on the velocity constant- of the reaction, and is not concerned with displacements of the equilibria of weak electrolytes. It is therefore best studied in solutions containing only strong electrolytes, and has been tho subject of a large mass of experimental work, (For references, *sec* Bell, " Acid-Base Catalysis," Oxford, 1941, p. 23.) The following generalisations emerge from this work:

(a) For a given reaction and a giver, added salt the percentage change in velocity is a linear function of the salt concentration. This law appears to hold almost universally up to about 0-2s. and is often valid up to much higher concentrations.

(6) The magnitude of the effect depends upon the individual nature of the reaction and of tho added salt, t jere being no general relation to the ionic strength.

(c) The addition of salt invariably causes an increase of velocity (positive salt effect) in reactions catalysed by hydrogen ions, while for hydroxyl ion catalysis the effect is sometimes positive find sometimes negative.

(rf) When the hydrogen ion is the catalyst the specific effect of an added salt depends chiefly on the nature of its an ion, while for hydroxyl ion catalysis the nature of the cation is the more important factor.

(e) The magnitude of the effect rarely exceeds 4-5% in O-lOir. aqueous solutions of uni-univalent salts, though in a few cases it may be as high as 10-12%.

The principle of the primary salt ^ffect is now understood from a theoretical point of view *(cf.* Bronsted, *Z.* physical. Chem. 1922, 102, 1<}9; 1925, ii5, 337; La Mer, Chem. Reviews, 1932, 10, 179). However, the most interesting predictions of the theory relate to reactions involving two ions, and for a reaction involving an ion and a neutral molecule (as do the majority of catalysed reactions) the theory only predicts that the effect will be a linear one (c/. (o) above), without giving either its sign or its magnitude. The theory ia therefore not described here. An interesting correlation between indicator measurements and primary salt effects in acid solutions has been demonstrated by Hammett and Deyrip (J. Amer. Chem. Soc. 1932, 54, 2721) and Hammett and Paul *\ibid.* 1934, 56, 830): this correlatbn has some theoretical basis and is ct-rtainly useful as a guide in practice.

It may be useful to su 111 ma rise briefly the chief practical consequoureB of primary and secondary salt effectB in catalysed reactions, *wish* some mention of how the complications thus caused may be avoided.

(i) In solutions containing a weak electrolyte the reaction velocity will be affected by changes m the total Bait concentration, whether these are brought about by adding a neutral salt or by changing the total concentration of a buffer solution.

(ii) In a solution of an ordinary weak add *{e.g.* acetic acid), or a buffer solution prepared from it, the reaction velocity is *increased* by the addition of salt. An increase in salt concentration from zero to 0-1 ON. usually increases the velocity by 16-20% in a solution containing only a weak acid, and 30-40% in a buffer solution.

(iii) Complications due to this secondary salt effect can be largely eliminated in a series of experiments by maintaining a constant total salt concentration (not greater than N./5) by adding the necessary quantities of neutral salt.

(iv) The primary salt effect modifies the velocity even when no weak electrolytes are present. It can frequently be neglected if the total salt concentration is not allowed to exceed N./10.

(d) MODERN VIEWS ON ACIDS AND BASES.

The understanding of acid-base catalysis has been closely connected with the development of ideas on the nature of acids and bases and the measurement of their strengths. It is therefore necessary to give some account of these ideas before describing further work on catalysis.

The Definition of an Acid has undergone a number of changes during the last fifty years. As soon as the ionic theory had become established an acid was defined as a substance containing hydrogen which gave rise to hydrogen ions in solution. Although acids were originally regarded as neutral molecules (like hydrogen chloride and acetic acid), it was soon found convenient to include negative ions such as HSO_4^-, $H_2PO_4^-$, which can also produce hydrogen ions in solution. These *anion acids* can of course only exist in practice in company with ions of opposite sign, and it might be suggested that salts like $NaHSO_4$, KH_2PO_4 should be regarded as acids. However, the sodium or potassium ions play no part in the acidic reactions of the salts, remaining unchanged throughout, and it is more logical to include only the anions in the definition. The modern definition of acids includes also *cation acids:* thus the acid character of solutions of ammonium salts is most simply explained as being due to the reaction $NH_4^+ \rightleftharpoons NH_3 + H^+$, and the ammonium ion can therefore be considered as an acid. (The older description of the "hydrolysis" of ammonium chloride solution in terms of the two reactions $NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl$ and $HCl \rightleftharpoons H^+ + Cl^-$ is only a more cumbrous way of expressing the same *facts,* since the chloride ion plays no part in the process.) In the same way the acid properties of solutions of many metallic salts (*e.g.* iron, aluminium, chromium, etc.) are best explained by the splitting off of hydrogen ions from the hydrated cations, sometimes in several steps, *e.g.*

$$[Cr(H_2O)_6]^{+++} \rightleftharpoons [Cr(H_2O)_5OH]^{++} + H^+$$
$$[Cr(H_2O)_5OH]^{++} \rightleftharpoons [Cr(H_2O)_4(OH)_2]^{+} + H^+$$

etc.

These hydrated ions can therefore be regarded as cation acids in the same way as the ammonium ion.

The Nature of the Hydrogen Ion in Solution has a considerable bearing on the definition of an acid. It was originally supposed to be simply a proton, the small size of which might serve to account for its high mobility, and possibly also for its catalytic power. However, there is now an overwhelming weight of both experimental and theoretical evidence to show that the hydrogen ion in solution is invariably solvated, and that no measurable concentration of free protons can be present. In particular, it is believed that the hydrogen ion in aqueous solution exists entirely as OH_3^+ (the oxonium or hydroxonium ion), which has a normal electronic structure with a completed octet and is analogous to the ammonium ion NH_4^+. In consequence all equations representing the production of a hydrogen ion in water should be rewritten so as to show the part played by the solvent, *e.g.* the dissociation of hydrogen chloride becomes

$$HCl + H_2O \rightarrow Cl^- + OH_3^+$$

However, it is still common practice to use the symbol H^+ for the hydrogen ion in solution, its solvation being tacitly assumed. It is clear that the nature of the hydrogen ion will actually vary from one solvent to another, *e.g.* in an alcohol ROH it has the formula ROH_2^+.

The term "hydrogen ion" which has been so far used in defining an acid is thus a somewhat ambiguous one. If it is taken to mean the actual species present in solution, the definition will vary from one solvent to another, while if it is taken to mean a free proton the definition is meaningless, since the production of this kind of "hydrogen ion" never takes place in practice. These difficulties are avoided by the modern definition, which reads : *An acid is a species having a tendency to lose a proton* (Brønsted, Rec. trav. chim. 1923, 42, 718; Lowry, Chem. and Ind. 1923, 1, 43). Although the production of a free proton is not possible, the tendency of the acid can be realised if some other species is present to receive the proton, and in the production of a solvated hydrogen ion the solvent acts as a proton acceptor. For example, all the following typically acidic reactions of hydrogen chloride involve the loss of a proton to another molecule or ion:

$$HCl + H_2O \rightarrow OH_3^+ + Cl^-$$
$$HCl + OH^- \rightarrow H_2O + Cl^-$$
$$HCl + EtOH \rightarrow EtOH_2^+ + Cl^-$$

(alcoholic solution)

$$HCl + NH_3 \rightarrow NH_4^+Cl^-$$

(no solvent necessary).

In exactly the same way the characteristic acid reactions of the ammonium ion involve the loss of a proton to give the ammonia molecule, *e.g.*

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + OH_3^+$$
$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$$
$$NH_4^+ + CH_3 \cdot COO^- \rightleftharpoons NH_3 + CH_3 \cdot COOH$$

One important consequence of the above definition is that *the oxonium ion* OH_3^+ *must itself be regarded as an acid,* its tendency to lose a proton being illustrated, for example, by the following reactions:

$$OH_3^+ + OH^- \rightleftharpoons 2H_2O$$
$$OH_3^+ + NH_3 \rightleftharpoons H_2O + NH_4^+$$
$$OH_3^+ + CH_3COO^- \rightleftharpoons H_2O + CH_3COOH$$

It will be seen that there is a close similarity between the oxonium and ammonium ions. In fact, although the oxonium ion is of great importance in aqueous solution owing to its close relation to the solvent, it is in no way unique, being one of a class of cation acids which includes the ammonium ion and many others.

The Definition of a Base has in the past been a subject of controversy, particularly as to whether the term base should be confined to hydroxy-compounds (*e.g.* NH_4OH), or whether it should be extended to other species which produce hydroxyl ions in solution (*e.g.* NH_3). The modern definition of a base avoids these ambiguities, and is closely related to the definition of an acid, *i.e.* : *A base is a species having a tendency to add on a proton.* Once again it is not a free proton which is involved, but a proton derived from another (acid) molecule or ion. For example the basic nature of the ammonia molecule is illustrated by the following reactions, in which it adds on a proton to give the ammonium ion:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$
$$NH_3 + OH_3^+ \rightleftharpoons NH_4^+ + H_2O$$
$$NH_3 + EtOH \rightleftharpoons NH_4^+ + OEt^-$$

(alcohol solution)

$$NH_3 + HCl \rightleftharpoons [NH_4^+ \; Cl^-]$$

(no solvent necessary).

The hydroxyl ion itself must also be regarded as a powerful base, since it readily adds on a proton to form water, *e.g.*

$$OH^- + OH_3^+ \rightleftharpoons 2H_2O$$
$$OH^- + CH_3 \cdot COOH \rightleftharpoons H_2O + CH_3 \cdot COO^-$$
$$OH^- + NH_4^+ \rightleftharpoons H_2O + NH_3$$

Not only the hydroxyl ion but also other anions must be considered as bases, especially those anions derived from weak acids. Thus the basic nature of the acetate ion is illustrated by the following reactions, in which it adds on a proton to form acetic acid:

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$
$$CH_3COO^- + OH_3^+ \rightleftharpoons CH_3COOH + H_2O$$
$$CH_3 \cdot COO^- + NH_4^+ \rightleftharpoons CH_3COOH + NH_3$$

The first equation represents the hydrolysis of an acetate like sodium acetate, and the third the " hydrolysis " of ammonium acetate. The recognition of this extended class of anion bases has been of considerable importance in the interpretation of catalytic phenomena. Cation bases also exist but are not common, being chiefly confined to the complex hydroxo-ions of heavy metals mentioned under the heading of cation acids.

The definitions of acids and bases already given can be summed up in the scheme

$$A \rightleftharpoons B + H^+ \quad . \quad . \quad . \quad . \quad (13)$$

where A is an acid and B a base. Two species related in this way are known as a *corresponding* (or *conjugate*) *acid-base pair*; examples are $CH_3 \cdot COOH$ and $CH_3 \cdot COO^-$, NH_4^+ and NH_3, $H_2PO_4^-$ and HPO_4^{--}, etc. There is no restriction as to the charge on A and B, but there must always be unit difference of charge between the members of *a* corresponding pair. In some cases the same species can act either as an acid or as a base, *e.g.* the water molecule is the acid corresponding to OH^- and the base corresponding to OH_3^+.

The scheme (13) is never realised in practice, all acid-base reactions actually observed being of the type $A_1 + B_2 \rightleftharpoons A_2 + B_1$. Thus the dissociation of a weak acid HX in water follows the equation

$$\underset{A_1}{HX} + \underset{B_2}{H_2O} \rightleftharpoons \underset{A_2}{OH_3^+} + \underset{B_1}{X^-} \quad . \quad . \quad (14)$$

and it will be seen that all the acid-base reactions given above (whether commonly described as " dissociations," " hydrolyses " or " neutralisations ") can be represented in this way. The *strength of an acid* is commonly defined in terms of the reaction (14), i.e. by the equilibrium constant.[1]

$$K = \frac{[OH_3^+][X^-]}{[HX]} \quad . \quad . \quad (15)$$

Exactly the same equation applies to charged acids, *e.g.* the acid strength of the ammonium ion is represented by the constant

$$K = \frac{[OH_3^+][NH_3]}{[NH_4^+]} \quad . \quad . \quad . \quad (16)$$

which in the older nomenclature is described as the " hydrolysis constant " of ammonium salts. In general the strength of an acid A in aqueous solution is represented by the constant

$$K = \frac{[OH_3^+][B]}{[A]} \quad . \quad . \quad . \quad (17)$$

where B is the corresponding base. The equilibrium governed by (17) is $A + H_2O \rightleftharpoons OH_3^+ + B$, and the constant K is thus in reality a measure of the strength of the acid A relative to that of the acid OH_3^+.

The *strength of a base* is commonly represented in terms of the equilibrium $B + H_2O \rightleftharpoons A + OH^-$, i.e. by the constant

$$K_b = \frac{[A][OH^-]}{[B]} \quad . \quad . \quad . \quad . \quad (18)$$

This constant is, however, closely related to the acid constant of the corresponding acid, *e.g.* for ammonia we have

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{K_w[NH_4^+]}{[NH_3][OH_3^+]} = \frac{K_w}{K}$$

where K is the acid constant of the ammonium ion, and $K_w = [OH^-][OH_3^+]$ is the ionic product of water. For a given solvent the dissociation constant of a base is therefore inversely proportional to the constant for the corresponding acid, and in fact all the properties of solutions containing acids and bases can be expressed in terms of acid constants. For example, the hydrogen ion concentration of any buffer solution is given directly as $[OH_3^+] = K\frac{[A]}{[B]}$

---

[1] The full equilibrium constant for the reaction (14) would contain the term $[H_2O]$ in the denominator, but this is omitted, since the concentration of water is effectively constant in all reasonably dilute aqueous solutions.

where A and B may be, *e.g.* CH_SCOOH and CH_3-COO-, NH_4^+ and NH_3, $H_?PO_4$- and KPO_4", *K* being in each case the acid constant. The inverse relation between the strengths of an acid and its corresponding base means that a very strong acid corresponds to a very weak base, and *vice, versa.* For example; the HCI molecule is such a strong acid that it reacts almost completely with water to give hydrogen ions and chloride ions: hence its acid strength cannot be measured directly, though it can be estimated indirectly to have a value of about 10^7. Consequently, although the chloride ion is formally a base, its basic properties are so^mall that they can invariably be neglected, and the same applies to the anions of other strong acids.

Finally it should be mentioned that the terms acid and base are now sometimes applied to a still wider class of 8ubstaui.es (c£ Lewis, J. Franklin Inst. 1938, 226, 293; Ludcr, Chera. Reviews* 1940, 87, 647). According to this definition an acid is a species having a tendency to accept electrons while a base is a species having a tendency to donate electrons. This formulation includes species which are acids and bases according to the definitions given above, but also includes other species whose functions do not involve the exchange of a proton; *e.g.* the molecule BF_3 is classed as an acid because of its incomplete octet and its consequent tendency to accept electrons. This wider definition has not BO far met with general acceptance, but it is interesting to note that its adoption would lead to the class ideation under acid catalysis of the reactions described in section *(k),* which are catalysed by BF_S, $AICI_3$, etc.

(e) GENERAL ACID-BASE CATALYSIS.

It has been shown in the preceding section that hydrogen and hydroxyl ions do not play any necessary or unique part in acid-base reactions, being merely particular members of large classes of acids niict bases. From this point of view there is no obvious reason why OHg^ and OH~ (or their analogues in other solvents) should possess the unique power of catalysing reactions, and it would seem more reasonable to expect that all acid species such as OH_3+, NH_4^+, CH_3COOH, etc^would act as acid catalysts: similarly the Bpeciea OH~ CH_3COO-, NH,, etc., mijht all be expectec to act as basic catalysts. This expectation has in fact been realised for a large number of catalytic reactions, and this kind of behaviour is known as *general acid-base catalysis.* From an experimental point of view it means a rev is ion of the simple kinetic equation (4), For example th- velocity of an acid-catalysed reaction in a solution containing acetic acid (HAc) will no longer be given by ik=VH*B+)$[.H^+]$, but by *=!,,+ (ifcat-)[H +]+ *HAC[HAc], and there will be similar additional terms in the case of basii catalysis.

The idea that hydrogen and hydroxyl ions are not the only effective catalysts is much olde than the revised concepts of acids and bases; in fact it was one of the earliest suggestion made to account for deviations from the clauaical kinetic equations. In particular the hypothesis hat undisaociated acid molecules like **HCI** and CH_3COOH could act as catalysts was known as the *dual theory* of catalysis. However, the lual theory originated before the development of modern views on electrolyte solutions, and the arguments on which it was based involved a neglect of both primary and secondary salt Sects, and the assumption that the degree of association of strong electrolytes is given correctly by the conductivity ratio. These arguments therefore need revision in the light of more recent work, and it is found in all cases hat the quantitative interpretation of the tnal theory is profoundly modified, while in most cases the supposed evidence for the theory s completely destroyed *(cf.* Bronsted, Chem. Reviews, 1928, 5, 245; Bell, "Acid-Base Catalysis," Oxford, 1943, pp. 48-59). No account therefore is given here of the rather jolcmical history of the dual theory. The following are examples of more modern work on the subject, largely due to Bronst«d and his collaborators:

The Decomposition of Nitramide was the irst reaction for which general basic catalysis was established. The decomposition takes place according to the equation

$$NH_2{\cdot}NO_2 \rightarrow N_2O+H_2O,$$

and the reaction can be conveniently followed jy measuring the pressure or volume of nitrous oxide evolved. In alkaline solutions the decomposition takes place at an immeasurably great -ate, but in solutions of strong acids catalysis by hydroxyl ion is eliminated, and the rate is measurable and constant over a large range of hydrogen ion conc&itrations (10~* to 0-2). This shows that there is no detectable acid catalysis, and the constant rate in these solutions is equal to the " spontaneous" rate. It is a simple matter to prepare many buffer solutions in which the hydrogen ion concentration is sufficiently great to eliminate the effect of hydroxyl ions, and it has been found by many workers that in such solutions the velocity is greater than the spontaneous rate, and depends on the concentration of the basic constituent of the buffer (Bronstal and Pedersen, Z. physikal. Chcm. 1924, 108, 185; Bronsted and Uuus, *ibid,* ***1926,*** **117,** 299; Bronsted and Volqvartz, *ibid.* 1931, A. 155, 211; Baughan and Bell, Proc. Roy. Soc. 1937, A, 158, 464 ; Marlies and La Mcr, J. Amer, Chem. Soc. 1935,67, 1812,2739 ; Tong and Olson, *ibid.* 1941, 63, 3406), A typical example is shown in Table IX, illustrating the

TABLE IX.—DECOMPOSITION OF NITRAMIDE AT 16°,

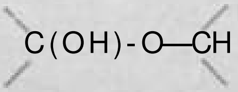
k=first-order constant, min."^{1}
" Spontaneous " rate=380x 10-*.

[CH,-COO-1.	[CH_a-COOHJ.	10^4k.	$\frac{(10^4k-380)}{[CH_3\text{-}COO^-]}$
000414	**0-0163**	246	0-504
(••<K)083	0-0135	382	0-605
00102	00101	651	0-603
00136	O0OC7	726	0-506

results of Bronsted and Pedersen (I,c.) for acetate buffers. It will be seen that the increase of velocity is directly proportional to the acetate ion concentration, and independent of the p_B of the solution (determined by the buffer ratio). These results demonstrate conclusively basic catalysis by the acetate ion and make it possible to determine its catalytic constant with accuracy. Similar results wore obtained with many other anion bases (both singly and doubly charged), with uncharged bases like aniline, and with positively charged bases of the type

$$[Co(NH\text{-}_3)_sOH]{+}{+}.$$

The Mutarotation of Glucose has long been known to be catalysed both by acids and by bases, and played an important part in establishing the theory of general acid-base catalysis (B rone ted and Guggenheim, *ibid.* 1927, 49, 2554; Lowry and Smith; J.C.S. 1927, 2539; Westheimcr, J. Org. Chera. 1938, 2, 431). The process observed is the in to reconversion of the isomcrs o- and |8-glueose, involving the rupture of a acmi-aeetal link



$$C(OH)\text{-}O\text{—}CH$$

The catalytic effect of hydroxyl ions is about 4x 10* greater than that of hydrogen ions, and there is a considerable rango of hydrogen ion concentrations (about p_B 4-6) over which catalysis by both OH~ and OH_3^+ can be neglected, enabling the " spontaneous " rate to be observed directly. The presence of general catalysis both by acids and by bases is most readily detected by using buffer solutions in this range, and experiment has shown that 43 other species are effective as catalysts, in addition to OH_a^+ and OH-, comprising the following types:

(o) Uncharged acids, *e.g.* CH_3COOH.
(6) Cation acids, *t.q.* N H / .
(c) Uncharged bases, *e.g.* NH_3.
\d) *Amoa* bases, *e.g.* CH_3COO", SO_4=.
(e) Cation bases, *eg.* $[Co(NH_3)_sOH]^{++}$.
(/) Amino-acids in the zwitterion form, *e.g,*

NHa+CHj-COO- .

The effect of this last type of catalyst is due primarily to the basic properties of the group COO-.

Fig. 1 shows data obtained by Bronsted and Guggenheim (J. Amer. Chem, Soc. 1927, 49, 2571) for sodium salts of various weak acids, a small quantity of the corresponding acid being added to bring the hydrogen ion concentration into the. range 10-' to $IO"^4$. (These amounts wero insufficient to cause any appreciable acid catalysis.) It will be seen that the velocity is in each case a linear function of the aryon concentration.

The Halogenation of Acetone was the first reaction for which catalysis by undis&pciated acid molecules was definitely established, and constitutes the only piece of evidence brought forward in support of the dual theory which has not been refuted by more modem work. The bulk of the work on this reaction is due to Dawson *et al.* (numerous papers in J.C.S. 1913-29). Much of this waa carried out before the importance of primary and secondary salt effects was realised, and the results are therefore often difficult to interpret. However, the general features of the reaction are clear, and have been confirmed by recent work (Smith, *ibid.* J934, 1744; Lidwell and Bell, Proc. Roy. Soc. 1940, A, 176, 88). The reaction velocity is independent of the concentration of the halogen, and is the same for bromine and for iodine: hrnce the process of which the rate is measured precedes the halogenation and involves only the acetone molecule and tile catalyst. (Modem views on the nature of this process are mentioned in section (?).) There is catalysis both by acids and by bases, hydroxy] ion being a much more powerful catalyst than hydrogen ion. The relative values for catalytic constants for OH~, OH_3^+.and the spontaneous reaction are such that there is no appreciable range of hydrogen ion concentrations over which catalysis by both OH- and OH_3+ can be neglected. This means that the spontaneous rate cannot be observed directly, and complicates the separation of tSe catalytic effects of different species. For example, in a solution containing a weak at id HX and its sodium salt the measured velocity *k* is equal to

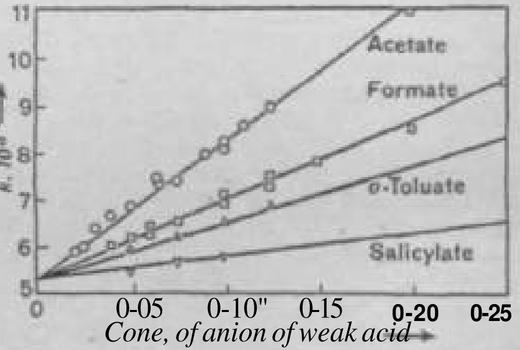


FIG. 1.

$$k_0 + (k_H O\ [H^+1 - H{*}OH-)[OH-] + \ldots HX] + (k_{X^-})[X^-]$$

where at the most one term (the second or third) can be neglected. A large numi>er of carefully planned experiments is therefore necessary in order tc determine the values of the individual catalytic constants.

Many other reactions are known which exhibit general acid-base catalysis in aqueous solution, of which the following may be mentioned: the bromiration of substituted ketoncs and of ketouic esters (Pederaen, J. Physical Chem. 1833, 37; 751; 1934, 38, 601; Lidwell and Bell, Proc. Roy. Soc. 1940, A, 176, 88), the bromination of nitromethane (Pedersen, Kgl. Danskc Vid. Selsk. Math.-fys. Medd. 1932, 12, 1), the hydrolysis of ortho-eaters (Bronsted and Wynne-Jones, Trans. Faraday Soc. 1929, 26, G9), the decomposition of the diazoacetate ion (King und Bolinger, J. Amer. Chem. Soc. 1936,68,1533), the depolymorisation of dimeric dihydroxyacetone **(BcO** and Baughan, J.C.S. 1937, 1947), the oxidation of phosphorous and hypo phosphorous acids;by iodine (Nylen, Z. anorg. Chem. 1037, 230, 385; Griffith, McKeown and Taylor, Trans. Faraday Soc. 1940, 36, 752), the formation and hydrolysis of Be mi car baz ones (Conant nnd Bartlett, J. Amer. Chem. Soc. 1932, 5*. 2881; Westheiraer, *ibid.* 1934, 56, 1062).

The theory of general acid-dasc catalysis puts s new interpretation upon *the " spontaneous " reaction, i.e.* that part of the reaction velocity which is independent of the concentration of dissolved catalysts. It is now supposed that this reaction is not truly spontaneous (though the term is still frequently used for convenience), but is due to acid or. basic catalysis by the water nirilncules, which can act either as acids or as bas&. Although the acid or basic strength of the H.O molecule is very a mall, it ia present in very liigh concentrations, and therefore its catalytic effect may well be appreciable. There are two pieces of evidence which favour this • interpretation. In the fiist place, all those reactions which exhibit general catalysis by acids or by bases also exhibit a measurable spontaneous reaction; conversely, those reactions which appear to be catalysed specifically by hydrogen or hydroxyl ions do not exhibit any measurable spontaneous reaction. In the second place, no spontaneous reaction can be detected in solvents which do not exhibit acidic or basic properties : *e.g.* nitrnmide is quite stable in chloroform solution, and tetramethylglueose undergoes no change in carefully purified hydrocarbon solvents.

The study of catalysis by acids* and bases in *non-aqueous solvents* throws an interesting light on general catalysis. In other hydroxylic solvents the condition hi similar to that in water, except that quantitative interpretation ia niort difficult on account of tile paucity of information about the behaviour of electrolytes in these solvents, and the increased importance of interionic effects. However, in inert solvents of the hydrocarbon type the position is very different. No free ions are formed in these solvents and, in particular, thejp are no analogues to tho hydrogen or hydroxyl ions, since the solvent molecule is unable to pick up a proton or to split one off. Any catalytic behaviour observed in this type of solvent must therefore be due to the molecules of the addc*l acid or base, since thera are no other catalysts present. A number of reactions ha* e been shown to exhibit general acid-base catalysis in 4jenzene and similar solvents, though more work is needed to clear up certain complications which arise in this type of medium (Bell and coworkers, J.C.S. 1930-11; summary given by Bell, Trans. Faraday Soc. 1038, 84, 229).,

(/) THE USE OF CATALYTIC MEASURE MKNTS FOB DETEHMININQ HY/DROOEN- AKD HYDROXYI,. ION C0NCENTEATI0N3.

Measurements of the velocity of a catalysed reaction have long been used as a method for determining the concentration of hydrogen or hydroxyl ions in a solution. According to the classical theory this determination is a very direct one, since the velocity is supposed to be a simple linear function of [OH_a+] or [OH~]. Later developments introduce some complications into this view. Thus it *is* abvious that a reaction exhibit ng general acid or base catalysis is unsuitab for this purpose, since the observed reaction veiucity will depend not only on the concentration of OH_3^+ or OH-, but also on the concentrations of other acid or basic species present in the solution. Fortunately there are a number of reactions which appear to exhibit *specific catalysis by hydrogen or kydroxyl ions,* and the most useful of these will bo described in this section. In another respect the modern theory has simplified the interpretation of the measured velocity, since it. is now believed that the velocity ia closely proportional to the concentration of the catalyst, and not {as has often been supposed) to its activity. This El illustrated by the data already given in Tables III and IV. In some ca^es it will be necessary to take into account the primary salt effect, but this is frequently Binall, and can be allowed for or minimised by keeping the salt concentration low.

The Decomposition of Diazoacetic Ester. —In acid aqueous solution the following reaction takes place:

CHN^OOEt+HgO
-*-CH,(OH)COOEt+N,

anil can be conveniently followed by measuring the pressure or volume of the evolved nitrogen. It has been shown (Brodig and Fraeukcl, Z. Elektrochem, 1905, 11, 525; Fracnkel, Z. physikal. Chem. 1907, 60, .202; Spitatsky, *Z,* anorg. Chem. 1907, 54, 278) that the velocity is proportional taiho hydrogen ion concentration in solutions of both strong an'd weak acids. Examples"of the results obtained are given in Table X.

TABLE X.—DECOMTOSITION OF DIAZOACETIC ESTER IN AQDEOUS SOLUTION (20").

£•= first-order constant, min. *K*

Catalyst.	lO'lOHj+J.	10*t.	**[OH.+]**
OOOOttOON. **H N O** . . „	009	*34b*	86-0
D00182K. HNO, . .	18-2	709	38-7
000030tIC. picric acid	**304**	**140**	884
(HXXHW9K. ptcrtc add	IKW	355	391
OOODOO**. m-nltroben- ?>>*f* acid	10-8	032	370
00162s acetic **udd** .	5-63	SIS	38-8

Measurements in buffet solutions ogree with the assumption that tho hydrogen ion is the only effective catalyst, provided that secondary salt effects are taken into account (c/. Tablo'VJIi. There is also an unusually large primary salt effect, and a further complication arises from the fact that in tho presence of many anions *a* second reaction takes place simultaneously, *e.g.* with {•hlnrirtes,

$$CHN_2 \cdot COOEt + H^+ + Cl^- \rightarrow CH_2Cl \cdot COOEt + N_2$$

This type of reaction has been found to tako place in solutions of chlorides, nitrates and sulphates, but not of perchlorates and picrate*.

In spite of these complications the diazoacetic ester reaction has been successfully used for the measurement of hydrogen ion concentrations, and hence of dissociation constants (*cf.* Bronsted *el a*\., Z. physikal. Chem. 1925, **117.** 299; 1927, 130,699; 1028,184,97).

The Hydrolysis of Acetals.—These reactions are of the Jjjrpe

$$CH_3\,CH(OR)_a + H_3O \rightarrow CH_3CHO + 2ROH$$

and are catalysed by acids but not by bases. They are more suited to the measurement of hydrogen ion concentrations than the hydrolysis of carboxyu'c esters, since these latter reactions produce acid, which interferes with the system under investigation. A large number of different acetals have been investigated by Skrabal by a chemical method. (For summary and references, *set* Skrabal, Z. Elektrochcm. 1927, 33, 322.) The possibility of catalysis by undissociated acid molecules was carefully investigated by Bronsted and co-workers using an accurate and convenient dilatometric method (Bronsted and Wynne-Jones, Trans. Faraday **Soo.** 1929,35, 59; BrcSnsted and Grove, J. Amer. Chem. Soc. 1930,52,1394). They found that no such effect is detectable, and that there is no measurable " spontaneous " reaction. The first point is illustrated by the last four rows in Table VIII, where a change in the concentration of formic acid from 0*02N. to 0*3N. has no effect on the reaction velocity when the buffer ratio and the ionic strength are kept constant. The reaction velocity is thus directly proportional to the hydrogen ion concentration without any complications), and by a suitable-choice of ftcetal a wide range of concentrations can be covered. Thus if *k* is the first order velocity constant at 20° (min.-^{1}) and *c* the hydrogen ion concentration, we have the following values of *kjc*;

Ethylacetal	19
Methylacetal	3>92
Etbyleneacetal	0-180

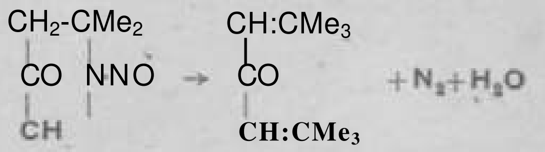
The primary salt effect is fairly large, but has been extensively studied (Bronsted and Grove, *id*

The Decomposition of Dlacetone Alcohol.—Tlu's ia a reversible reaction,

^ r i i ' u U WMv W \ V* Pl i>Jrtf Pl ^j— A u n V v U ' w r l q

which, however, goes practically to completion, in ilil ute aqueous solutions. It is catalysed by bases, but not by acids, and is accompanied by a large volume change ao that its velocity can conveniently be followed by a dilatometric method. Data have already been given in Table IV to show the direct proportionality between reaction velocity and hydroxyhion concentration in solutions of NaOH. (For other d^ta, *see* French, *ibid.*, 1929, 51. 3215; Murphy, ***ibid.*** 1931, 53, !)77.! An exhaustive study has been made of the primary salt effect in this reaction {Akerlof, *ibid.* 1920, 48, 3046; 1927. 49, 2955: 1928, 60, 1272). There is no catalysis by water molecules or by the anirws of weak acids, but primary and secondary (though not tertiary) amines doexert a catalytic effect, and therefore the reaction cannot be used for determining hydroxyl ion concentrations in solutions containing these molecules. It is believed that this catalysis by amines is due to a specific chemical mechanism, and cannot be described as general basic catalysis (Miller and Kilpatrick, ***ibid.*** **1981,** 53, 3217; Westheimer and Cohen, *ibid.* 1938, 60, 90; Ann. New York Acad. &ci. 1940,39,401; Westheinier ami Jonea, J, Amer. Chem, Soc. 1941, 63, 3283).

The Decomposition of Nitrosotriacetonamine.—This ia a first order reaction taking place according to the equation •



and its velocity can be conveniently studied by measuring the pressure or volume of nitrogen evolved (Clibbens and Francis, J.C.S. ,1912,**101,** 2358; Francis and Geake, *ibid.* 1913,103, 1722; Francis, Geake and Roche, *ibid.* 1915,107,1651; Bronsted and King, J. Amer. Chem. Soc. 1925, 47, 2523). The reaction velocity is directly proportional to the hydroxyl ion concentration up to about 0-5N., above which concentration the reaction appears to be more complex. There is no evidence of general base catalysis, though no investigations have been specifically directed to this point.

The above four reactions are probably the most convenient for measuring hydrogen or' hydroxyl ion concentrations. It should, however, be mentioned that for most purposes the *inversion of sucrose* and the *acid hydrolysis of carboxyiic esters,* both in aqueous solution, can bo regarded **« examples of specific catalysis by hydrogen ions. It is a matter of some dispute how far undissociated acid molecules can exert a catalytic effect, but from a practical point of view such effects are certainly very SUM 11.

(g) RELATIONS BETWEEN CATALYTIC POWER AND ACID-BASE STRENGTH.

If the catalytic effects of several acid species for a given reaction can be compared, it is natural to expect that they will bear some relation to the acid strengths of the various species, in the sense that the stronger acid will be the more effective catalyst!* It has in fact been found that ftu's parallelism is a quantitative one, and it is usually referred to as the *Bronsted relation,* since it was first formulated by Bronsted and Pedersen in 1924 as a result of their work on the decomposition of uitramide (Z. physikal. Chem. 1924, **108,** 185). Tho rclntiCn can be written in the form

$$k_A = G_A K_A^{\alpha}, \text{ or } \log k_A = \log G_A + \alpha \log K_A. \quad (19)$$

where k_A is the catalytic constant of a **dr«B** acid catalyst, K'_A its dissociation constant, and G_A aad a are constant for *a,* given reaction, solvent, temperature and series of similar catalysts. The constant a is at wave positive and less than unity. An exactly analogous equation holds for biieuc catalysis, i.e.

$$k_B = G_B K_B^{\beta}, \text{ or } \log k_B = \log V_B + p \log K'_B. \quad (20)$$

K_B is here the ordinary basic dissociation constant of the catalyst as defined in equation (18). It is however convenient for many purposes to express the basic strength of the catalyst by means of the reciprocal of the acid strength of the corresponding acid. As shown in section *(d)*, this will not alter the form of equation (20) or the value of the constant β, though the value of G_B will be changed, and the equation can therefore be written

$$k_B = G'_B\left(\frac{1}{K_A}\right)^{\beta}, \text{ or } \log k_B = \log G'_B - \beta \log K_A \quad (21)$$

The Bronsted relation is analogous to several other relations which have been found to exist between reaction velocities and equilibrium constants, and some progress has been made towards a molecular interpretation of such regularities (*cf, e.g.* Hammett, Chem. Reviews, 1935, 17, 125; Trans. Faraday Soc 1938, 34, 156; Horiuti and Polanyi, Acta Physicochim. U.R.S.S. 1935, 2, 505; Bell, Proc. Roy. Soc. 1936 A, 154, 414), However, there is no strict theoretical basis for these relations, and their accuracy or range of validity can only be determined by appeal to experiment. Actually the Brönsted relation has been found to hold without systematic deviations in all the reactions for which general acid-base catalysis has been established, though the closeness with which it is obeyed varies somewhat from case to case. In the exact application of this relation to the experimental data it is necessary to take into account the so-called *statistical effect,* depending upon the number of points in the catalyst molecule at which a proton can be lost or picked up. However, the application of this correction rarely has much effect on the degree of agreement with the Bronsted relation, and in any case the way in which it should be applied in particular cases is often a matter of dispute, and is not discussed here *(cf,* Bronsted and Pedersen, Z. physikal. Chem. 1924, 108, 185; Bronsted, Chem. Reviews, 1928, 5, 322; Pedersen, J. Physical Chem. 1934, 38, 581; Trans. Faraday Soc. 1938, 34, 237; Westheimer, J. Org. Chem. 1938, 2, 431).

Typical examples of the validity of the Bronsted relation are shown in Figs, 2 and 3, in which the symbols *p* and *q* refer to the *statistical effect* mentioned above *(cf.* section *e,* pp. 249c and 250a).

In each case the logarithm of the catalytic constant is plotted as ordinate against the logarithm of the dissociation constant of the corresponding acid as abscissa : *cf.* equation (21). For the decomposition of nitramide (Fig. 2) the points lie well on four straight lines, one corresponding to each class of bases investigated. The concordance is good, and usually within the limits of the experimental error.

For the mutarotation of glucose the agreement is not so good for any one class of catalyst, with the result that any differences between the classes as a whole are masked. As will be seen from Fig. 3, the data for a very varied selection of catalysts can be represented with moderate accuracy by a single relationship. There are no other reactions which have been investigated in such detail as the two illustrated, above, but the available data indicate similar behaviour for both acid- and base-catalysed reactions in many other cases.

Catalysis by the Hydrogen Ion, the Hydroxyl Ion and the Water Molecule should in principle be governed by the Bronsted relation. It is not, however, easy to test this, since there is some difficulty in giving a satisfactory numerical measure of the acid-base strengths of the species OH_3^+, OH^- and H_2O. By formal analogy with the usual expression for the dissociation constant of an acid HX, i.e.

$$K_A = \frac{[H^+][X^-]}{[HX]}$$

we can write

$$K_A(H_2O) = \frac{[OH_3^+][OH^-]}{[H_2O]} = \frac{K_w}{55 \cdot 5} = \begin{cases} 1 \cdot 07 \times 10^{-16} \text{ at } 18^\circ \\ 1 \cdot 8 \times 10^{-16} \text{ at } 25^\circ \end{cases}$$

where 55·5 is the number of gram molecules of H_2O in a litre of water. Similarly, the formal expression for the acid strength of the ion OH_3^+ is (cf. equation (16) for the ammonium ion)

$$K_A(OH_3^+) = \frac{[OH_3^+][H_2O]}{[OH_3^+]} = [H_2O] = 55 \cdot 5 \quad (23)$$

The basic strengths of OH^- and H_2O are then conveniently measured by the reciprocals of the acid constants for their corresponding acids H_2O and OH_3^+. These values cannot be directly compared with the corresponding ones for other acids and bases, since they involve the supposed volume concentration of H_2O molecules in water, a quantity which is clearly unsuited for use in the calculation of a mass action

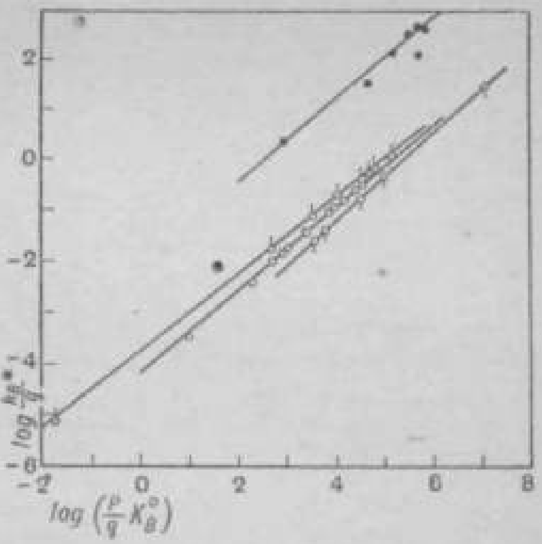


Fig. 2.—THE DECOMPOSITION OF NITRAMIDE.

● Bases with two positive charges, *e.g.* $[Co(NH_3)_5(OH)]^{++}$.
▲ Bases with no charge, *e.g.* aniline.
○ Bases with one negative charge, *e.g.* acetate ion.
♀ Bases with two negative charges, *e.g.* oxalate ion.

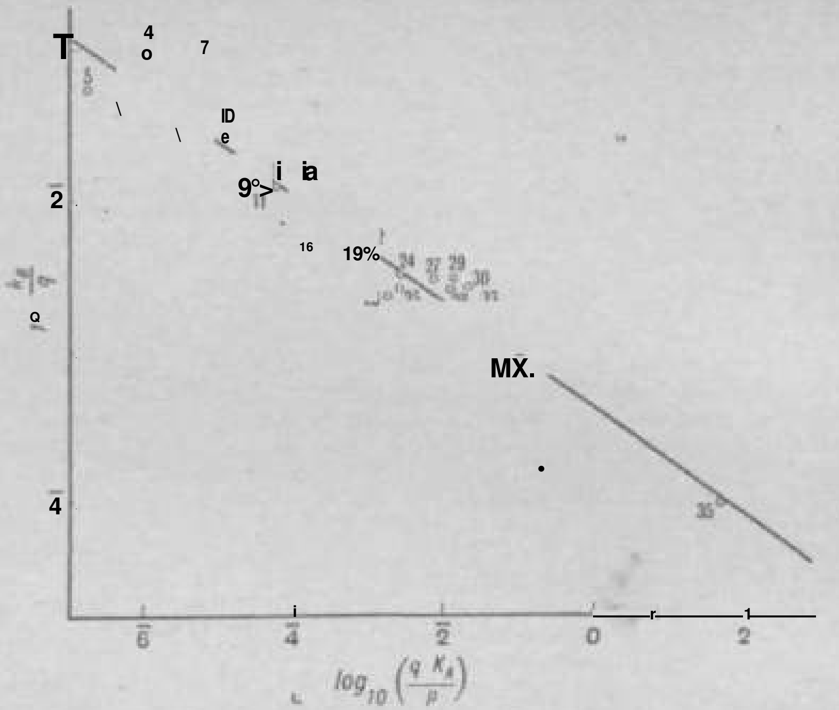


FIG. 3.—THE MUTAROTATION OF GLUCOSE.

Key to figures: 4 hist id in i;, 5 a-jiicullne, T pyridine, 8 trfmcthylacatatfl ion, (t propkmate Ion, *U)* (iiiiiioline, 11 scctnU' iuii, 12 pbainrlaOBiatt ion, 13 glutamate Ion, 14 bonxoatt loo. Hi o-toluate ion, 17 gfycollatc lorn, 18 uspurtatc ion, IU hippuxate ion, *'Zo* formate ion, 21 a-tiliiniur, !i- mmidi'late Ion,*Z'S* BaHcylftt.tr inn, *-i o-chlorobe***izoatc** ion,25 **cbJcTOacetatt** ion,'2fl cyano-acetato ion, 27 jt-benzototftiiK.', 2S sarctwiiit!, 20 lysints hydrodiloride, 30 arginiuc tiytlrodttoritlu, 3t sulphate *ion, 2'1* prulini;, *ZH* dimctliylijlytinu, 34 bctniuc, 35 witer.

constant: however, the values may serve to give a rough estimate of the a c id -bus e strengths concerned. Moreover, in the case of catalysis by the water molecule the catiilytic constant for HJJO has to *be* evaluated by dividing the " spontaneous " velocity k_0 **bytheeonoeDtntfoa** of water molecules (55-5), eo that the hitter figure enters into the calculation of both the catalytic constant and the acid-base strength, and the uncertainty attached to its use may to some extent cancel out in the comparison.

Some of the experimental data for catalysis* by hydroxyl ions and w&tot molecules are shown in Table XI_K The water molecule is throughout acting as a base, uml the calculated values of i'Oii- and &j|jo are obtained from equation (21), using values of O'n and j3 derived from the experimental data for other basic catalysts.

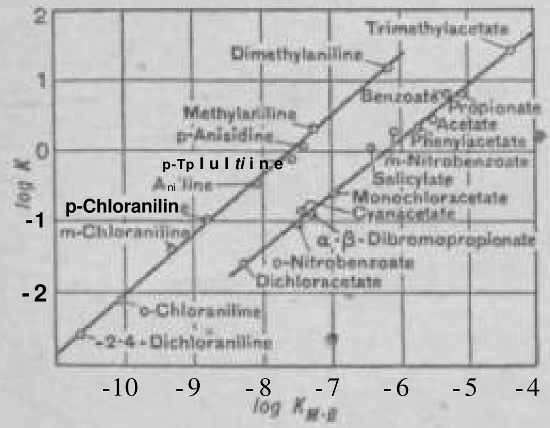
TABLE XL—CATALYSIS BY HYDHOXYL loss SXD WATER MOLECULES.

Reaction.	k_{H_2O}		Sw-	
	OU.	**Calc.**	OtM.	Calo.
Decomposition of nitramide * . , • .	B-8X1CT*	**S-2X1O"^{9}**	I-OX 10^{s}	1·0 × 10^{s}
Mutarotation of glucose [a] .	iKixlO"*	**i.tixio-^{6}**	3HxlO^{3}	7-4 x ln-
Iodination of acrtone *	o0xl(r^{1u}	**SOxlO"**	l-BX 10	B-2X10*
Iodination of acetonylacgtone [a] .	2-CXKT'	**l-HxlO-»«**	*l(IX* 1d^{a}	*5-5x1^*
Iodinatitin of monochloroacetone [3] .	S-8xI0n«	**1'liXlO-^{8}**	6-6 X10^{1}	)-8X10*
Iodination of monobroinoacetone * .	20X10"^{7}	**44xlO~^{8}**	1-2x10*	l-oxio^{7}
[T]Jromination of dichloroacetone [3] . .	7-9XKT'	**S-0X10-'**	27x10«	14X10^{7}
Bromination of acctoat'c-tk[1] ester [a]	i-3xur^{3}	**4-3X'10-»**	—	—
Broroination of acetyldct.-ttine [a] . ,	l-2x 10"*	**(i i)X 10-«**	—	—
Brom ination of acetoa' •> -t i • • m id[a] .	14X1U '	**6-5 X10"^{1}**	—	—

[1] Marlicii mid Ln iicr, J. AUKT, **Chan.** Sac. 1035, 67, Igl"*
[2] 1-owry ami WHMHI, Trans, l'araday Soc. 1925\ 42, GS3~
[3] **Hell** uuiJ **Udwell,** l'rou. Hoy. Soc. 1940, A, 176, WJ.

Tlia calculation normally involves an extrapolation through at least four powers of ten, and hence no weight can be attached to the presence or absence of exact agreement between observed and calculated values. In fact, the agreement to within *a,* power of ten found for water catalysis is probably as good as can be expected, and confirms the view that the " spontaneous " reaction is in fact due to basic catalysis by water molecules. On the other hand, there is in all cases (except in the mutarotation of glucose) a large systematic discrepancy for catalysis by the hydroxyl ion, and it is likely that this represents a real effect, i.e. that the Bronstcd relation is not applicable over the very wide range of basic strengths involved *(ef.* Bell and Lidwell, *I.e.).*

The application of the Erönsted relation to catalysis in *non-aqueous solutions* baa been tested for a number of reactions and solvents. In many caiies there are no data available for the acid-base strengths of the catalysts in the solvents in question, and in such cases the strengths in water have been commonly used for comparison. This procedure is justifiable, since there is much evidence to show that the relative strength of two acids of the same charge type is little affected by change of solvent: hence the use of strengths appropriate to another solvent will only have the effect of changing the value of the constant *0* in equations (19)-(21).



FIQ. 4.—THE DECOMPOSITION OF NJTKAMIDE • IN m-CRKSOL.

Figs. 4 and 5 illustrate the usual loghrithmic plot for two catalysed reactions in non-aqueous solvents. In the decomposition of nitramide in tti-creuol (Briinsled, Nicholson and Del banco, Z. phyaikal. Chem. 1934, **169,** 3711) the baric constanta (A'u.u) were obtained directly from indicator measurements in the same **solvent**. On the other hand, in the rearrangement ol N-bromoacL'tanilitle (togiveji-broHiaiicetfiiiilJile) (Bell, Proc, Roy. Soc. 1934, A, 143, 377) the ;u ill constants given ($/T_o$) are those in aqueous solution.

(A) THE MECHANISM OF ACID-BASE CATAI>Y8I3.

The term " catalysis " is often used to describe the promotion of a chemical change by som<e physical agency, as, for example, the effect of a urface in a heterogeneous gas reaction, or of jaramagnetie molecules in the conversion of >ara- to ortho-hydrogen. It was originally bought that catalysis by acids and bases was due to some physical effect of this kind, which was vaguely connected with the supposed small size of the hydrogen ion or the high mobilities of hydrogen and hydroxyl ions. However, modern views accept a much more " chemical" explanation, according to which catalysis by acids and bases is due to *an acid-base reaction /etiveen the catalyst and the substrate.* This view eads to the same kinetic laws as the physical picture of catalysis, provided that the extent of >f the reaction between the catalyst and the sulist.ra.te is small, and that the catalyst emerges unchanged from that reaction. The catalyst is thus supposed to take an essential part in the reaction mechanism, and not merely to speed up an uneatalyeed process. In confirmation of this view, it is generally found that reactions catalysed by acids and bases do not take place at all in the absence of catalysts (including catalytic impurities fortuitously present). An already indicated, the so-called " spontaneous " reaction in aqueous and similar solutions is not a truly spontaneous react ion* but depends upon ACid-base catalysis by the solvent molecules. Further, the assumption of an acid-base **reaction** between catalyst and substrate provides a reasonable explanation of the existence*of general catalysis by acids and bases, and of relation* between catalytic power and acid-base strength,

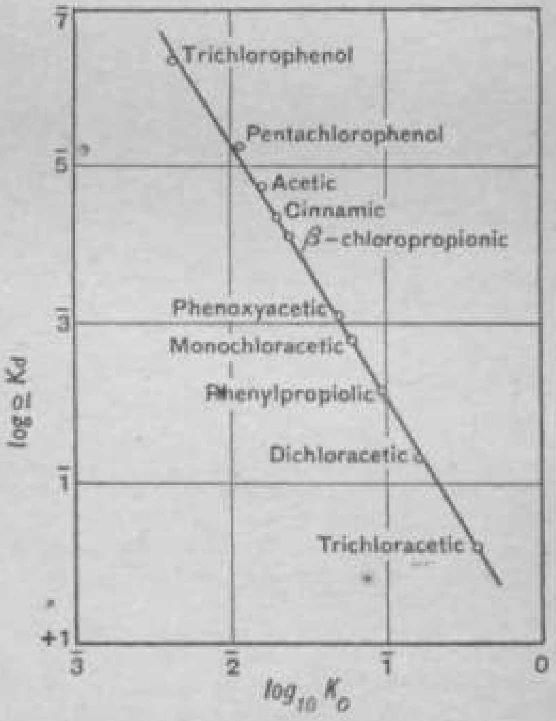


FIG. 6.—THE REARRANGEMENT OF N-BHOMO-ACETAMIL1DE IN CLILOILOBEUGENE.

Substances commonly acting as substrates are such weak acids or bases that their acidic or baaic properties are barely detectable, and a simple acid-base reaction between catalyst and substrate will normally proceed to such a small extent that no observable result is **produced.** In an actual catalysed reaction the products of this initial acid-base reaction must be capable of undergoing some further change leading to an observable result. For example, in the decomposition of nitra-mide it is suggested that the basic catalyst acts by removing a proton from NH:NOOH, the tautomeric form of nitramide, forming the ion [N:NOOH]-~, which is unstable and decomposes rapidly. In other cases it may bo necessary to add another reagent to produce the reaction : *e.g.* in the reaction of acetone with halogen? (basic catalysis) it is believed that the effect of the basic catalyst is to produce very small quantities of the ion [CHjCOCHj1", which then reacts rapidly with the halogen.

Acid-base reactions *(e.g.* the neutralisation of acids and bases) usually take place at a rate too great for measurement, but it is believed that this is not always the case for the reactions between catalyst and substrate. Such .downraf of reaction ia associated -with *mesomertim,* i.e. the existence of two possible electronic ptructures for the ion produced. This kind of behayiour is met with in an extreme form in substances known as paeudo-acids and **inoodo** bases. For example, the normal form of nitrumethane has the structure CH_3-NO_2, and would not be expected to ionise to any appreciable extent in the presence of sodium hydroxide. Actually it reacts completely with HOI Hum hydroxide to give a salt, though the reaction takes place at a measurable speed. This i* because the ion formed is not $\overset{\ominus}{C}H_2{\cdot}NO_2$, but has the alternative electronic structure

The reaction with hydroxyl ions would not normally be **dasaed** as an example of catalysis, but the bruin ination of nitro me thane is catalysed by bases like the acetate io«, and no dbubl involves the formation of the eame nitroniethv! ion.[1]

In many cases, however (particularly in acid catalysis), the reaction between catalyst and substrate is assumed to be a rapid one, ami **the** products of this reaction then undergo further but slow .transformation. It is often difficult to determine the relative rates of the sucre?aive stages, and the matter is often complicated by the fact that acids and bases may take part in several stages of the observed change *(e.g.* Pedereen, J. Physical Chem. 1934, 38, 581; Trims. Faraday Soe. 1938, 84, 237; Bell, Proe. Koy. Soc. **1936,** A, **154,** 414 ; " Acid-Base Catalysis," Oxford, 1flJ1, Chapter VI; Wkrabal, Z. Elektrorhem. 1927, **33,** 32$.

A very large amount of work liaa been done during the last twenty years on the mechanism of individual catalysed reactions (c/. Watson, " Modern Theories of Organic Chemistry," 2nd ed., Oxford, 1941; Hammett, " Physical Organic Chemistry," New York, 1940). The following examples are given of the kind of conclusiona reached in two important groups of reactions—the prototropy of ketones, and the hydrolysis of estera—without going into the evidence on which these conclusions are based.

(i) The Prototropy of Ketones.—A large group of tautnmeric changes are commonly described as *protolrapic changes* and can be represented by the general schome

HX-Y:Z ^ X:YZH

where X, Y and Z'are normally either carbon, nitrogen or wxygen. The following are examples:

HC'CiO-ii-OH

(keto-euv)).

HN·C :O^N: C·OH

(lactam-lactim).

HCN:O^C:N'OH

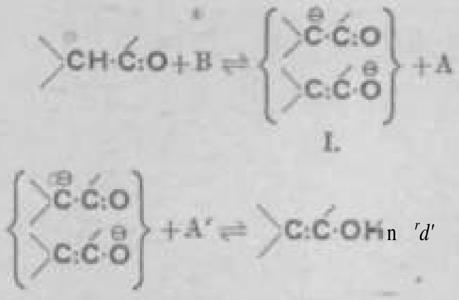
(111 *i* roso- *isotii* t roso).

HCC:C^C:CCH

(three-carbon tautomerism).

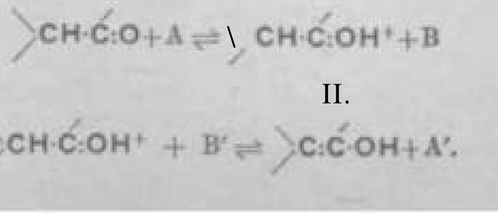
All these reactions are catalysed by acids and/or bases, and the accepted mechanisms involve the addition of a proton at .one point of the molecule and the **removal** of a proton from another point; 'hence the term *prototropic.* In the **iateroaaveqpon** of a keto form and an cnol form *(i.e.* of kelones or related compounds) the supposed mechanisms are as follows, A representing an iwid and B the corresponding base.

Basic Cfatnhjsh.



I.

Acid Catalysis,



II.

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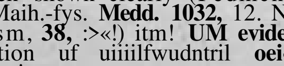
[1] It was formerly assumed that both the neutralisation and the bromination of nitro-paratlins **Involved** cti^ intermediate formation or the *aei-form, e.g.*



"OH

However, It hits been shown clearly (Pedmcn, Kill. Danskc Vid. Sdsk. Maih.-fys. **Medd. 1032,** 12. No. 1 - **J.** Physical Chem. ism, **38,** :>«!) itm! **UM evident** is **M*in«t** the formation uf uiiiilfwudntril **oei-nitro-**methane **la** these reactions.

It will bo seen that in basic catalysis the second stage of the reaction involves reaction with an acid, while the second stage of acid catalysis involves reaction with a base. Normally it is not necessary deliberately to add both an acid and a basic catalyst. In a hydroxylic solvent the solvent molecules can ajt either as acids or bases as required, while in a solvent not possessing acid-base properties the acid or baae required in the second stage can be identical with the product of the first stage: i.e. A'=A and B'=B in the above schemes.

The ion ([) formed in basic catalysis has been written with two different structures, differing only in their electronic distribution. In older views of the process it was supposed that the upper of these two structures was first formed from the ketone, and that it then changed rapidly into the lower structure. According to moilern *iv.** these two forma have no separate ejd*ten«e, the actual state of the ion being a *r?aoiiunce. hybrid* {or mesomeric state) of the two classical structures represented by the formula given. The excess negative charge is distributed between the carbon and oxygen atoms, and **when** the ion take* up a proton it may produce either the keto or the enol form.

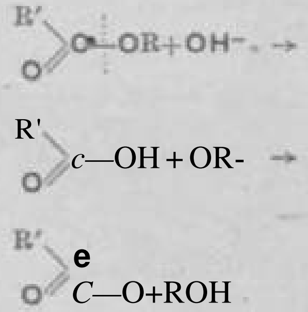
The actual intereon version of keto and enol forms has only been studied in a very few cases, and cannot be observed in the case of simple ketones on account of the instability of the enol form. There are, however, a number of observable processes which are closely relate] to the reaction schemes given above. The ion (I) formed in basic catalysis reacts very rapidly with halogens, and many measurements have been made on the *hflogenation of ketonrt* **sad** related substances. The rate of reaction#ia independent of the nature and concentration of the halogen, being determined by the rate at which the ion (I) is formed by the reaction between the ketone and the catalyst. The rate of *isotopk exckaiKje* between the ketone and a hydroxylic solvent containing deuterium is also determined by the rate of formation of the ion (1), and has been measure* in a few instances. Finally, in an **optically** active ketone of the structure RJRJCHCO-R, the *rate of racemisation* under conditions of basic catalysis will also be equal to the rate of formation of the ion {I), which is equally likely to revert to either optical antipode.

The halogenation ami raAenoisation of ketones was originally believed to involve the actual production of the enol form, which is known to react rapidly with halogens and which cannot retain optical activity. However, it in now believed that under conditions of basic catalysis the formation of the ion is **Bidfidsnt** for both halogenation and racemisation, the enol not being produced. In acid catalysis, on the other hand, formation of the ion (II) will not lead to either racemisation, isotope exchange or reaction with halogen, and under these conditions actual formation of the enol is necessary for any of these processes to take place.

Tin: above interpretation can he tested by comparing the rates at which the different processes take place under identical catalytic conditions. Under conditions of basic catalysis it has been shown in one instance that the rates of racemisation and bromination are identical (Hail and Wilson, J.C.S. 1936, *623), and in another instance that the rates of raceniisstion and deuterium exchange are identical (Hsu, Ingold and Wilson, *ibid.* 1938, 78). Similarly, for acid catalysis the equality of the rates of bro m [nation and racemisation baa been established for two ketones {Ingold and Wilaon, *ibid.* 1934, 773; Bartlett and Stauffer, J. Amer. Chem. Soc. 1935, 57, 2580) and equality in the rates of broroination and deuterium exchange for another ketone (Reitz, Z. physikal, Chem. 1037, **179,** 119): this would be expected if the equilibrium amount of onol is so small that the back reaction can be neglected.

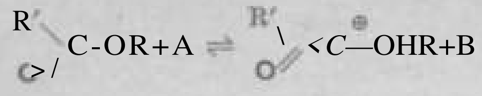
(ii) The Hydrolysis of Esters.—The mechanism of this important class of reactions has been formulated in a large number of different ways. However, many of these differ only in a formal way, or in some details which cannot be tested experimentally. The schemes given here represent one of the simplest possible formulations *(cf.* Day and Ingold, Trnna. Fara* day Soc. 1941,37, 68«).

The hydrolysis of an ester by means of hydroxyl ions probably represents a specific reactitAi which is not properly classed aa basic catalysis. It has been maintained *(e.g.* Dawson and Lowson, J.C.S. 1927, 2444) that other basic species such as the acetate ion ran exert a catalytic effect, but the evidence for this is at best inconclusive. The probable mechanism for the reaction with hydroxyl ions can be written

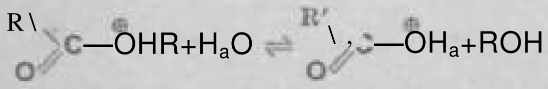


The first step of the reaction ia in principle reversible, but since the second step goes to completion this reversibility is never observed. It will be seen that the bond between car bun and oxygen is broken (acyl fission), **a SUppodtiDn** which is supported by experiments on oxygen isotope interchange and also by the retention of optical activity during hydrolysis when the group It is asymmetric.

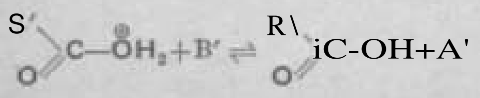
The acid hydrolysis of an est«r, on the other hand, represents a true case of acid catalysis. Attempts to establish catalysis by species other than hydrogen ions in aqueous solution (Dawson and LowKon, »6/d.*1929, 393) are difficult to interpret with certainty **owing** to the high salt concentrations used. However, there is good evidence that the reverse reaction (esterifi cation) is caAlysed by undissociated acid molecules in alcohol solution (Uolfe and Hinshelwood, Trans, **Fuaday** Soc. 1W34. 30. 935; Hinshelwdod and Legard, J.C.S. 193(5, 687), and any proposed mechanism must therefore be eoiisor.a. ' **with** general acid catalysis. The first step can be written



where A is an acid (which may be the **hydrogen** ion) and B its corresponding base. The further reaction of the ion formed takes place according to the scheme



This change need not take place as a simple bimolecular reaction, but may involve preliminary fission of the ion. There are various possibilities for this detailed mechanism, which can in some cases be distinguished by the kinetic behaviour of the reaction, or by the optical behaviour (racemisation, retention of configuration or inversion) when R is asymmetric. The extent to which the different possibilities have been realised in practice is discussed in detail by Day and Ingold (*l.c.*). Finally the ordinary acid molecule is formed by the reaction :



where the acid-base pair A'-B' may or may not be the same as that involved in the first step of the reaction. All the stages given are reversible, and the mechanism therefore applies both to hydrolysis and to esterification in the presence of acid catalysts.

(t) OTHER TYPES OF POSITIVE CATALYSIS IN SOLUTION.

There are a number of instances of **homo**geneous catalysis in solution which do not fall under **the** head of acid-base catalysis. In some of **these** enough is known about the mechanism to show that it depends on *alternate oxidation and reduction of the catalyst,* while in other cases the existence of several valency states makes it probable that the same type of explanation holds. The following examples illustrate the kind of behaviour met with.

The Decomposition of Hydrogen Peroxide is catalysed by iodide ions in neutral solution, the reaction velocity being directly proportional to the concentrations of hydrogen peroxide and of iodide ion. The reaction mechanism has been elucidated by a number of workers (*see* summary by Bray, Chem. Reviews, 1932, 10, 172; *cf. also* Liebhafsky and Mohammed, J. Amer. Chem. Soc. 1933, **55,** 3077). **The** following reactions can take place :

$$(a)\quad H_2O_2 + I^- \rightarrow H_2O + IO^- \text{ (slow)}$$
$$IO^- + I^- + 2H^+ \rightarrow I_2 + H_2O \text{ (fast)}$$
$$(b)\quad H_2O_2 + I_2 \rightleftharpoons 2H^+ + 2I^- + O_2$$

In a solution containing originally only iodide **ions**, reactions *(a)* only can take place to begin with. However, as soon as some iodine has been produced reaction (*b*) sets in, and after a very short time the velocities of the two reactions become equal, the net result being $2H_2O_2 \rightarrow 2H_2O + O_2$. Since the reaction *(b)* has a much greater velocity constant than (a), the equilibrium amount of I_2 is much smaller than that of I^-. The reaction velocity is therefore given by $v=k[H_2O_2][I^-]$, where I^- is practically equal to the original concentration of iodide ion. The velocity of reaction (a) can be measured separately by using solutions buffered at a moderate hydrogen ion concentration sufficient to prevent *(b),* and the velocity of iodine reduction is found to equal the rate of decomposition of hydrogen peroxide in neutral solution.

The Reaction of Hydrogen Peroxide with Thiosulphates is also catalysed by iodide ions. In this case there is an uncatalysed reaction represented by

$$H_2O_2 + 2S_2O_3^{=} + 2H^+ \rightarrow 2H_2O + S_4O_6^{=}$$

the velocity of which is proportional to $[H_2O_2][S_2O_3^{=}]$, and independent of $[H^+]$. The addition of **iodide** ions causes an increase in velocity which is proportional to $[H_2O_2][I^-]$, and independent of both $[S_2O_3^{=}]$ and $[H^+]$. This is explained (Abel, Z. Elektrochem. 1907, 13, 555) by the reaction scheme:

$$H_2O_2 + I^- \rightarrow H_2O + IO^- \text{ (slow)}$$
$$IO^- + 2S_2O_3^{=} + 2H^+ \rightarrow S_4O_6^{=} + I^- + H_2O \text{ (fast)}$$

The same reaction is catalysed by molybdic acid, but in this case the products are different, the change being

$$4H_2O_2 + S_2O_3^{=} \rightarrow 2SO_4^{=} + 2H^+ + 3H_2O.$$

The total rate of sulphate production (which must be disentangled from the tetrathionate production mentioned above) is given by an equation of the form

$$v=(k_1+k_2[H^+])[MoO_4^{=}][S_2O_3^{=}]$$

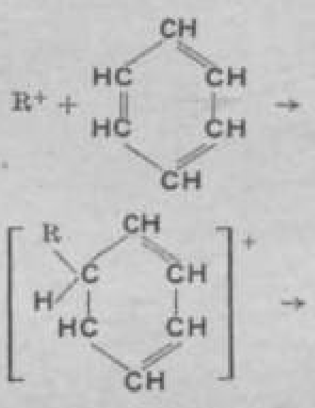
being independent of the concentration of hydrogen peroxide. It is assumed that all the molybdate is converted immediately by the **hydrogen** peroxide into the permolybdate ion $MoO_5^{=}$, a small proportion of which reacts with the hydrogen ion to give $HMoO_5^-$. Both **the ions** $MoO_5^{=}$ and $HMoO_5^-$ oxidise **the** thiosulphate to sulphate at measurable but different rates, forming molybdate, which is immediately reconverted to permolybdate by the hydrogen peroxide (Abel, *ibid.* 1912, 18, 705; Monatsh. **1912,** 34, **425,** 821).

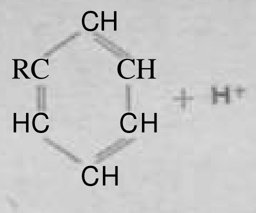
Catalysis by Metallic Ions is met with in many reactions, though the mechanism is usually a matter of speculation. Many of the reactions involve oxidation or reduction, and in such cases the catalysing ion is normally **one** which can exist in more than one valency state: for example, it is well known that the decomposition of a hypochlorite solution to give oxygen is catalysed by cobalt salts, and it is supposed that the cobalt is alternately oxidised to **the** cobaltic state and reduced to the cobaltous state. Other examples are the decomposition of hydrogen peroxide, catalysed by chromate ions (**Spitalsky** and Koboseff, Z. physikal. Chem. 1927, 127, 129); the oxidation of iodides by hydrogen peroxide, catalysed by iron and copper ions, molybdates and tungstates (Brode, *ibid.* 1901, 37, 257); the oxidation of sulphites by oxygen, catalysed by iron and copper ions (Titoff, *ibid.* 1903, 46, 641); and the anodic oxidation of many substances, catalysed by ceric ions. A special type of behaviour is met with in some reactions of this kind, in that when two catalysts are present simultaneously, their effect is greater than the sum of their catalytic effects when present singly. This behaviour is often referred to as *promoter action.* Examples are the effect of copper and iron salts in the reaction between persulphates and iodides (Price, *ibid.* 1898, 27, **474**), in the reaction between hydrogen peroxide and iodides (Brode, *ibid.* 1901, 37, 257), and in the reaction between sulphites and persulphates (Schilow and Buligin, Chem.-Ztg. 1913, 37, 512); also the effect of copper and mercuric salts in the oxidation of various organic compounds by concentrated sulphuric acid (Bredig and Brown, Z. physikal. Chem. 1903, 46, 502). It is possible to obtain a general explanation of this promoter action in terms of intermediate compounds even without a knowledge of the actual intermediate stages in any particular case (Spitalsky, ***ibid.*** 1926, 122, 257).

Catalysis of Organic Reactions by Metallic Halogenides (notably of aluminium, iron and boron) constitutes a different class of homogeneous catalysis. There is of course a large mass of literature on preparative organic chemistry which deals with this type of reaction, but only a few examples of recent work will be referred to in which evidence has been obtained of the mechanism of catalysis. The best known example is the *Friedel-Crafts reaction,* in which a hydrocarbon (usually aromatic) is alkylated or acylated by alkyl- or acyl-halogenides in the presence of *aluminium chloride* or other halogenides. It is now generally agreed (cf. Wertyporoch, Ber. 1931, 64 *[B],* 1375; Linstead, Chem. Soc. Annual Rep. 1937, 34, 251; Nightingale, Chem. Reviews, 1939, 25, 329) that the first step consists of the addition of the aluminium chloride to the organic halogenides to give a complex which is readily ionised, *e.g.*

$$RCl + AlCl_3 \rightarrow [R]^+[AlCl_4]^-$$

Recent evidence of this has been provided by exchange experiments using radioactive chlorine (Fairbrother, J.C.S. 1937, 503). The positive ion R^+ or RCO^+ then acts as the alkylating or acylating agent, *e.g.* with benzene :

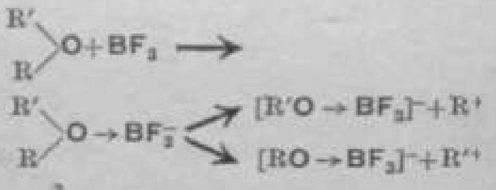




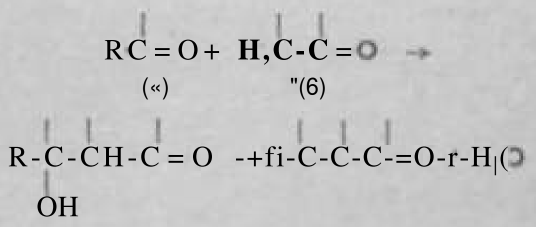
the aluminium chloride being regenerated by the reaction :

$$AlCl_4^- + H^+ \rightarrow AlCl_3 + HCl.$$

Of recent years *boron trifluoride* has been increasingly used in conjunction with alcohols, ethers and esters as an alkylating agent for hydrocarbons. The mechanism assumed is similar, i.e. (Price and Ciskowski, J. Amer. Chem. Soc. 1938, 60, 2499)

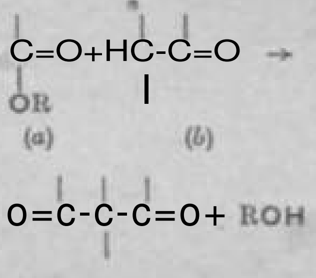


where R is an alkyl group, R' either alkyl, acyl or hydrogen, and the choice between the alternatives in the last stage depends on the nature of the groups. The positive ion then reacts with the hydrocarbon as above. As in all mechanisms of this kind, it may be left an open question whether the ion R^+ exists in the free state, or whether the complex undergoes ionisation in this sense on the approach of the hydrocarbon. There is, however, a good deal of independent evidence of ionisation when BF_3 interacts with organic oxygen compounds (Meerwein and Pannwitz, J. pr. Chem. 1934, [ii], **141,** 123). Boron trifluoride has also been found to catalyse another class of reactions, which are usually effected by means of basic catalysts, though acid catalysts have also been used (Hauser and Breslow, J. Amer. Chem. Soc. 1940, 62, 2385). Among these are the aldol condensation, sometimes followed by loss of water, i.e.



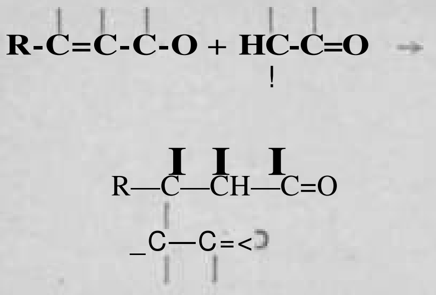
$$RC{=}O + H\text{-}C\text{-}C{=}O \rightarrow R\text{-}C(OH)\text{-}C\text{-}C{=}O \rightarrow R\text{-}C\text{-}C\text{-}C{=}O + H_2O$$

the Claisen condensation,

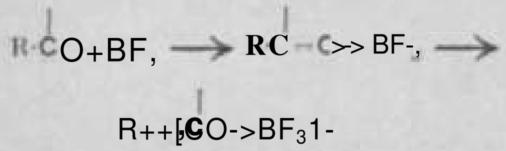


$$C(OR){=}O + HC\text{-}C{=}O \rightarrow O{=}C\text{-}C\text{-}C{=}O + ROH$$

and the Michael condensation,

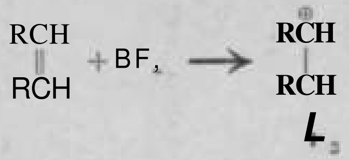


In the basic catalysis of these reactions it is supposed that the component marked *(b)* loses a proton to the basic catalyst, leaving behind n negatively charged earbonium ion which then reacts further, just aa in the base-catalysed prototropy of ketones *(see* p. 25Gc). In catalysis by BF_3, on the other hand, the catalyst is supposed to add on to the component marked *(c), i.e.*



subsequent reaction being due to the ion R^+.

In addition to this vide range of reactions, it has been found that *cut-trans* isomerisation is also catalysed by BF_3 (Price and Meiater, J. **Amer.** Chem. Soc. 193ft, 61, 1/595). The proposed mechanism is



followed by rotation about the single bond. The srfme equation is supposed to represent the first stage in the alkyktion of benzone by olefins in presence of boron trifluoride.

As already mentioned at the end of section *(d),* boron tritiuoride ranks as an acid if we accept the definition of an acid as an electron-acceptor, although it is not termed an acid if (as is usual) this term is restricted to proton-donors. It i» therefore of interest that ***liquid** hydrogen fluoride* (an acid according to either definition) has been found to act as a catalyst in many of the above **reactions** and rearrangements (c/. Simons, Archer and **Randall,** *'ihid.* 1039, 61, 1821; 1940, 62, 485). It is known that practically all organic compounds containing oxygen dissolve in liquid hydrogen fluoride with the production of ions (Fredenhagen, Z. anorg. Chem. 1339, **242,** 23), and the mechanism of catalysis may be jnsunied to take place along similar lines. For example, when benzene is alkylated by an ester in liquid hydrogen fluoride, the first 8ta₀e is

$$2HF + R'COOR \rightarrow R'COOH_2^+ + R^+ + 2F^-$$

and the ion R^+ then acts as an alkylating agent ss before.

(ii) NEGATIVE CATALYSIS IN SOLUTION.

Cases of negative catalysis (or inhibition) in solution are comparatively rare. It is fairly often found that the addition of small quantities of a substance may cause a considerable diminution in the velocity of a reaction, but in most cases this is due to *TZMOVOI of* a *positive wbtlyat* by *a.* chemical reaction. For example, in the esterification of carboxylic acids in alcohol solutions the addition of small quantities of water decreases the velocity, owing to the re'aetion :

$$C_2H_5OH_2^+ + H_2O \rightarrow C_2H_5OH + OH_3^+$$

The effective catalyst is the solvatcd hydrogen Jon $C_2H_5OH_2^+$ in comparison **with** which **the** hydrated ion OH_3^+ has a very small effect (Goldschnridt and Udby, Z. physikal. Chem. 1007, 60, 728; 1910, 70, 627). The effect of the inhibitor thus depends on the relation between its concentration and the concentration of positive catalyst, and the phenomenon would not usually be described as genuine negative catalysis. In some cases the concentration of the positive catalyst may be extremely small anil its presence may be fortuitous. For example, the mutarotation of tetramethylglnoose is difficult to arrest in most solvents, but does cot take place in chloroform solution. This is attributed to the presence of traces of phosgene as an impurity, which reacts with and removes traces of catalysing amines, also present as impurities (Lowry *et al,* J.C.S. 1925, 127, 1385, **2883).** Similarly, the inhibiting effect of gelatin on the decomposition of cbioramitie has been attributed to the formation of a complex **jvith** minute amounts of copper ions, which exert a positive catalytic effect (Bodenstein, Z, physikftl. Chem. 1928, A, **189,** 397).

A different type of negative catalysis is met with hi a number of oxidation reactions, notably the *oxidation of sulphites* to sulphates by oxygen gas. This reaction has been studied by many workers over a long period, but most of the modern work is ^due to Backstrom and his collaborators **(B&ckstr&m,** J. Amer. Chem, Soc. **1927,** 49. 14M; Biiokstrom and Alyea, ***ffnd.*** 1929, 51, 90; Alyea, *ibid* 1930, 62, 2743; Alyea and Jeu, ***ibid.*** 1933, 55, 575; Backstroui, Z. physical. Chem. 1934, B, 26, 122). The rate is independent of the oxygen concentration, but depends on the hydrogen ion concentration and is increased by very small concentrations c' various metallic ions, notably Cu^{++} The rate is also greatly increased by illumination by ultraviolet light, the quantum efficiency of the photochemical reaction being in the neighbourhood of 50.0CO. Both the thermal and ***photochemical*** reactions are greatly inhibited by the addition of s*aall concentrations of various organic compounds (notably alcohols), and this is true both in the presence and absence of cuprie'ions. It is now agreed that the oxidation consists of a *chain reaction,* and that the action of the inhibitor depends upon the breaking of the chains and the consequent shortening of their length. **Since** the chains in the uninhibited reaction involve the oxidation of many thousands of sulphite ions (as shown by the ^ quantum efficiency) the destruction of a very

HiuaU number of intermediates in these chains can produce a large decrease in reaction velocity. It is assumed that the act of chain breaking involves the oxidation of the alcohol (or other inhibitor), and it has proved possible to detect the very small amounts of oxidation products formed, and to show that the rate at which they are produced agrees with the shortening in the chain length of the sulphite oxidation.

There is still some difference of opinion as to the actual nature of the reaction chain. Most workers agree that the primary process is the production of the singly charged ion SO_a~~ by loss of an electron from SO_3^-, as suggested byJHuber (Naturwiss. 1331, 19, 450; Haber and Franck, yiUungsiber. **Preote.** Akad. Wiss. Berlin, 1931, 250). The positive catalytic effect of cupric ions is then explained by the reaction

$$Cu^{++} + SO_3^{=} \rightarrow Cu^{+} + SO_3^{-}$$

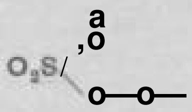
According to Haber the subsequent chain process is

$$SO_3^- + O_2 + H_2O + SO_3^= \rightarrow 2SO_4^= + OH + H^+$$
$$OH + SO_3^= \rightarrow SO_3^- + OH^-, \text{ etc.}$$

where the chain can be broken by the oxidation of the inhibitor by the radical OH. Other writers prefer a mechanism involving hydrogen peroxide in place of the radical OH, while Backstrom (Z. physikal. Chem. 1934, B, 25, 122} writes

$$SO_3^- + O_2 \rightarrow SO_5^-$$
$$SO_5^- + 2HSO_3^- \rightarrow 2HSO_4^- + SO_3^-, \text{ etc.}$$

the chain breaking being caused by oxidation of the inhibitor by the ion SOf, considered to have the structure



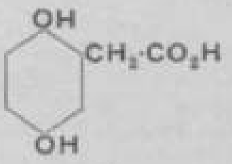
Similar behaviour is met with in the *oxidation of aldehydes* in solution by gaseous oxygen, this reaction also being a chain reaction promoted by metallic ions and by ultra-violet light, and inhibited by alcohols (*cf.* Backstr6m^(,c). In this case, however, the position is more complicated, since the amounts of inhibitor oxidised do not agree with those calculated on the basis of a simple chain-breaking mechanism. The literature contains many other examples of negative catalysis which have not been studied in detail, but which probably all depend on breaking of reaction chains. For exampjp, the no-tailed " activated oxalic acid " {prepared by the action of potassium permanganate on an excess of oxalic acid) probably involves free radicals of long life, and its activity is greatly reduced by small concentrations of many oxidisable substances, notably phenols and certain dye-stuffs in concentrations as low as 10"'TN. {Weber, *ibid.* 1934, B, 26, 3<B).

Bibliography.—E. K. Rideal and EL S. Taylor, " Catalysis in Theory and Practice," Macmillan, 192t> ; J. N. Brtinsted, " Acid and Basic Catalysis," tkw. Reviews, 1928, 5, :m ; G.-M. Schwab, II. S. Taylor and R. Spence, " Catalysis," Maemillan, 1937; R. P. Bell, " Acid-Base Catalysis," Oxford, 1941.

R. P. *a*.

HOMOGENISERS (i. Vol. IV, 295c).

HOMOGENTISIC ACID,



I.

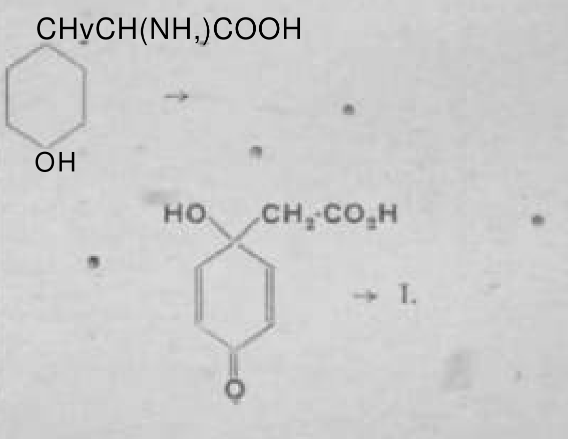
2:i>Dihydroxyphenylacetic acid, m.p. (anhydrous) 152-154°.

The acid occurs in the urine of individuals suffering from alkaptonuria, the urine becoming brown on the addition of alkali in the presence of oxygen. It also occurs in the blood of alkaptonurics. The acid was first isolated and identified by Wolkow and Bauinann (*Z.* physiol. Chem. 18S», 15, **241).**

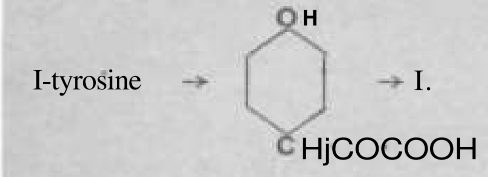
To 100 ml. of urine 5-6 g. lead acetate are added, boiled, and the p_a adjusted to 5-6 by the addition of aqueous ammonia, and the lead salt allowed to crystallise. After recrystallisation under similar conditions the salt is decomposed with hydrogen sulphide. Finally the solution is concentrated under reduced hydrogen pressure and saturated with sulphur dioxide, the acid separating on cooling (G. Medes, A. 1934, 206).

The homogentisic acid found in the urine probably arises from degradation of tyrosine and phenylalanine {O. Neubauer, Chem. Zentr. 1909, II, 50; L. Blum, Arch. cxp. Path. Pharm. 1908, 59, 273). Whether its presence is due to the failure of the alkaptonuric to destroy the homogentisic acid when formed, or to abnormal katabolism is not known (O. Gross, Biochem. Z. 1914,, 61, 165; A. J. Wakeman and H. *D.* Dakin, J. Biol, Chem. 1911, 9, 139; H. D, Daitin, ***ibid.*** 1911. 9, 151).

According to Blum *{I.e.)* and K. Fri<-dmaun (Beitr. chem. Physiol. Path. 1908, 11, 304), in the conversion of tyrosine into homogentisic acid the side chain is first degraded, then a relative change of position of the side chain and the hydroxyl group takes place, with a secondary oxidation concurrently; finally a reduction occurs,

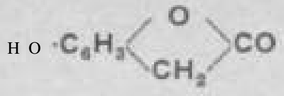


According to Y. Kotake (Chera. Zentr. 1923, I, 117) the change occurs as follows :



Homogentisic acid may be synthesised by heating quinol dimethyl ether dissolved in carbon disulphide with ethyl chloroacetate and aluminium chloride and subsequent demethylation with fuming hydriodic acid and red phosphorus {Osborne, J. Physic-1. 1903, 29, 14; Baumann and Frankd. Z. physiol. Chem. 18951 20, 224). Also from the allyl ether of quinol monobenzoate (G. Hahn and W. Stenner, *ibid.* 1929,**181,** 88).

Homogentisic acid passes into the *lactone,*



m.p. 191°, on heating. The *lead* salt has m.p. 214-215°, it is soluble in 675 parts of writer at 20°. *Ethyl enter,* m.p. 119-120°.

Homogentisic acid readily reduces copper and silver salts; it gives a blue colour with ferric chluride and on distillation from ferric chloride solution gives a substance, m.p. 89-90° (C. T. Momer, *ibid.* 1921, **117,** 67). It yields *gentisic* acid (hydroquinone carboxylic acid) on fusion with potassium hydroxide at 196-198°. With amines it gives characteristic colours {C. T. Momer, *ibid.* 1910, 69', 329,.

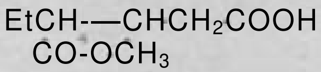
Estimation.—The acid may be estimated in milk ami blood by precipitating the albumin with 8odiupi tungstate and estimating the acid in the filtrate colorimetrically with phosphotungstic acid (Ii. Lieb and F. Lanyar, *ibid.* 1931, 203, 135; *cf.* H. P. Briggs, J. Biol. Chem. 1922, 51, 453, and *G.* Katsch and E. Metz, Cbem. Zentr. 1928.1,386).

In urine the homogentisic acid may be estimated iodometrically (H. Lieb and F. Lanyar, Z. physiol. Chem. 1929, **181,** 199; E. Metz, 1'iKhem. Z. 1927, **190,** 261). The method depends on the oxidation of homogentiste acid to the qtnnone with O-OSAModine in bicarbonate or borax solution until a blue colour is obtained **witli** starch. Providing no other interfering substances are present to react with the iodine, the method is quantitative. Addition of & large amount of sulphuric acid liberates the iodine which can be titrated with sodium tliiosulphatc, and where small amounts of homogentisic acid are present, addition of potassium iodide is advisable. The amount of thiosulphate in determining the anjount>of the acid in 10 ml. urine is about 0-2 ml. too iimall and this correction must be added to give the true value, maximal error 0-5 mg, in 10 ml. 0-05iV-8olutioiis are used : 1 ml, thiosulphale is equivalent to 0-0042016 p. homogentisic acid.

For further details on the identification and estimation of homogentisic acid, *see* Abdenhaklen, " Handbuch der biologische Arbcitsuiethoden," Abt. 4, Tril. 5, i, 551 (1931).

HOMOPHLEINE (». Vol. IV, 336a).

HOMOPILOPIC ACID, a-ethylbutyrolactone acetic acid (H. A, D. Jowett, J.C.S. 1901, **80,** 1345),



$$\begin{array}{l}\mathrm{EtCH{-}{-}CHCH_2COOH}\\ \quad\mathrm{CO{\cdot}OCH_3}\end{array}$$

Oxidation of isopilocarpine with permanganate gives homopilopic acid, and pilopic acid, $C_7H_{t0}O_4$, and the former on fusion with potash yields o-ethyltricarballylic acid. The acid is an oil, b.p. 235^237°/20 mm. It has been synthesised by [1]N. A. Preobrashenski, A. It Poljakowa and W, A. Preobrashenski (Ber. 1935, 68 [BJ, 844), and by 'Dey (J.C.S. 1937, 1057). These authors obtained the raceraic acid in the solid form, m.p. 100°C. N. A. Preobrashenski and his colleagues have also synthesised d-homopilopic acid (Ber, 1935, 68 [B], 850),

HOMORENON *(v.* Vol. I, 147d).

HOMRA{y. Vol.11, 145a").

HONEWORT, Corn Parsley *(Petroaelinum segelum),* American names, *Cryplotsenia canadensis$_t$ Sison Amomum,* an umbelliferous plant used as a salad in China and Japan. The leaves are also cooked and eaten as a vegetable. Chung and Kipperton (Hawaii Agric. Exp. Sta. Bull, 1929, No. 60) report the composition of marketable leaves as : water, 89-53 ; protein, 2-33; fat, 0*23; N-free extract, 437; fibre, 1-45; ash, 2-09%. Among mineral constituents of the leaves, Ca 0-114, Fe OOlfl and P 0-0(3% are noteworthy.

(Gf. Murray's "New English Dictionary," and Britten and Hollaiid, " Dictionary of English Plant Names," 1886. The plant was believed to cure a swelling, " hone," in the cheek.)

A. G. Po.

HONEY. The syrupy excretion of the working bee *(Apis mellifica)* derived from nectar collected from flowers. It is deposited in the honeycomb cells £s a reserve food-stock for the colony when external supplies are no longer available. The yellow syrupy fluid consists of nearly equal proportions of glucose and fructose with water and small quantities of nitrogenous matter, .pollen, wax, mineral matter and acids, and occasionally sucrose and hiannitol. Traces of alcohol are generally present. Honey also contaifls invertase, and possibly other enzymes derived from pollen, and traces of vitamins.

The colour of honey varies considerably with the source of nectar, heather honey being a rich golden-yellow and clover honey a pate greenish-whit<fc In stored honey the colour may change somewhat during processing or subsequent storage according to conditions adopted. The specific gravity of honey is largely controlled by climatic conditions, values quoted in the literature varying from 1-10 to 1-45. The *p*^ value ranges from 3-8 to 4-3. Honey is usually Itevorotatory (-91 to —3-0°) although dextrorotary samples occur. Heather honey may **uchifajt** the property of thixotropy. A physical examination of such a honey is recorded by G. W. S. Blair (J. Physical Chem. 1935, 39, 213).

Analyses of honeys show considerable differences according to their place of origin. Excluding obviously abnormal samples the following ranges of composition apply to honeys from all parts of the world :

	%
Water	8-25
Glucose	30-42
Fructose	23-39
Sucrose	0-4
Astf	0-2-2-5

The ratio fructose : glucose.is regarded by some analysts as sufficiently characteristic to ser\e as an index of the purity of commercial honeys. Thus Auerbadh and Bodlander (Z. Untera. Nahr.-u. Genussm. 1924, 47, 233) state that the ratio should be 100-119:100 for genuine honey and may be <90:10O in artificial honeys. This viejp is not generally upheld and analytical data from numerous sources throw doubt, on the validity of this statement. In Italian honeys, for example, Canneri and Sulnni (Ann. Chiru. Appl. 1935, 25, 397) find **the** uitio for a great many samples to lie in the range 101-113:100 but also record others showing ratios up to 168:100.

The sucrose content of honey also shows considerable variation, and although lc-is than 1% in most European honeys it may **reach** much higher values under certain **condition*.** A sample of Hungarian honey examined by Berko and Kardos (Menog. Kutat. 1937, 10, 177), in a season when the nectar flow was exceptionally high, contained mo.re than 10% of sucrose. Follett-Smith (Div. Repts. Dept. Agrie. Brit. Guiuna, 1934. 100) reports British Guiana honey containing 8-67% of sucrose, the total sugars being 75-8% and the p_H 4-23.]t ia said that liees fed on large proportions of **morose** invert only a portion of it and an abnormally large amount remains in the honey. Honey collected in the neighbourhood of Cuban **sttgar** fadurics is reported to contain *artificially* inverted sugar. Bees fed exclusively on glucose produce honey containing that sugar only. ("Certain varieties of Sumatra honey produced by *Apis indir.a* consist largely of glucose and fructose but contain neither sucrose nor dextrin. " Honey," without **comb,** made by an^Cthiopia.11 mosquito in tree hollows, is recorded by ViUierB (Compt. rend. 1878, 88, 292) to contain^ water. 25-5; gfucose and fructose, 32-0; mannitol, 3;0; dextrin, 27-9; ash, 2-5%. The Mexican honey-ant produces " honey " consisting of iin almost pure solution of fructose; The product from *Polybiu apicipennis* frequently includes lan*e crystals of sucrose. " Eucalyptus Hbney," made by an Australian Muck bee, is a thick syrup having a strong aromatic odour. " Palm h'Hiey," the concentrated sap of *Jubcea spectabills,* is commonly utilised in Chile and differs from genuine honey in its high suciose content. Schmidt-Hebbel and Toledo (L'harm. Zentralk. I **B38,** 79, 033) record numerous analyses of this product, the notaUft **figntet** in their average values *being,* wnter, up to 38%. and ratio sucrose : ylucoso ifniutosi! **not** leas than •*i* (the corresponding values for Chilean honey are •*20%* and 0-1 respectively). American honey-dew honey occasionally contains /ndezitose in considerable amounts (Hudson and Sherwood, J. Amer. Chem. Soc. 1920, 43, 116). This polysaccharide is also reported in conifer honey by T. von Fellenberg (Mitt. Lehensm, Hyg. 1937, 28, 139) who describes methods for its determination.

Both conifer and honey-dew honey frequently contain dextrins (Hilger, *Z.* Nahr.-u. Genussm. 1904, 8, 110; Haenle and Scholz, *ibid.* 1903, 6, 1027). After removal of protein matter by tannic add, dextrin is separated from honey by precipitation with ether from acidified alcohol; it is strongly dextrorotatory, and probably accounts for the supposedly abnormal dextrorotation of honey samples, long regarded as a definite indication of adulteration by commercial syrups.

Small amounts of organic acids are commonly found in honey. Formic acid is said to be **added** by the bees prior to capping the comb, and possibly explains the small tendency of honey to ferment. Recorded formic acid contents of.honey range from 0006 to 001%. Nelson and Mottem (Ind. Eng. Chcm. 1931, 23, 335), in an examination of very acid honeys, found "acetic acid (up to 0-04%), citric acid (0-008%), malic acid (0-05%) and small amounts of succinic acid.

Honey usually contains traces of nitrogenous matter which is partly precipitated on dilution with water. Hungarian honey is said to contain peptones, globulin and some albumin, but not protamines, h intones or albiunoses. A considerable proportion of the nitrogen compounds in honey exists in colloidal forms and, in the case of American honeys, these show an isoclectric point in the neighbourhood of p_H 4-3 (Lothrop and Paine, Ind. Eng. Chem. 1931, 23. 328). The colloidal matter contains 8-11% of nitrogen and is closely related to the colour of the honey. Dark-coloured honey is of high colloid, content and removal of the colloid by ultrafiltration or by r) a rifi cation, with bentonite improves the colour of the honey and in many case's its flavour and atnrage properties. Paine, Gertier and Lothrop record 0-08% of colloids in pale (clover) and 0-80% in dark buckwheat honey (Ind. Eng. Chem. 1934, 26, 73). The non-colloids include a proportion of ammo-acids which react with glucose and fructose to produce dark mclaninoid colouring matter (Watanabe, J. 'Biochem. Japan, 1932, 16, **188).** The darkening of honey on heating or during storage is **attributable to** this reaction.

It ia nut clear whether these nitrogenous colloidal substances are essential constituents of honey itself or whether they are derived from pollen which is almost invariably present. According to Butcher.(Food, 1935,4,169) water-insoluble matter in honey should consist only of pollen grains. These may bo separated by flotation on a 30-50% solution of honey. Microscopical examination of the pollen is frequently" of value in honey investigations. A detailed system of microscopical examination of honey is described by Zander fAngew. Chem. 1935,48. 147).

Knymt'S occurring in honey include invertase, catalase, amylase and diastase. Neither luetasc, proteases nor lipases have been detected. The invertase, which is destroyed by heating honey to 60°, effects the slow hydrolysis of sucrose during storage of honey (Kardos, Z. Unters. Lebensm. 1938, 76, 354). Diastase is. probably derived from pollen, and the diastatic activity of honey is often regarded as an index of its genuineness. Diastase is destroyed by heating honey to 70° for 1 hour. After 24 hours at 60° however the enzyme is still active.

Cold-run or " virgin " honey is obtained by uncapping the comb with a warm knife and either allowing the syrup to flow out at ordinary temperature or, more rapidly, by means of a centrifugal " extractor." Extracted comb may be replaced in the hive for refilling by the bees, or warmed and pressed to remove residual honey. The product thus obtained is usually inferior in colour to cold-run honey. In the latter, inversion of sucrose takes place fairly rapidly during the first 10-12 days of storage and much more slowly afterwards. The changes are accelerated by high storage temperature, as also is the rate at which the colour deepens (Lynn, Englis and Milum, Food Res., 1930, 1, 255). The latter phenomenon is dependent on the decrease in stability of fructose with rise in temperature and the greater tendency to react with amino-acids to form coloured substances (V. G. Milum, Amer. Bee J. 1939, 79, 445). In general, high temperatures of processing merely facilitate changes which take place slowly at lower temperatures, and do not introduce new factors. Freshly-drawn honey can be stored in darkness without change for some considerable time, but exposure to light accelerates sugar crystallisation.

Fermentation of stored honey is uncommon, and is dependent on the water content and on storage temperature; it is unlikely to occur at temperatures below 11° or above 26°. Honeys of high water, nitrogen, acid and ash contents are b'able to ferment when stored at 11-18°. According to Lochhead (Prog. Rept. Dominion Agric. Bact. Canada, 1934, 12) honey containing less than 17% of water does not ferment even after storage for a year. With 20% moisture, however, fermentation may occur at any time. Addition of 0-25-0-50% of sodium benzoate effectively prevents fermentation for a considerable period. The alcoholic beverage, mead, has been made since very early days by the controlled fermentation of honey. A supplementary source of nitrogen for the yeast, is now usually added (Osterwalder, B., 1932, 858). According to Boussingault (Ann. Chim. 1872, fiv], 26, 362) the amount of carbon dioxide and of alcohol produced during fermentation is greater than would- be expected from the quantity of sugar destroyed. Neither acetic nor lactic acid is produced during fermentation and the diastatic activity of the honey remains unchanged.

Honey is used medicinally as a mild laxative for children; it also acts as a demulcent, relieving dryness of the mouth and throat and facilitating swallowing. For these purposes honey is purified by farming and straining through wurm flannel. The product is known as *Mel depuraturn.*

Nottbohm (Arch. Bienenkunde, 1928, 8, 32) gives the following analysis of the ash of honey :

(% of ash.)

	K_2O.	Na_2O.	CaO.	MgO.	P_2O_B.
Blossom honey	30-50	5-5-100	2-1-80	1-5-21	1-6-12-5
Honey-dew honey	52-57	3-2-4-3	0-5-1-3	0-7-2-3	6-6-9-5

Paine, Gertler and Lothrop *(I.e.)* find that the separated colloids of honey include 2-9% of ash material. The ash of the colloids of sumac honey has the percentage composition:

SiO_2.	Fe_2O_3.	CaO.	P_2O_5.	K_2O.	MgO.
420	22·6	14-3	9·0	9-6	trace

Spectroscopic examination of honey ash by Gorbach and Windhaber (Z. Unters. Lebensm. 1939, 77, 337) revealed the presence of Ca, Mg, Fe, Mn, P, Si, Cu and Ni in all honeys, but the spectrum region used, 210 m/x to 460 m/x is not suitable for detecting'the alkali metals Li, Na, K. Forest honeys frequently contained Ba, Ag, Pd, V, U, Al, Ir, Co, Zn, As, Sn, Pt, Mo, and occasionally Ti, Cr, K and Sr. Admixture of 1% of forest honey with floral honey could be detected by this means.

The colour of natural honey appears to be related to the amount and composition of the ash as well as to its N and colloid contents and to its diastatic activity *(see above).* Whether these are related or independent phenomena is not clear. Schuctte and Triller (Food Res. 1938, 3, 543) note a parallelism between colour and S and Cl contents and also between colour and Na and K contents *{ibid.* 1939, 4, 349). Lothrop and Paine (J.c.) also find that the percentage of nitrogen and the total ash in American honeys increases with depth of colour. Buttner (Z. Unters. Lebensm. 1935, 70, 475; 1938, 76, 351) records that the S content of floral honeys is extremely small, that of conifer honey somewhat greater (1-3-^3 mg. [as SO_4] per 100 g.) and that of synthetic honey may be as high as 36mg.perl00g.

The vitamin content *(A, B_t C and D)* of honey is very small (Kifer and Munsell, J. Agric. Res. 1929,-39,355). Griebel (Z. Unters. Lebensm. 1938, 75, 417) reports that "honey mainly derived from *Meniha* species contained 1-6-2-8 and that mainly from buckwheat 0-07-0-22 mg. of vitamin-C per gram.

According to Dingemanse (Acta brev. neerl. Physiol. Pharmacol. Microbiol. 1938, 8, 55) certain honeys contain a volatile cratrogeniu substaflce which may belong to the propylene-phenol group.

Much of the analyst's interest in honey centres round the distinction between genuine natural and adulterated or purely synthetic honeys, the position being complicated by the fact that hot-processed honey may have lost certain of the characteristics of natural honey (enzyme activity, etc.) and taken on certain of the attributes of adulterated honeys. The customary adulterants are commercial syrups, starch sugars, invert sugars, molasses, etc. Commercially inverted sugars normally contain by-products (*e.g.* furfuraldehyde derivatives) which give colour reactions with 0-naphthol or resorcinol. Fiehe's test (Z. Nahr.-u. Genussm. 1908, 16, 75; *see also* Fiehe and Stegmüller, Arb. Kais. Gesundh. 1912, 40, 305; J.S.C.I. 1912, 31, 943) is the most popular of this kind. This is carried out by treating the filtered and evaporated ether extract of honey with a solution of resorcinol (1%) in 25% hydrochloric acid. An orange-to-red colour indicates the presence of artificially inverted sugar. Genuine honeys normally give only a faint transient colour, even after processing at 60-65°. The reaction is more marked if the honey has been autoclaved 113-115° (Moreaux, Ann. Falsif, 1936, 29, 22). Exceptional cases have been recorded in which genuine honeys give a positive Fiehe test. Mathieu (*ibid.* 1938, 31, 97) considers that honey should not be regarded as adulterated unless it gives a more marked test than does genuine honey mixed with 2% of sucrose.

More recently the original Fiehe test has been largely replaced by the phloroglucinol test for hydroxymethylfurfuraldehyde. The technique is the same except that phloroglucinol replaces resorcinol in the acid reagent (Fiehe and Kordatzki, Z. Unters. Lebensm. 1929, 57, 468). The reagent gives no colour with pine honey, a temporary coloration with over-heated honey, and a deep red colour and red-brown precipitate with adulterated honey.

/?-Naphthol used similarly gives a red-to-violet coloration with honey containing commercial invert sugar (Litterscheid, J.S.C.I. 1913, 32, 376).

Hydroxymethylfurfuraldehyde may also be detected and estimated by Weiss' method (Z. Unters. Lebensm. 1929, 58, 320). An eth^l acetate extract of the honey is treated with *p*-nitrobenzhydrazide in acetic acid. Lemon yellow crystals of the hydrazone of the aldehyde are formed, m.p. 206-208° (decomp.), and may be dried and weighed. No precipitate is formed from genuine honey and that from heated honey is extremely small.

Dextrins present in starch syrups may be detected in adulterated honey by precipitation with methyl alcohol from a concentrated aqueous solution of honey. Alternatively, honey is dissolved in glacial acetic acid (4-5 *g.* of honey in 1 c.c. of acid) and dextrins if present in appreciable amounts separate from the solution (Raikov, Z. anal. Chem. 1939, 116, 40). Fiehe tests for dextrins in honey, after precipitation of protein matter with tannic acid, by addition of hydrochloric acid and alcohol. Pure honey remains clear under these conditions, whereas added starch syrup causes a turbidity.

According to Elsdon (Analyst, 1938, 63, 422) added glucose may be detected by the lowered freezing-point of a 10% solution of honey.

Adulteration of honey with molasses may be detected by Beckmann's test for raffinose. Sucrose is readily determined by means of the reducing power of honey before and after inversion. Although gross adulteration with sucrose may thus be shown, the sucrose content of genuine honey is itself variable over a considerable range and a limiting value indicative of adulteration is not easily decided. For similar reasons the diastatic activity of honey, at one time taken as a criterion of purity, can no longer be regarded as trustworthy (Vansell and Freeborn, J. Econ. Entom. 1930, 23, 428; Lampitt, Hughes and Rooke, Analyst, 1930, 55, 666). Schou and Abildgaard (Dansk Tidsskr. Farm. 1931, 5, 89; Z. Unters. Lebensm. 1934, 68, 502) distinguish natural from artificial honey by differences in the ultra-violet absorption spectra. The curve for natural honeys rises smoothly from A380 to 220 m/i whereas that of adulterated samples shows a well-defined maximum at 282*5 m/* due to the presence of hydroxymethylfurfuraldehyde, of which invert sugar may contain up to 5%.

According to Gottfried (Z. Unters. Lebensm. 1929, 57, 558) the formol titration of genuine exceeds that of adulterated honey.

An ammoniacal solution of silver oxide (Ley's reagent) on warming with a concentrated solution of honey in water gives a greenish coloration; with adulterated samples the liquid becomes dark brown or black (Utz, Z. angew. Chem. 1907, 20, 993).

A. G. Po.

HONEYSUCKLE PERFUME. There are a large number of species of *Lonicera* (Fam. CaprifoMaceffi), and in Provence the flowers of *L. caprifolium*, *L. etrusca* and *L. gigantea* are processed for the natural perfume of honeysuckle. Ingolen (Parfums France, 1937, 15, 299) obtained 3-3% of a green concrete extract from the flowers of *L. gigantea*, by extraction with light petroleum. From this 2-14% of essential oil was obtained, which had a^{*15} 0-9012; optically inactive ; n^{*} 1-4613°; ester value 145-6. The perfumers sold is practicably entirely artificial, with a little natural ylang-ylang and neroli oil. Linatool, geraniol, hydroxycitronellal, phenylethyl alcohol and similar bodies are used in its preparation, but it does not in any way approach the perfume of the flower.

E. J. P.

41 *HQNTHIN.*" Trade name for keratinised tannin albuminate, used in treating intestinal catarrh (Von Sztankay, Pharm. Zentralk. 1932, 73, 630).

HOOLAMITE (r. Vol. Ill, 21a).

HOPCALITE (*v.* Vol. II, 347a; III, 196, 20(/f 21a).

HOPEITE. Hydrated zinc phosphate,

$$Zn_3(PO_4)_2,4H_2O,$$

crystallised in the orthorhombic system. The crystals are remarkable in consisting of an intimate zonal intergrowth of two modifications —a-hopeite and /Miopeite—differing in their optical characters and in the rate at which water is expelled by heat. They are colourless, white or brownish; sp.gr. 3-0-3*1; hardness 3£. For many years hojTeite was known only as a rare mineral from the zinc mine of A1 ten berg, or Vieille Montagne, between Liège and Aachen; but in 1907 it was found finely crystallised and in considerable quantity in a cave with bone-breccia and associated with ores of zinc and lead at Broken Hill in Northern Rhodesia. In 1916 it was incorrectly described under the new name hibbenite from the Hudson Bay zinc mine near Salmo in British Columbia.

ParaJiopeite, from Broken Hill, Northern Rhodesia, has the same composition as hopeite, but the crystals are triclinic with sp.gr. 3-31 (L. J. Spencer, Min. Mag. 1908,15,18).

L. J. S.

HOPKINSON PRESSURE BAR TEST *[v.* Vol. IV, 549a).

HOPS (v. Vol. II$_V$ 91c).

HORDENINE *[p-(* j8-dimethylaminoethyl) phenol],

$$HO{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2NMe_2,$$

was discovered by Léger (Compt. rend. 1906, 142, 108) in malt culms. No hordenine has been detected during the germination of wheat, peas or lupins *{cf.* lleilhes, Amer. Chem. Abstr. 1936, 30, 7146) nor is it present in ungerminated barley (c/. Torquati, Chem. Zentr. 1911,1, 166). During the process of germination the amount of hordenine is said to be increasing until the 11th day and then gradually diminishing (Raoul, Compt. rend. 1937, 205, 450; *cf.* Torquati, *I.e.).* For further-constituents of the malt germs, *see* Hashitani (J. Tokyo Chem. Soc. 1919, 40, 647). Hordenine *{Anhaline)* occurs also in Anhalonium species (Spath, Monatsh. 1919, 40, 129; 1921, 42, 263). For extraction of hordenh e from barley germs, *see e.g.* Gaebel (Arch. Pharm. 1906, 244,436) or Raoul (Compt. rend. 1934,199,425); the yield is stated to be 0-13% of the air-dried malt germs. Hordenine forms colourless orthorhombic prisms, m.p. 117-118°, b.p. 173-174°/11 mm., subliming at 140-150°. The free base is readily soluble in EtOH, $CHCl_3$ or Et_aO, soluble in H_2O (7 in 1,000 parts) and sparingly so in C_6H_6, toluene or xyfcne. It is a strong base, alkaline towards litmus and phenolphthalein, and liberates ammonia from its salts. It also reduces acid solutions of $KMnO_4$ in the cold, and iodic acid and ammoniacal solutions of $AgNO_3$ on warming.

The salts are crystalline: *hydrochloride,* m.p. 176-5-177-5°; *hydrobromide,* 173-174°; *sulphate,* 209-211°; *methiodide,* 229-230° (479-130°, Hashitani, *I.e.). Benzoylhordenine,* m.p. 47-48° *(see* Léger, Compt. rend. 1907, 144, 208). For colour reactions of hordenine, *see* Denigès (Bull. Soc. chim. 1908, [iv], 3, 786) and Labat (J. Pharm. Chim. 1909, [vi], 29, 433).

. By oxidation of O-methylhordenine with $KMnO_4$ anisic acid was obtained (Gaebel, *I.e., cf.* Léger, Compt. rend. 1906,143,916) and a Hofmann degradation of the same substance afforded trimethylamine and vinylanisole (Léger, *ibid.* 1907, 144, 488).

Hordenine was first synthesised by a series of reactions starting with phenylethyl alcohol (Barger, J.C.S. 1909, 95, 2193). Since then numerous other syntheses have been effected (Rosenmund, Ber. 1910, 43, 306 ; Ehrlich *et at.,* Ber. 1012, 45, 2428; Spath and Sobel, Monatsh. 1920, 41, 77; Kindler *et al.,* Annalen, 1923, 431, 22*; Arch. Pharm. 1927, 265, 394; 1933, 271, 441; Raoul, Compt. rend. 1937, 204, 74; G.P. 233069, 248385).

Hordenine salts have been employed as a remedy in cases of typhoid, dysentery, enteritis, etc. For furtner details of its pharmacology, *see* Rietschel, Arch. exp. Path. Pharm. 1937,186, 387. The *methylurea* derivative of hordenine shows myotic action (Stedman, Biochem. J. 1926,20,719). o-(/3-Dimethylaminoethyl) phenol (o-hordenine) has been synthesised by Von Braun and Bayer (Ber. 1924, 57 [B], 193); its physiological action is much weaker than that of hordenine.

Schl.

HORMONES. The term hormone denotes a number of physiologically active substances secreted directly into the blood stream or the lymphatic system of animals by various organs named endocrine glands. These internal secretions serve to regulate various functions of the body, often in a part of the body remote from their source, and very small amounts of them' in most cases suffice for the purpose.

The deficiency of a given hormone gives rise to characteristic symptoms in the animal—the effect of castration in domestic animals is a familiar example—and these can usually be alleviated or cured by the administration of the pure hormone, or of an extract containing it. The general principle of the biological assay of hormone preparations'depends on the production of such effects. The League of Nations Health. Organisation (Quart. Bull. Health Organisation, League of Nations, 1935, 4, 618; 1938, 7, 887) has established standards for the sex and pituitary hormones, some of which consist of pure crystalline substances.

Following upon the isolation of the pure hormones, the chemical constitution of a number of them has been determined; the chemistry of the most important hormones is summarised below.

Hormones of the Pituitary Gland (Hypophysis).—The *anterior lobe* of the pituitary gland produces a large number of hormones, and appears to act as a central co-ordinating mechanism controlling the secretions of other endocrine glands. The following glands arc dependent on pituitary control: pancreas (insulin secretion), thyroid, parathyroid, the sex glands, and adrenal (medulla and cortex); there are also hormoncs*controlling lactation, carbohydrate metabolism apart from insulin secretion, etc. An important function of the -pituitary gland is the control of growth, and acromegaly and gigantism, and also insufficient growth are associated? with disturbances ofJth* hypophysis.

Of the above hormones, -those controlling the sex glands *(gonadotropic hormones)* have been particularly widely studied, although their chemistry has not been elucidated. Two effects on female animals can be distinguished, one the ripening of ovarian follicles, the other the formation of corpora lutea; in the male they produce sjermogenesis and the proliferation of Jhe interstitial cells. Although Zondek has given the names " prolan A " and " prolan B " to the substances responsible for these effects, and materials, exerting mainly one or other of these effects, can be prepared, separation is difficult if not impossible. The beginnings of chemical study are made possible by the fact that pregnant women excrete material with high hormone activity, derived probubly from the pluralta ; it may be noted that this secretion is utilised in the widely used method for the diagnosis of pregnancy in its early stages (Aschheim-Zondek test). The active material is obtained from urine by precipitation with, phosphomolybdic acid, the precipitate is dissolved in ammonia, baryta water added and the hormone precipitated from the filtrate by adding alcohol and ether (G.P. 588047). In U.S.P. 2035642 ; B.P. 406531, acetone saturated with benzoic acid is added to the hormone solution acid with acetic acid. The precipitate contains the hormone. A later method is the adsorption of the active material on benzoic acid, followed by dialysis and precipitation with tannic acid or other reagents (Gurin, Bachman and^ Wilson, J. Biol. Chem. 1939, **128,** 525). Another important source of gonadotropic hormones is the serum of pregnant mares, from which a potent preparation can be obtained by removal of the inactive proteins with salicylsulphonic acid, followed by dialysis and precipitation with acetone (Rinderknecht, Noble and Williams, Biochem. J. 1939, 33, 38f>. The active material is classed as a mucoprotein and contains a carbohydrate-polypeptide complex.

fhe secretion of prolars can be influenced by the administration of the sex hormones proper, and a delicate balance between them is maintained in the body (for an account, *see* Ammon and Dirscherl, " Fermente, Hormone, Vitamine," Leipzig, 1938; Berblinger, " Ergebnisse der Vitamin- und Hormonforschung," I, 191, Leipzig, 1938).

The *posterior lobe* of the pituitary gland is comparatively poor in hormones, which are distinguished **as the** ***pressor (pitressin, vasopressin)*** which causes a rise in blood pressure, the *oxyiocic (pitocin)* with an effect on the irritability of uterine muscle, and the *melanophoric,* which controls pigmentation in some animals. Thfise hormones have been tolerably well separated from one another and characterised as belonging to the proteins. The same applies to the anterior lobe hormones; their chemistry is otherwise obscure.

Thyroid Hormone.—The essential nature of the thyroid hormone has l#en recognised for a long time; removal of the gland leads to symptoms known as myxoedema, whilst goitre and cretinism have been traced to thyroid insufficiency, usually due to an inadequate supply of iodine in the diet. Hyperfunction 06 the gland, as seen in GraVes's disease, loads on the other hand to increase in the metabolic rate accompanied by tachycardia, exophthatihia and nervous symptoms.

The gland contains a gelatinous " colloid," which is a globulin-like protein (thyroglobulin), but it contains a comparatively large amount (0-6%) of iodine; indeed, nearly the whole of the iodine content of the body is concentrated in the thyroid gland in a non-ionisable form.

Extraction.—The physiologically active iodine-containing portion of the thyroglobulin molecule was isolated by hydrolysis of thyroid gland tissue with sodium hydroxide (Kendall, J. Biol. Chem. 1919, 39, 125) in the form of the crystalline *thyroxine,* $C_{15}H_{11}O_4NI_4$, m.p. 231-232°, which has the characteristic physiological activity of the thyroid hormone. The yield of thyroxine was greatly improved by Harington (Biochem, J. 1926, 20, 293), who used stepwise hydrolysis with baryta: thyroglobulin (or gland substance) is boiled for 5 hours with 10% aqueous baryta, and the filtered solution acidified ; the acid-insoluble portion is re-hydrolysed for 18 hours with 40% baryta at 100°. 'The insoluble barium salts yield thyroxine, obtained crystalline by acidifying an alkaline alcoholic solution with acetic acid at the boiling-point. Harington and Randall *(ibid.* 1929, 23, 373) have shown that the acid-soluble portion of the hydrolysate contains 3:5-diiodotyrosine and that this and the thyroxine account for the whole of the iodine content of the gland *(cf.* Meyer, " Fortschritte der Chemie Organischer Naturstoffe," II, 103, Vienna, 1939).

Reactions.—A few milligrams of thyroxine in aqueous-alcoholic hydrochloric acid give with sodium nitrite a yellow colour which deepens to orange on boiling; addition of ammonia produces a rose-red colour. This test is characteristic of compounds containing the 2:6-diiodophenol grouping and is also given by diiodotyrosine; both compounds also -give the ninhydrin reaction *(v.* Vol. I, p. 3246).

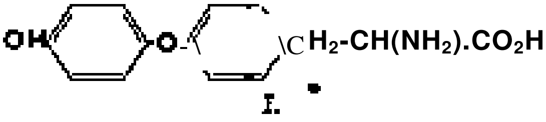
Biological Assay.—Estimating the percentage of the alkaline hydrolysate of thyroid gland tissues which is insoluble at p_H 5 (Harington) or extractable by butyl alcohol (Leland) is a reasonably accurate method of chemical assay. The biological tests depend on measurements of the increase in metabolism, the diminution of the liver glycogen content or the accelerating effect on the development of tadpoles; the Reid-Hunt test measures the increases in the resistance of thyroid-treated mice to poisoning by acetonitrile.

Constitution.—TJiyroxine on catalytic reduction loses its iodine, giving *thyronine,*

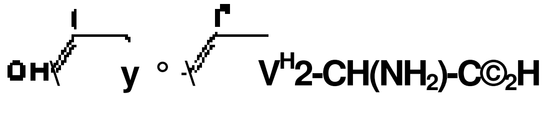
$$C_{15}H_{16}O_4N.$$

This has been degraded by fusion with potash to oxalic acid, ammonia, ^-hydroxybenzoic acid, quinol, and a phenol which was shown by synthesis to be ^-(p'-hydroxyphenoxy)-toluene. Thjs, and the degradation of thyronine by exhaustive methylation and graduated oxidation show that it must have the structure (I), which has been confirmed by synthesis (Harington, Biochem. J. 1926, 20, 300).

Thyroxine itself gives on alkaline fusion products of the pyrogallol type and no p-hydroxybenzoic acid, from which it follows that 2 atoms of iodine must be adjacent to the hydroxyl and two more must be in the second ring. This, and the analogy with diiodotyrosine leads to the formula (II) for thyroxine.

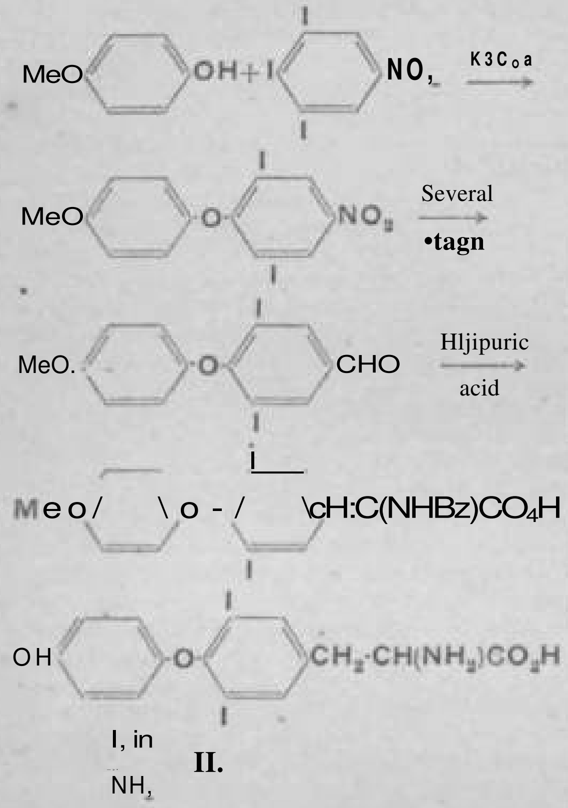


I.



II.

This structure is confirmed by the exhaustive methylation and oxidative degradation of thyroxine. The synthesis of thyroxine (Harington and Barger, *ibid.* 1927, 21, 169) was carried out as follows:



II.

TJio penultimate stage involves simultaneous demethylation, loss of the benzoyl group and reduction of the double bond.

Thyroxine was resolved (Harington, *ibid.* 1928, 22, 1429) and the /-(-)form, m.p. 236-236°, [a|slfII—3-5° proved to be physiologically somewhat more active than the racemie, which is obtained by the alkaline hydrolysis of thryoid tissue ; the active form was later obtained from thyroglobulin by intensive peptic digestion, followed by tryptic digestion (Harington «nd Suitor, *ibid.* 1930, 24, 456). Both it and the physiologically inactive Z-(+)-diiodotyrosine are constituent ammo-adds of thyroglobulin (Glutton, Harington and Yuill, *ibid.* 193fct, 32, **1119)!** in configuration /-(—)-thyroxine ia related to (-{—}-tyrosine (Canzanelli, Harington and Randall, ***ibid.*** 1934, 28, 68).

The active hormone of the thyroid cannot bo thyroglobulin, because thyroid preparations are active when administered by the mouth to thyroidectomised individuals, and in Harington's view it is probably a peptide containing both *l-(* —)-thyroxine and (-(-(-J-diiudotyrosme.

Clinicaliy, thyroid preparations (dried gland or **synthetic)** *tliyroxiiui)* are used in the tn.it-ment of **myxoedema** and other **caaes** of thyroid insufficiency and also of ob&ity, owing to their capacity for increasing the metabolism, particularly that of proteins.

Parathyroid Hormone.—The **parathyroid** fjiund controls the calcium metabolism ef **the** iKxly by **means** uf a n^tecial **hormone** ; removal uf the gland *leads* to symptoms **known** as tetwty, which can be alleviated by ml in in is (ration of caluuin and of extracts of the gland (Collip). The hormone is not dialysablc, it appears to be akin to insulin, but nothing ifl known of its cheinistry.

Pancreatic Hormone.—The hormone of the pancreas is *insulin (q.V,).*

Secretin.—The mucous membrane of the small intestine gives on extraction with acids a preparation -which, when injected into the blood stream, causes a secretion of pancreatic juice (Bayliss and Starling, J. Physiol. 1902, 28, 325). The active compound, secretin, is a complex polypeptide of unknown constitution *(cf,* Agren, *J.* Physiol. 1938-39, 94, 553; Niemann, Proc. Nat. Acad. Sci. 1939, 25, 207).

CEstrogenic 'Hormones.—Substances.capable of inducing the phenomena of oestrus (hqat) in ovariectomised animals have been isolated from **a** variety of sources, but principally ovaries, placenta and pregnancy urine.

Biological Assay.—This is generally carried out by the vaginal smear method of Allen and Doisy (j. Amer. **Mad.** Assoc. 1923, 81, 819).

Isolation.—Pregnancy urine is extracted with ether, the extract evaporated, the residue diesolved in methyl alcohol and shaken with light petroleum. The akaholic solution is diluted and extracted with ether, the extract again evaporated and subjected to partition between 00% alcohol and benzene. The alcohol solution contains mainly cestriol, the benxene solution cestrone. The crude hormones are subjected to hydrolysis with hydrochloric acid; their ether solution is then freed from acids with aodium carbonate, and extracted with sodium hydroxide. This removes the hormones, leaving the inactive pregnanediol in the ether; the hormones are finally re precipitated with acid and taken up in ether. LEstrone is distilled in a high vacuum, whilst cestriol is precipitated from an alcoholic solution by means of ether {Biitenandt and Hildebrandt, *Z.* physiol. Chem. **1981,** 199, 243). A later method (Cohen and Marrian, Biochem. J. 1936, 30, 57; Cohen, **Manias** and Odeli, ***ibid.*** 2250) involves concentration of the urine to one-eighth and extraction at p_a 2-5-30 with butyl alcohol after saturation with salt; tho hormones can be extracted with alkalis and purified, the cestriol being obtained us the sodium salt of the glycuronide *(see below)*; more usually, this complex is broken up by acid **hydrolysis.**

Girard aad Sandulesco (Helv. Ohim. Actft, 1930, **19,** 1095) describe the isolation of oestrono from the crude concentrate, obtained by solvent extraction of the urine of pregnant mares, with the aid of (Jirard's reagent T *(q.v.).* Theketonic constituents are isolated in this way and can be further split up into phenolic (tustrone) and non-jjhi'uolic compounds by means of alkali.

The ftmt crystalline compound to be **isolated** by three groups of workers was *a&tronc,*[1] CigHjjO, (Doisy, Veler and Thayer, Amer. J. Physiol. 1929,90,329; Butenandt, NaUirwisa. 1929, **17,** 879; **Diagemaose,** de Jongh, Kober and Laqucur, **Dent.** nuul. Woch. 1930, 56, 301) **from human pregnancy** urine. **Later** it was found **that** u-strone is even **more abundant** in **the mane of pregnant mans,** in which it

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[1] A variety of mimes **«*m given to the different preparations,** Bueh «s theclin, Iblliculln. etc., ami Uieto *wm* eonie uncertainty abutit **theti** prorcr rornmrntlon, tint In the pi-mom **tec**......t tiitBc Itl»tork;il dftuil are oiuittiu.

is accompanied by several related compounds, *eqailin, equilenin.* and {?) *hippulin* (Girard, Sanduleseo, Fridenson and Rutgers, Compt. rend. 1932, 194, 909; **195,** 981; Girard, Sandulesco, Fridenson, Gaudefroy and Rutgers, ***ibid.*** 1932,**194,** 1020), which can be derived from cestrone by the loss of 2 or 4 atoms of hydrogen. Following the observation of Zondek that the urine of stallions also contains cestrogenio material (Nature, 1934, 133, -209, 494), pure cestrone has been isolated from this source (Deulofou and Ferrari, Z. physiol. Chem. 1934, 226, 192; Hausler, Helv. Chim, Aeta, 1934. **17,** 531) and from the urine of normal men (Dingemaiie, Laqneur and Muhlbock, Nature, 1938, 141, 927}; and the occurrence of oeatrone in material of purely botanical origin (palm kernel oil) has been shown by Butenandt and Jacobi (Z. phyaiol. Chem. 1933, 218, 104).

The alcohol *cestriol,* **C^H^O^** was isolated from human pregnancy urine by Marrian (**JJ3.0.I.** 1930, 49, 237, f>15; Biochem. J. 1930, 24, 435, 1021) and converted into cestrone by dehydration (Butenandr and Hildebrandt, Z. phyaiol. Chem. 1931, 199, 243; Marrian and Haslewood, Biochem. *J.* 1932, 26, 25). It was detected in female willow catkins (Skarzvnski, Nature, 1933.131, 7<i6).

An even more potent oestrogen was isolated from sow's ovaries (McCorquodale, Thayer and Doisy, Proc. Soc. Exp. Biol. and Med. 1935, 32, 1182; J. Biol. Chem. 1936,**115,**435) and proved to be identical with the lower-meltiug or a-form of *oestradiol,* the two epimeric forms of which result from the reduction of the carbonyl group of cestrone (Schwenk and Hildebrand Naturwis9. 1933, 21, 177; Wintersteiner, J. Amer. Chem. Soc. 1937, 59, 765). The £-dioI, together **with** the corresponding alcohol derived from equilenin, was found to be a constituent of " 8 follicular hormone " obtained from the urine of pregnant mares (Wintersteiner *et al., J.* Amer. **Chem.** Soc, 1936. 58. 2052; J. Biol. Chem. 1937, **119,** cvij).

Water-soluble ccftnptexe* containing a'strioJ have been isolated from the placenta and from pregnancy urine *(emmenin* or oestriol glyeuronide) and mares' urine (oeatrone conjugated with sulphuric acid). Nearly the whole of the ODStrogenic material of pregnancy urine is excreted in this combined form, doubtless because the complexes are less toxic to the organism; they exhibit only a fraction of the cestrogenie potency of the hormones themselves when injected into the blood stream, but are almost as potent when administered orally.

Properties. — *(Estrotte,* 3 - hydroxy -17 - keto- Δ i^s-cestratriene,[1] crystallises in 3 • forms : m.p. 254° (rhombic metastable), m.p. 256* {monoclinie metastable) and m.p. 259° (rhombic stable), and has $[a]_D$ +170° (in dioxan). The *acetate* has m.p. 126°, the *benzoate* m.p. 218-219°, the *methyl ether* m.p. **168*S-1W°,** the *oximr,* m.p. 241-242° (eorr.), the *aemicarbazove* (+&H_2O) m.p. 266-267° (corr.). O;lfxg.ofcestrone* constitutes one international unit of cestrogenic activity.

a. - (Sstradid, 3:17 - dihydroxy - ^$^{1:3;a}$-cestratriene. has m.p. 176-178° (corr.), $[o]_D$ +81^{6} (in alcohol); the 3 *acetate* has **m.p. IS6-6-1S7-8^{0},** the ***ll-acetate,*** m.p. 215-217-5° (corr.) and the *diaeetate* m.p, 127°. The physiological activity of a-csstradiol Is higher than that of o?strone and is -enhanced by eaterirication (Miescher, Schok and Tschopp, Biochem. J. IMS, 32, 725).

$-<Estrwliol has m.p. 220-223° (corr.), $[a]_D$ +54° (in dioxan; the *diacdate* has m.p. 139-141-5° (corr.).

(Estrial, 3:16:17-trihydroxy-A$^{1:*3}$-^{OBstratrieiie}> has m.p. 281° (corr,), $[a]_D$ +61° (in alcohol); the *tt iacelale* has m.p. 126°, the *methyl eth?,r* m.p. 162-5-184° (cnrr.).

Equilin, 3-hydroxy-17-ketO- A$^{1:3:*:7}$-<»stratetraene'hasm.p. 238-240°, $[o]_D$+308*(indioxan); the *benzoate* has m.p. 197-198°, the *methyl ether* m.p. 160-5-161-6°.

Bippnlin has m.p. 233° (eorr.), $[a]_D$ +128° (in dioxan).

Equilenin, 3-hydroxy- 17-keto-A$^{1:3;0:i:8}$-aJStrapent&ene, has m.p. 258-259° (corr.), $[a]_D$ +87° (in dioxan), and forms an *acetate,* m.p. 15(5—157°, a *benzoate,* m.p. 222^223° (corr.) and a *methyl ether,* m.p. 197-198° (corr.).

Colour ***Beactiont.***—The natural oestrogens give with sulphuric acid an orange colour (.Marrian), with a fluorescence which is green with restrone and ojatriol, blue with **cnbradiol** (.Schwenk and Hildebrand). Kober modified this test by adding phenol to the aoid, and several colorimetriu methods of estimation were based on this test (Cohen and Marrian, ***ibid,*** 1934, 28, 1603; Pincus, Wheeler, Young and Zahl, J. Biol. Chem. 1936, **116,** 253; Ziinmermann, Klin. Woch. 1938,17, 1103); the most useful of these is Kober's modified test, using a-naphtliol in place of phenol (c/. Biochera. J. 1938, 82, 357).

Constitution.—The structure of cestrone was ascertained us follows: the general type of ring structure and the presence of two active groups at opposite end.s of the molecule were deduced from a crystallo^rnphic study of cestrone and gestriol by the A'-ray method (Bernal, J.S.C.I. 1932, 51, 259), and by an examination of their monomolecular *lilms* (Adam, Danielli, Haslewood and Marrian, Biothom J. 1932, 26, 1233). Marrian and Haslewood (J.S.C.I. 1932, 51, 277) suggested a structure based on that of the sterols, which was further elaborated to (I) by Butenandt (Nature, **1932, 130,** 238) andwhia was confirmed by later work. Thus, oastriol (11) gives on fusion with potash the acid (III) (Marrian and Haslewood, *be.),* which is dehydrogenated by selenium to the phenanthrol (IV) and the latter is converted into 1:2-dimethylphenanthrene (V), identical with a

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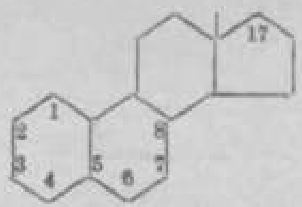
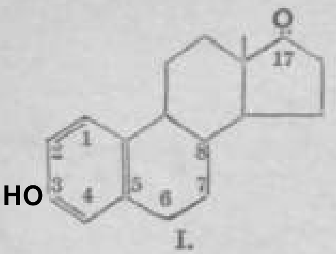
[1] The nomenclature is based on the hydrocarbou cpstranu



(Adam. Datikill, Dodds, King, Marrian, J'arkes and Uoseiihelm, Nature, 1033, 132, 205).

synthetic specimen (Butenandt, Weidlich and Thompson, Ber. 1933, 66, [B], 601):



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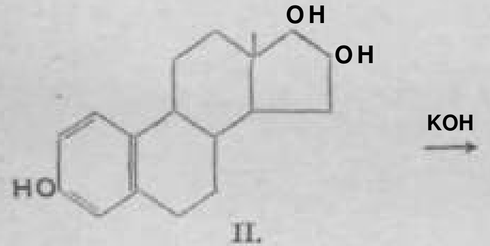

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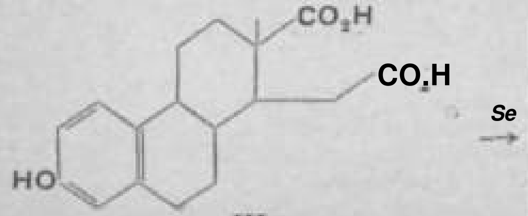

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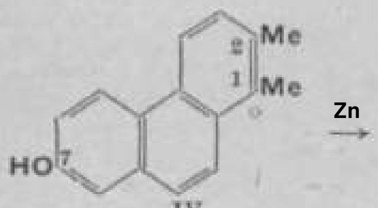

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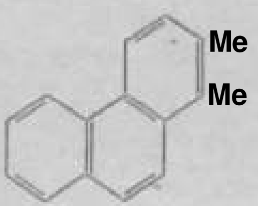
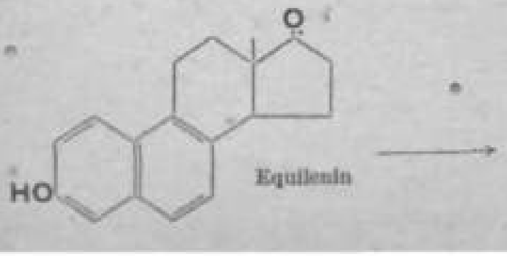
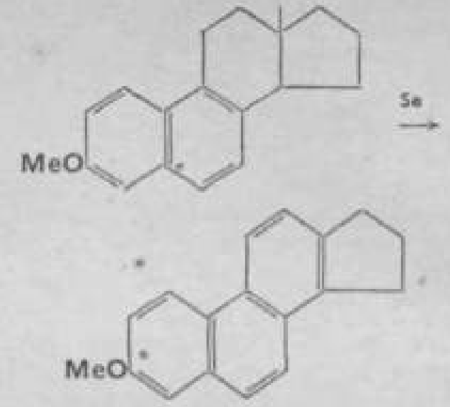


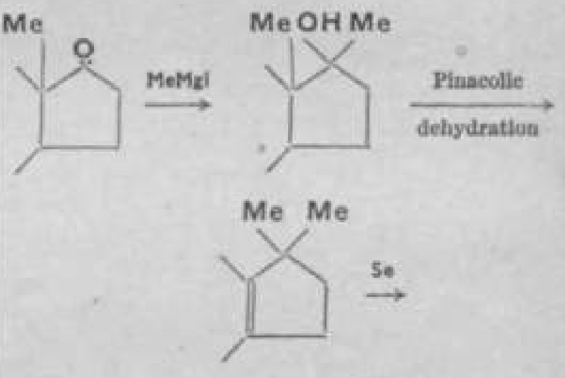
V.

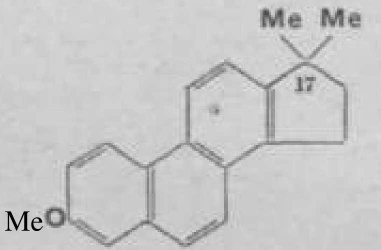
Later, 1:2-dimethyl-7-phenanthrol was synthesised by Haworth and Sheldrick (J.C.S. 1934, 864). Final proof of the skeleton assigned to oestrone and equilenin was afforded by Cook and Girard (Nature, 1934, **183,** 377) and Cohen, Cook, Hewett and Girard (J.C.S. 1934, 653) by converting the methyl ethers of these compounds, after reduction of the ketone group, into the same methoxy- compound, which was synthesized: «





The position of the ketone grouping was proved as follows:





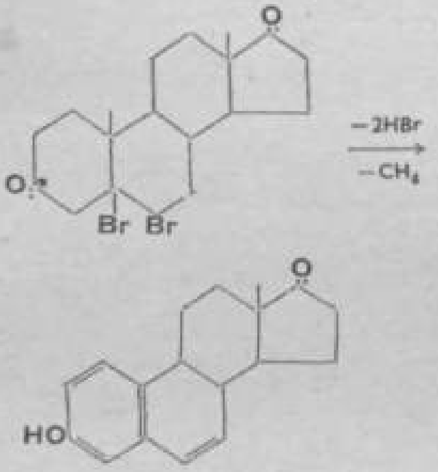
VI.

(Cohen, Cook and Hewett, *ibid.* 1935, 445). A similar pinacolic migration occurs when oestradiol methyl ether is dehydrated: the product on dehydrogenation. gives a methoxy-compound analogous to (VI), but with only one methyl group in position 17-

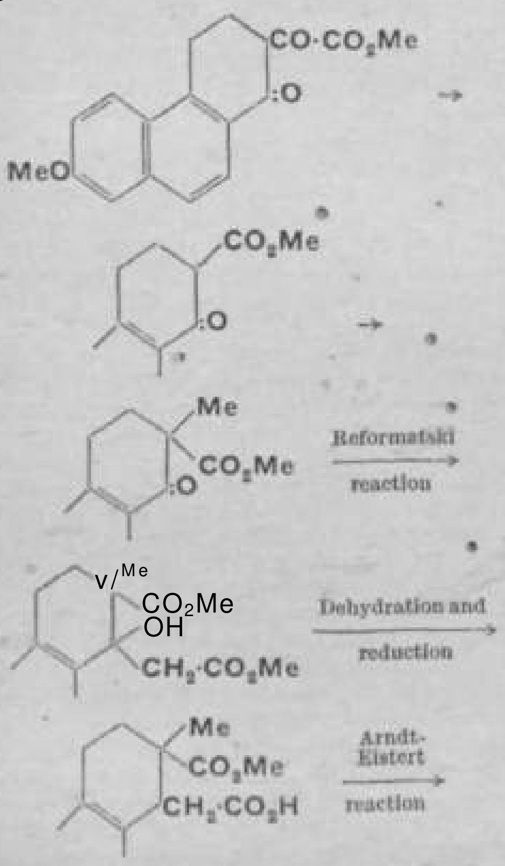
Equilin has been dehydrogenated to equilenin with palladium black, showing that the skeleton and the position of the functional groups are the same (Dirscherl and Hanusch, Z. physiol. Chem. 1935, S33, 13; **286,** 131); as the absorption spectrum of equilin is similar to that of more oestrone, the additional double bond is not conjugated with those of the benzene ring and probably occupies the position 7:8 (Cook and ftoe, J.S.C.I. 1935, 54, 501).

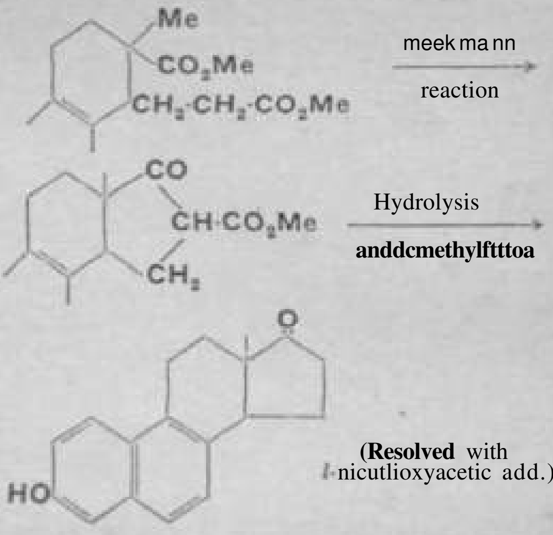
Origin of the Œstrogens.—Following Butenandt, it is commonly assumed that the œstrogens are formed in the body by a degradation of cholesterol involving the removal of the side-chain and partial dehydrogenation of the resulting compound. This view receives support from the definite oestrogenic activity of testosterone and Δ-androstenedione, which might be expected to undergo such a dehydrogenation in the body; it is also in keeping with the occurrence of androgenic substances in the ovary and of cestrogens in the test is, but is nevertheless purely speculative. The metabolism of steroid hormones generally is discussed by Marker (J. Araer. Clieni. Soc. 1938, 60, 1725}.

Synthesis of (Estrogens.—A feebly ncstrogenic compound was prepared by heating the debromination product of dibromonndrosterone, when a phenolic substance was produced with loss of methane; - the substance is isoecjuilin, m.p. 252?, [<»]D +170°, and may perhaps be identical with hippulin (Inhoffen, Naturwiss. I9:i7, 25, **125):**



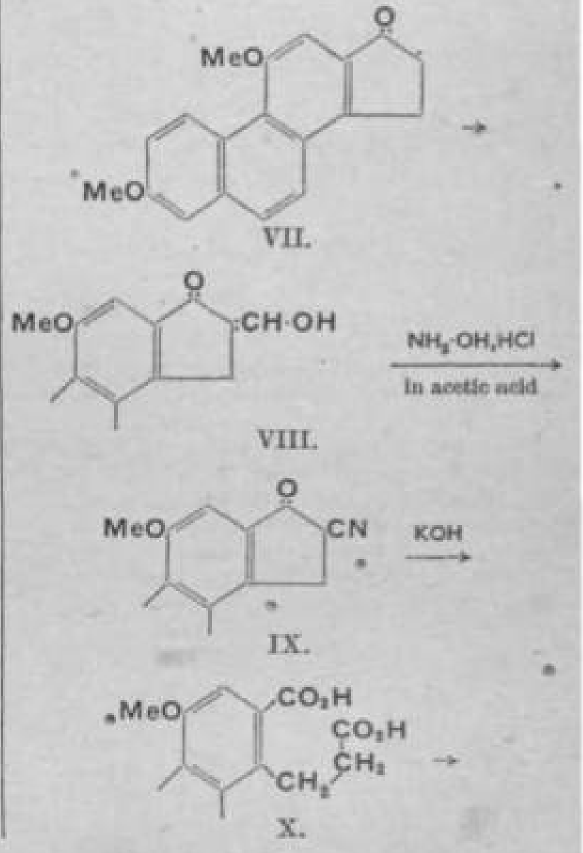
The synthesis of equBenin has been announccd, although full details are not yet available, by Bachmann, Cole and Wilds (J. Amer Chcm. Soc. 1939, 61, 974), who used the following route:

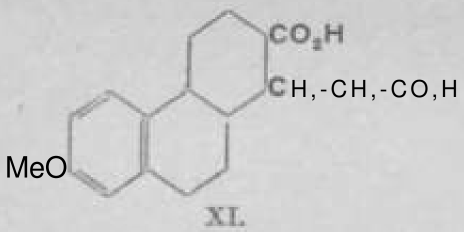




(**Resolved** with l-nicutlioxyacetic add.)

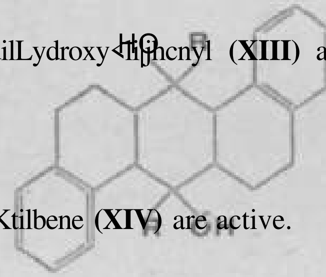
The synthesis of a compound having the skeleton structure of cquilenin, but lucking the angular methyl group, has been achieved by Koebnerand Robinson (J.C.S. 1938, 1994); this is termed *x-nortquiUnin* to denote that the stereo-chemical configuration of the compound is unknown, An analogous *x-ttoraxtrone* has also been prepared by Robinson and Rydon *{ibid.* 1939, 1394); the compound (VII) was synthesised by the method of Robinson *(ibid.* 1938, 1390), but it could not be reduced **direct** to norastrone, although norequilenin was prepared in this way. The five-mem bereti ring was therefore opened by way of the steps {VIII) and (IX) and the resulting compound hydrogenated in several stages. The final product (XI) gave noroestronc **methyl** eTher on cyclisatiofl :





XI.

Artificial (Estrogens.—Apart from the synthesis of the natural festrogenic compounds, a vast number of potentially active compounds have been prepared and tested. The first compound with a measurable activity was I-ketO-1:2:3:4-tetrahydrophenanthrene (Cook, Dodds and Hewett, Nature, 1833,**181,** 56). A series of dialkyl-dihydroxy-coropounda of the type (XII) was prepared and the dip ropy 1 compound ($R=C_3H_7$) found, to have an activity comparable with that of cestriol; some other members of the series were also active (Cook, Dodds, Hewett and Lawson, Proo. Roy. Soc. 1034, B, 114, 272). The phenanthrene skeleton present in these compounds and in the natural cestrogen3 is not, however, essential for activity, lor ;);/-dilLydroxy<lijjhcnyl **(XIII)** and *pp'-di-*liydroxyKtilbene **(XIV)** are active.

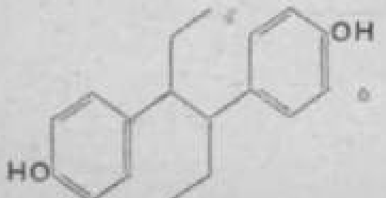


XII.

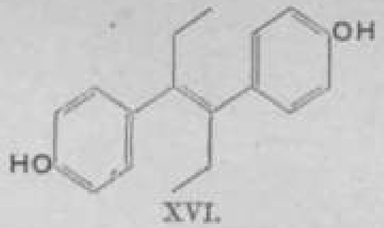
XIII.

XIV.

Recently a compound, of tho formula (XV), with a potency approximately equal to that of o-cest radiol was found in the by-product of the demcthylation of anethole **(Campbell,** Dodds and Lawaon, Nature, 1938, **141,** 78), and an equally **active** compound is the corresponding stilbene, " diothylstilbcestror **(XVI)** (Dodda, Uolberg, Lawson and Robinson, Proc. Koy. Soc. 1039, B, **127,** 140); this* produces 100% **responw** in doses of 00004 mg. when; tested on spayed rats.



XV.



XVI.

A atereoisomeride, thought to he the *cis-com*-pound (^r-diethylstilbcestrol), has only one-tenth the activity of (XVI). The latter la the most active of, a series of homologuua which have been prepared and tested; another compound of comparable potency is 4:4'-dihydroxy-y8-dipheiiyl-A^-hexadiene, which also has a chain of 8 carbon atoms.

Diethylstilboestrol can be administered orally or subcutaneously, and shows all the biological properties of the natural (estrogens;, it confers the mating instinct on ovariectomised animals, sensitizes the rabbit uterus to progesterone, anil acts on the anterior lobe of the pituitary gland.

The duration of oestrus induced by diethylstilboestrol is brief, but may be prolonged by ficlnrinistoring it in the form of esters (propionatfi), just as is the ease with oestradiol.

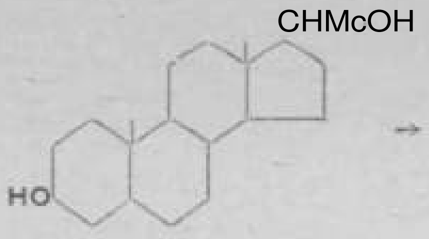
Corpus Luteum Hormone (Progesterone).—The corpus **tatenm** of the mammalian ovary produces a hormone indispensable to pregnancy. This causes characteristic changes in tho mucous membrane of the uterus: the mucous membrane proliferating as the result of the action of rcstrogenie hormones is changed into a secreting membrane, and thus adapted for the reception of the fertilised ovum ; the hormone also assists in the maintenance of pregnancy, and the removal of the corpus luteum during that. period causes the ejection or absorption of the developing ovum. Later in pregnancy the placenta takes over the task of supplying the hormone. The restrogenic hormones are in some respects inhibitory of the physiological activity of progesterone.

Biological Assdty.—Tho assay of the hormone is based on the changes it produces in the uterus of a rabbit previously treated with (Estrogens (Allen and Corner test); the preliminary proliferation of the endninctrium can be induced in an immature rabbit by administration ofcegtrone (Clauberg test). An international unit is equal to 1 TOg. of progesterone.

Extraction.—Sow's ovaries (or corpora lutea) arc the best source of the hormone. These are generally extracted with alcohol, the solvent is removed and the residue taken **no** in ether; phospholipoids are precipitated with acetone, *cholesterol* and *fats* arc frozen out from a mpthyl alcohol solution, acids are removed with sodium bicarbonate; ceetrone may be eliminated by partition between light petroleum and alcohol (Corner and Allen, Amer. J. Physiol. 19ii9, 88. 326; Allen, *ibid.* 1930, 92, 174; J. Biol. Cheni. 1932, 98, 531 ; Allen and Meyer, Amer. J. Physio], 1933, l(W, 55). The final step in the purification is carried out with oarbonyl reagents. The yield is about 50 mg. from 100 kg. of ovaries.

The pure crystalline hormone, *proyesterone,* was isolated l>y four independent groups of workers (Butcnandt, Westpbal **and Hohlireft Z.** physiol. Chem. 1034. 227, H4: Slottn, **Rusehlg** and Fels, Bcr, 1934, **67** [B], 1270; Allen and Wmterstciner, Science, !!)34, **80,** 100; **Kartmann** and Wctlstcin, Helv. Cliim. Acta, 1934,**17,** 878, 13C5}. It is an nn saturated diketone $C_2,H_{3((}O_{!}$, and occurs in two polymorphic varieties, m.p. 128° and 121°, $[a]_D$ +187°; jt is accompanied by the physiologically inert af/oprcgnanol-20-one.[1]

Constitution.—The constitution of progesterone was at first deduced by analogy and finally confirmed by syntheses. The first of **then** stdRs IVom pregnanediol (I), a physiologically inactive compound which ia found in pregnancy urine, and may be produced from progesterone in the) course of metabolism, it is converted by partial oxidation into the keto-alcohol **(II), which** gises f he uns&turated compound (III) by bromination and removal of hydrobromic acid; gentle oxidation then gives progesterone (A*-pregnene-3:20-dione) (IV) (Butenandt and s.in,,i,it, **Bcr. [934, 67** [BJ, **18M, 19011** i



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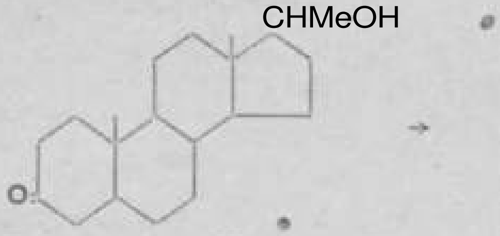

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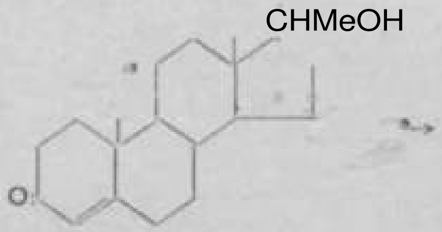

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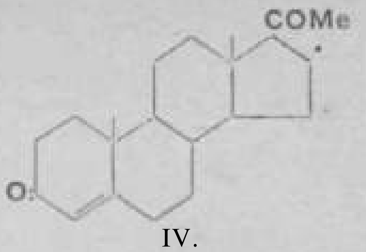
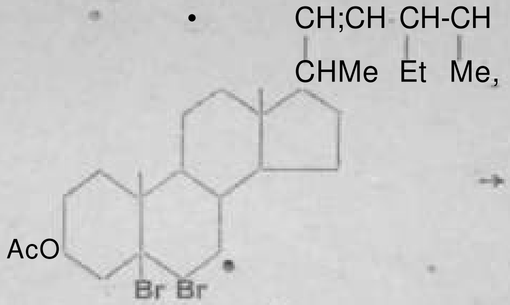
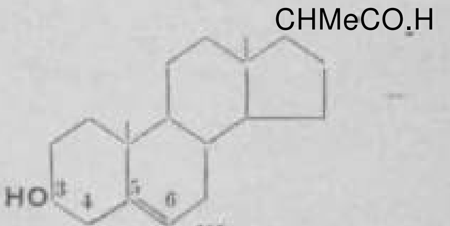


IV.

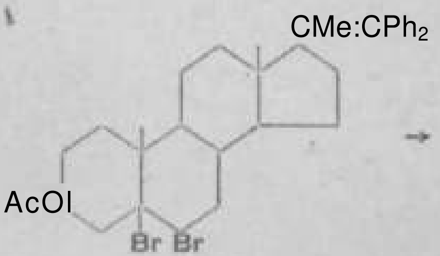
Another synthesis (Fernholz, ***ibid.*** 1934, **67** \B.]. ***1855;*** **Fernholz** and Cliakravarti, *ibid.* lu35, **88** [H], SiiS) starts from a vegetable material, stiginaattirol, the acetate of which is **ozonised** after protecting thu nuclear double bond lty bromination (V); **the** product **is** debrominnted and **hydtolysed to 3-hydroiy6wnorchoIflnic** acid (VI). The aide-chain is then shortened by the action of plienyl magnesium bromide on the **ester and** oxidation of the acetate of the product, the double bond beinii again protected by bromination (VII). The acetate < VII1J is **hydrolyBed** to the. alcohol, which is oxidised to the ketone and **the** latter debrominated to progesterone, the double bond migrating spontaneously into the £.*-positiori:



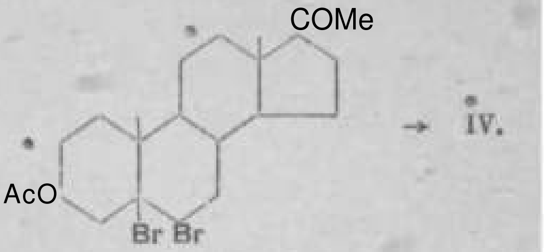
V.



VI.



VII.



V(It.

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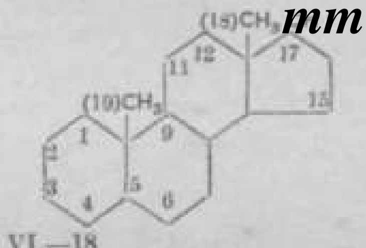
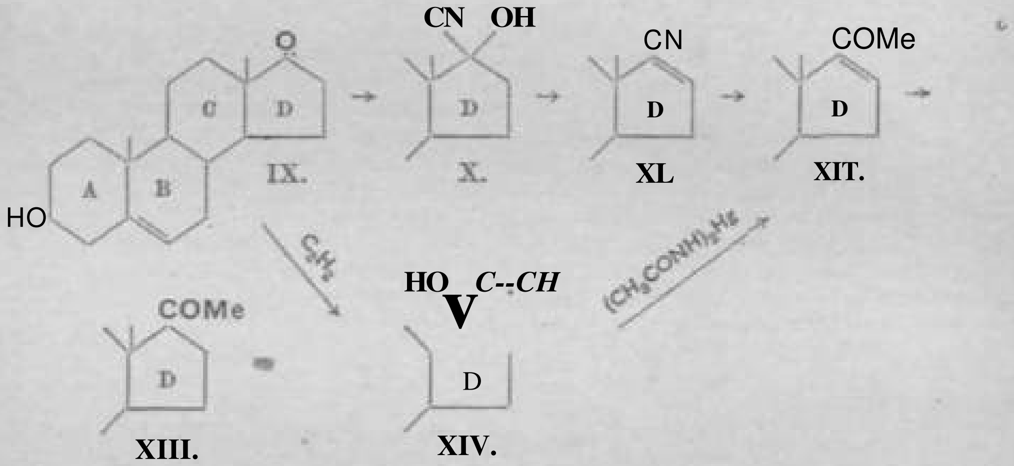
[1] Tlio nomrndittiirt; t« Imsc-ii on tlio hydrocarbon pregnane or 17-othylatKtrortnoo,



This process is used for the large-scale preparation of progesterone, which is in great demand for clinical purposes, but many attempts have recently been made to devise a synthesis from readily available starting materials. Thus, cholestenone has been oxidised with chromic acid to a mixture of progesterone and androstenedione, although the yields are not stated (Diraeherl and HumiBch, Z. physiol. Chem. 1938, 252, 4'J). In the more recent syntheses the comparatively accessible C_{19} compounds of the androstane series are converted into C_{21} compounds. In one of these (Butenandt and Schmidt-Thomé, Ber. 1939, 72 [B], 182) *trans*-dehydroandrosterone (IX) (*see* p. 275a) is converted into the cyanhydrin, which is dehydrated and the unsaturated nitrile treated with methyl magnesium bromide. The product **(XII)** is reduced to the compound (XIIJ) without reducing the double bond in ring B. The final oxidation of the hydroxyl in ring A is achieved by a modification of the Oppenauer method with aluminium isopropoxide and cyclohexanone, which brings about the migration of tho double bond into ring A at the same time.

The compound (XII) has also been obtained (Goldberg and Aesehbacher, Helv. Chim. Acta, 1939, 22, 1185) by the addition of the elements of water to the condensation product of *tra*6*. dehydroandrosterone and acetylene (XIV) (Ruzieka and Hofmann, *ibid.* 1937, 20, 1280); the reagent used was mercury acetamide in alcohol, the mercury complex formed being decomposed with hydrogen sulphide. Other methods bring about enlargement of the five-membered ring. Two other syntheses (Butenandt, Schmidt-Thome" and Paul, Ber. 1939, 72 [B], 1112; Miescher and Kfigi, Helv. Chim, Acta, 1939, 22, 184} are chiefly of academic interest.



Progesterone, unlike oestrone, is highly specific in its action and is completely inactivated by reduction of the double bond; some derivatives of testosterone alkylated in the 17-position possess, however, some degree of activity (Klein and Parkes, Proc. Roy. Soc. 1937, B, **121,** 574).

Androgenic Hormones.—Substances with male hormone activity have been isolated from vertebrates only, although certain plant extracts are said to exhibit androgenic activity (Loewe). Early experiments showed that materials were formed in the testicles which were indispensable for the proper functioning of the male genital organs and the preservation of the secondary sex characteristics; without them the well-known phenomena accompanying- castration are observed. Active extracts of testes were obtained by F. C. Koch, C, R. Moore and their collaborators ; the presence of active material in urine was demonstrated by Loewe and Voss end by Funk.

Biological Assay,—The increase in growth of a capon's comb under the influence of androgenic materials was first utilised as a quantitative test by Gallagher and Koch (1929) And adopted at the London Conference for the Standardisation of Sex Hormones in 1935; a " capon unit " is equal to 100μg. of androsterone. Another test depends on the increase in the size of seminal vesicles in castrated rodents (Loewe and Voss, Horenchevsky); the two tests do not always give equivalent results (for a detailed account, *see* F. C. Koch, " The Male Sex Hormones," Physiol. Reviews, 1937,17).

Isolation.—Lipoid-soluble active bodies have been isolated from testes and human urine, of men or castrates, and even from the female organism. It was eventually found that the activity of extracts of male urine was due to androsterone (Butenandt, Z. angew. Chem. 1931, **44,** &05; 1932, 45, 655; Nature, 1932, **130,** 238; Butenandt and Tscherning, Z, physiol. Chem. I9'U, 229, 167, 185) and that of testes extracts to testosterone (LaqueUi*, David, Dingemanse and Freud." Aeta brev. neerl. 1935, 5, 84 j Z. physiol. Chem, 1935, **233,** 281); *trans*-dehydroandrosterone, about one-third as active as androsterone, was isolated from urine by Buteuandt and Danncnbaum (Z. physiol. Chem, 1934, 229, 192; Butenandt, Dannenbaum, Hanisch and Kudszus, *ibid.* 1935, **237,** 57) and it was found that adrenosterone, from adrenal cortex (p. 2786), possesses androgenic activity.

The method of extraction of androsterone from male urine was similar to that employed for oestrone (p. 268c), except that androsterone is not phenolic and is therefore found in the neutral portion of the extract. As a method of preparation this process has been superseded by the synthetic method described on p. *215a.*

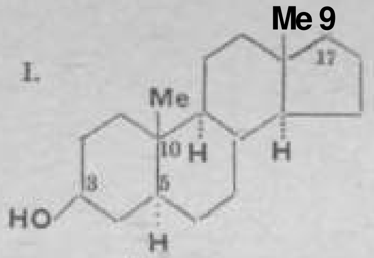
Properties.—Cia-androsterone has m.p. **184-** !*•>• (corr.), [o],, +94'fl'J (in alcohol), the *acetate* m.p. lti4fM65o° (corr.), the *oocimt* m.p. •209-211" (corr.), the *aemicarbazonc* m.p. 276° (corr.). 1(%g. equal 1 International unit.

Trams-testosterone has m.p. 154-5-lu5-5^{c} (corr.), $[_{a}]_{D}$ +109^{0} (in-alcohol), the *acetate* m.p. 140-111° (corr.), the *propionale* m.p. 121-123° (corr,), the *benzoate* m.p. **198-200"** (corr.). 15^-equal 1 International unit.

JVaas-dehydroandrosterone occurs in two forms, m.p. 140-141* (corr.) and 152-153° (corr.), $[a]_{D}$ +10-9° (in alcohol), the *oxime* haa m.p. 188-189°, tho *acetate* m.p. 171-172° (corr.). 200fig. equal 1 International unit.

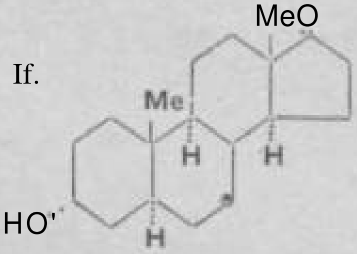
Constitution.—The amount pf androsterone isolated by Butenandt and Tscherning *(ibid.* 1984, 229, 167, 185) was barely sufficient to establish the formula as $C_{1V}H_{M}O$, and the correct constitution was put forward by analogy with that of oestrone. This and the configuration of the compound were established by the eyiithesjp of androsterone by Ruzicka, Goldberg and Briingger (Helv. Chim. Acta, 1934,17, 1389) and Ruzieka, Goldberg, Meyer, Briingger and Eichenberger *(ibid.* p. 1305). They oxidised the acetates of cholestanol, eoprosterol and their *epi*-compounds with chromic acid and obtained the acetates of four stereotuisoeric hydroxyketonea:

I.



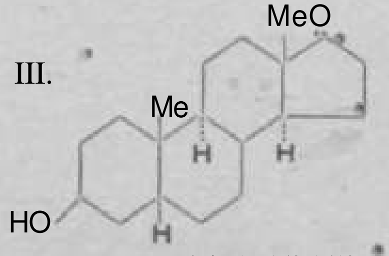
From cholestanol |i*unndrofllcronc), m.p. 175-17(5°.

If.



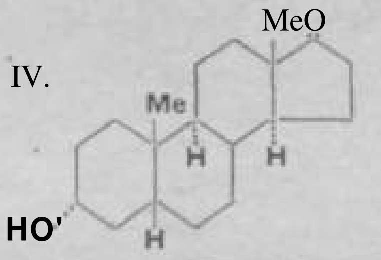
From epi'choteauool (androsteroue), m.p. 184".

III.



From coprostt-rol, in.]). 150-151°.

IV.

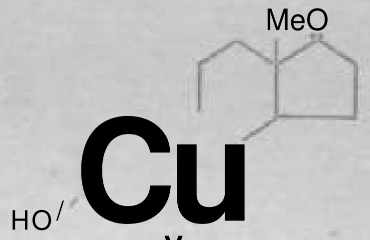


From ffificoprosterol, m.p. 152-113".

(M.p.'i us corrected.)

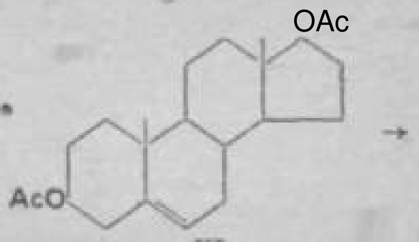
Of these, (II) 3-ep*hydroxyaetioaHocholane-17-one proved to be identical with aYidrosterone; wo- or *trans*-androsterone (I) showed one-eighth the activity of androsterone in the capon test and (III) and (IV) were inactive; the great importance of the stereochemical configuration will be noted. Androsterone is prepared on the large scale by the above method.

Oxidation of dibromocholeateryl acetate (Ruzicka and Wettstein, *ibid.* 1935, 18, 986; Butenandt, Dannenbaum, Hanisch and Kudszus, t.c.; Wallis and Feroholz, J. Amer. Chem. Soc. 1935, 57, 1379, 1504) and denomination of the product gives (rarw-dehydroandrosterone (V); the configuration of the hydroxyl group in this compound is like that of tsoandrosterone (for nomenclature, *v.* Schonheimer and Evans, J. Biol. Chem. 1936, **114,** 567). In accordance with this configuration, the compound is precipitated with digitonin, whereas androaterone is not. Cis-dehydroandrosterone has been prepared, and is biologically more active than the natural *trans*-compound.

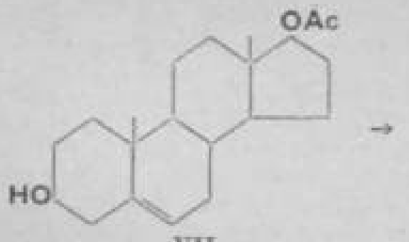


V.

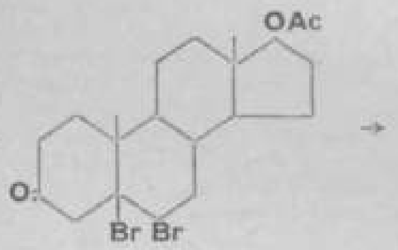
Testosterone, isolated from testes proved to be different from, these; it was unsaturated and hence unstable to alkali and permanganate and was much more active than androsterone in the rat test (Laqueur *el al., I.e.*; Callow and Deanealy, Lancet, 1935, ii, 77). It was isolated in minute amount from the testes of steers {David, Dingemansc, Freud and Laqueur (Z. physiol. Chem. 1935, 233, 281) and proved to be an a/J-un saturated kctone, $C_{18}H_{M}O_{2}$; on careful oxidation it gave A*^{6}-androstene-3:17-dione, also obtained by the oxidation of (TO/M-dehydroandroaterone (David, Acta brev. m*rl.. Physiol. 1935, 85, 108). It was then synthesised from the above compound (Ruzicka anrl Wettstein, Hdv. Chim. Acta, 1935, 18, 1204; Butenandt and Hanisch, Ber. 1935, 68 [B], 1859; *Z.* physiol. Chem. 1935, 237, 39) ᐅy reduction to amirostcnediol, the acetate of which (VI) can be hydrolysed to *a* inonoacetate (VII), the acetyl group in ring A being removed before that in ring D. After protecting the double bond by bromination the monoacctate waa oxidised to (VIII) and on removing bromine testosterone acetate (IX) was obtained;



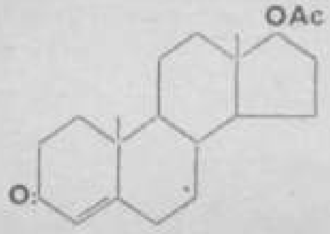
VI.



VII.



VIII.



IX.

Testosterone when injected in oil solution is about 7 times more active than andronterone in the capon test. In the rat test its activity is increased by the presence of an acidic material (Laqueur's "X-Stotf") in extracts of testes, probably fatty acids, which have no effect in the capon test. This increased activity is probably connected with the rate .of absorption of the active material. Similarly, the activity of testosterone and androsterone can be enhanced by esterification with fatty acids up to valeric acid; testosterone valerate is 10 times more active than testosterone in the rat test, but not in the capon test. Testosterone propionate has the highest activity of any known substance in both tests. Modern theory inclines to the view that testosterone is the only natural androgenic compound and that androsterone is probably a secondary product derived from it (N. H. Callow, Biochem. J. 1939, 83, 559; Dorfman, Cook and Hamilton, J. Biol. Chem. 1939, 130, 285).

A very large number of derivatives of these fiompoimrffl have been prepared by varying the groups attached to the carbon atoms 3 and 17 in androsterone and testosterone. A number of these compounds have been found to possess considerable biological activity, which is also < losely bound up with their stereochemical configr'&tion ; a discussion of them is beyond the scope of this article, but reference may be made to a review by Goldberg in " Ergchnisrio der Vitamin- und Hornionforsehung," Leipzig, 1!t:ts, 1, 391; *see also* Airnnon and Dirscheri, • Kerroente, Hormone, Vitamine," Leipzig, LOSS.

A number of androstane derivatives, particularly unsaturated compounds, have some biological activity as female sex hormones and, on the other hand, nitrogens have a stinrulatinu effect on certain of the male sexual organs. The physiological significance of this is uncertain, but reference may. be made to Korencheveky, " ErgebnisBo der Vitamin- und Hormonforschung," Leipzig. 1938, II, 420, for a discussion of the subject. Some male hormone activity may be derived from the adrenal cortex *[see below)* and it is known that tumours of the adrenal cortex in women may lead to virilisation; an abnormally high secretion of (mns-dehydroandrosterone has also been observed in such cases.

Adrenal Hormones.—The adrenal gland consists of two parts, the medulla and the cortex. The former secretes adrenalin *[q.v.).* The cortex is essential to life and, in man, atrophy or destruction of this part of the gland is the cause of Addison's disease. Removal of the gland is rapidly fatal, especially in birds, and gives rise to the following symptoms : disturbances of the equilibrium between potassium and sodium in the blood as well as in the amount of water in the blood, adynamia (ready onset of muscular fatigue), difficulty in the assimilation of fats and in the absorption of carbohydrates. It is thought that the last two processes an- connected with phosphorylation (Verzar) and that this process is controlled by the adrenal hormones. These deficiency symptoms are relieved by extracts of the adrenal gland, the composition of which has been intensively studied in recent years.

Biological Assay,—In the survival test (Caftlaod and Kuizenga) adrenalectomised animals (rats) are kept alive by injections of the material to be examined. The dog test (Pfiffner, Swingle and Vars) similarly measures the amount of hormone preparation necessary to maintain a dog in good condition. The muscle fatigue test (E verse and de Froinery) measures quantitatively the diminished resistance to muscle fatigue in rats; the-Inglo test is similar, *»ho* the swimming test (Ga&reaBtrom, Waterman and Laqueur). The glucose test is based on the absorption of glucose in rats.

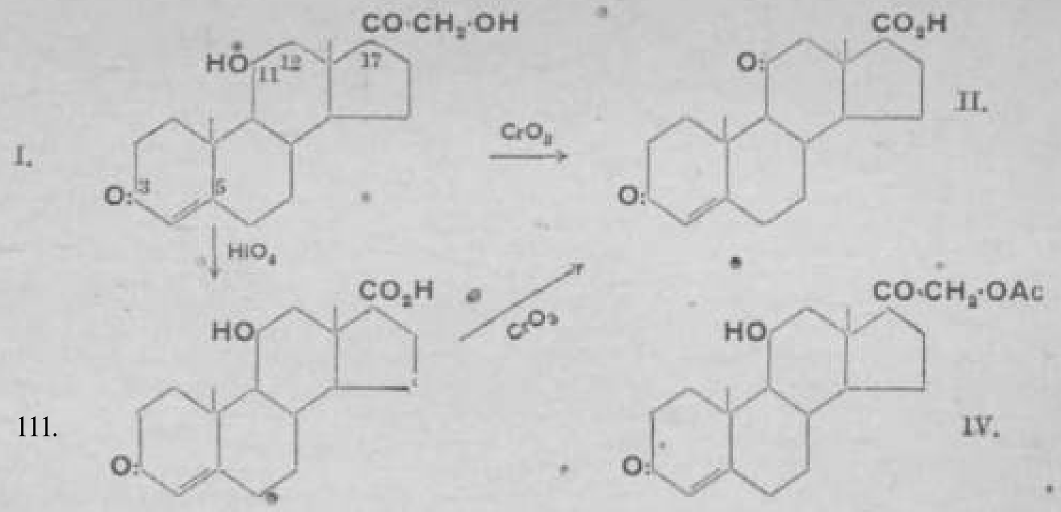
Isolation.—The separation of the cortex from the meduTtfi of the adrenal glanr} is not practicable on a large scale^ and whole glands are used; the inaetivation of the hormones by heat and alkali must also be borne in mind.

The glands are extracted with alcohol at room temperature, the extract is evaporated, the residue taken up in benzene, then in acetone; after partition between 70% alcohol and hexaoe the alcoholic layer is filtered through " *p*r~ mutite* " to remove adrenalin (losses are sometimes experienced at this stage), evaporated, the residue taken up in water to precipitate resins and again re precipitated from an alcoholic solution. The yield at this stage is equivalent to 60 g. of dry material from 1,000 kg. of gland (from some 20.000 head of cattle) and contains 1-2 million dog units (Swingle and Pfiffner, Amer. J. Physiol. 1931, 96, 153, 164, 180! Pfiffner, Vars and Taylor, J. Biol. Chem. 1934, 106, 625; Pfi$ua and Vars, *ibid.* p. 845). An alternative method (Cartland and Kuizenga, *ibid.* 103(1, 116, 57) involves extraction of the glands with acetone, two partitions between 70% alcohol and petroleum and an extraction with ethylene dicbloride; the yield of (dry) material is somewhat less (18 g. from 1,000 kg.) but the total activity is higher (2-5 million dog units).

The active material is soluble both in watt* and in solvents such as ether and benzene and the further purification of the hormones is **based** on repeated partition between solvents; this has been employed by three groups of workers, namely those of Kendall, Win tors teiner and Pfiffner, and Reichstein. The 'final isolation of the pure compounds is carried out with carbonyl reagents ; Oirard's reagent has been particularly valuable in Reichstein's hands. In this way 5 pure active compounds have been isolated, together with 7 or 8 closely related but inactive ones; nevertheless, the amorphous, water-soluble material remaining in the residues appears to be more active than any of the pure compounds hitherto isolated.

Chemically, all the pure compounds found in the adrenal cortex belong to the sterol group; those which are saturated belong to the chole-etane type and are characterised by an oxygen atom (in addition to one on C»), the position of which is almost certainly on C_{11}, although this has not yet been strictly proved. They also have an oxygenated side-chain of varying length on C_{17}.

Proper ties and Constitution.—C'ortt *costerone,* A^prcgnene-ll^l-diol-S^O-dioiietll.CjjHggO., has in.p. 180-182° (corr.), {a]$_0$ +223° (in alcohol) (Beiehstein, Laqueur, UyJdert, de Fremory and **Spanhoff,** Proc. K. Akad. Wetensch. Amsterdam, 1936, 39,1218 ; Nature, 1937, 139, 26); it forms an alcoholate, reduces ammoniacal silver solutions and gives the characteristic spectrum of an o^-unsat u rated ketone. Oxidation with chromic acid gives the acid (II) (Heichstein, Helv. Chim. Acta, 1&37, 20, 953). The hydroxylic nature of the oxygen atom * (originally pj&ced on C_{ia}) was recognised by Kendall, Mason, Hoehn and Mackenzie (Proe. Staff Meet. Mayo Clinic, 1937, 12, 136), who showed that the acid (III) was produced by oxidation of corticoaterone (I) with periodic acid and (III) could be further oxidised to (II) :



Corticosterone forms a ruonuauetate (IV) which can be oxidised by chromic acid in the same way, the product being identical with the^ acetate of dehydnxMiiiri **•twone** (below).

The position of the side-chain on C_{17} has been proved by convei-aion, of corti«jate*one into aMopregnane (Steiger and Reichatein, Nature, 1938, **141,** 202; Helv. Chim. Acta, IMS, 21, 161).

Corticosterone possesses a high degi-ee of cortin activity, I mg, being equivalent to 60-^00 g. of a -prarenal gland; its esters are equally active, but the activity is almost completely destroyed by the reduction of the double bond.

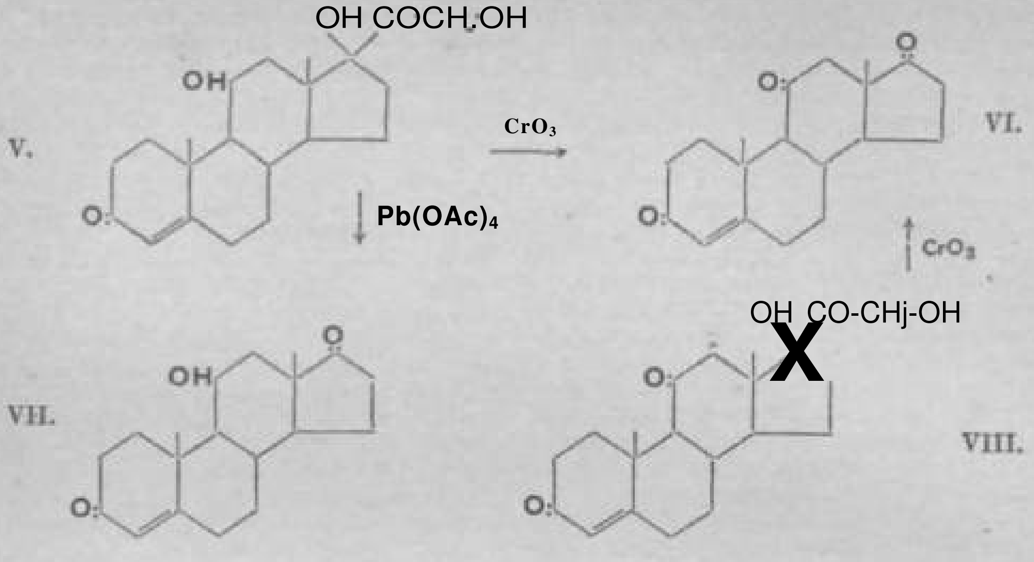
Dehydrocortkosterone, $C_{ai}H_{as}O_4$, m.p. 174-181-5°, [o]$_D$ +299° *(acetate,* m.p. **173-180-6°), hu** been isolated by Mason, Myers and Kendall (J. Biol. Chcm. **1986,**114, 613) arid prepared by Keichatein by the oxidation of cortieosterone acetate and hydrolysis; it gives the acid (III) on oxidation **with** either periodic or **chromic** acid. Its biological activity is inferior to that of corticosterone and it differs from the latter in not giving the characteristic green fluorescence with sulphuric acid.

Δ p gl h n 2: 1-triol-3:20-dione* (V),

$C_{21}H_{30}O_5$,

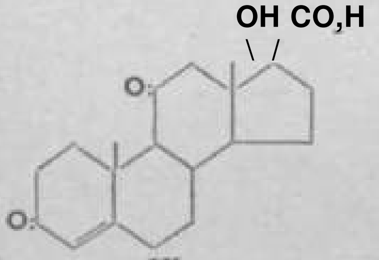
m.p. about 207-210°, [a]$_D$ +167-2° (Reichstein, Helv. Chim. Acta, 1937, 20, 1164) has some activity in the Everae and de Fremery teat, reduces silver solutions and gives a green fluorescence with sulphuric acid. On oxidation with chromic acid it gives adrenostinmc (VI), whereas lead tetra-acetate# gives the hydroxy-ketone (VII); the acetate of (V), m.p. 223-225°, passes on mild oxidation into the acetate of the compound (VIII) described at the top of the next page.

A'-Preffnent-l~:2l-diol-3:lh2Q-trione (VllI), C n ^ ° s . m-P- aboufc 208°. HD +209°, was first isolated by Wintersteiner and Pfitfner (J. Biol. Chem. 1935, 111, 585; 193(5,**114,** Ixxx; 116, 291). It is very similar to the triol (V), but can be distinguished by its crystalline form (shining rhombohedra); it has a bitter taste.



V. VI. VII. VIII.

Oxidation with chromic acid gives adrenosterone and with periodic acid the hydroxyacid {IX):



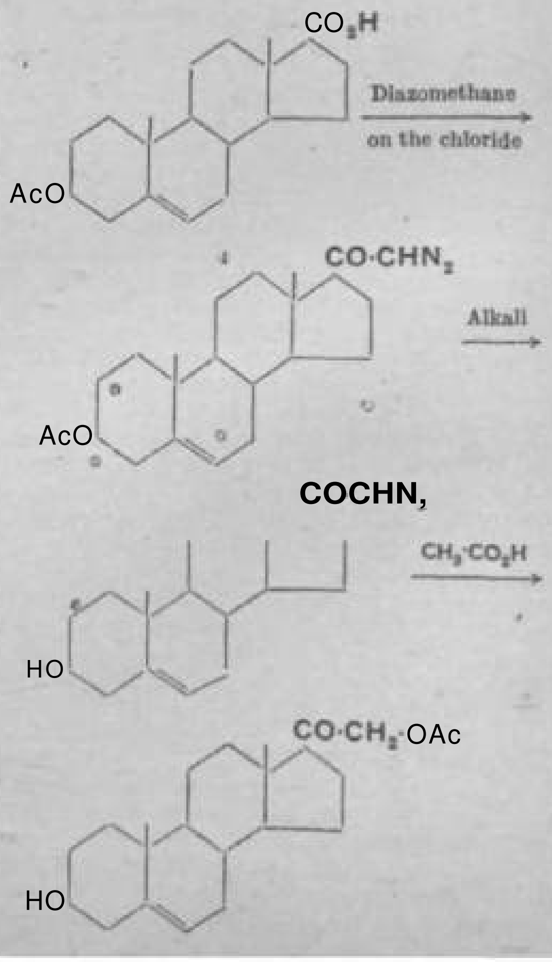
IX.

Its activity is somewhat less than that of (V).

Adrenoslerone, A *-androstene-3:11:17-trione (VI), $C_{]tt}H_{24}O_3$, was isolated from the portions of the adrenal extract more soluble in ether and petroleum by Rcichatein (Helv. Chim. A eta, 1936, 19, 29) and has m.p. 222°, $[a]_D$ +262°*;* it has no cortin activity but a considerable an^lrogeRic acitivity (about one-fifth that of androsterone in the capon test) and this provided a clue to its structure. It is hydrogenated to a saturated trikotone, m.p. 178°, which has been reduced by Clemmensen's method to androstane, thus fixing the ring structure present in this, and hence also in the other compounds of the group which have been correlated with it. A by-product of the reduction is 17-androstanol, which fixes the position of the side-chain in these compounds, whilst the position of one oxygen **atom** on C« follows from the fact that the hydroxylftted compounds of this series are precipitated by digitonin.

In addition to thejibove compounds, a number of physiologically inert compounds have been isolated ; these have proved*useful in elucidating **the** chemistry of the whole group, and an account of them by Reiehstein will be found in " Ergebniase der Vitamin- und Horraonforschung," Leipzig, 1938,1, 334. *

A synthetic compound possessing an even greater biological activity than corticosterone (5 to 7 times greater in the dog test and about 10 times greater in the Everse and de Fremery test) is deoxycortiraaterone or 21-hydroxyprogesterone, m.p. 141-142" (corr.), $[a]_D$ +178° (Reichstein and Steiger, Nature, 1937,**139,** 925; Helv, Chim. Acta, 1937, 20, 1164); it lacks the characteristic inert hydroxyl group on C_{lv} but embodies the other features which appear to be essential for cortin activity, namely a double bond a/S with respect to the carbonyl group on C_3 (since all the active compounds are inactivated on reduction) and the terminal hydroxyl group on C_{tt} (since progesterone itself has no cortin activity). The compound was prepared from the acetate of A'-3-hydroxycholenic acid as follows:



The last compound is brominated to protect the double bond, oxidised and denominated (c/. the preparation of progesterone, p. 273c), yielding the acetate of deoxycorticosterone. This synthesis is of great importance in view of the clinical uses of the compound. Deoxycorticosterone has recently been isolated in minute amount from the suprarenal gland (Reichstein and Von Euw, *ibid.* 1938, 21, 1197).

G. A. R. K.

HORNBLENDE. An important rock-forming mineral belonging to the monoclinic series of the amphibole group, consisting mainly of metasilicates of calcium, magnesium and iron. The name hornblende is sometimes applied to the group itself, which includes the useful minerals asbestos *(q.v.)*, nephrite and crocidolite *(q.v.)*. More usually, however, it is restricted to the darker-coloured (green, brown, black) aluminous varieties, the composition of which is expressed by mixtures in various proportions of the molecules

$$Ca_4Na_2(Mg,Fe)_{10}Al_aSi_{14}O_{44}(bH,F)_4,$$
$$Ca_4Na_a(Mg,Fe)_8AI_6Si_{12}O_{44}(OH,F)_4,$$

etc. It forms part of many kinds of igneous rocks, *e.g.* hornblende-granite, syenite, basalt, etc., and crystalline schists, *e.g.* hornblende-schist.

L. J. S.

HORNFELS *v.* HORNSTONE.

HORN LEAD: Lead chloride, $PbCI_2$.

HORN-QUICKSILVER. *Calomel,* Hg_aCI_2, occurs native in small quantities.

HORNSILVER. Native silver chloride *v.* CEBARGYBITE.

HORNSTONE and **HORNFELS,** narifes applied to a variety of* hard and tough, fine-grained and compact, splintery, siliceous rocks with a horny appearance, which have generally been formed by the baking action of igneous rock-masses on surrounding sedimentary rocks (sandstones, grits, shales, slates, etc.). They frequently show a banded structure representing the original bedding planes, but they do not break along these directions. The name hornstone is more usually applied by mineralogists to the highly siliceous kinds, and regarded as a variety of quartz allied to flint, chert, novaculite and jasper; whilst the German name hornfels is applied by petrographers to materials more of the nature of rocks, *e.g.* biotite-liornfels, andalusite-hornfels, tourmaline-hornfels, calc-silicate-hornfels, etc., the last-named having been produced by the thermal metaniorphism of impure siliceous limestones. The Swedish *Hälleflinta* (meaning rock-flint) is also very similar in character; this may in some cases represent an altered felsitic lava, but in others it does not differ from hornfels. These materials are used as hones *{Whetstones).*

L. J. S.

HORSE-CHESTNUT. The horse-chestnut tree, *JEsculus hippocastanum,* is a native of Persia and Northern India, and is said to have been introduced into Europe in the sixteenth century. The nuts, closely resembling those of the sweet (edible) chestnut, are the " conkers " of school boys, but are injurious if eaten owing to their content of toxic saponin and other bitter substances. When extracted with boiling water or preferably with dilute sodium carbonate solution the nuts leave a harmless residue of value as a cattle food (Sasaki and Kandatsu, J. Agric. Chem. Soc. Japan, 1936,12, 675). According to Dechambre (Compt. rend. Acad. Agric. France 1917, 3, 927) the extracted nuts may be ground and used in breadmaking.

The bark of the tree contains the glucoside *sescvlin (q.v.)* (6-j8-glucosidoxy-7-hydroxycoumarin, Head and Robertson, J.C.S. 1930, 2435; Macbeth, *ibid.* 1931, 1288) with small proportions of the aglucone sesculetin (6:7-dihydroxycoumarin, Gattermann and Köbner, Ber. 1899, 32, 288). iEsculin, m.p. 200-202° is extracted from the bark with boiling water, and the extract after treatment with lead acetate, and subsequently with hydrogen sulphide to remove excess lead, is concentrated' until crystals are formed. iEsculin is hydrolysed by mineral acids or by the enzyme emulsin to glucose and sesculetin, m.p. 270°.

A second glucoside *fraxin* is also present in the bark. Hydrolysis of fraxin, $C_{16}H_{18}O_{10}$, yields glucose and *fraxetin,* $C_9H_5O_5OMe$, a methoxysesculetta (Koerner and Biginelli, Gazzetta, 1891, 21, ii, 452).

Horse-chestnut leaves contain quercitrin and the flowers contain quercetin.

Baker and Hulton (Analyst, 1917, 42, 353) give the composition of the hulled nuts as: water, 1-85-3-5; ash, 245-2-90; oil, 5-0-7-2; protein, 7-25-10-8; reducing sugars (as dextrose), 1-6-9-1; sucrose, 7-27-17-5; starch (Lintner), 21*9-47-8; starch (taka-diastase), 15-2-39-0: pentoslns, 4-75-5-44; crude fibre, 2-0-2-6%. In an examination Of the hulls Hilpert and Kruger (Ber. 1939, 72 [B], 400) give the following analytical data:

C, 54-5; H, 4-8; methoxyl, 2-2; lignin, 5-2; pentosans, 5-7%.

The nuts are of value in the manufacture of n-butyl alcohol and acetone by fermentatign processes; yields of alcohol may reach 11-12% of the weight of the nuts (Henley, J.S.C.I. 1919, 38, 281T; Gill, *ibid.* p. 41 IT). Hirst and Young (J.C.S. 1939, 951) obtained yields of 10-20% of a starch having [a]^+151° and by means of the methyl derivative obtained three fractions of molecular weight 700,000, 650,000 and 430,000. Tho starch molecule probably corresponds with a chain length of 28 glucose units.

Belozerski and Dubrovskaja (Biochimia, 1936, 1, 665) isolated from the cotyledons of the nuts a globulin, *Mppocastanin,* and a nucleoprotein. Hydrolysis of tho latter yielded a protein having a nitrogen-distribution similar to that of hippocastaniA and a nucleic acid yielding guanine, adenine, cytosine, thymine and lsevulic acid but not uracil.

The use of the saponin of horse-chestnut as a substitute for white soap bark in certain therapeutic preparations is suggested by Roberg and Hoffmann (Dent. Apoth.-Ztg. 1939, 54, 416).

For an examination of the seed oil, *see* Masson (Bull. Sci. pharmacol. 1918, 25, 65).

A. G. Po.

HORSE-FAT. The fat obtained from the horse is of &> yellowish colour and buttery consistency : as the rendering of horse-fat is not as a rule so carefully carried out as that of other edible animal fats, it is liable to be contaminated with remnants of tissues, to rancidify easily and to develop an unpleasant odour. On standing, it separates into a solid and a more unsaturated liquid portion, the latter being known as " *horse oil*" (not to be confused with horse's foot oil, *see below).* Both the fat and oil have weak drying properties and are, therefore, unsuitable for use as lubricants. In consequence of the increasing consumption of horse-meat, the fat has become a commercial article; it is used by the poorer classes on the Continent as a substitute for lard, and is no doubt used, upon occasion, as an adulterant of more expensive edible fats.

Low grade horse-fats are used in the manufacture of soaps and leather-greases. A process for protecting calcium carbide from the action of water vapour by a coating of oil from horse fat was patented by McRae (B.P. 25046/1905).

Horse-fat melts at about 34-39°C., and has an iodine value varying from *65* to 94 according to the part of animal from which it is derived: *cf.* Amthor and Zink, Z. anal. Chem. 1S92, 31, 381; Kalmann, Chem.-Ztg. 1892, 16, 922; Gill and Rowe, J. Amcr. Chem. Soc. 1902, 24, 46t>; Dunlop, Analyst, 1907, 32, 317 (the fat from the kidney-bed was found to have an iodine value of 110-6, the highest figure recorded for any horse-fat); Rosello, Chim. et. Ind., 1929, Spec. No. (8e Congr. de Chim. ind., Strasbourg (1928) 520C. (examination of horse oils: the presence of palinito-dilinoliiys reported).

The higher iodine value, and refractive index of horse-fat t51-59° Zeiss at 40°, *i.e.* n_D 1-4600-1-4653) have been used in Germany as an official means of identifying horse-meat *(cf.* A. Beythien, " Laboratoriumsbuch f.d. Nahrungsmittelchemiker," 1931, 13. According to Pritzker and Jungkunz (Z. Unters. Lebensm. 1932, 63, 30), however, the upper limit of 69° for the refractive index originally given by König (" Chem. d. nienschl. Nahr.-u. Genussin," 1910 (3) 1,420) and reproduced by Beythien and others is probably a misprint for 59°, a figure which is consistent with the iodine value and is also the one given in " Das Schweizerische Lebensinittelbuch," 1909 ed.).

Horse-fats contain about 24-33% of saturated acids, consisting of palmitic acid, with a small proportion (from 5-13%, on the whole fat) of stearic acid, oleic acid (50-55%) and linolic acid (about 10%) *(v.* Heiduschka and Steinruck, J. pr. Chem. 1921, [ii], **102,** 241; Grossfold, Z. Unters. Lebensm. 1931, 62, 553; Pritzker and Jungkunz, *I.e.).* The presence of 1-7% of linolenic acid in horse-fat was reported by Heiduschka and Steinruck (v. Klimont, Meisl and Mayer, Monatsh. 1914, 85, 1115) and rather more (about 4-5%) in the abdominal fat from the wild Western range horse (iodine value 82-7; Schuette, Garvin and Schwoegler, Jc Biol. Chem. 1934,**107,** 635) which appears to be more unsaturated than the fat of the ordinary domestic horse.

The identification of horse-fat may be of importance in the examination of meat products such as sausages, etc. According to Pritzker and Jungkunz, horse-fat may be differentiated from lard by the fractional precipitation method of Kreis and Roth (Z. Unters. Lebensm. 1913, 25, 81), and fractional crystallisation of the acids from alcohol is suggested by G. Wolff (Chim. et Ind. 1934, Spec. No. (13e Congr. de Chim. ind., Lille, 1933), 885S): detection of it in admixture with lard or tallow is, however, a very much more difficult matter. It is stated to be detectable by biological methods depending upon the differentiation of albumins from different sources *(cf.* Wittels andWelwart, Seifens.-Ztg. 1910, 37, 1014; Allen, " Commercial Organic Analysis," 5th ed., Vol. IX, p. 244; "Schweizeriscl.es Lebensmittelbuch," 1917 ed.), but such methods would fail if all albuminous matter had been removed by refining. Paschke (Z. Unters. Lebensm. 1938,76,476) relies upon the detection of linolenic acid in mixtures containing horse-fat, and has described a delicate modification of the hexabromide test for this purpose. The identification of horse-fat in lard by means of its characteristic absorption spectum (max. at 310 m/z) is claimed by Dorta and Reggiani (Z. Unters. Lebensm. 1939, **77,** 449).

Horses' Crest-Fat (" adeps colli equini") which is prized in Switzerland as a remedy for baldness and is obtained from the crest on the back of the neck, has been studied by Pritzker and Jungkunz (Pharm. Acta Helv. 1931,6, 201). Its refractive index (52-5-54-5° Zeiss at 40°, *i.e.* w_D 1-4610-1-4623) and iodine value (75-84) are similar to those of horse-fat, but the content of unsaponifiable matter (0-13-0-19%) is distinctively lower than that of the body-fat (0-3-0-5%); the paler colour of the unsaponifiable matter derived from the crest-fat further serves to differentiate it from the body-fat. The body-fat gives orange-red colorations in the Bellier test, which is negative in the case of the crest-fat. Some 3-5% of paraffin wax or beeswax appears to be commonly added to the commercial crest-fat as a stiffener.

***Horse- (Bone-)Merrow Fat,* a non-drying fat of** iodine value 77-5-80-5 (Zink, Forschungsber. ii. Lebensm. 1896, 3, 441), and *horse-bone fat,* iodine value 89-6 *(v.* Schenk, Mitt. Lebensm. Hyg. 1918, 9, 215), are also obtainable from the horse.

Horse's Foot Oil is obtained from horses' feet by boiling them with water: samples examined by Lewlfowitsch (" Chemical Technology of Oils, Fats and Waxes," 6th ed., Vol. 2, p. 495) and Amthor and Zink had iodine values of 74 and 90 respectively. As a rule the oil is not met with in commerce under its own name, as the feet are usually boiled out together with cattle feet and sheep's feet and the resulting oil is sold indiscriminately as "neat's foot oil," or as " animal oil."

E. L.

HORSE-FLESH-ORE *(v.* Vol. II, *S2d).*

HORSE-RADISH. The fleshy root of *Cochlearta armoracia* L., a cruciferous plant native to eastern Europe. The sliced or grated root is used as a condiment. Its characteristic flavour is largely due to the presence of propyl and wobutyl wothiocyanates. Recorded analyses show the root to contain (%):

Water	738-76-7
Protean	2-7-3-4
Fat	0-3
N-free extract	16-9-18-3
Fibre	2-B-2-8
Ash	1-5-1-6

More recently **Frieae** (Z. Unters. Nahr.-u. Genussm. 192f>, 49, itH) gives the following data(%):

	Wdter.	Adi.
Whole root	72-07	**2-11**
Inner layer	**M-86**	1-79
Outer layer	7305	2-09

The **percentage** composition of the ash recorded by Frieze (I) and by Ktinig (II) is as follows:—

	O.	Na^O.	CiO.	MgO.	Fe_sO_3.	AI,O_9.
r.	1-34	11-00	**9*27**	2(i7	0 0 9	0-21
II.	8	4-0	8-2	2*0	**l-fl**	—

	Mn	**W**	SO_3.	SiO_4.	Cl.
I.	0 0 9	7-54	27 Ott	9-37	0-84
II.	—	7-8	308	12-7	0-9

According to Noetze) (Pharin. Zcntralk. 1935,36, 221) horse-radish '"juice" contains **1*5(1**-2·3% of dry matter, 0-3-0-5% **of** ash and **G-22-O-2B%** of mustard oil. The original roots (25-80% of **water)** contained 0-12-0-16% of mustard oil.

Peroxidase, present in horse-radish root, provided tho basis of Buck's early studies of this ensv me. Elliot and Keilin (Proc. Roy. Soc. 1934, B, **114,** 210) record an examination of horse-radish peroxidase in relation to ita bfematin content. No relation was apparent between the proportion of heematin and the activity of **tfie** enzyme. All tlie ha[1] matin occurs free in t lir-root as acid hsiuatiu.

Horse-radish is a good source of vitamin-C. According to Kedrov (Problems of Nutrition, **U.8.S.B.** 1934, 3, No. 5, 20) 20 g. of root dailj suffices to prevent scurvy in man if used as solo source of the vitamin. *

A. G. Po

HOWLITE(i>.Vol. I,58Grt).

HUCKLEBERRY. The fruit of ***Gaylus*** *eacia resinom* Torr. and Gray, a native of the western hemisphere. In the central*states o: America the name is also given to the swam] blueberry, *V actinium corymbomm.* T£e frui is eaten raw or cooked, and is frequently dric(or canned.

Tho following percentage composition of thi **true** huikl"lk.Try is recorded by Atwater nut **Bryant** *[U.8.* Dept. Agrio. Off, Exp. Sta. Bull 1900, No. 28): •

Water, 81-S); protein, 0-1}; fat,. OH; N-fre extract, 10G ; fibre, 16 G; ash, 0-3%.

A. G. Po

HULSITE. A black, opaque, orthorhombi (?) mineral originally described us n hydron **borate** of ferrous and ferric iron and magnesium but subsequently found to contain some- tin **(SnO,**, 7*07% in a sample with a consiclcrabl amount of insoluble gangue), **the formula beta gives** as

$12(Fe,Mg)O\cdot 2Fe_2O$, $SnO_2\cdot 3B_3O_a$-$2H_2O$.

Is occurs as small crystals and tabular masses in a metamorphic limestone, near* the contact of this rock with granite, at Brooks Mountain, Seward Peninsula, Alaska, and is associated with magnetite and tin-ore (A. Knopf and W. T. Schaller, Amer. J. **Sd.** 1908, [iv], 25, 323; 1910, [iv|T 29, 543).

L. J. S

HUME.ROTHERY'SRULE. In general,' when one metal is alloyed with another, the first addition of\ metal Y to a solvent metal X results in tho formation of a homogeneous alloy with the aaino crystal structure as the parent metal X, and which may bo called a *primary solid, solution* of Y in X, These primary solid solutions are of two kinds, namely, *siibstitut-ional solid solutions* in which the solute atoms.replace those of the solvent in ita lattice, and *interstitial solid solutions* in which the solute atoms occupy the holes or interstices between those of the solvent. The extent of these primary solid solutions varies from complete miscihility of the two metals in the solid state *[e.g.* copper--nickel, silver-gold) to a soluhility which if too small to l>e measured. When the concentration of soluto atoms exceeds that of the limit of the primary solid solution, a new phase makes its appearance. In **Borne systems** *(e.g.* copper-silver) the new phase is *a,* solid solution of X in f, and in such cases the alloys, according to their compositions, fall into one of three typos, **a** nil nary solid solution of Y in X, a primary solid solution of X in Y, and a mixture of the two jriinary solid solutions. In other systems intermediate phases are also formed, and these may je of fixed or variable composition., It is well tnown that, in the **gBoertd** <';tse, the compositions of many of these intermediate phases **are** difficult to reconcile with the ordinary valencies of the elements, and it was first pointed out by Hume-Rothery [1] in 192(5 that this is only to be ' expected when a truly metallic **compound is** formed. The valency compounds of ordinary chemistry are the result of tho valency electrons being bound into stable groups (usually octotal, and if metallic properties are regarded aB resulting from tho presence of free electrons, *n.* **metallic** compound will not bo expected to follow the usual valency relations. In searching for an alternative explanation of the compositions of the intermediate phases in, alloy syatemB, Hume-Rothery was guided by the Electron Lattice Theory of Lindemann * which was attracting attention at the time. This theory has been discarded, but it led to the hypothesis that certain intermediate phases in alloy systems might be characterined by definite ratios of valency **ekc-**tiona to atoms, and this has been confirmed for a number of systems. •

The first kind of alloy considered was that of the a/0 brass type, and Fig. 1 shows the equilibrium diagram of the system copper-zinc. Here the primary or a-solid solution of zinc in ro|>per is followed by a 0-phasc which has a **body-**centre<*eubic structure, in contrast with the fara-. ccntred cubic structure of copper **itself** Thu composition of the-jS-phaso is in the region **of the** equiatomic composition **CuZn,** although **then** is a wide range of Bolid solubility. The next phase, denoted *y,* is in the region of 62 atomic per cent, zinc, and has a characteristic crystal structure, and this in its turn is followed by the «-phase with a close-packed hexagonal structure, and a composition extending from about 78 to 81 atomic per cent, zinc, *i.e.* to the zinc-rich, side of the composition 75 atomic per cent, zinc which would correspond with the formula CuZn$_3$.

Fig. 2 shows the equilibrium diagram of the system copper-aluminium, and this clearly haa a general resemblance to that of the system copper-zinc. The 0-phase in the system copper-aluminium haa a body-centred cubic structure, and ita composition is in the region of Cu$_3$AI. The equilibrium diagram of the system copper-tin has some of the same characteristics, and here the composition of the 0-phase is in the region of Cu$_s$Sn. It was pointed out by Hume-Rothery that, if the elements were given their normal valencies Cu I, Zn 2, Al 3 and Sn 4, the compositions CuZn, Cu$_3$AI and Cu$_s$Sn all corresponded with a ratio of 3 valency electrons to 2 atoms. Other examples were quoted, and

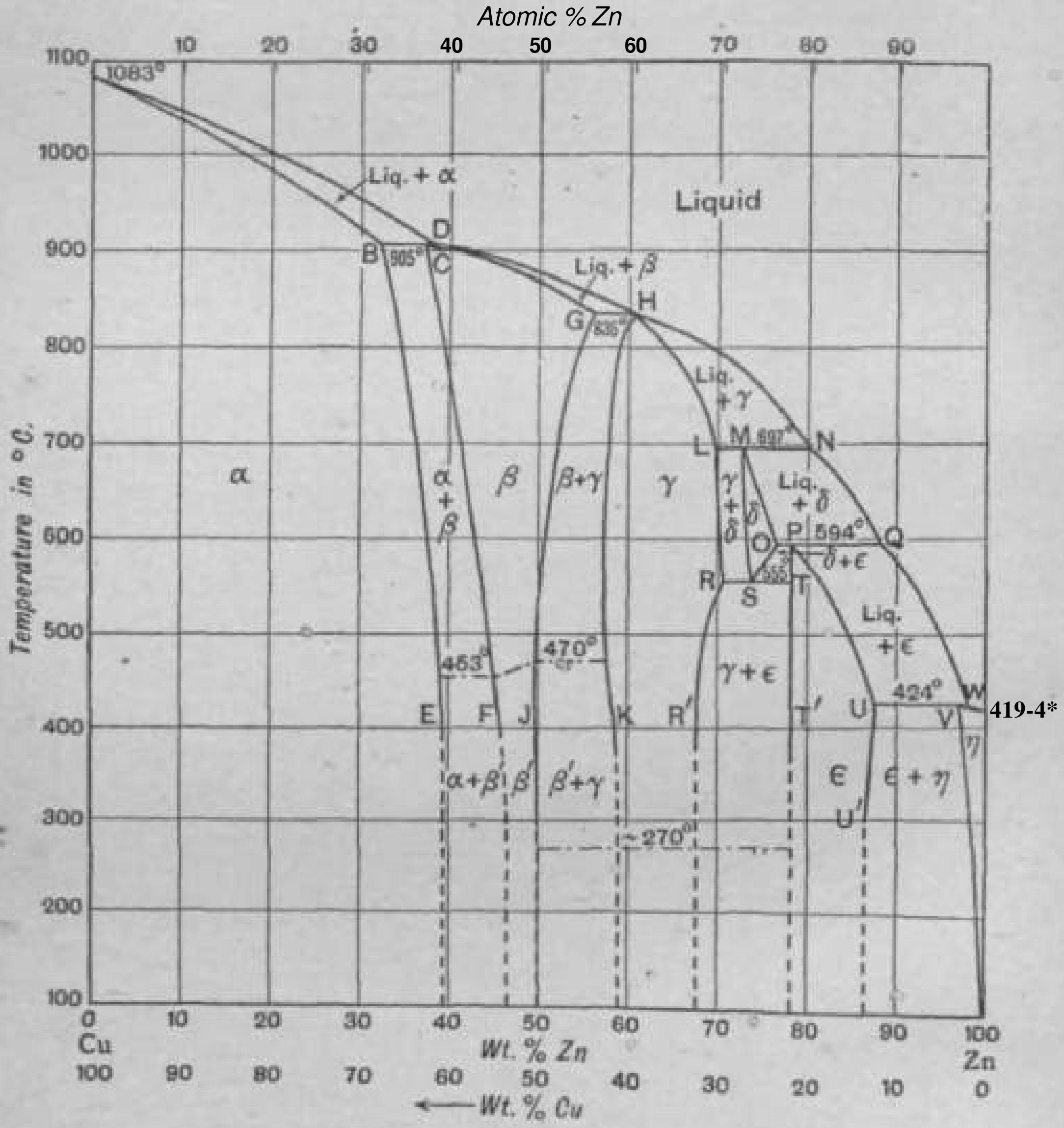


FIG. 1.

he idea was takt.i up by Westgren and his collaborators,[3] As a result of this and later work it was shown that in a number of alloys of copper, silver and gold with the elements of the B-sub' grc ups, and with Be, Mg, Al and Si there was a general tendency for body-centred cubic st natures to occur at a valency eleetnfii/atom ratio of 3/2, whilst y-brass structures were found at an electron/atom ratio of 21/13, and close-packed hexagonal structures at an electron/atom ratio of 7/4. These phases may conveniently be called electron compounds. The work of Bradley and Gregory • showed that terna'ry electron compounds could be prepared, the type of crystal structure remaining the same when the prOfwrtions of the atoms were adjusted so that the electron concentration (i.e. the ratio of valency electrons to atoms) had the value characteristic of the structure concerned. This conception was carried further by the work of Ekiimn [B] and others, who showed that the same principle was followed in some alloys of the B-sub-group metals with elements of Group VUI. provided that the latter were assumed to possess a zero valency. Thus in the system iron-zinc, a phase with the y-brass structure was found to occur at a composition corresponding to the formula Fe_5Zn_{21}. Here, if the iron is assumed to possess zero valency, there are 42 valency electrons.to 26 atoms, which gives the characteristic ratio 21:13 found in Cu_6Zn_8 and **Cu,AI$_4$.**

The above relations were discovered empirically, and clearly suggested that in this class of alloy the electron concentration was sometimes the predominant factor in determining the type of structure, although in .other cases it was clear that the effect of electron concentration was outweighed by other factors. Of these the most important factor is the relative size of the different atoms, and, speaking generally, electron compounds are only formed in cases where the atomic diameters of the two elements do not differ too widely, the limiting difference being of the order of 25%. In cases where the two metals differ widely in electrochemical properties there is a tendency for electron compounds to disappear, and to be replaced by compounds which begin to resemble those of a normal valency type.

In Fig. 1 it will be seen that the a/a-f/} and *a+fljfl* phase boundaries have a characteristic shape showing that the solubility of zinc in copper diminishes at high temperatures. It has been shown empirically by Hume-Rothery and collaborators • that this kind of phase boundary js controlled largely by the electron concentration, although the effects are modified by the relative sizes of the atoms in the alloy systems concerned, and these effects have been studied in detail by Hume-Hothery and Andrews.[7] From the empirical point of view, therefore, the position may be summarised by saying that in this class of alloy there are many cases in which both the type of structure and the form of the phase boundaries are determined largely by the electron concentration, although this simple principle is often obscured by the effect of other factors such as the relative sizes or electrochemical characteristics of the atoms concerned.

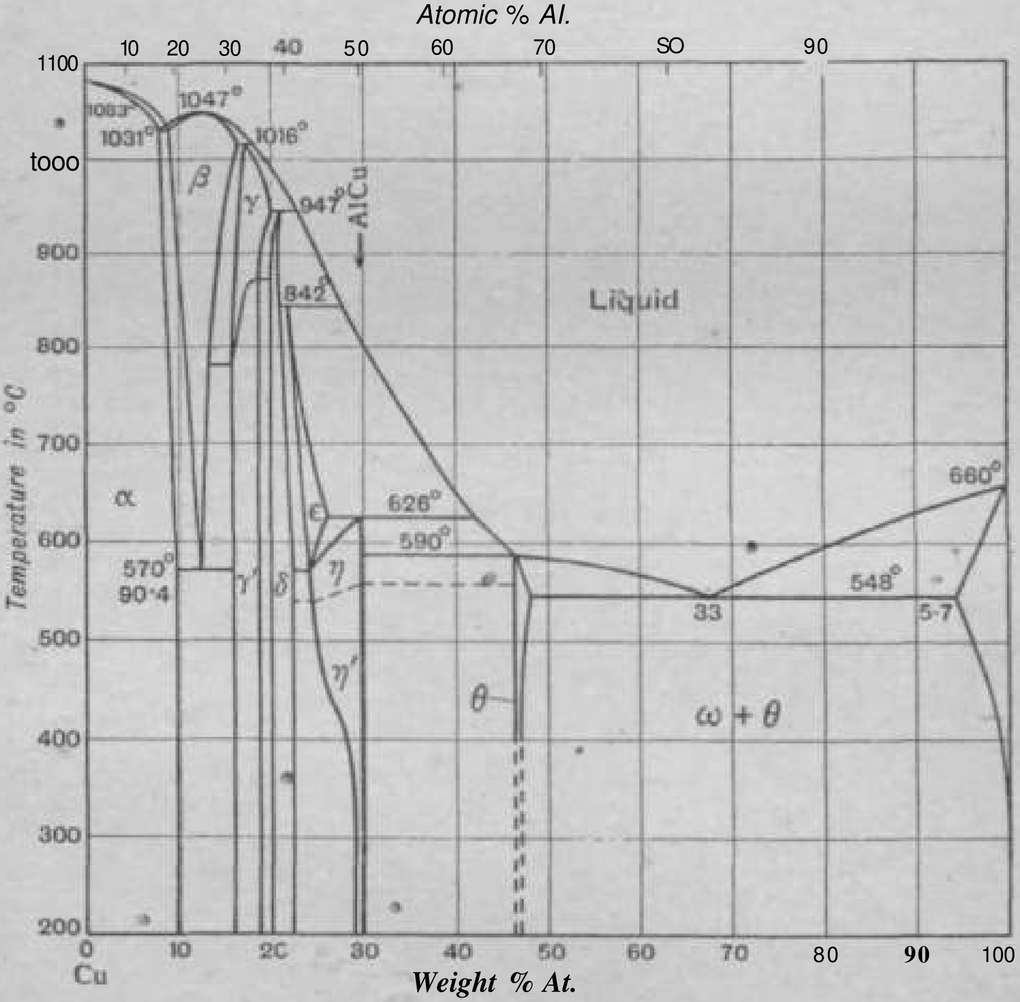


Fig. 2.

These empirical relations received remarkable support from the theoretical work of Mott and Jones[a] on the modern electron theories of metals, •especially as regards the theories of lirilluuin zones {Brillouin, " Quantenstatistik," Ikrliii, 1931), Jones* was able to show that for the y-brass structures the electron concentration was nearly that required to fill the first Brillouin zone. Although in other cases the explanation was more complicated, the electron theory clearly supported the view that electron concentration was sometimes the predominant factor in determining the type of crystal structure or the form of phase boundaries, and Jones even developed a theory of the a/0 brass equilibrium in reasonable agreement with the facts. The work of Jones suggests that whilst the electron concentration is often the important factor, there is no reason why this should correspond with simple whole number ratios of atoms; In the above description reference has been made to formulae such as CuZn, Cu_3Al, etc., in order to illustrate the principle in a simple way, but it must not be imagined that these exact ratios have any particular significance, or that any definite molecular species exist with these compositions. The important fact is that in the different systems, phases of the same structure tend to occur at roughly the same electron concentration.

Recent work by Lipson[10] has extended the principle to defect lattices. These are structures in which variation in composition takes place not by a process of substitution of one atom for another, but by one kind of atom dropping out of the lattice. In such cases it has been shown that characteristic changes occur at compositions such that the number of electrons per unit cell remains constant, and this is in agreement with the expectations of the electron theory. In normal structures with no defects, a constant number of electrons per unit cell is equivalent to a constant number of electrons per atom, or a constant electron concentration, but in defect lattices the number of electrons per unit cell is the fundamental characteristic.

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W. H.-R.

HUMIC ACID. The term applied from time to time to various acidic constituents of the black, spongy, semi-colloidal matter (humus) present in soils, peat, etc., resulting from the chemical and microbiological decomposition of plant and animal residues. Typical samples of humic acid are prepared by extracting soil or peat with very dilute alkali (concentrated alkali causes decomposition) and precipitating the brownish-black humic acid with dilute mineral acids. Numerous systems of purification or further fractionation have been adopted by different investigators. An average analysis of humic acid is C 61-9, H 4-2, N 3-3, O 30-6%.

Much discussion has centred round the nitrogen content of humic acid. Artificial humic acids, closely resembling the natural product, may be prepared by heating sugars with mineral acids. This suggests that the humic acid does not contain nitrogen as an essential constituent. The nitrogen invariably present in natural preparations has been regarded as ammoniacal nitrogen in ammonium humate. Not all this nitrogen, however, can be removed by customary methods for decomposing ammonium salts.

Preparations still more closely resembling natural humic acid are obtained by heating sugars with amino-acids under conditions favouring the production of hydroxymethylfurfuraldehyde. The latter substance on exposure to air is shown to be polymerised in the course of some months, to yield a black substance, possessing the general properties of humic acid.

Attempts to prepare artificial humic acid have been numerous, but although there is a general similarity in the nature of the synthetic products, it cannot be established that any individual substance has been isolated. Nor can it be proved that any of the synthetic preparations is identical with the natural substance. Moreover, humic acid preparations from soil or peat vary considerably in their composition and properties according to the process of isolation adopted, and have not yet afforded proof that natural humic acid exists as a chemical entity. Many modern workers favour the view that the numerous preparations of natural humic acid consist of varied mixtures of substances similar in character but not chemically identical. Indeed Waksman, " Humus," Bailliere, Tindall and Cox, 1938, suggests that to avoid misconception the term " humic" acid should be abandoned altogether.

A. G. Po.

HUMIDITY AND HUMIDITY CONTROL. ***Introduction.—Humidity*** **is a general** term applicable to the water vapour content of any gas. It is rarely used for gases other than air, and this restricted meaning is used throughout this article, but the application of the statements to other gases will be obvious.

There are three general methods of stating the humidity of air. The most fundamental is the *absolute humidity* which is the mass of water per unit volume of air, and is usually expressed in terms of grams per cubic metre or grains per cubic foot. The absolute humidity at any temperature can be increased by adding water until the air becomes saturated, at which point it is in equilibrium with liquid water at the same temperature. (It is true that in the absence of nuclei such as dust particles or ions a supersaturated state may be obtained, but this is an unstable condition.) Humidity may also be quantitatively stated as the *vapour pressure* of water present in the air, but this is the least used of any methods of defining humidity, probably owing to the difficulty of measuring water vapour pressure in air by any simple direct method. Since water vapour obeys Boyle's law with considerable accuracy, the vapour pressure is proportional to the absolute humidity.

A much more useful measure is the *relative humidity* or *percentage saturation,* which is defined as the active absolute humidity expressed as a percentage of the maximum or saturation humidity at the same temperature. An alternative definition based on vapour pressures can be used and the difference between the two results is negligible in practice. Relative humidity is much more important than absolute humidity because it is closely related to the equilibrium moisture content of hygroscopic substances regardless of temperature changes, and has very direct application to such practical problems as drying. It should be noted that since the saturation absolute humidity and the vapour pressure of water increase with temperature, the relative humidity of a given quantity of air can be lowered by heating and raised by cooling, although no water is added or taken from the air.

Although humidity may be stated in these three ways it is always possible to relate one to the other if the temperature is known. Tables of saturation absolute humidity and of vapour pressure at various temperatures are available and therefore all measurements of humidity can be expressed in the way most convenient to the purpose in hand.

Measurement of Humidity.—*Absorption Method.*—The most fundamental method of measuring humidity is by absorption. A known volume of air is drawn over substances which completely remove the water (*e.g.* phosphorus pentoxide or silica gel). The mass of water absorbed can then be determined by weighing. This method is, however, cumbersome and slow and is little used in practice except for basic calibration purposes.

Wet and Dry Bulb Hygrometers.—The most usual method is to make use of the wet and dry bulb hygrometer, which consists of two mercury-in-glass thermometers, one of which has its bulb covered with muslin provided with a wick dipping into a water reservoir in order to keep it wet. Water then evaporates off the muslin at a rate depending on the relative humidity of the air, and the absorption of latent heat causes this thermometer to indicate a lower temperature (the wet bulb temperature) than the other which gives the dry bulb temperature. The difference of the readings is known as the bulb difference and from this the relative humidity is determined by reference to tables.

It is essential that the muslin and wick should be clean and be renewed frequently, and that the water should be pure. It is possible to use a wet and dry bulb instrument when the covering of the wet bulb is frozen but care must be taken when the film of ice is thin. Detailed instructions for such measurement will be found in the "Observer's Handbook "issued by the Meteorological Office in Great Britain, or similar publications in other countries.

The tables generally used in Great Britain for this type of hygrometer are " Hygrometrical Tables adapted to the use of the Dry- and Wet-Bulb Thermometer," by James Glaisher (4th ed., Taylor and Francis, London, 1866). To avoid the trouble of using tables, nomograms and various humidity-calculating devices have been produced and these are often a help in reducing observations to terms of relative humidity. The Meteorological Office issues a set of tables (M.O. 265) for use with wet and dry bulb thermometers exposed in Stevenson screens out of doors and these are intended for use in " light airs," whereas Glaisher's tables refer to the thermometers in still air. If still air were realised in practice, the sample of air which the hygrometer measured might not be the same as the rest of the space in which the observer was interested. If moving air be used it is found by experiment that for the same relative humidity the bulb difference increases with the velocity, but fortunately above a speed of 3 metres per sec. this increase is negligible. This fact forms the basis of two of the best types of wet and dry bulb hygrometer.

In the *sling* or *whirling psychrometer* two thermometers are fastened to a frame provided with a handle which enables them to be rotated, thus causing a stream of air to flow over the bulbs. This instrument is adopted as the standard for the measuring of humidity by the U.S. Weather Bureau, and detailed instructions for its use will be found in " Psychrometric Tables," published by the U.S. Government Printing Office, Washington. Briefly, these may be stated as follows: The bulb of one thermometer is covered with a wick and moistened, and the instrument whirled rapidly for 15-20 seconds, stopped and quickly read, the wet bulb having attention first. The whirling and reading are repeated until the wet bulb reaches its lowest temperature. While whirling the psychrometer the observer should walk to and fro thus obtaining a better average reading.

The other hygrometer employing moving air is called the *Assmann psychrometer* and is regarded as the best instrument of this type for standardisation purposes. A constant current of air is drawn by a fan driven by clockwork or by an electric motor over the bulbs of the two thermometers, one having the usual wet muslin cover. The bulbs are surrounded by highly polished metal shields so that the instrument is unaffected by radiant heat. The tables for use with it are practically identical with those of the whirling instrument, but the best tables are " Aspirations Psychrometer Tafeln " issued by the Prussian Meteorological Institute. These tables originally covered the range to 40°c. (104°F.), but this range has been extended by Awbery and Griffiths (Proc. Physical Soc. 1932, 44, 132) up to 100°c. (212°F.).

It is not necessary to use mercury-in-glass thermometers, and mercury-in-steel thermometers, electrical resistance thermometers, thermo-couples or even bi-metallic temperature indicators are used in cases where the extra cost can be justified. With the mercury-in-steel thermometers it is possible to obtain enough power for a direct reading of relative humidity by means of a linkage system connecting the two indicating mechanisms to a pointer *(e.g.,* Bateson, J. Sci. Instr. 1932, 9, 94). With these variations from the usual mercury-in-glass thermometers records can be obtained and these are often of great value in industrial applications of humidity.

Hygroscopic Methods.—Other methods of measuring humidity depend on the change of length of hygroscopic substances when in equilibrium with atmospheres of different relative humidities. The most commonly used substances are hair, gold-beaters* skin, animal or vegetable membranes or textile fibres. Temperature changes of normal magnitude have little effect on these materials, and when cleaned from grease they can therefore be used for indicating and recording instruments calibrated directly in relative humidity. Unfortunately, the accuracy of such instruments is not great owing to lag and to changes of reading after they have been subjected to high or low humidities. It has been shown (D.S.I.R. Food Investigation Special Report No. 8, 1933) that gold-beaters[1] skin has the smallest lag and that horsehair maintains its calibration better than other substances. Incases where extreme accuracy is not necessary such instruments are very useful as they can be read directly; but they should be checked at intervals against a standard hygrometer.

Dew Point Method.—When air is cooled the relative humidity increases until the air becomes saturated. At this point (the dew point) water will be deposited as dew and this forms the basis of an accurate method of measurement. In order to detect the formation of dew a highly polished silver thimble is used and arrangements are made for cooling it, for instance, by the evaporation of ether. The temperature of the surface when the dew forms is best determined by means of a thermo-couple attached to the thimble. This method is not suitable for general use but forms an excellent. means of calibrating empirical hygrometers. Full details of refinements obtaining high accuracy will be found in D.S.I.R. Food Investigation Special Report No. 8, 1933.

Other Methods.-Many other ways of measuring humidity have been proposed from time to time but the only one which will be mentioned here is that based on the different thermal conductivities of humid and dry air. The method is therefore identical with ordinary methods of gas analysis by *katharomeRr* which were described originally by Shakespear and Daynes (Proc. Roy. Soc. 1920, A, 97, 273). It is a very accurate way of determining small amounts of water vapour in gases. (For further details, *see* H. A. Daynes, " Gas Analysis by Measurement of Thermal Conductivity," Cambridge University Press, 1933.)

Control of Humidity.—It will be clear from what has been said that the relative humidity in any enclosed space can be changed by heating or cooling the atmosphere, but there is usually a very severe limitation to what can be done in this direction and therefore control is effected by adding or taking water from the air. Air is saturated at room temperature when it contains about 1J% water by weight. The weight of water, therefore, required to change the humidity by 10%, which, is a normal amount, is only 0*15% of the weight of the air if there is no leakage of air or condensation of water. The amount of water needed is therefore in general small and in some cases very crude methods can be used.

Humidification.—To increase the humidity in a room it is often sufficient to sprinkle water on the floor with a watering can or to allow steam to blow into the air from jets. The latter method usually results, however, in the introduction of much heat and the humidity in some cases is lowered when the steam is turned on. A far better way of introducing water is by means of specially designed humidifiers which break up the water into very small drops in which condition it readily evaporates. The absorption of heat in this process is often a great help in increasing the relative humidity in factories where machinery is giving off heat. The water may either be sprayed into the air, being atomised by compressed air, or the spraying may occur in an enclosure, through which air flows, and in its passage is consequently humidified and washed. A third type combines the function of a humidifier and ventilating plant, since air is humidified at some central point and distributed to various parts of the room or building by a trunking system. The relative advantages of these three types of plant depend greatly on the local conditions and cannot be discussed in detail here.

Dehumidification. — Interest in humidities lower than those normally occurring is generally the reason for installing a drying process. If it is allowable to heat the air this is clearly the easiest way of obtaining the necessary low humidity and is the general practice in drying methods. If heating is not allowable it is necessary to absorb the water from the air. When relatively small volumes of air are to be handled, fused calcium chloride is a very useful substance as it is cheap and the solution produced when water is absorbed is easily carried away by a drain. It has been found very useful in dehumidifying small laboratories and testing rooms. Sulphuric acid has been considered for the same purpose but has usually been rejected because of corrosion difficulties.

It is often preferred to use an adsorbent substance which can be regenerated. Silica gel, which is the best known example of this type, is pure silica manufactured in such a way as to have a porous structure which makes it capable of adsorbing up to 40% of its own weight of water without appearing wet or increasing in volume. When saturated it is heated and the water is given off, allowing the substance to be used repeatedly (*v.* Vol. I, p. 1506). In practice it is arranged that three or four units are available, one being in use while he others are being regenerated or cooled. The change-over between the units can be effected at definite intervals by automatic means if desirable. A full description of such plant by Lees will be found in Engineering, 1932, 184, 458. Alumina has been put forward as an alternative to silica gel and is used in very much the same way (Engineering, 1941, 152, 406).

Air-Conditioning Plants.—The plants which have been described above are designed to correct humidity by the direct addition or removal of water vapour, little regard being paid to temperature. The object of an air-conditioning plant is to deliver at every point in the region served air which has been washed free from dust, at the desired temperature and humidity and with the correct air movement. The basic principle of such plants is that air is saturated with water at such a temperature that when it is heated to room temperature it will have the correct relative humidity. This may be a process of humidification or dehumidification according to circumstances, and air may also be heated or cooled during the process. The air is saturated by passing it through a very dense spray of water in a large chamber. Baffle plates remove any water drops and the air then passes through a heating chamber to give it the correct temperature. After this a fan delivers it to the distribution system. Details of the construction of such plants will be found in Moyer and Fittz, " Air Conditioning," McGraw Hill Book Co., New York, 1938. The control of these plants may be effected in many ways. The simplest of them is to use two thermostats which control the temperature of the spray-water and of the air as it leaves the plant.

When air is saturated in the manner described it is brought to a temperature known as the " temperature of adiabatic saturation " which, as pointed out by Carrier (Trans. Amer. Soc. Mech. Eng. 1911, 33, 1005), is the same as the wet bulb temperature obtained in a ventilated wet and dry bulb hygrometer. The connection between the two cannot be explained on a theoretical basis, but the agreement in most cases is so close, that the adiabatic saturation temperature is often spoken of as the wet bulb temperature.

When very low humidities are required with an air-conditioning plant it is necessary to cool the spray-water by a refrigerating plant or by some method such as rapid evaporation in a vacuum.

Automatic Humidity Controls.—The best results with a humidifying or dehumidifying plant can only be obtained with automatic control. An instrument for this purpose is essentially a hygrometer, fitted with some device to start the plant when the humidity departs from the desired value. The commonest form of control or " hygrostat" makes use of the change of length of hairs, textile threads or goldbeaters' skin. This type usually behaves very well as it is not subjected to large changes of humidity if the plant is kept running continuously. Another type is based on the wet and dry bulb hygrometer, which, if it works on a true humidity basis, is complicated because the readings of two thermometers have to be subtracted and then corrected for temperature. This can be avoided by using a wet and dry bulb thermostat, but a small error in either instrument may then cause a considerable error in humidity.

The transmission of the indication of the hygrometer to the plant being controlled can be carried out electrically or by compressed air. The electrical method of transmission appears to be the simplest, but chattering of contacts often causes trouble with relays and this problem has to be given special consideration. With the compressed air method the sensitive element opens and closes a small leak in a system which is supplied through a smaller orifice, and consequently the presence or absence of the leak causes a large change of pressure which is employed in operating diaphragm valves or dampers. Space does not allow mention to be made of the many ingenious applications of these principles under practical working conditions *(see Bibliography).*

Humidity Control in Experimental Work.—In any research or testing work with hygroscopic substances it may be necessary to control the humidity under which the work is carried out. If all the necessary operations can be carried out in an air-tight box it is often very simple to control the humidity by means of a large tray of saturated salt solution in the enclosure. This has a definite vapour pressure and therefore at a given temperature a fixed relative humidity. Tables of values will be found in " International Critical Tables " (Vol. I, p. 67). Sodium chloride may be specially mentioned, since its solubility changes little with temperature and therefore over a range of temperature it gives a relative humidity of approximately 73-75%. Sulphuric acid and glycerin solutions have been used for a similar purpose, but as they absorb or lose water their strength is changed and therefore the humidity is not constant as in the case of saturated salt solutions. Tables relating to sulphuric acid were given by Wilson (J. Ind. Eng. Chem. 1921, 13, 326).

Where it is impossible to work in a small enclosure it is necessary to humidify the whole of the room. As accurate humidity control can only be effected when the temperature is also controlled, it is advisable to choose a room the temperature of which can be maintained constant. It should therefore have few or no windows and if possible an air-lock at its entrance. The humidity can be lowered by fans drawing air through a tower containing calcium chloride and raised by passing it through a similar tower containing wet pumice or coke. The fans can be controlled by any suitable type of electrical humidity control operating through relays.

Industrial Importance of Humidity.—In the Application of scientific principles to industry, humidity is assuming an ever increasing importance. This is obvious in connection with all problems relating to drying processes but there is also a much wider scope. When industrial materials are reviewed it is found that a very large proportion are hygroscopic in character. A close investigation of their working properties shows that weather often has profound effects even in a building where the temperature is maintained approximately constant. These effects are therefore due to the changes of humidity and it is often economically sound to change the humidity artificially to ensure the best working conditions.

The behaviour of hygroscopic materials is to a large extent bound up with the formation of electrostatic charges. At high humidities the rate of leakage of these charges is so great that they are not detectable, but at low humidities they may become so marked as to exert considerable forces on the material being worked. Thus, in the textile trades threads and fabrics under dry conditions are often distorted from their normal paths through machines and become attached to any neighbouring earthed conductor with a resultant breakdown of the working. Another effect of these electrostatic charges is that dust or other small particles are often thrown off into the air causing discomfort and contamination. This effect is enormously reduced by the increase of humidity. Further, electrification may become so serious in some cases that sparks occur and in the presence of inflammable fibres the risk of fire is very considerable. Humidification has been used to reduce such risks.

Low humidities are of great value in works producing cables, transformers and other electrical apparatus in which the insulation must be kept in a very dry state.

Humidity and Human Comfort.—While the full consideration of this subject is outside the scope of this article, it should be noted that humidity is a large factor in the comfort conditions of an atmosphere especially in hot climates, the other factors being temperature and air movement. In Great Britain this subject has not therefore received as much attention as in America. The plants for giving comfortable conditions in large buildings are usually of the air-conditioning type fitted with refrigerators. The design of these plants is based on the results of much research work and excellent results are obtained.

Various instruments have been designed for measurement of comfort conditions, the best known of which is the *katathermometer* designed by Sir Leonard Hill. This is essentially an alcohol thermometer with a large bulb. The time for the temperature to drop from 100°F. to 95°F. is measured. From this a " cooling power " is determined and this has been related by much experimental work to comfort conditions. Another instrument is the *eupatheoscope* which is a black-painted copper cylinder 22 in. high by 7J in. in diameter heated to 75°F., the loss of heat from this being recorded and scaled in figures of " equivalent temperature." For a full description, *see* D.S.I.R Building Research Board Technical Paper, 1932, No. 13 (H.M. Stationery Office).

Bibliography.—The subject matter of this article is treated in a much fuller way, especially from the practical and industrial standpoints, in M. C. Marsh, "Controlled Humidity in Industry, C. Griffin, London, 1935. Air-conditioning plants have been largely used in America and there is now considerable literature on this subject: *see* A. M. Green, Jr., " Principles of Heating, Ventilating and Air Conditioning," Wiley, 1936; W. H. Scverns, " Heating, Ventilating and Air Conditioning Fundamentals," Wiley, 1937; C. A. Fuller, " Air Conditioning," Pitman, 1938; R. E. Holmes, "Air Conditioning in Summer and Winter," McGraw Hill Book Co., 1938; J. A. Moyer and R. U. Fit-tz, " Air Conditioning," McGraw Hill Book Co., 1938; J. R. Allen and J. H. Walker, " Heating and Air Conditioning," McGraw Hill Book Co., 1939; W. H. Stangle, " An Air Conditioning Prinw," McGraw Hill Book Co., 1940. Reference should also be made to the " Journal of the Institution of Heating and Ventilating Engineers," London, and the " Transactions of the American Association of Heating and Ventilating Engineers," New York, also to two American periodicals, " Heating, Piping and Air Conditioning " and " The Aerologist."

M. C. M.

HUMULENE (P. Vol. II, 92<i, 408</).

HUMULON (v. Vol. II, 92a).

HUNGARIAN TURPENTINE is the oleoresin obtained from *Pinus pumilio* Haenkc.

HUTCHINSONITE. Sulpharsenite of thallium, lead, silver and copper,

$$(Tl,Ag,Cu)_2S\text{-}As_2S_3 + PbS\text{-}As_2S_3,$$

crystallised in the orthorhombic system, and one of the few minerals that contain thallium (18-25%) as an essential constituent. It is of rare occurrence as minute, red, transparent crystals in the white, crystalline dolomite of the Binncnthal in Switzerland.

L. J. S.

HYACINTH or **JACINTH.** A name loosely applied to several kinds of gem-stones of a yellowish-red or red shade, but more usually to *zircon* (native zirconium silicate, $ZrSiO_4$). Other stones of similar colour to which the name is sometimes applied include: ferruginous quartz from Santiago de Conipostella in the north of Spain (Conipostella hyacinth); hessonite (*v.* GARNET) ; brown iodocrase or vesuvianite from Vesuvius t yellowish-red spinel from Minos Novas, Brazil; topaz from Brazil; and reddish-brown corundum (Oriental hyacinth). The *vaKivOos* or *hyacinthus* of the ancients was, however, a blue or purple stone, probably corundum (sapphire), or perhaps amethyst.

L. J. S.

HYACINTH (Artificial). Practically all hyacinth perfumes are based on two important synthetics, the natural perfume being rarely used. These two synthetics are cu-bromostyrene, PhCH:CHBr, m.p. 7°, b.p. 2≥0° *d* 1-4220, *,, M>094; and phenylacetaldehyde, $PhCH_2\cdot CHO$, b.p. 205-207°, *d* 1·050-1·085, *n* 1-52U5-1-5345. The latter important modern synthetic perfume is necessary in all the more delicate perfumes of the hyacinth and narcissus types, for which bromostyrene is rather coarse ; but it is very apt to polymerise, and should be kept in dilute alcoholic solution.

E. J. P.

HYJENIC ACID ($C_{26}Hs_0O_t$?) has been stated to occur as a glycenue in the secretion of the anal glandular pouches of the striped hyivna (CariuH, Annalen, 1864, 129. 168); the acid, which was stated to melt at 77-78°, probably consisted of a mixture of homologous fatty acids with an even number of carbon atoms.

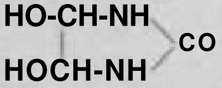
E. L.

HYALOPHANE («. Vol. I, 6316).

HYDANTOIN, gly colly lurea,

$$\mathrm{CO}<\begin{matrix}\mathrm{NHCH_f}\\ \mathrm{NH{-}CO}\end{matrix}$$

is found together with allantoin in the leaf buds of *Piuianus oriental*** (Linn.) (Schulze and Barbieri. Ber. 1881, **14,** 1834); in beet juice (p. Lippmann, *ibid.* 1890. 29, 2052); also in the pale sprouts growing from beets in moist warm weather* (Pauly and Sauter, *ibid.* 1930, 63 [B], 2063). It ia prepared (1) by reducing allantoin or aUoxanic acid with concentrated hydriodic acid at 100° (Bayer, Annalen, 1864. **130,** 168); (2) by the action of excess of alcoholic ammonia on bromoacetylurea at 100° (Baeyor, Ber. 187S, 8, 612); (3) by the condensation of sodium dihydroxytartrate and urea in the presence of hydrochloric acid at 50-60° (Anschiitz, Annalen, 1889, **254,** 258); (4) by the condensation of glyoxal and urea in the presence of hydrochloric acid (Siemonsen, *ibid.* 1904, **333,** 109); (5) from the compound:



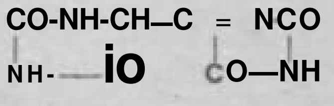
$$\begin{matrix}\mathrm{HO{-}CH{-}NH}\\ \mathrm{HOCH{-}NH}\end{matrix}>\mathrm{CO}$$

(which is formed from formaldehyde and urea in water) by heating with hydrochloric acid (['auly and Sauter; *I.e.);* (6) from anunoacetouitrile by the action of potassium cyanate (Biltz and Slotta, J. pr. Chem. 1926. [ii], **113,** 233); (7) from ethyl hydantoate by heating at 135° for 7 hours or bv warming with 25% hydrochloric acid (Harries and \Tfeiaa, Bor. 1900, 33, 3418), or by heating with alcoholic ammonia at 100° (Harries, Annalen, 1808, **361,** 69); the ethyl hydantoatc is prepared by the condensation of glycine ethyl ester hydrochlori.de with potassium cynnate (Harriet and Weiss, *l.c.)* or by tha interaction of glycine ester and sodium ethyl carhoiiate (Diela and HeintzeU Ber. 1905,38, **306).** It may be prepared from hippuric acid by converting it into 1 - benzoyl- - thiohydiintoin (formerly 3-benzoyl-) (Johnson and Nicolet, J. Araer. Chem. Soc. 11*11, 13, 1973) and then desulphurising this compound with an aqueous Hu'ution of chloroacetic add (Johnso'h and Bengis, ibid. 1913, **35,** 1005}- It it) obtained from glycine by treatment with potassium evanate and glacial acetic acid und evaporating the hydantoic acid so obtained to drynesis with hydrochloric acid (West, J. Biol. **Chem,** 1918, **34.** 188 ; Wagner and Simons, J. Chem. Education, 1936, 13, **265),;** and a yield of 90%_ is obtained by the condensation of glycine with nitrourea (Sah and Uu, A. 1937, 390).

Hydantoin crystallises in colourless needles, m.p. 216° (Schulze and Barbieri, Anschiitz, *U.c,};* 217-220° (Harries and Weiss, *U.);* its heat of combustion at constant volume iti.-f 312-4 kg.-cal., and heat of formation -f 109 kg.-cal. {MatignoQ, Ann. Chim. 1893, [vi], 28, 70). Its dissociation constant A^*_a is 7-59 x $10''^{10}$ (Wood, Phil. Trans. 1906, 1833); the dielectric coefficient -j~=6-4 (<=dielectric constant, c=concentration) (Devoto, Gazzetta, 1933, 63, 50). For the absorption of light by hydantoin, *set* Asahina, Bull. Chem. Soc. Japan, 1929, 4, 202. Irradiation with a quartz lamp causes opening of the ring since no ammonia is evolved but the amino-N (van Slyke) increases considerably (Lieben and Cctreuer, Biochem. Z. 1933, 259, 1). It is sparingly soluble in cold, readily in hot water, and the solution has a sweetish taste; it is soluble in 10 parts of boiling acetic acid. Hydantoin is not attacked by ammonia, hydrochloric acid or dilute nitric acid ; when boiled with baryta water it is converted into the barium salt of hydantoic at'id, the heat of combustion of which is 308-9 kg.-cat. and heat of formation + 1810 kg.-cal. (Matignon, I.e.), m.p. 179-180°. Heating with ammonium sulphide at 150-155° in a scaled tube or boiling for 120 houra with dilute ammonium sulphide gives glyciue (Hank* and Weiss, Annalen, 1903, **327,** 380; Bovd and Robson, Biochem. J. 1935, 29, 542). The*action of reductases from milk, blood, pancreas or liver extract causes cleavage with liberation of ureu (Wada, Proc. Imp. Acad. Tokyo. 1934, 10. 17). Iti its physiological action, hydantoin has a slight hyperglycffimic effect, counteracting to some extent the influence of insulin (Isshiki, Folia Pharmacol. Japan, 1932, **15,** No. 1, Breviaria 4).

Hydantoin formft *sodium* and *potassium sails* which are soluble in alcohol with difficulty and are hydrolysed by water (Bailey, J. Amor. Chem. Soc. 1906, 28, 392). The *silver derivative,* **$C_3H_aO_gNjAg,H_ap$,** is precipitated by silver nitrate from an ammoniaoal solution of hydantoin (Weiss, Annulcn, 1903, 327,375; *ef.* Buoyet, Annalen, **1864,** 130, 160).

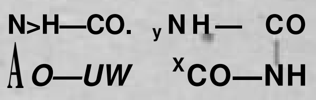
When equal weights of hydantoin and par£-bantc acid are heated at 150° for 1$ hours, 1:5 *deJi t/dro-5:5 '-dihydaniyl,*



$$\begin{matrix}\mathrm{CO{-}NH{-}CH{-}C} & = & \mathrm{NCO}\\ \mathrm{NH{-}{-}io} & & \mathrm{CO{-}NH}\end{matrix}$$

m.p. 178°. is formed; its sodium salt is yellow and crystallises from 20% sodium hydroxide with **$4H_2O$,** m.p. about 140°; reduction with hydriodic acid regenerates hydantoin (Biltz and Lachraann, J, pr. Chem. 1933, [ii], **136,** 217).

Spiro • 5; 5 • *dihydan loin,*



$$\begin{matrix}\mathrm{N{>}H{-}CO.} & {}_y\mathrm{NH{-}} & \mathrm{CO}\\ \mathrm{A\,O{-}UW} & {}^x\mathrm{CO{-}} & \mathrm{NH}\end{matrix}$$

prepared by boiling 5-amino-4-hydro.icy-4T5-dihydrouric acid with concentrated h'ydrochloric acid, it crystallises in stout rhotnbohedra which slowly blacken and decompose above 400°. It is remarkably stable towards acids, and is not attacked by alkaline permanganate; it is converted by hot concentrated aqueous barium hydroxide into altantoin. It is the parent substance of *kypocaffeinc (frimelhiff-spiro~5:!}-dihydanloin)* (Biltz and Heyn, Annalen, 1016,413,38).

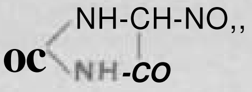
With 3:5-din]trobenzoic acid in alkaline solution, hydantoin gives a. purplish-rose colour {also given by many creatiniiie derivatives) which ciui be used for coloriraetric determination (Benedict and Behre, J. Biol. Chem. 1936, **114,** 515).

Substituted derivatives of hydantoin are referred to the ring,

$OC\langle^{NH\cdot CH_2}_{NH\cdot CO}$

With regard to the isomerisation of hydantoin, *see* Hahn and Seikel, J. Amer. Chem. Soc. 1938, 68, 647.

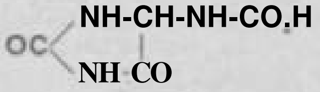
5-Nitrohydantoin,



$OC\langle^{NH-CH-NO_2}_{NH-CO}$

prepared by the action of nitric acid on hydtintoin, forms shining crystals, melting and decomposing at 170° (Franchimont and Klobbie, Rec. trav, ehim. 1888, 7, 12; Harries ant} Weiss, Annalen, 1903,327, 373).

5-Aminohydantoin hydrochloride, 5-Carboxyaminobydantoin *(hydroxonic add)* (I), obtained by the reduction of potassium allantoxanate (Ponomarev, Annalen, 1870, 226. 228, 461 ; *v.* Vol. I, 23tW) when hoiled with acetic anhydride yields l:3-di(i<'C-tyl-r>-ji(etvlatninohydantoin (II) which is hydrolysed by boiling with a methyl alcoholic solution of HCI to give the hydrochloride of 5-aminohyunntoin, m.p. **218"** 222D (III). The free base has not been isolated (Biltz and Gieslcr, Ber. 1913, 46, 3423; Biltz and Hanisch, J, pr. Chem. **1928,** [ii]. Hi, 140):



$OC\langle^{NH-CH-NH-CO_2H}_{NH-CO}$

I.

$OC\langle^{NAc-CH-NHAc}_{NAc-CO}$

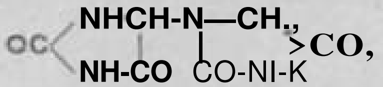
II.

$OC\langle^{NH-CH-NH_2,HCl}_{NH-CO}$

III.

t:3-Diacetylhydantofn, obtained by the action of acetic aghydride on hydantoin, has m.p, 104-105°, and yields ***1-acetyUtyiaiiioiii,*** m.p. 143-144°, when boiled with water, and this forms a sparingly soluble *had salt* (Harries and Weiss, Annalen, 1903, 327, 355; Siemonsen, I'MB. 1904,888. 101).

1;3-Dlchlorohydanto!n, obtained ip the form of lustrous crystalline leaves, m.p. 120-121°, by the action of chlorine on an aqueous solution of hydantoin, has the characteristic properties of a chloroimino compound (Harries and Weiss, *i.e.;* Siemonsen, i.e.; Biltz and Behrens, Ber. 1010, 43, 1984). Attempts to prepare bromine derivatives of hydantoin have been unsuccessful; by the action of J mol, of bromine, hydantoin is converted into *iaoaltiftiric arid,*

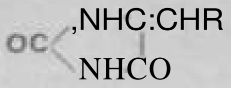


$OC\langle^{NHCH-N-CH_2}_{NH-CO\quad CO-NH}{>}CO,$

m.p. 258-260°; when a larger proportion of bromine is employed, parabanic acid (oxalylurea) ia formed, probably from an intermediate 5:5-dibromo-derivative.

Condemsationwith Aldehydes.—Hydantoin condenses with formaldehyde (1-3 mol.) in aqueous solution to form 1 - (or 3-) *hydroxymethyl-hydanioin.* m.p. 125-135°; this yields *cklaro-mrlhylkydantnin,* $CjH_5O_2N_2CI$, m.p. 150-157°, when treated with phosphorus pentaehloride or concentrated h3'drochloric acid. When hydantoin is warmed with formaldehyde in the [m'senee of acids, more complex products are **obtained** (Behrend nnd Niemeyer, Annalen, lfHMl,365,38).

Hydantoin condenses with aromatic aldehydes in the presence of glacial acetic acid and sodium acetate or in pyridiae solution in the presence of piperidine or diethylamine, to form compounds of the type (I), whieh on reduction, *e.g.* with ammonium sulphide in aqueous or alcoholic solution or with hydrogen sulphide in pyridine, yield the corresponding 5-aryI-sub**sntated** hydantoin (II),



$OC\langle^{NHC:CHR}_{NHCO}$

1.

$OC\langle^{NH-CH-CH_2R}_{NH-CO}$

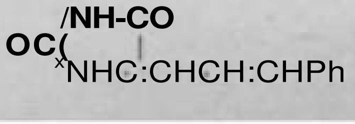
JI.

The following compounds have been described:

5-Fitnzalhydantoin, m.p. 220°; Johnson and Bates (J. Araer. Chem. Soc. 1015, 37, 383) record two isomeric modifications of *hen*zalhydantoin : the ordinary form *(cis),* m.p. 220°, and a *trans*-form, m.p. 246", which crystallines in aggregates of distorted needles (c/. Komatsu, Mem. ColL Sei. Eng. Kyoto, 1912, S, 13); for the absorption **spectra** of the two forms, *see* Hahn and Evans, J. Amer. Chem. Soc. 1928,60, 806; and Asahina, Boll. Chen. Soc. Japan, 1930, 5, 354.

5'Aniaalhtfdantoin, m.p. 243"-244° (decomp.) yields a *bro*wo-dciivative, m.p. **247";** and on reduction with hydriodic acid forms 6-p-*kydToxybenzylhydan'toin {ii/ra$inekt/dantoin),* m.p. 257-258°, from which tyrosine is oDtained by prolonged boiling with hydriodic acid. The tyrosinehydantoin, m.p. 275-280°, described by Blendermann (Bied. Zentr. 1883,209) ia probably an optically active isomeridc of this compound, •*p-Iiydroxybcnzalhydantoin* has m.p. 315° {Boyd and Robson, Biochem. J. 1035, 29, 542); *piperonalhydantoin,* m.p. 245°. For the methyl ethers and acetoxy-derivatives of 3':4'-dt-hydroxybenzalhydnntoin, *see* Deulofeu and Mendivclxim, Z. physiol. Chem. Ifl33,**219,** 233.

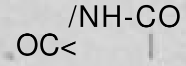
6-Cinna malftydantoin,



$OC\langle^{NH-CO}_{NHC:CHCH:CHPh}$

crystallises from hot glacial acetic acid in cluetere of canary-yellow needles **which** melt at 272-273° to a red oil (deeomp.) (Johnson and Wrenshall, J. Amor. Oliem. Hoc. **1916,** 37, 2133). *Ti-FumU hydantoin* has in.p. 232°; for the **absorption** spectrum, *see* Asahina, Bull. Chem. Soc. Japan, 1030, 5, 354.

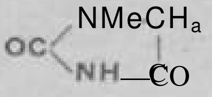
3': 5" - *Dichloro-i'-hydroxybenzaIhydantoin,*



$$OC<^{NH-CO}$$

m.p. 300°. *5-'P'Nitrobenzalhydantoin,* m.p. 254° (W^heelcr and Hoffman, Amer. Chem. J. 1911, 46, 368). *5-0-Nitrobenzalhydatitoin* has m.p. 278-280°; nitration gives l-nitro-5(o-nitrobenzal)-hydantoin, m.p. 224-226°; bromination in acetic acid gives the yellow l-bromo-5(o-nitrobenzal)-hydantoin, m.p. 247-248°; while chlorinaAion in acetic acid gives 1:3-dichloro-5-(o-nitrobenzal)-hydantoin, m.p. 180-182° (decomp.) (Kozak and Mutual, Bull. Acad. Polonaise, 1930, A, 432(.

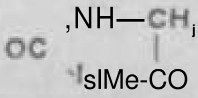
A Iky I and aryl substituted derivatives, 1 -*Jtfethylkydantoin,*



$$OC<^{NMeCH_a}_{NH-CO}$$

may be prepared (1) by fusing sarcosine and urea (Huppert, Ber. 1S73, 6, 1278; Horbaczewski, Monatsh. 1887, 8, 580); (2) by passing cyanogen chloride through fused sarcosine (Traubo, Ber. 1882, 15, 2111); (3) by heating hydrocaffuric add with baryta water (Fischer, Annalen, 1882, **215,** 286); (4) by reducing 3-methylallantoin with hydriodic acid {Fischer *id Ach, Ber. 1809, 32, 2748); (5) from methylhydantoic acid by long heating at 100-120* (Baumann and Hoppe-Seyler, *ibid.* 1874, 7, 37; Salkowski, *ibid. p.* 188); (0) from the urea obtained by the action of potassium cyanate on mcthylamingacetonitrile hydrochloride by treatment with hydrochloric acid (Biltz and Slotta, J. pr. Chem. 1926, [ii], 113, 233). It forma easily soluble prisms, m.p, 156°, from aqueous alcohol but sublimes in leaflets; the *silver* derivative, C^HjOaNjAg, forms difficultly soluble leaflets which become browx at 100°, It is considerably oxidised when administered stibcutaneously to dogs (Gaebler and Kelteh, J. Biol. Chem. 1926,70,**768).** When heated with methylparabanio acid, 1-methy Ihydantoin yields dimethyI-5:5'-bihydantylidene, m.p. 273° (Biltz and Lnehmann, *I.e.). l-Ethylhydantmn,* obtained by heating cquimolecular quantities of ethylglycine and urea at 120-125" ffieintz, Annalim, 1865,**133,** 65) or from N -cyan o methyl -N-ethylurea (Biltz and Slotta, *I.e.),* crystallises from alcohol and ether in rhombic plates, m.p. 103-104°, sublimes and is very easily soluble in alcohol and water, less so in ether; with diazomethane it gives \-*elhyl-1&-mvihylkydanloin,* ra.p. 93° (Siemonaen, Annalen, 1904, 333, H3).

3- *Alethylht/dantoiHf*



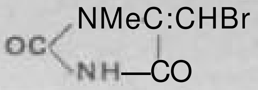
$$OC<^{NH-CH_j}_{NMe-CO}$$

obtained by methylating hydantoin by means of methyl iodide, potassium hydroxide and methanol at 100° (Franchimont and Klobbie, Rec. trav. chira. 1880, 8, 289 ; Siemonsen, *I.e.),* or with mothyl sulphate (BHtz and Slotta, *I.e.);* from methylurea and glycine (Guareschi, Chem. Zentr. 1892, I, 140); or by heating j3-methylallantoin with hydriodic acid on the water bath (Fischer and Ach, Ber. 1899, 32, 2746); it crystallises in prisms, m.p. 182° and is very easily soluble in alcohol and boiling water, with difficulty in ether. The l-nifro-derivutive has m.p, 168° (Franchimont atnl Klol>bio, *I.e.)* and the *l-acftyl*-derivative forms needles, m.p, 134-135° (Siemonsen, *I.e.).*

3-Etkylk-ydantain crystallises in leaflets from water, in prisms from alcohol, m.p. 103° (Bailey and Randolph, Ber. 1908, 41, 2498; Harries and Weiss, Annalen, 1903, 327, 378); nitration gives *X-nitroS-tthylkydantoin.*

1:3- *Dimeihylhydanioin* is formed by the action of diazo methane on 1-methylhydantoin; it has b.p. 174°/34 mm.

1:6- *Divielkylhydantoin* lias m.p. 161-162° (Pinner, Ber. 1888, 21, 2320) and yields \-*mtthyt-5 - bromomethylenehydanioin,*



$$OC<^{NMeC:CHBr}_{NH-CO}$$

m.p. 143-144°, by the action of bromine (Gabriel, Annalen, 190S, 348, 50).

l-Phenylhydn/itoin from N-phenylglveins and urea or from chloracetylurea and aniline crystal-**HMB** in needles, m.p. 191°; *^r^.itn potassium in alcohol it gives* tho potassium derivative, $C_eH_7O_2N_aK$, which decompose? at 370 378°, and is hydrolysed by water; bromination iti acetic acid leads to substitution in the **phtaiy]** group (*p*-position) (Breustedt, J. pr. Chem. 1902, [ii], 66, 254), *l-PJicnyl-Z-methylhydantom* melts at 185°; \.*pMn.yl-Z-ac£tylhydantoin* has m.p. 145-146° (Biltz and Slotta, *I.e.). l-p-'Joi.yl-hyd"avinin* has m.p. 210° (SCIIADIX:., Her. 187,7, 10,2045; 11,1128); *Z-v-Tolylhydanfoin,* from p-toly)urea and glycine, has m.p. 2%° (Quenda, Chem. Zentr. 1^02, I, 140); 3-ity/5:5-*dimethyl hi/ttantoi a,*

$$MeC.H.N-CO.\atop{CONH}>CMe_2$$

crystallises in thin prismatic plates, m.p. 172° (Bailey and McPherson, J. Biol. Chem. **1916,11,** 2526 ; Ber, **1908, 41,** 2497). *l-Amsyl-3-metkylhydanloin* has m.p. 194°; *l-anisyl-S-acetylhydantoin,* m.p. 172°.

Homologuesof hydantoin Sontainingoneor two substituents in position *5* arc most numerous and are prepared by the following general methods; (1) from the eyanhydrin of an aldehyde or ketone containing the group

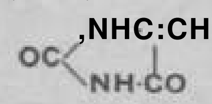
• -CO-CH,-

by the action of urea (Pinner, Ber. 1887, 20, 2351; 1888, 21, 2300; 18R0. 22, 685) or ammonium carbonate (Buchercr and Stetncr, J. pr. Chem. 1934, [ii], **140,** 291; Wagner and Simons, *l.e.).* Modifications of this method are due to Herbst and Jfohnson (J. Amer. Chem. Soc. 1932, 54, 2463) who prepared the aminonitrile from the carbonyl compound by the action of hydrocyanic acid and ammonia, converted this to the ureidonitrile with potassium cyanate and then cycliaed by warming with 20% hydrochloric acid. Bergs (G.P. 566094) and also Slotta, Behnisch and Szyszka (Ber. 1934, 67 [BJ, 1529) heat the carbonyl compound with a cyanide and ammonium carbonate under pressure of carbon dioxide. (2) By the action of dilute hydrochloric acid on the hydantoic acid obtained by evaporating to dry ness & solution of an a-amino-acid and potassium cyanate (Dakin, Amer. Chem. J. 1910, **44,** 48). This reaction is proposed for use in characterising and isolating amino-acids (Boyd, Biochem. J. 1933, 27, 1838). Alternatively, the amino-acid may react with urea and baryta water (Lippich, Ber. 1908, 41, 2953). (3) *By* reducing the compound obtained by the condensation of hydantoin with an aromatic aldehyde (Wheeler and Hoffmann, *I.e.;* Boyd and Robson, i.e.) and *(i)* from a substituted malondiamide by treatment; with hypochlorite, the intermediate chloroamide

RR'C(CONH,)CONHCl *{e.g.* R = n'=Et,

m.p. 135°) cyclising spontaneously in solution at room temperature (Rinkes, Rec. trav, chim. 1927, 48, 268). 6-Substituted hydantoins can show optical activity and may be obtained in active forms by resolution with bases, *e.g.* brucinc, or from optically active hydantoic acids or amino-acids by method (2) above (Sobotka, P.P. 736319; Sobotka, Holzman and Kahn, J. Amer. Cbem. Soc. 1932, 54, *397).

5'Methythy^nnloin (lactylurea), has m.p. 140° or 145=" (Heintz, Annalen, 1873,**169,** 125; Urech, Ber. 1873, 6, 1113) and on brotnination yields 5- *bromomethyUnekyda ntoin,*


$$OC\begin{array}{l}\diagup NHC{:}CHBr\\ \diagdown NH\text{-}CO\end{array}$$

m.p. 241-242° (Gabriel, Annalen, *l,c.)*; *5-rnetkyl-S -nitrohydan toin,*

.NHCMeNO.

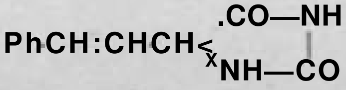
\NHCO

m.p. 148" (Franchimont and Klobbie, Rec. trav. chim. 1888, 7, 13), *5-Ethylkydantoin,* m.p. 117-118°, yields *S-brotnoethylidenehydanioin,* m.p. 230-236°, on bromination (Gabriel, I.e.); *5-propylhydantoin* has m.p. 136-5°; *&-isopropyl hydantoin,* m.p. 146° (Bergs, *I.e.)*; *5-isobutylhydantoin,* m.p. 209-210° (Pinner and Lif•chutz, Ber. 1887, 23, 2351), 212° (Lippich, *ibid.* **1908, 41,** 2953); *IS-isobutylhydantoin,* m.p. 212*, [a]g" -68-2° in normal Bodium hydroxide solution, becoming zero in 30 hours owing to the abiLty of thq ring carbonyl groups to enolise. *5-Phenylhydanioin,* ra.p. 178°; the 5-ocetyl-rlerivative has m.p. 145° (Pinner, *I.e.);* the 5-frfomo-derivative melts above 200°, and is decomposed by hot water yielding *5-hydroxy-5-phenylhydantoin* (Gabriel, Annalen, 1906, 350, 118), 1:3- *Dimethyl-S-hydroxy-S-phenylhydantoin* **has** m.p. 115-118° (Biltz and Billow,*I.e.). S-Mtlhyl-5-phenylhydarUoin* has m.p. 161-162° (Pinner, Ber. 1888, 21, 2320).

dl-5- *IJenzylhydantoih* was prepared by Wheeler and Hoffman (Amor. Chem. J. 1911, 45, 372) by heating benzalhy dan toin with phosphorus and hydriodic acid. It crystallises from alcohol in lancet-shaped crystals or in prisms, m.p. 194-195°. Dakin and Dudley (J. Biol, Chem. 1914, 17, 35) prepared d- and 1-5-benzylhydantoins by hydrolysis of *I-* and rf-jS-phenyl-a-ureidopropionic acids,

$$C_BH_6CH_a\text{-}CH(NHCONH_£)CO_aH;$$

d-5-benzylhydantoin has m.p. 181-183° and [al^ + 96-4° in 50% alcohol; it racemises completely on standing in alkaline solution at room temperature ; \-*5-benzylhydantoin* has m.p. 181-183°; on prolonged heating with concentrated acid it racemisea completely. *S-ji-NiUobtmylkydantoin* crystallises in pale yellow prisms, m.p. -38—240° (decomp.); *5-p-aminobemylhydantoin* **has m.p.** 145°; when diazotised and heated it yields tyroBinehydantoin (JohnBon and Brautlecht, J. Biol. Chem. 1912, 12, 187). *5-Anisylkydantoin* **has m.p. 188-189°;** *&-cinnamylh,ydantoin,*


$$PhCH{:}CHCH\begin{array}{l}\diagup CO\text{—}NH\\ \diagdown NH\text{—}CO\end{array}$$

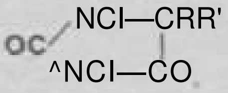
m.p. 171-172° (Pinner and Spilker, Ber. 1889, 22, 685).

ir.!i-*liimethylhytiantoin,,* formed from acetone cyanhydrin, has m.p. 175° (Urech, Annalen, 1872, **164,** 264; Errera. Gazzetta, 1896, 26, i, 210), the *1-nitro* derivative has m.p. 161-162°, the *l-acetyl* derivative m.p. 192°; ehlorinntion in'\;oid aqueous solution gives *l:3-dichloro-5:5-dimethylhydanloin,* while the action of diazomethane or methyl sulphate gives 3:5:5-(n"-*methylhydantoin. l;3:5:S-Tetramtlkiflhydantoin* obtained by methylation of the l:5:5-com pound, **has** m.p. 85°. *<il'5-Methyl-5-ethylkydantoin* has m.p. 149°; the optically active specimen prepared by Dakin (frj.) had m.p. 172-173° and ["I'D + 32°, this value remaining constant in alkaline solution. *5:5-Diethylhydantoin,* m.p. **166°;** *5:5-dipropylhydantoin,* m.p. 199" (Errera, *I.e.;* Biltz and Slotta, *I.e.;* Rinkes, *I.e.).* *5-Mdhyl5-phenythydantoin* has *ni.p. 197°; *6-ethyl-5-pkenythydantoin* (" *nirvanol* ") m.p. 197° and its spdium salt are hypnotics. it is tasteless but the sodium salt has a bitter taste (Wemecke, Deut. med. Woch. 1916, 42, 1193; Piotrowski, Ohem. Zentr. 1916, II, 1182; from Munch, mod Woch. 63, 1512; and Farbw. vorm. Meister, Lucius and BrUning, Swiss P. 72561); it has been resolved by means of brucincin absolute alcohol; *d-5.5-etkylphenylhyd<int<>in,* m.p. 237°, $[a]_D$ +123° (in alcohol), +169° (in alkali) j the *l-isomer* has m.p. 235-237°, [«],,• -121°= (alcohol), —167° (alkali) (Sobotka, Holzman ana Kahn, J. Amer. Chem. Soc. 1932, 54, 4697). *5-Pr vrropyt.5.pheTiylkydan(oin,* m.p. **170**° (Farbw. vorm Meister, Lucius and Briining, Swiss P. 741;

™*il°}⁹⁰)*⁵-methyl-i>-P-pl'enyte.tkylh!/daiitoin* m.p **180** , and *5-ethyI-5-p-phenyMht/lhydttntoin* also nave hypnotic properties. Fur the prepar«on of other soporifics of this group, «<

Chemise-he Fabrik von F. Heyden, G.P. 300508, 310426; .Swisa P. I7446L *5-Methyl-5-be.nzyl-kydanioin* hat m.p. 226°: *5:5-dibenrylkydanhin* ro.p, 305" (decomp.); *5'phenyl'5-benrylhydantain,* m.p. 210° (Slotta, Behniseh and Szyszka, *I.e.).*

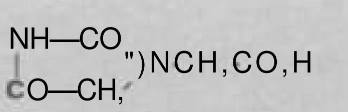
The action of sodium hypochlorite and free KvpochlorouH acid on 5:5-disubstituted hydan* toins yields the l:3-d»cA/wo-derivative,



Tk • compounds GUI be t:rvst;illiaed from t hloroform, but are decomposed by water, alcohol or hydriodic acid regenerating the original hydantoin (Biltz and Behrens, Ber. 1910, 43, 1984).

l:3-Dichloro!):5-diphenylhydantoin* has m.p. 164° (decomp.) and yields *\:3-dimethyt-5:5-diphe.iiylhydantoin* when treated with methyl sulphate.

11ydantoin-i-acetic acid,



The ethyl eater condenses with anisaldehyde giving *ethyl 5-auisalhydantoin-*1 *-acetate* which crystallises with 1 raol. of alcohol, m.p. 215-216°. Digestion of the ester with sodium methoxide and methyl iodide yields *ethyl Z-mztkylhydanUrin-I-acetate,* m.p. 91-92° (Renfrew and Johnson, J. Amer, Chem. Soc. 1929, 51, 1784). *6-Btmzylhydantoin-l-acetic acid* is a polypeptide , hydantoin derived from phenylalanineglyeine, has m.p. 184-185° and crystallises in flat prints or rhombic plates (Johnson and Bates, *ibid.* 1916,88, 1087).

Hydantoin-3-acetic acid, obtained by refluxing ureido-bismalonic eater

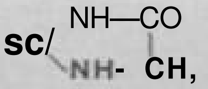
$$CO[NH\text{-}CH(CO_8Et)_a]_8$$

with 10% hydrochloric ac?d, has m.p, 196° (Cerchez, Bull. Soc. chim. 1931. [iv], 49, 52); *amide,* m.p. 225-226°; *anilide,* m.p. 215°; *methylamtde, m.p.* 223°, *bemylamide,* m.p. 209-210°. A number of esters of hydantoin-3-acetic acid have^becn described: *methyl,* m.p. 91°; *propyl,* m.p. 116°; *butyl,* m.p. 95"; sec-*butyl,* m.p. 142°; *iaobutyl,* m.p. 124°; *hoamyl,* m.p. 104"; *cydokexyl,* m.p. 184°; *pkenyl,* m.p, 205-206°; *benzyl,* m.p. 142°; *choUtteryl,* m.p. 304-300° (Locquin and Cerchez, Compt. rend. 1929. 188, 177; Cerchez, Bull. Soc. chim. 1931, [iv], 49, 600, 602; Locquin, Cerohv- and Pol.card, *ibid.* 595; Policard, *ibid.* 607). Hydrolysis of hydantoin -3-acetic acid given carbonylbisglycine (Wessely and Komra, Z. physiol. Chem. 1928, 174, 306).

Hydnntoin-5-acelic acid, m.p. 213—214°, U obtained together with its ureide,

m.p. 273-274°, by condensation of ethylmaleato or funoarate with urea in the presence of sodium and alcohol at 75° (Jensmanowska-Sicnkiewiczowa, Rocz. Chem, 1935. 15. 202, 510: Amer. Chem, Abstr. 1936, 30, 2025). *5-Mefkylliydantoin-5 acetic acid* has m.p. 214-215°. The *ethyl ester,* obtained by the method of Bergs from acetoacetic ester, has m.p. 138° and gives an *amide,* m.p. 252° (decomp.) and *hydrazide,* m.p. 104-105°; hydrolysis with potassium hydroxide yields homoaspartic acid, m.p. 233° (decomp.) (Pfeiffer and Heinrich, J. pr. Chem. 1936, [ii], **146,** 105). *Hydantoin~5-propionic acid* has m.p. 165°; *hydanloin-5-f}-bromopr&pi<mic acid,* m.p. 228-230°; *A'-hydantoin-^-propionic acid,* m.p, 222-223°; *hydantoin-5-fi-chloropropionic acid,* forms rectangular plates; *kydanloin-R-acrylic acid* m.p. 256-258° (Dakin, Biochem. J, 1919, 13, 398). For other derivatives of hydantoin *see* West, J. Biol. Chem. 1918, 34, 187.

Thiohydantoins.—*2-Tkivhydantoin.*



was obtained by Klason (Cheni.-Ztg. 1-S90. 14, Hep. 200). It may be obtained, quantitatively by hydrolysis with hydrochloric acid of 2-thio-l-acetylhydantoin or of 2-thio-l-ben7.oyUhydantoin (produced respectively by the action of potassium thitj cyan ate on glycine or on hippnrio acid in the presence of acetic anhydride). Optically active derivatives may be obtained from optically active a-aminoacids by treatment with acetic anhydride and ammonium thiocyanate; if the thiocyanate ia added after an interval, the thiohytlantoin is racemised (Csonka and Nicolet, J. Biol. Chem. 1932* 39, 2J3). It crystalheea in yellow prisms, m.p, 227-228* (decomp.). It is stable and yields stable eodium and potassium salts (Johnson and Nieolet, J. Amer. Chem. Soc. 1911, 33, 1973; 1913, 35, 780). 5-Methylthiohydantoin is a catalyst for the decomposition of sodium azide with iodine (Friedmann, J. pr. Chem. 1936, [ii}(**146,** 179). *2-Tkio-Z.p.tolylhydantoin,* m.p. 228°, is converted into *3-p-tolylkydantoin* on heating with an aqueous solution of chloroacetic acid (Johnson, Ffaw and Hodge, J, Amer, Chem. Soc. 1912,34, 1045). *2.Thio-5-o-hydro3ybenzyl-hydantoin,* m.p,)07°, is readily desulphurised in the same way, yielding *5-o-hydroxybenzyl-hydantoin.* *5:5~Dimethyl'3-o-tolyi-2tkiohydan-Coin,* m.p. 195-5% is prepared from o-tolyl mustard oil and potassium aminotjobutyrate (Bailey and McPherson, J, Amer. Chem. Soc. 1916, 38, 2525).

2-Thiohydantoin-H-propionic acid has m.p. **165**° (Johnson and Guest, Amer. Chem. J. 1912, 47, 242).

The benzal derivRflves of thiohydantoin are dyes for wool, silk and cotton, giving yellow, orange and red tints. *5-Bf.nzal-2-thiohytiayito^n,* microscopic needles, m.p. 259° (Johnson and NieoleUJ. Amer. Chem. Soc. 1912, 34. 1048; *ef. also* Ruhcmnnn and Staplctnn, J.C.S. 1900. 77, :M«); *acetyl* derivative, m.p. 260°. 5- *Vanillal-2*thiohydanloin,* m.p. 24l>\ *tliacetyl* derivative, m.p. 261°; *&cinnamal-2-thiohydantcnn,* m.p. 260°, *aceiyl* derivative, m.p. 267°; *b-phydrory-*

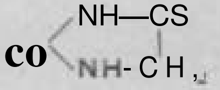
benzal-2-thiohydantoin, m.p. 305° (Boyd anc Hubson, Biochem. J. 1935, 29, 542; Namjoah and *Dutt, J.* Indian Chem. Soc, *1931, 8,* 241, Johnson and Brautlccht, J. Biol. Chem, **1812,** 12, **184);** *5.W-A'-di€Ketvxybtnzal)-*-ikioh.ydantotn,* m.p. 224-225°; *5-{3'-methoxy-i'-acetoxy. bemal)-2-thiohydanU>in,* ra.p. 246-247° (Deulofeu and Mendivelzua, Z, physiol. Cbem. 1933, 219, 233).

l-Acetyl-2-lhiohytlantoin crystallises from absolute alcohol **in** beautiful squint tables; it melts at 175-176° to a clear oil without effervescence, *l-AcetyLo-methyl-'2-tkiohydantoin* prepared by the action of potassium thiocyanatc on i-alanine, in the presence of acetic anhydride. crystallises in stout prisms, m.p. 161-162°, [«'$^{20}_{D}$ + 118-5° and the itf-forai, m.p. 168-109° (Csonka and Nicolet, i.e.; Johnson and Nicolet, J, Amer. Chem. Soc. 1911, 83, 1975; 1912, 34, 1041; 1913, 35, 1130; Amer. Chem. J. 1913, 49, 200; J. Biol. Chem. 1912,11, 98).

2-Thiohydantoin reacts with/ aromatic aldehydes and acetic anhydride giving acetyl arylidene derivatives, the acetyl group being situated on the enolic form of the CO group (Naiujoshi and Dutt, *I.e.).*

4-Tkiohydantoin is formed by the condensation of carbethoxyaminothioacetamide in presence of alkali

$$EtOOCNHCH_aCS{\cdot}NH_8$$



It crystallises from hot water in spear-shaped twinned crystals and gradually decomposes above 200°; it hydrolyses with hydrocliloric acid, yielding hydantoin and hydrogen sulphide (Johnson and ChemofF, J. Amer. Chem. Soc. 1912,84,1208).

It A. W.

HYDNOCARPIC ACID *{v.* Vol. I I. 521&).

JHYDNOCARPUS OIL *(v.* Vol. U, *5'2ld).*

" HYDRALDITE " (v. Vol. V, 320c).

"HYDRAMIN." Trade name for a com1 • i nation of p-phenylenediamine and quinol. The siime name has more recently been applied to a textile assistant (Krais, Alonatschr. **Textal-** Tnd. 1034,49, **138).**

HYDRARGILL1TE *(v.* **VoL** V, 532a).

" HYDRARGYROL" Trade name for the mercury salt of phenol-JB-SU!phonic add,

$$tC_eH_4(OH)SO_3)_2Hg,$$

stated to be a useful non-corroBivo antiseptic. " *Asterol "* is its mgre stable addition compound with ammonium tartratc.

HYDRAST1NE, $C_{21}K_{s1}OoN$. An alkaloid occurring together **with berwrme** and eanadine in.^he root of " Golden Seal," *J/yt!raslti canadentis* Linn., **to** the extent of about *1-5%.*

Its preparation and **physical** properties are described by Diirand, Anicr. .1. Pharm. **1861, 23,** 112; Perrins, Pharm. J. 18tJl-18(52, [ii], 3, G*«; . HiihltL, Amur. J. **8ci.** 1802, [ii], 36, 57; Vower, **Pharm.** J. 1884-1885, *[in].* 15. **297**j tiijkinan, R«». trav. clum. 18BC, 5, 290; Freund and Will, Ber. 1886, 19, 2797; 1887, 20, 88; Schmidt and Wilhelm, Arch. Pharm. 1888, 226, 329; and Elsa Schmidt (Amer. J. Pharm. 1919, 91, 270).

Preparation.—Hydrastine niuy be **Isolated** from the sulphuric acid *m*other-liquor from which the berl>erine salt has crystallised *(see* BEKBKKINE), This is largely diluted with water, and almost neutralised with ammonia. On evaporation, ammonium sulphate, resin, etc., are filtered off, and the hydrastine precipitated from the cold lilt rate by ammonia. The coloured precipitate ia dissolved in alcohol (I'err ins, Power), or ethyl acetate **(Schmidt** find Wilhelm), and the colouring matter removed by digeat'on with animal charcoal; the alkaloid crystalb'ses from the concentrated solution. Purification of **the hydrastine** is effected by repeated crystallisation from alcohol.

Some authors prefer to extract hydrastine from the root before berberine, thus, According to JTreuntl and viil], hydraatine is most readily obtained by percolating finely powdered *hy*draatis root with ether, and crystallising the ethereal residue from alcohol. Elaa Schmidt employs a similar method, using oenzene as the solvent.

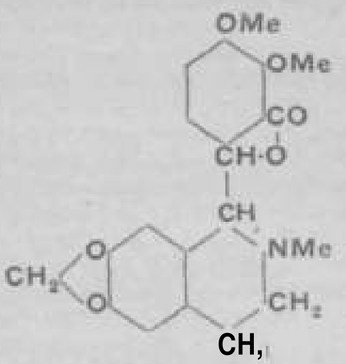
Properties.—Colourless, rhombic prisms, m.p. 132°. Insoluble in water, readily soluble in chloroform or benzene; less readily so in ether or alcohol; [a]j> in chloroform, —67-8° (Fiemid and Will); in chloroform, -638°; in dry alcohol, -49-8° [• in 50% alcohol, +115° *{Cair* and Reynolds, J.C.S. 1910, 97, 13:14). The ordinary salts of hydrastine are soluble in water, giving dextrorotatory solutions, but do not crystallise well (c/. Schmidt and Kerstein, Arch. **Piiarm.** 1890, 228, 49). Hydrastine and its hydrochloride, a hygroscopic powder, were official in the United Stntcs Pharmacopoeia 1916, but have been dropped from the United **States** Pharmacopoeia 1936; they are chiefly employed for the arrest of uterine hemorrhage in doses of **i** to y grain. Hydrastine ia poisonous in larger **dotes.**

Detection and estimation.—The most characteristic colour reaction of hydrastine is the production of a fluorescent solution (due to the formation of hydrastinine) by the addition of permanganate to an aqueous solution of its sulphate *{cf.* Lyons, Pharm. J. 1885-86, [iiil, 16, 880V For other colour **refections** of hydrastine, *see* Power, ***ibid.*** 1885-86, [iii], 16, 1092; Labat, Bull. Soc. chiin. 1909, fiv], 5, 742, 745. The assay of hydrastis rhizome prescribed in the United States Pharmacopeia 1916 consists in the gravimetric estimation of the ether-soluble alkal<Jids, which should amount to not less tlian 25%. For other methods of assay, *see* Gordin **md Presoott,** Arch. Pharm. 1899, 237. 439; 1901, 239. 638; van der Haar, Pharm. **Weekdad.** 1911,48, 1302.

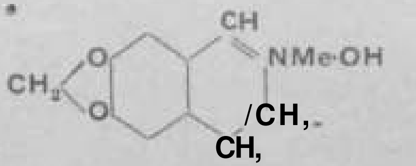
Constitution.—He oxidation of hydrastine by aitrfe **add** yields opianic acid and hydraatinine.

C >i H >• O*. N ~*r*- H O i n ~ r t-i f\ 1 /-* u /"i w
fir l™«t - -ll)" 10 6"i Wi"i3'-':(
iittirastint', Upmiili: neltl. Jis'ilrAstiiilin.'.

The **determination of** its constitution H bound uj> with, that of these fission-products and is due mainly to the researches of Freund and Rooer. The work, -which has been reviewed *by* Freund *(Anirnhn, 1892, 271, 311), leads* to the following constitutional formate ;



Hydras tine.

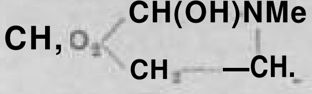


Hydnistinlne,

The complete synthesis of natural hydrastine haw not been effected so far. Hope, Pyman, Remfry, and Robinson (J.C.S. 1931, 236) have described the synthesis of two optically inactive stereoisomeridea of hydrastine but they have not yet been resolved. The mixture of nitrohydrastines obtained by the interaction of hydrastinino with nitromeeonine was reduced to a mixture of two aminohydrnstines. These were separated, and the amino-group wasteplaoed by hydrogen by way of the hydrazinohydrastincs, yielding *iM-kgdrastine-a,* m.p. 137°, and *dl-hydrastine-b,* m.p. 150-151°, The former was also obtained by the racemisation of natural f-hydrastine by means of aqueous alcohol under pressure (Marshall, Pyman and Robinson, .I.I[1] .S. L954, 1MB). •

Hydrastinine, $CMH_{13}O_3N$, is prepared by the oxidation of hydrastine (Kreund and Will, Bte. 1887, 20, 88), u4 baa been Byntheaiaed by ritzsch (Annalen, 1895, 286, 18); Decker (G.P. 234850, U)10); Roscnraund (*er. dent. pharm. ties. I9j\ 29, 200).

It may also be prepared from bcrberine (freund, G.P. 24113G, 1910), cot ami tic (Py man and Remfry, J.C.S. 1912, 101, 1806; *see also* Toptschiev. J. Appl. Chcm. U.S.S.R., 1933, 6, 529) or safrole (Kindlcr and Pcschke, Arch. I'harm. 1932, 270. 353). Like berberine *(q.v.), t* li« free brine occurs in two isomeric founts, in ivciueoiis solution as the quaternary hydroxide shown above, and in the solid state *;M* the t.irbinolamine,



$$CH_2O_2\langle\begin{matrix}CH(OH)NMe\\ CH_2\ —CH_2\end{matrix}$$

(<•/. **Uobbie** and **Tinktcr, J.C.S. Km!. 85, 1005).**

It mclte nt tHi-117[1], **CTyatallimw from light** petroleum, and i» easily soluble in alcohol or L-thcr, but sparingly so in **water.**

The hydro^hlorid«, properly hydraatuuniuia chloride, $C_nH_{13}O_3NCI$, like hydrastine and its hydroeliJoride, is not official in the United States Pharmacopoeia 1936. It melts and decomposes at 210°, and is easily Bolubie in water, giving a neutral solution showing a blue fluorescenoe. It gives no turbidity with ammonia, but sodium hydroxide causes a milky turbidy which disappears on shaking, and, on keeping, the solution deposits free hydrastinine.

Canadine, $C_{.0}H_{21}O_4N$, oooun with crude hydraatine *(see above),* from which it may be isolated by fractional crystallisation of the nitrates, the canadine salt being *lean* soluble. Silky needles, m.p. 182-0°, $[a]_D$ -298° in chloroform (Schmidt, Arch. Pharm. 1894, [iii], 232, 1 !•()). On oxidation with iodine it is converted inlo bcrberine. By fractional crystal lisa* tit in of tetra hydro be rberi ne d-broniocamphorsulpbonate. Gadatner *(ibid.* 1901, 239; 648) isolated a laevorotatory base identical with canadine, winch is therefore itetrahydroberberine. Jowett and Pyman have found 1-a-cattad ine *metho' chloride* in *XanOtox^lum brachyacanthtim* (J.C.S. 1313, 103, *-2.\YA)* (r/. Spath and Julian. Ber. J931, 64 [BJ, 1311; lierseii and Seupert, *ibid.* 1987, 7O[B3,J121).

F. L. P.

HYDRATION OF IONS.—Prom the early days of the theory of electrolytic dissociation, it has been recognised that the ions of salts might be hydrated (or in general *solvated)* by attachment to solvent molecules, but it is only fairly recently that any quantitative results in this field have been obtained. With the hydrogen ion, the free proton H* is linked with 1 mol.t>f water to form the hydroxonitmi ii)n $H_aO\backslash$ which is generally called tho " hydrogen ion." In other solvents sitni]a.r ions, *e.g.* $(C.H_5'OH)H*$ are probably formed. In some other cases also solvent molecules are thought to be attached by co-ordinate links to the solute ions.

Several methods have been used for tho study of hydration of ions: •

(1) Absorption spectra.
(2) Conductivity and viscosity measurements.
I'S) Distribution ratios and the solubility of gAMt iti salt solutions.
(4) Transport measurements.
(5) Application of Stokes's law.
(ti) Knergy changes in solvation of ions,

H. 0. Jones in 1907-15 obtained evidence for the hydration of ions from absorption spectra of aqueous solutions of electrolytes. He found that certain salt solutions have a smaller capacity for absorbing radiation than pure water, and concluded that water was combined with solute ions, and that such water has a smaller capacity for absorbing radiation than freo water. NH_4CI, NH,NO_3 anil KCI solutions showed little difference from pure wate*r in this reject. If *a,* salt was dissolved in a mixture of two HolvimtH, two nliHurjitioh spectra were fiiiuut, and <m changing the composition of the solvent, tho absorption spectra changed corrc**•ponriingly in** intensity, ghowtng that the **solvent** molecules, were in some wuy combined with

Kohite iong. If calcium chloride or aluminium chloride was added to a solution of cobalt chloride, the effect on the absorption spectrum was the same as if the solution had been concentrated. Hence it was assumed that the calcium chloride had taken some of the water molecules, and decreased the amount of " free " water for dissolving the cobalt chloride {Jones, Z. Elektrochem. 1914, 20, 552; Camegie Inst. Pub., No. 60, 1907).

From his conductivity measurements Kohlrauseh concluded that the ions were surrounded by atmospheres of water molecules, and that the electrolytic resistance was due to friction, which increased with the size of the ion atmosphere. In the case of highly hydrated ions the friction becomes almost the same as that between pure water molecules. Jones obtained further evidences of solvation from conductivity and viscosity measurements by working with mixed solvents, such as glycerin and water containing LiBr, The results were mainly qualitative.

Distribution experiments have been used as a means of determining the degree of hydration of ions (c/. J. 0. Philip, J.C.S. 1907, 91, 711). The method depends on the assumption, that if the ions are combined with water the amount of " free " water in the solution which is available for dissolving another substance, is reduced. The distribution of a substance between a non-aqueous solvent and a salt solution was studied, and assuming that the solubility in " free" water is the same as in pure water, the following results were obtained for molecular hydration: Na_2SO_4. 28-5; HC1, 4-4; NaOH, 20-5; LiCI, 8. Sugden {ibid. 192\ 174) used acetic acid distributed between amyl alcohol and salt solutions, and found that in many cases the degree of hydration is independent of temperature. H. A. Taylor (J. Physical Chem. 1925, 29, 995) determined the partition ratio of hydrogen chloride between benzene and salt solutions and came to the conclusion that aqueous solutions behaved like pure water, and that there was no difference between " free " and combined water. These measurements are primarily concerned with the activity of the solvent in various salt solutions and are not necessarily to be interpreted as a result of hydration.

A similar method used by Philip (J.C.S. 1907, 91, 711) depended on the difference between the solubility of a sparingly soluble gas in a salt solution and pure water. In some cases the absorption of the gas was found to be practically independent of the salt concentration, but where this was not so, hydration was assumed to have rWurred, and the degree of hydration was calculated from the decrease in absorption.

Hufner (Z. phyiJikal. Chem. 1907, 57, 611) measured the decrease in solubility of nitrogen and hydrogen in solutions of organic substances, *e.g.* arabinoee, and found that the decrease was proportional to the weight of substance in the solution. By this method Philip calculated the hydration of KCi as 6-11, NaCI as 14-16 and BaCl, as 26-30.

When determining Hittorf transport numbers (this Vol., p. 2374) it is assumed that only the ions more and that the water is not transferred. However, it was shown by Nernsfc in 1900 tha the ions carry water with them, and that in concentrated solutions this effect is quite appreciable. He added an indifferent substance such as raffinose to the electrolyte solution and determined the concentration of the raffinose in the anolyte before and after electrolysis. If the electrolyte ions were unhydrated there would have been no change in the distribution of the raffinose throughout the solution, but a definite change round the anode was found. The results were not very conclusive, but with improved experimental technique later workers were able to calculate the relative hydration of the ions. Wash bum (J. Amer. Chem. Soe. 1909, 31, 322), using a similar method to that of Nemst, determined the water so transferred, and calculated the true transport numbers n_c^T and n_a^T from the Hittorf values n_c^H and n_a^H. If ΔN_w g.-mol. of water are transferred per faraday, F, to the cathode, and the solution contains N_s equivalents of solute to N_w equivalents of water, the solute corresponding to ΔN_w of water is $\frac{\Delta N_w N_s}{N_w}$. Too little solute by this amount will be found in the cathode compartment.

$$n_c^T = n_c^H + \frac{\Delta N_w N_s}{N_w} \quad . \quad . \quad . \quad . \quad (1)$$

$$n_a^T = n_a^H - \frac{\Delta N_w N_s}{N_w} \quad . \quad . \quad . \quad . \quad (2)$$

In very dilute solutions $n_c^T = n_c^H$.

TABLE I.—TRUE AND APPARENT CATION TRANSPORT NUMBERS AT 25°C. IN 1·25N SOLUTION, AS DETERMINED BY WASHBURN.

	HCl.	LiCl.	NaCl.	KCl.	CsCl.
	0'820	0-278	0-300	0-462	0-485
	0844	«0304	0 383	0-495	0-491
Ax* . .	024	2-5	078	060	0-58

Since ΔN_w is the net transfer of water,

$$\Delta N_w = w_c n_c^T - w_a n_a^T \quad . \quad . \quad . \quad (3)$$

where w_a and w_c are the amounts of water carried by the anion and cation respectively. Hence from (3) $w_c = \frac{\Delta N_w}{n_c^T} + \frac{n_a^T w_a}{n_c^T}$ and it is possible to calculate the relative hydration of the ions. If it is assumed that the hydrogen ion has 1 mol. of water, then the numbers of molecules of water associated with other ions are $Li^{\cdot} = 14$, $Na^{\cdot} = 8{\cdot}4$, $K^{\cdot} = 5{\cdot}4$, $Cs^{\cdot} = 4{\cdot}7$.

Table I shows the remarkable fact that the cation transport numbers of the alkali metal chlorides increase with increase of atomic weight, whereas it would be expected that the mobility of the unsolvated ions would decrease with rise of atomic weight. Bredig in 1804 had suggested that the metal ions carried with them water which increased their size and thus slowed them down, lithium carrying the moat water and caesium the le&flt, and this view is in accordance with the above results.

Remy (Z. physikal. Chem. 1925, **118,** 161; Trans. Faraday Soc. 1927, 23, 381) measured the amount of water transported when the intermediate liquid was gelatinised, and in later work a parchment membrane wag used. The change in volume of the liquids round the electrodes waa measured by the rise of the meniscus in capillary tubes. Allowing for electro-end osmosis, and assuming that the parchment did not affect the movement of the ions, he calculated the following results for hydration. If it in assumed that one water molecule is associated with the hydrogen ion, the numbers associated with other ions arc: K" 5, Na* 8, Li^p 14. Cl' 4.

Baborovsk^ (Z. physikal. Chem. 1927, 129, 129; **131,** 129) carried out similar experiments but weighed and analysed the contents of the anode and cathode compartments. The results are as follows-:—If one water molecule is associated with H\ then the numbers associated with other ions are: U" 14, Na' 8-9, K" 6, Cl' 4, Br' 2, I' 2 in normal solutions, bnt the hydration increases markedly in more dilute **solutions.**

The results of Washbum, Remy and Baborovsky are in fair agreement, and those of Washbum were confirmed by Taylor and Sawyer {J.C.S. 1929,2095) using urea as the reference substance.

Riesenfeld and Reinhold (Z. physikal. Chem. 1909, 66, 672) stated that the true transport number is independent of concentration, nil such changes being due to hydration of ions. If |p-«, then *n**-»*f*+*c*4N_u from (1). If T »c is const-ant $\frac{dn*}{}$-p=$J_J Y_w$ and the slope of the *I* graph made by plotting *v*^ against c ia ΔN_w. They combined this equation with the assumption that the water molecules form a shell round the ion, the volume of which can he calculated from Stokee's law,* which states that w=g$\frac{JJI}{\pi r\eta}$ where *u* is the velocity, r the radius of the spherical ion, *F* the force moving it, and *T]* the .viscosity of the medium. If tho volume of the ion in negligible compared wi£h that of the water envelope, the volume of tho latter can be found. If /,, *I*,, are the mobilities o£ ions of radii r_v r_{Jt} then -±=^, and if A_v A_t are the numbers of molecules of water attached to the ions, 'T=\='r*- *n tW8 w*y tne foPowing values were found at infinite dilution, assuming that the hydrogen ion is unhydrated : OH' 11, K* 22, Cl 21, Br' 20, I' 20. NO,' 26, Ag* 37, **CIO/** 37, |Cd" 55, |Cu" 56, Na* 71, Li* 158. The values seem unreasonably Urge, and the modern theory of electrolytes indicates that the true transport number is not independent of concentration {Glasstonc, " Electrochemistry of Solutions," Methuen. 1937, p. 16(i).

Reiny (Z. physikal. Chem. 1915, 89, 529) assumed that certain largo organic ions are unhydrated, and from Kopp's atomic volumes calculated the supposed volume of the unhydrated hydrogen ion. By using Stokes's law, he found that the difference in radius between the hydrated and unhydrated ion was usually equal to the diameter of a water molecule. This calculation, however, involves rather uncertain ionic radii.

Clich in 1926 took into account the volume of the ion and the compression of solvent molecules by electrostatic forces (electrostriction of the solvent).

All calculations based on Stokes's law give improbably high results, and it is very doubtful if the simple law holds for spheres of ionic dimensions.

A new approach has been opened by the study of energy changes in the solution of gaseous ions (i.e. unsolvated ions assumed to be in the gaseous state), W. M. Latimer (J. Amcr. Chem. Soc. 1926, 48, 1234) calculated the energy of solution of gaseous ions in water, and obtained good agreement with the -values which Bom had found from a simple electrostatic expression for the energy change in bringing a charged sphere from a vacuum into a medium of dielectric constant) *D.* Latimer found that the entropies of solution of gaseous ions vary linearly with the radii, and hence it is apparent that 'the energy effects on the solution of gaseous ions are determined by tho size and charge of the ionB. T. J. Webb {*ibid.* 1926, 48, 2589) calculated similarly the energy of solvation and the effect of electrostriction of the solvent. Fa j arts regarded the heat of solution of salts as due to two effects, *(a)* the energy required to dissociate the salt into free gaseous ions, and *(b)* the heat evolved when these are dissolved ii* water. Very high hydration values were obtained by this method of calculation, *e.g.* LtCI 187, NaCl 180'5.

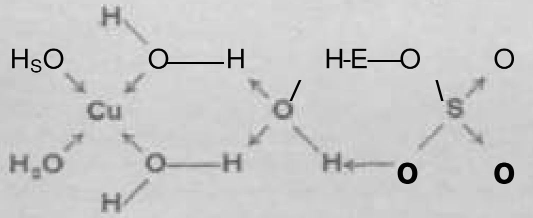
More recently Bern a I and Fowler {J. Chem, Physics, 1933, 1, 515) have derived expressions for the heat of hydration of ions, and their method is used as the basis of most of the recent work in this field. ,

The values of the hydration of ions obtained by different methods show very poor agreement, and there is still no unanimity of opinion as to the exact relationship between tho ions and solvent molecules.

Physical solvation doubtlessly explains many cases of hydration. This assumes that there is an increased concentration of water molecules in the immediate vicinity of an ion, and that the water molecules are held by electrostatic forces. Water is polar, and the molecular dipole orients itself so that in the case of a cation the negative or oxygen of the dipolo is attracted to the ion. In tho case of an anion, the hydrogen of the water molecule is attracted.*[1] There may be an induced dipole in tbo solvent molecule due to the field of the ion, and in the case of a small ion with a large charge, this induced dipole is large. Under the influence of an electromotive force the water molecules are dragged along with the ions. Born stiowed that the dipoles could be held so strongly by small ions that they would lose all degrees of freedom.

It is possible to obtain an expression for tho electrical contribution to the heat of solvation of *iom,* and if the force is purely electrostatic, this urll be the total heat of solvation. The differon co between the heats of solvation in two **solvents** should be equivalent to the heat of transfer of the ion from one solvent to another. The agreement between experimental results jinil those calculated on the assumption of **physical** solvation is not good. It is generally considered that when the sequence of ionic velocities is independent of the solvent, the solvation is physical.

Solvation can also be considered from the point of view of Werner's Co-ordination Theory. If one atom or group supplies both the electrons necessary to form a bond, the latter is known as a co-ordinate link, and the capacity of a group for co-ordination depends on its power of giving or accepting tlcctrons. Six water molecules can co-ordinate with a **metal** ion to form a cation complex, and examples of such complexes are $\backslash Co[H_{2}0)_{t}V^{+}$ (the anion being 2Br', 2CI', 21') or $[Cr(H,,O)_{B}]CI_{2}$ and similar compounds with Ni. Zn,"Cd, Fe'^{1}, Fe^{1}", Ca and Al **M** nuclei. Copper sulphate pentahydrate has ***i*** **mol.** of water co-ordinated with the nation **and 1 moL co-ordinated with** the anion as shown below :



It is seen that the anion *and* cation are bound together by ro-ordination of an anion water molwule with two of the cation water molecules. M'ost cation water complexes are known to **exist** in solution, but anion complexes are in most etiaes only definitely known to be **present** in the solid state. Sidgwick, " Electronic Theory of Valency," Oxford University Press, 1927, has considered aolvation from the electronic point XT view, and has emphasised the importance of the donor and acceptor properties of hytlroxylic solvents in forming co-ordinate links. This js shown by the **itrtiotare of** CuSO,,5H.,O, in which it is seen that the oxygen atom of the **OH group i« capable** of giving electrons, whilst the hydrogen atom can receive an electron. The solvation of ions increuses the size of **the** ion and reduces the likelihood of ion **Association,** since the ion centres have to be u mtuin minimum distance apart for association to take place. It was found **that** the ions of lithium Its undergo association in nitromethane, although the solvent him a large dipole moment **which** would induce physical snlvation. It Is thought that since nitri; methane is a nonhydylic solvent, **and can** only **coordinate With** the **cation,** salvation is thereby reduced anil ion **association** occurs. The velocity of the lithium ion is :V:ili timi's *»n* fust in. liquid **ammonia** ns in water, **whereon the surer, ion** is only 2-1 :*» times ***m*** flint li i> probable **that** tin' silver itin tends In hitm it **complex** in **lOnmonfai, reuniting** in **a reduction** of t)u- **velocity,** and thut the lithium ion hus a **great** affinity for water and undergoes hydration in aqueous solution, which diminishes the velocity. This would explain the above observations on their relative velocities.

The general view now taken is that in & few cases chemical combination probably occurs between the ion and solvent molecules, and that other solvent molecules can be held by electrostatic forces. It is quite possible that in eases of physical solvation, a Grotthuss effect is produced in the electrolyte when the solute and solvent molecules have an atom or group in common. This implies a constant interchange of the common group or atom as the ion moves through the solution under the influence of an applied electromotive force.

Bibliography.—H. S. Taylor, " Physical Chemistry," Macmillan, 1930, Vol. I, p. 686; Glasstone, " Electrochemistry of Solutions," Methuen, 1937, p. 45; Annual Reports of the Chemical Society, 1026, p. 27, and 1930, p. 351.

T n p.

HYDRATO-KANTEN-S and -y <«. Vol. 1, 103a).

HYDHATOPEKTIN **[».VoLV, 162o).**

HYDRAZINES. The term " hydrazine " was first applied to the then unknown diamide, NHJ'NHJ, by E. Fischer, but is commonly understood to include those derivatives in which the hydrogen atoms are replaced by **other** radicals. The reactions of such compounds divide them sharply into (a) those still containing an NH, group and (6) those in which at least one of the hydrogen atoms of each amino group has been replaced. As all the compounds of any importance under *(b)* are hydrnzo-compounds this **account** includes only those hydra - **zmea** containing the grouping **p**N'N**H**$_{a}$ **embracing** hydrazine itself, mono- and unsym.-dialkyl, -aryl. **-acyl,** and aralkyl **hydxazines.**

Hydrazine, $NjH_{<t}$ was first obtained by Cu it ins (B«. 1887, 20, 163:!) **in** the form's of its hydrate and its salts by hydrolysing triazoacetic acid, $(CWN_{2}\text{-}CO_{2}H)_{3}$. The formation **of** liydrjr/.iue from many other organic compounds hns IIIHO bren reported, but it was **a considerable** time **before** simpler preparations **from inorganic materials were** elaborated. Thus trace 8 **of** hvdru/Jne are formed on exposing nitrogen and **hydrogen** to uItfn-violet light, by pass mjj^a spark fliNchurjie through nitrogen-ammonia mixtures, by **the** direct oxidation uf **ammonia hy enpric** wulfihatc, **by** air **akme** {Ruschig, Her. 1907, **40,** 4")88), or in **proience of** noble mctalH (Krmiss, Z. **phynikal. Chem.** lilUtl, B, 39, **83**):

$$4NH_{3}1\ O,\ 2H_{2}O\ t\ 2N_{2}H,.$$

Hydrazino is also **formed** in small amount by **the** reduction \iith sodium amalgam of nitric oxide potassium sulphite, $K_{3}SO,\text{-}2NO$ (Duden, Ber. *l»\n,* 27, 3408) prepared by the interaction ofmtnc nxide and **patosdam sulphite** (Divers and Hagtt, **J.C.S, 1890, 69.** lrtlO).

Hyrlmxinr m **moat readfry** obtaint'd. **howerer, h> oxidising ammonia with sodium hypodtlorite** (Ras• hig, ***l.r.*** , ,***f.*** **Mollor,** Kong, dausk. Vidensk. **Selfik. 1034;** 12, No. Iti) when chloramidc initially formed reacts with excess of ammonia. The yield is remarkably dependent on the presence of glue or gelatin *(see also* Joyner, J.C.S. 1923, 123, 1114), an effect which has been attributed to the influence of the colloid on the viscosity of the solution (dilution with a mobile solvent euch as acetone exerts an unfavourable influence) or alternatively to the adsorbent properties of the colloid (the action of other strong adsorbents such as charcoal, colloidal **ailietfl** acid, etc., is in some measure com parable with that of glue}. The base* is conveniently isolated (preparation : Organic Syntheses, Coll. Vol. I, 1932, 302) as its sulphate, **N_2H_4H,SO_t,** distillation of which **with** aqueous alkali yields hydrazine hydrate, **N_nA_4,H_aO (Curtiua** and **Schnlte,** J. pr. Cliem., **1890, [fit** 42, **521}, b.p.** 119°. Its dehydration was **achieved by** de Brnyn (Bee. trav. chim. 1894, 13, 433; 1895, **14,** 83; 189(5, 15, 174; 1899, **18,** 207) using barium oxide (bnrimn **and** sodium hydroxides, calcium oxide and sodamulc have since been used) and yields anhydrous hydrazine as a **corrosive** liquid, b.p. 113-5°, m.p. + 1-4°, fuming strongly in air.

Pure hydrazine and its aqueous solutions are relatively stable but decompose rapidly in preaenco of alkali and air to nitrogen and water. With (stronger oxidising agents, *ejj,* hypochlorites, reaction is very vigorous with rapid **evolution** of nitrogen.

Hydrazine is basic in character and although the pure compound reducea sulphuric and other oxygen-contain ing acids, a range of compounds containing tctra- and hexa-valent sulphur, etc., have been described. Hydrazine also **fol**ms metallic derivatives, thtis excess of sodamide yields sodium hvdr.i/.iue and an explosive zinc hydrazine has been described. Hydrazine is a good solvent for many inorganic salts some of which, however, suffer reduction,

Hydrazine condenses **with** carbonyl compounds to give azines which are often difficultly soluble compounds of high melting-point:

$$2RR'CO+N_{i!}H_1 = RR'C:NN:CRR'.$$

Hvdru/.ine is used only to %* minor extent in technical practice, *e.g.* as an antioxidunt (U.S.I'. 1973724) or in the application **of azo-dyofl** {!•.!'. 7(Jfi957) but is **a** valuable laboratory reagent as a reducing agent and for the precipitation of metals. Thin it affords a sensitive micro- ' In mical test for zinc (Kay ind Sirkar, Mikro them., Kmich Featschr., 1930, 243) n«d **may** be used to separate aluminium' and **chromium (Maljarow,** Chem. Zentr. 1930, II, 1408); iron from manganese (Jilek and Vicovsky, Coll. Czech. Chem. Comm. 1931, 3, 379); and to precipitate nickel, cobalt **and** cadmium in^ forms suitable- for gravimetric **estimation** (Hay and Sirkar, J. Indian Chem. Soc. 1930, 7, 251).

Hydra/.ine may be detected by its ability to reduce gold salts (Curtiua and Scbrader, J. pr. Chem. 1894, \i\], 50, 318) or by the red acid- -<• native coloration given with ferric chloride alter (txidiwing with alkaline ethyl nitrite to hydrazoic acid.

Semicarbazide. NH,-CO-NH-NH,, is p«*. pared :

(I) *iiy* boiling hydrazine with («) **urea** (Uurtjus and Hcidenrcich, Ber. 18i)4, 27, 0% or (/<) potassium **cyanatc** (Biltz and Arnd, Annalen, L905, 339, 250; *cf.* **Bonveanlt** and **Locqirin,** Bull. Soe. chim. 1905, [iii], 33, **168).'**

(2) From nitrourea by reduction either with zinc duet (Thiele and Heuser, Annalen, l8!>r>. 288, 312) or electrolytically (Organic Syntheses, Coll. Vol. I, 1932, 472). The last method has the advantage of yielding the pure compound directly **whilst** in the older preparations it was necessary to convert it into a **derivative** *{e.g.* >f acetone or bonzaldehyde) from **which** the semicarbazide was regenerated.

Seroicarbazide forms prisms, in,p. 90°, **bui** s **usually** employed as its more stable salts **with** one equivalent of and. It is used as **reducing** agent and boili (ilriinetric (Maselli, Gazzetta, **L905,** 35. i, 271) and gasometric (Datta, J. Amer. Chem. Soc. 1914, 36, 1014; **1916,** 38, 2737} estimations depend upon this **prop***rty.

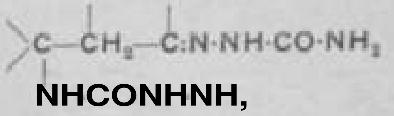
Semicarbazide readily reacts with earbonyl compounds to give characteristic semienrba zones:

$$RR'CO' NHj\text{-}NH\text{-}CO\text{-}NH,$$
$$= RR'C{:}N\ NH\ CONHj,\text{-}j\ H_2O$$

This reaction is usually carried out by **mixing** cold or warm solutions of **a** semicarbazide **But [hydrodSoride)** and the carbonyl compound in **water, with** alcohol if necessary, and buffering excess acidity with sodium acetate when the derivative crystallises out. Occasionally, if the solution is subjected to long heating, the product contains hydrazine diearbondianiide. The reaction ia normal for most carbonyl compounds though abnormal **reactions** as with chloral are sometimes encountered :

$$CCl_3\text{-}CHO\text{-}f\ NH_2\cdot NH\cdot CONHg$$
$$= CCl_3\cdot CH\,;f\ NH\text{-}NH'CO\text{-}NH,$$

(Klitig, Compfc. **rend.** 1!)09, 148, .%0 ; Bull. Soc. chim. 1909, [iv], 5, 412), and a^-unsaturated carbonyl compounds often yield scmicarbazidg-seniicarbazones of the type (Rupe and Hinterlach. **Bar. 1907,40,4764):**



$$>C-CH_2-C{:}N\cdot NH\cdot CO\cdot NH_2$$
$$NHCONHNH,$$

Thiosemicarbazide, $NH_2NH\text{-}CS'NH_2$, in ..p. 181-1S,')^0, w prepared by boiling hydrazine hydrate with aqueous potassium carbonate and tliiocyanatc (l'reimd and Schander, Ber. 1896, 29, 2501). Thiosciniearbazones which are propinrtl similarly to the oxygenated compounds usually have low uiefting-points but are of value in that thc)(give complex compounds with salts of heavy metals, particularly mercury (Ncubcig and Neimann, ***ibid.*** 1902, 35, 204U ; Jensen **and Etanflke-HadBftn,** Z. anorg. Cb*m. 103U, ^27, 25). Thiosctniearbuzide U **a** reluuvHy nuii-toxiu antioxidant auitublti for spraying dried frtiit.4 **to** prevent discoloration ($I^1.S.I^1$. **2088458) and** for **utobiliaing** adn-iialiii^ (U.S.P. 2017144). It exerts a specific iiilliicncu on the tjuulity of silver electroplating (Egeberg and Promisel, Trans. Eleetrochem. Soc. 1938, 74, Preprint 13) and acts as an anticorrosion assistant on iron or iron alloys (F.P. 652598}.

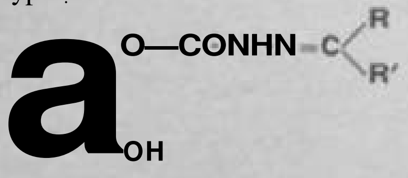
4'Phenylsemicarbazide,

PhHN-CONH-NH,,

m.p. 122", is formed on boiling semicarbazones with aniline and then hydrolysing and separating the ketonic constituent (Borache, Ber. 1905, 38, 832), but is best prepared by heating phenylurea with hydrazine hydrate (Organic Syntheses, Coll. Vol. I, 1932, .439). Phcnylaemicarbazide ia occasionally used as a ketone reagent (Braun and Steindorff, Ber. 1905, 88, 3097; Sah and Ma. J. Chinese Chem. Soc. 1934, 2, 32) giving derivatives which form complexes with heavy metals auch as iron, cadmium, cobalt, etc. (Smith, J.C.S. 1937, 1354; Jenaen and Rancke-Madsen, Z. anorg. Chem. 1936, 227, 25); it has also been incorporated in therapeutic preparations (Svensk Farm. Tidakr. 1938, 42, No. 15, Suppl. 1).

Benzhydrazide, o-, *m-* and *pnitrobenz-* and other aryl *hydrazides,* obtained by heating the carboxylio amides or esters with hydrazine hydrate, give well-defined crystalline aldehydic or ketonic derivatives which are aometi-ies more conveniently handled than the phenyl hydrazones (Curtius *et at.,* J. pr. Chem. 1894, [ii], 50, 275, 295; 1895. 51, [ii], 165, 353). Like other hydrazides benzhydrazide undergoes chemiluminescent oxidation by hypochlorite (Courtot and Bemanoae, Compt. rend. 1937. 205. 989). Sah and his co-workera have prepared a large number of nitrobenzhydnizonea (Sci. Rep. Nat. Tsing Hua Univ. Ser. A, 1934, 2, 357; Chen, J. Chinese Chem. Soc. 1995, 3, 251) some of which seem **6ft** be of distinct value, *e.g.* for the complete isolation of vanillin (Schorigin and Smoljaninova, A, 1935, 750; for mi cm chemical use. *tee* Griebel and Weiss, Mikrochem. 1927, 5, 146). Aryl acid hydrazides are efficient oxidation-inhibitors (G.P. 504436).

Einhorn (Annalen, 1898, 300, 135; 1901.817, J90) has shown that hydroxyacyl hydrazones of the type":



are formed particularly easilj by aldehydes but **much** leas readily by ketonw and poiess the property of dissolving in alksli and being precipitated unchanged by acid.

Semioxamazide, NH,-CO-CONH-NH. m.p. 220-221°, prepared by boiling hydrazine with oxaniethane in alcohol, ia recommended as a reagent for aldehydes, *e.g.* furfural and cinnama.1-dehyde (Kerp and Unger, Ber. 1897, 80, 585}

Phenylhydrazine, H,NNHPh, is conveniently prepared by reducing benzene diazonium salt* with atannous chloride (Hqfitzsch *ibid.* 1898, 81, 346), zinc dust (Meyer and Lecco' *ibid.* 1883, 16, 2970). alkali aulphite {Fischer *ibid.* 1875, .8, 590; Annalen, 1878, **190.** 73; Organic Syntheses, Coll. Vol.- I, 1932, 432) or electrolytically (Fichter and Willi, Helv. Chim. Acta, 1934,17, 1416). The manufacture by the reduction of nitrobenzene using lead oxidea is the subject of patent claims {G.P. 480598) and. it is also produced by the very remarkable action of fluoramine **(NH_2F)** on aniline (F.P. 735020).

Phenylhydrazine haa m.p. 19-6° (Fischer, Ber. 1908, 41, 74), b.p. 243-57760 mm. (corr.), d" 1-0970 (Perkin, J.C.S. 189R, 69, 1209). It ia very susceptible to oxidation and the hydrochloride is usually used for the prepp ration of phenylhydrazonea. It is weakly basic and forms mono-acid salta, although easily dissociable salts with two equivalents of inorganic acids have been described. The base and many of its derivatives are toxic.

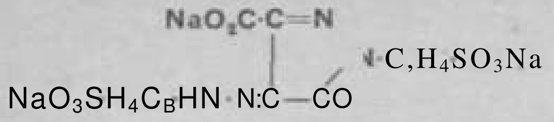
Phenylhydrazine may be detected by its colour reactions with sodium hypobromite (Dehn and Scott, J. Amer, Cfiem, Soc. 1908, 30, 1422), 2:4-dinitrobenzaldehyde (Sachs and Kemp, Ber. 1902, 35, 1230) or formaldehyde anJ sodium nitroprusside (Simon, Compt. rend. 1898, 126. 483; Bull. Soc. chim. 1898, [iii], 19, 299). The ox alate crystallises well and provides a means of identification (Bamberger and Suzuki, Ber, 1912,45,2752). More conclusive is its characterisation as a phenylhydrazone *(see* HYDKAZONES). It ia estimated by its reducing action on Fehling's solution (Strache, Monateh. 1891, 12, 525; *cf.* Maclean, Biochem. J. 1913, 7, 611) or on arsenic acid (Causse, Compt. rend. 1897,126, 712; Bull. Soc. chim. 1898, [Hi], 19, 148).

Phenylhydrazine ia used in the laboratory to characterise carbonyl compounds as phenylhydrazones and sugars as osazones (mechanism : Kennerand Knight, Ber. 1936, 69 [B], 341) and as an analytical reagent, *e.g.* for molybdenum (jfge Schmidt, " Anwendung der Hydrazine iif der analytisehen Chemie," Stuttgart, 1907. p. 31), for aluminium in presence of iron (Ishiroaru, Sci. Rep. Tohoku Imp. Univ. 1936. 1,25,780), for mercury (Miller, Chem.-Analyst, 1938, 27, 9). In technical practice phenylhydrazine is the Bource of pyrazolone mcdieioala (" *arUipyrin"* " *pyramtdone* "), .bactericidal azo-coin pounds (Jug.P. 13777) and" of some azo dyes such as Erioehrome Red (U.S.P. 1856413). Attempts have also been made to put some of its derivatives to therapeutic uses in the treatment of tuberculosis (review: Sehnitzer, Z. angew. Chem. 1930, 43, 744). Phenylhydrazine is an efficient antioxid*nt {B.P. 312774) and an effectivi softener for natural and synthetic rubber (B,P. 488701) particularly when protected by the presence of another antioxidant, and that it similarly improves eellulosie materials Buch as those **intended** for surgical use ie claimed (.Swis&jP. 183210).

Phenylhydrazinejj-sulphonic **acid,**

$$H_BN\text{-}NH\text{-}C«H_4\text{-}SO_9H,$$

m.p. 286°, is prepared by sulphonating phenyl hydrazine or reducing diazotiaed sulphanilir acid. Its reactions are often abnormal as when it forma addition compounds with aromatic aldehydes and ketonea *l(ct.* however, its use in g the corpus luU;um tn.riiu.iir, LSWISS P. **170618,** and its reaction with sugars, B. 340619). It oevertheleas yields pyrazolo with aliphatic diketoncs, and the yellow dyeatuff *tartrazine* with dihydroxytartaric acid,



(G.P. 34294; Swissa P. 119718); it is also the source of dipyrazolones (F.P. 44843) and nitrocolours (H.P, 409512). Phenylhydrazine-jj-aulphonic acid bag been applied in the form of long-chain hydrazones *(r..g.* of l&uric aldehyde) as a textile assistant (F.P. 755143). Its possible therapeutic action on malignant tumours has been investigated {Boyland, Biochem. J. 1938, 32, 1207).

ji-Brornophenylhydrazine,

$$H_2N\text{-}NH\text{-}C_6H_4Br,$$

m.p. 105-5°, prepared by brominating a phenyl hydrazone and hydrolysing the product (Humphreys, Bloom and Evans, J.C.S. 1923, 123, 1768) or directly by brominating phcnylhydrazine and reducing the resulting bromodiazonlum bromide (Michaelis, Bor. 1893, 26, 2190) is a useful reagent for carbonyl compounds and particularly for sugars (Nouberg, *ibid.* 1899, 32, 2395; Z. physiol. Chem. 1900, 29, 256; microchemical use, Feigl, Mikrochim. Acta, 1937, 1, 127; Wageaaar, Pharm. Weekblad, 1934, 71, 229).

p-Nitrophenylhydrazine,

$$H_2NNHC_6H_4NOj,$$

m.p, 167°, p-Nitraniline is duizotised, tMe diazdnium salt reduced by alkali bisulphite and the resulting aj9-disulphonic acid hydrolysed by mineral acid (Bamberger and Kraus, Ber. 1890, 29,281; c/. G.P. 62004). The sparing solubility of p-nitrophenylhydrazunes haH been utilised in the estimation of aldehydes (Feinberg, J. AIIUT, Chem. Soc. 1927,49,105), andfef acetone in urine (Dehio, Z. anal. Chem. 1936, **104.** 417); for chemical use, see Feigl (Mikroehim. Acta, 1937, *1.* 127).

2:4-Dinitrophenylhydrazine,

$$H_2N\cdot NH\text{-}C_6H_3(NO_2)_2,$$

m.p. 198°, is beat obtaiaed by the' interaction of 2:4-dinitro-cliloro- or -bro mo-benzene with hydrazino in alcoholic solution. It yields an orange pigment, m.p. 298°, on heating with acetoacetaniudo in alcohol (G.P. 269065^ and is **a** valuable reagent for carbonyl groups *(tee* HYDRAZONES) both for qualitative and quantitative purposes, *e.g.* for estimating furfural and camphor in galenical preparations (Hampshire and Page, Quart. J. Pharm. 1934, 7, 558). Its use according to the original method of Brady (J.C.S. 1931, 766) sometimes gives rise to hydrazones of slightly varying melting-point, a phenomenon at one time ascribed to stereoisomorism but believed by Campbell (Analyst, 1936, 61, 391) to bo due to aldol condensation products. This worker re-examined the melting-points of dinitropheoylhydrarones of approximately 100 aldehydes and ketonea and recommends their preparation in iropropyl alcohol using hydrochloric acid.

Methylphenylhydrazine, $H_2N\cdot NMePh$, b.p. I31°/35 mm., is best prepared by reducing N-nitrosomethylaniline with zinc dust (Fischer, Annalen, 1886, 236, 198) or e lee truly tically (Wells, Babcock and France, J. Amer. Chem. Soe. 1936, 68, 2630). This base is useful for identifying sugars in particular, the hydcazones or osazones being crystallised from glycerin (Wagenaar, Pharm. Weekblad, 1934, 71, 229). Methylpb.enylhydra.zine heated with dihydroxynaphthalenes, yields hydroxynaphtbocarbazolep used as intermediates for azo colours (G.P. 548819).

Diphenylhydrazine, $H_2N\text{-}NPh_2$, m.p. 44°, prepared by reducing N-nitrosodiphenylamine (Fischer, Annalen, 1878, **190,** 175; Stahel, *ibid.* 1890, 258.243), may be used to characterise simple aldehydes but is moat valuable aa a reagent for reducing sugars with which it gives beautifully crystaUine hydrazones. Its use as an antioxidant in gasoline and in petroleum cracking distillates has been claimed (U.S.P. 1906044, 4793635).

Benzylphenylhydrazine,

$$H_2NNPhCH_2Ph,$$

b.p. 216-218°/38 mm., is prepared by the action of benzyl chloride on phenylhydrazine. When free from phenylhydrazine it reacts with sugars to give only hydrazones and not osazones.

0-Naphthylhydrazine, $NH\cdot NH_{1}C_{0}H$,(^ m.p. 124-125°, is made by rmlurihg jS-naphthyl diazonium salts (Fischer, Annalen, 1886, 232, 242) or by the action of hydrazine on j9-naphthol in a sealed tube fFranzen, Ber. 1906, 38, 260). This hydrazine forms highly crystalline, very sparingly soluble hydrazones, particularly with **•qgars.** but it **tomttarkabk that diffianat products,** probably stcreoinomeridca, ara obtaineu when they are prepared in acetic acid or alcoholic solution (Hilger and Rothenfusser, Ber. 1902, 86, 1841, 4444). Naphthocarbtizoles may be obtained technically by heating naphthylhydrazine with hydroxynaphthalene carbojcylic acids (U.S.P. 1948923).

A number of new chloro- and bromo-nitrophenyl hydra zincs and alkyl-aryl-hydrazines have lii-i'ii prepared by Maaskant (Kec. trav. chini. 1937, 56, 211) by replacing halogen atoms in halogenonitrobenzenes by hydrazinc, and representative hydrazones have also been described.

A. H. C.

HYDRAZOBENZENE, fhNH NHPh. *is* prepared by reducing nitrobenzene in hot alcoholic solution with zinc dust or iron in presence of alcohol or solvent naphtha, and also by electrolysis, M.p. 126-127° (Darmst&dtwr, G.P. 189312; Chem. Zentr. 1907, II, 2002; Ismailflfi and Kolpenuki. *ibid.* 1933, II, 3049). Decomposes at the melting-point to give aniline and azobenzene. Hydrochloric acid converts it int* benzidinc.

HYDRAZOIC ACID (tr. Vol. I, 580a).

and Promise], Trans. Electrochem. Soc. 1938, 74, Preprint 13) and acts as an antieorrosion assistant on iron or iron alloys {F.P, 652598).

4-Phenylsemicarbazide,

$$PhHNCONHNH_a,$$

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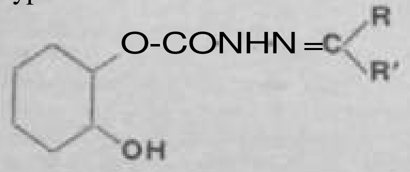


are formed particularly easily by aldehydes but much less readily by ketones and possoaa the property of dissolving in alkali and being precipitated unchanged by acid.

Semioxamazlde, NH, COCONH NH$_r$ m.p. 220-221*, prepared by boiling hydrazine with oxametbane iii alcohol, is recommended as a reagent for aldehydes, *e.g. f* arfural and einnamaldehyde (Kerp and Ungcr, Ber. 1897, 80, 585).

Phenylhydrazine, H,NNHPh, is eonvehiently prepared by reducing benzene di-Kzonium saltawith stannoua chloride (Hentzsch, *ibid.* 1898. 81, 346), zinc dust (Meyer and Leeco, *ibid.* 1883, 16, 2976), alkali sulphite (Fischer, *ibid.* 1875. .8, 590; Annalen, 1878, **190.** 73; Organic Syntheses, Coll. Vol.- I, 1932, 432) or eleetrolytically (Fjchter and Willi, Helv. Chim. Acta, 1934,17, 1416). The manufacture by the reduction of nitrobenzene using lead oxides is the subject of patent claims (G.P. 480598) and <t is also produced by the very remarkable action of fluoraiuine **(NH_aF)** on aniline (F.P. 735020).

Phenylhydrazine has m.p. 19-6° (Fischer, Ber. J908. 41. 74), b.p. 243-5°/760 mm. (corr.), d^n 10970 (Perkin, J.C.S. 1896, 69, 1209). It is very susceptible to oxidation and the hydrochloride is usually used for the prepcration of phenylhydrazones. It is weakly basic and forms mono-ncid salts, although easily dissociable salts with two equivalents of inorganic acids have been described. The base and many of. its derivatives arc toxic

Phenylhydmzino may be do tec ted by its colour reactions with sodium hypobromite (Dehn and Scott, J. Amer. Cnem. Soc. 1908, 80, 1422), 2:4-dinitrobenzaldehyde (Sadia and Kemp, Ber. 1902, 85, 1230) or formaldehyde ami sodium nitropruB8ide (Simon, Compt. rend. 1898, 126. 483; Bull. Soc. chim. 1898, [iii], 19, 299). The oxal&te crystallises well and provides a means of identification (B&mberger and Suzuki, Ber. 1912,45,2762). More conclusive iBits characterisation as a phenylhydrazone *(see* HYDRA ZONES). It io estimated by its reducing action on Fehling'o solution (Strache, Monatah. 1891, 12, 525; *cf.* Maclean, Biochera. J. 1913, 7, 611) or on arsenic acid (Causae, Corapt. rend. 1897, 125, 712 ; Bull. Soc. chim. 1898, [iii], 19, 148).

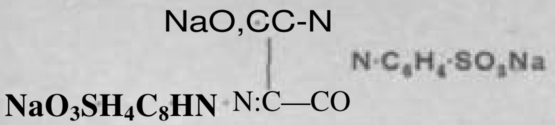
Phenylhydrazine is used in the laboratory to characterise carbonyl compounds as phenylhydrazones and sugars as osazones (mechanism : Kenner and Knight, Ber. 1936, 69 [B]. 341) and as an analytical reagent, *e.g.* for molybdenum (*se* Schmidt, " Anwendnng der Hydrazine iiTdcr analytischen Chemie," Stuttgart, 1907, p. 31), for aluminium in presence of iron (Ishiraaru, Sci, Rep. T6hoku Imp. Univ. 1936, I. 25, 780), for mercury (Miller, Chem.-Analyst, 1938, 27, 9). In technical practice phenylhydrazino is the source of pyrazolone juedicinals (" *antipyrin,"* " *pyramidoTK* "), .bactericidal azo-coin pounds (Jug.P. 13777) and of some azo dyes such as Eriochrome Red (U.S.P. 1856413). Attempts bave also been made to put some of its derivatives to therapeutic uses in the treatment of tuberculosis (review: Schnitzer, Z. angew. Chem. 1930, 43, 744). Phenylhydrazine is an efficient antioxid&nt (B.P. 312774) and an effective softener for natural and synthetic rubber (B.P. 488701) particularly when protected by the presence of another antioxidant, and that it similarly improves cellulosic materials such as those intended for surgical use is claimed (Swiss P. 183210).

Phenylhydrazine-ju-sutphonic acid,

H,N·NH·C_6H_4·SO_3H,

m.p. 286°, is prepared by eulphonating phenyl lydrazine or reducing di&zotised sulphanilio acid. Its reactions are often abnormal as wben it forms addition compounds with aromatic ildehydcs and ketones *(cf,* however, its use in isolating the corpus luteum hormone, Swiss P. 170618, and its reaction with sugars, B.P. 340619). It nevertheless yields pyr&zolones

with aliphatic diketones, and the yellow dyestuff *tartrazine* with dihydroxytartaric acid,



$$\begin{array}{l} \qquad\qquad NaO,CC\text{-}N \\ \qquad\qquad\quad | \qquad\qquad N\cdot C_6H_4\cdot SO_3Na \\ NaO_3SH_4C_8HN\ N{:}C\text{—}CO \end{array}$$

{G.P. 34294 ; Swiss P. 119718); it is also the source of dipyrazolones (F.P. 44843) and nitro-colours (£.P. 409512). Phe ny Ihydrazine-p-sulphonic acid has been applied in tho form of long-chain hydrazones *(e.g.* of lauric aldehyde) as a textile assistant (F.P. 758143). Its possible therapeutic action on malignant tumours has been investigated (Borland, Biochem, J. 1938, S2, 1207).

y-Bromophenylhydrazine,

$$H_aNNHC,H_4Br,$$

m.p. 105-5°, prepared by brominating a phenyl Jiydrazone and hydrolyBing the product (Humphreys, Bloom and Evans, J.C.S. 1923, 123, 1768) or directly by broininiUing phtmylhydrtt. zine and reducing the resulting bromodiazonium bromide (Michaelis, Ber. *ISM,* 28, 21EK>) is a useful reagent for carbouyl torn pounds and particularly for sugars (Neuberg, *ibid.* 1899, 32, 2395; Z. pliysiol, Chera. 1900, 29, 256; microchemical use, Feigl, Mikrochim. Acta$_f$ 1937, 1, 127; Wagenaar, Pharm. Weekblad, 1934, 71, 229).

jj-Nitropheny I hydrazine,

$$H,NNHC,H_t\text{-}NOj,$$

m.p. 157°. p-Nitraniline is diazotised, tMb diazoniuin salt reduced by alkali bisulphite and the resulting ajS-disulphonic acid hydrolysed by mineral acid (Barubergcr and Kraus, 13er. 189U, 29, 281; c/. G.P. 62004). The **sparing** solubility of f>-nitrophenylhydrazones 1ms **been** utilised in the estimation of aldehydes **fFeinbwg,** J. Amer. Chem. Soc. 1827,49, **105),** and*>f acetone in urine (Dehio, *Z.* anal. Chem. 1936, **104.** 417); for chemical use, *see* Feigl (Mikrochim. Acta, 1937, i, 127).

2:4-Dinitrophenylhydrazine,

$$H_2N\cdot NH\cdot C_6H_3(NO_2)_2,$$

m.p, 198°, is best obtained by the' interaction of 2:4-dinitroehloro- or -bromo- benzene with hydrazine in alcoholic solution. It yields an orange pigment, m.p. 298°, on heating with acetoaeetanilido in alcohol (G.P. 2696651 and is a valuable reagent for carbonyl groups *{see* HYJ}RAZONES) both for qualitative"and quantitanv purposes, *e.g.* for estimating furfural and camphor in galenical preparations (Hampshire and Page, Quart. J. Pharm. 1934, 7, 558). Its use according to the original method of Hrady (J.C.S. 1931, 766) sometimes gives rise to hydrazones of slightly varying melting-point, a phenomenon at one time ascribed to sterco-isomemm but believed by Campbell (Analyst, 1930, 61, 391) to be due to aldol condensation products. This worker re-examined the melting-points of dinitrophenylhydrazones of approximately 100 aldehydes and ketonea jind recommends their preparation in taopropyl alcohol using hydrochloric acid.

Methylphenylhydrazine, $H_2NNMePh$, b.p. 131*735 mm., is best prepared by reducing N-nitrosomethylaniline with zinc dust (Fischer, Annalen, 1886, 236, 198) or electrolytically (Wells, Babcock and France, J. Amer. Chem. Soc. 1936, 58, 2630). This base is useful for identifying sugara in particular, the hydcazones or osazonea being crystallised from glycerin (Wagenaar, Pharm. Weekblad, 1934, 71, 229), Methylphenylhydrazine heated with dihydroxynaphlhalenes, yields hydroxynaphtbocarbazoles used aa intermediates, for azo colours (G.P. 548819).

Diphenylhydrazine, H_aN-NPh., m.p. 44°, prepared by reducing N •nitroswdipbenylamine (Fischer, Annalen, 1878, **190.** 175; Stahel, *ibid.* 1890, 268,243), may be used to characterise simple aldehydes but is most valuable as a reagent for reducing sugars with which it gives beautifully crystalline hydrazones. Its use as an antivxidant in gtululiiiu til ill in petroleum cracking distillates has been claimed (U.S.P. 1906044, *793635).

Benzy I phenyl hydrazine,

$$H_sNNPhCH_2Ph,$$

b.p. 216-218°/38 mm,, is prepared by the action of benzyl chloride on phenylhydrazine. When free from pheuylhydrazine it reacts with sugars to give only hydrazones and not osa*2ones.

0-Naphthylhydrazine, NH$_a$NH-C$_{1o}$H,(/9), m.p, 124-125°, ia made by reducing 0-naphthyl diazonium salts (Fischer, Annalen, 1886, 232, 242) or by the action of hydrazine on 0-naphthol in a sealed tube (Franzen, Bcr. 190C, 38, 26(1). This hydrazinu forms highly crystalline, very sparingly soluble hydrazones, particularly with sugars, but it is remarkable thsit different products, probably stercoisomerides, are obtained when they arc prepared in acetic acid or alcoholic solution (Hilger and Rothenfusser, Ber. 1902, 35, 1841, 4444). Naphthocarbazoles may be obtained technically by heating naphthylhydrazinc with hydro*xy*naphthalene carboxylic acids (U.S.P. 1948923).

A number of new chloro- and bromo-nitro. phenylhydrazines agd alkyl-uryl-hydrazines have been prepared by Maaskant (Rec. trav. chim. 1937, 56, 211) by replacing halogen atoms in halogenonitrobenzenes by hydrazine, and representative hydrazones have also been described.

A. H. C.

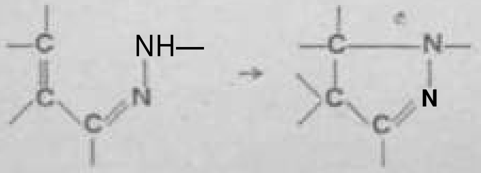
, **HYDRAZOBENZENE,** PhNHNHPh, ia prcjiiired by miming nitrobenzene in hot alroholie solution with zinc dust or iron **in** presence of alcohol or solvent naphtha, and also by electrolysis. M.p. 126-127° (Darmstadt*-, G.P. 189312; Chem. Zentr. 1907, II, 2002; Ismailslfl and Kolpenski, *ibid.* 1933, II, 3049). Decomposes at the melting-point to give aniline and azo benzene. Hydrochloric acid converts it **into** benzidine.

HYDRAZOIC ACID («. Vol. I, 680a).

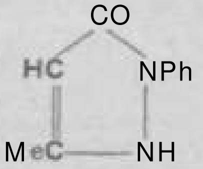
HYDRAZONES. Compounds obtained by eliminating water between carbonyl compounds and hydrazine or mono- or unsym.-disubstituted hydrazines:

$$RR'CO + NH_2NR''R''' \rightarrow RR'C:NNR''R''' + H_2O$$

Simple mono-carbonyl compounds react with hydrazine itself under mild conditions to give monohydrazones, or azines, R'RC:N-N:CRR', according to the proportion of base employed. On the other hand polycarbonyl compounds (*e.g.* benzil) usually afford polyhydrazones although 1:3- and 1:4-diketones react with hydrazine itself to give pyrazoles and pyrazines respectively and β-ketoesters react smoothly to give pyrazolones (*cf.* JPusco and Ju-stoni, Gazzetta, 1937, 67, 3), sometimes with intermediate formation of true hydrazones which can be isolated; dihydropyrazoles (pyrazolines) are often obtained from α/β-unsaturated carbonyl compounds in addition to unsaturated hydrazones (Raiford and Peterson, J. Org. Chem. 1937, 1, 544):



An important technical application of such reactions is the interaction of ethyl acetoacetate with phenylhydrazine when the first-formed phenylhydrazone loses a molecule of alcohol to give (I), the N-methyl derivative of which is the drug "*antipyrine*."



I.

The substituted hydrazones of carbohydrates are readily oxidised by excess of the hydrazine, an adjacent —CH·OH group being oxidised to a —CO group which condenses with the hydrazine to form a dihydrazone or osazone:

$$RCH(OH)CHO \rightarrow RCH(OH)CH:NNHR' \rightarrow RCOCH:NNHR' \quad (A)$$

or

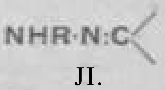
$$RCOCH_2OH \rightarrow RC(:NNHR')\cdot CH_2OH \rightarrow RC(:NNHR')CHO \quad (B)$$

$$(A) \text{ or } (B) \rightarrow RC(:NNHR')CH:N\cdot NHR'$$

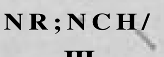
Whilst the mono-hydrazones of sugars are appreciably soluble in water the osazones often crystallise well from water or very dilute acetic acid, and their characteristic crystalline forms serve as a ready means of identifying sugars microscopically (*v. infra*).

All of these compounds are normally obtained by interaction of the components in cold or warm alcoholic, aqueous or weakly acid solution.

Constitution.—Whilst hydrazones derived from bases $NRR'\cdot NH_2$ can only have the constitution $NRR'N:CR''R'''$, a number of alternative structures have been proposed for the derivatives of primary hydrazines, $NHR\cdot NH_2$, *e.g.*

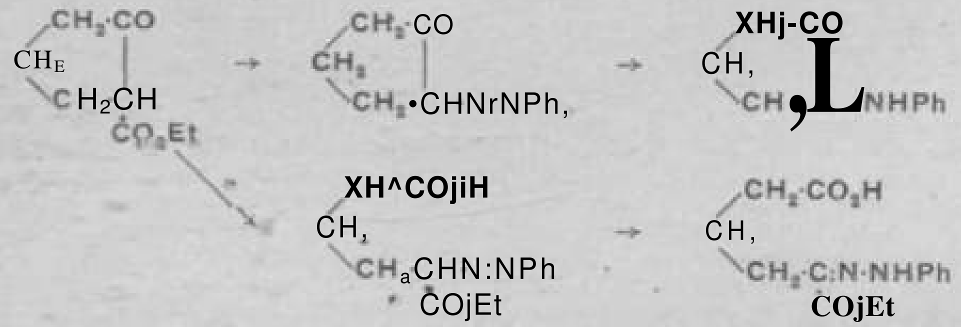


II.

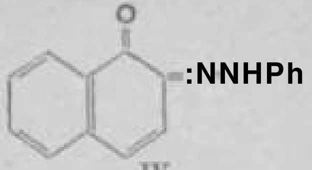


III.

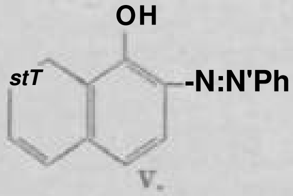
Although there is known to be a close connection between hydrazones (II) and azo-compounds (III) all normal hydrazones are believed to be of form (II). In other cases the problem is not easily decided. Thus many compounds which may be regarded as hydrazones are obtainable by the action of diazonium salts on phenols or compounds with reactive methylene groups. Hydrindene-1:3-dione gives a "hydrazone" which is hydrolysed to ninhydrin (1:2:3-triketohydrindene) and β-ketoesters exhibit similar reactions, usually with "acid" or "ketonic" hydrolysis (Japp and KJingemann, Ber. 1887, 20, 2942, 3284, 3398; Annalen, 1888, **247**, 190). So ethyl *cyclo*-pentanone- and -hexanone-2-carboxylates yield with phenylhydrazine, dione monophenylhydrazones or phenylhydrazones of acyclic keto-acids according to the conditions (Linstead and Wang, J.C.S. 1937, 808; *see also* Pieckmann, Annalen, 1901, 317, 27; Lyons, J. Proc. Roy. Soc. New South Wales, 1932, 66, 516; Mansko and Robinson, J.C.S. 1927, 240):



Among aromatic compounds the question of hydrazone or azo structure has given rise to discussion extending over many years. Zincke and Bindewald (Ber. 1884, 17, 3026) studied the monophenylhydrazone of o-naphthoquinone (IV) and observed that the same compound is obtamed from **a-naphihol** and **booamo** diazoninm chloride and might bo thought therefore to possess structure (V):



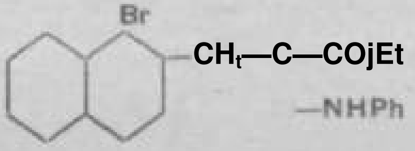
IV.

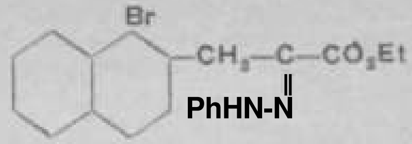


V.

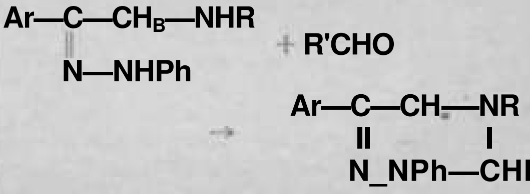
Many similar instances among *o-* andphydroxy- azo-com pounds have since been noted. The evidence in favour of one or the other form in these instances in conflicting and ranges, for example, from the formation by <>-hydroxyazo-compounds of chelate bodies in support of the azo structure to their unwillingness to form alkali metal salts as would be anticipated from a hydrazone structure. The chemical evidence has been summarised by Auwers (Annalen, 1931, **487,** 79; 1933, **505,** 283), who concludes on thia basis that the p-compounds are azo bodies whilst their o- isomcra behave as o-qu in onoid derivatives. Kuhn (Naturwiss. 1932, 20, 622) had suggested a betaine structure, but his Inter spcctroscopic evidence (Kuhn and Bar, Annalen, 1935, **516, 143)** indicates that the two forms are in equilibrium in solution, one or other form pa-dominating according to the solvent; this interpretation, however, is not wholly accepted by Burawoy *{ibid.* 1936, **521,** 298; J.C.S. 193(i, 30). (For a review of the spectrochemistry of hydrazones, see Ha mart-Lucas, Bull. **8OC** ehiin. 1936, [v], 3, 723).

Hydrazouesof the form **SRR':NNR"R"',** whore R, R' are different, are theoretically capable of existing in two stereocheniical modifications according to the direction of the N-N linkage with respect to the double bond and a large number of ijsoruers of this type a» known (.see Mcisenheimcr and Thielacher in Freudenberg'a " Stereochemie,** 1933, p. 1095); quite stable ieomers of certain tli- «and tn-nitro-phenylhydrazones *{e.g.* of furfural) have been prepared (Bredereck and Fritzsche, Ber. 1937, 70 [B], 802) and Sempronj (Gazzetta, 1938, 68, 263) starting with l:2-bronionaphthyltnethy] bromide prepared ethyl a-acetyl-£-{l-bro«o-2 naphthyl) propionate, which on hydrolysis and treatment with benzene diazonium eliloride gave t* *a* isomcra of I -broDio-2-naphthyI-pyruvic ft rid phenylhydrazone which must be regarded as stereoisomers as each gives rise to the same indole by the Fischer reaction :



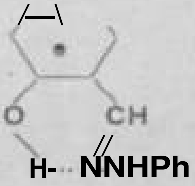


In these instances the configuration is rarely established with certainty as no general reaction is known to nfford any distinction such as does the Beckmann rearrangement in the case of stereoinomeric oximt!3; isoraeric phenylacylamino hydrazones have been diatinguiahed by the ability of one isomer to Form cyclic condensatiun products with aldehydes



$$\begin{array}{l}\mathrm{Ar—C—CH_B—NHR} \\ \qquad \| \\ \quad \mathrm{N—NHPh}\end{array} + \mathrm{R'CHO} \rightarrow \begin{array}{l}\mathrm{Ar—C—CH—NR} \\ \qquad \| \qquad\quad | \\ \mathrm{N\_NPh—CHR'}\end{array}$$

(**Bosch,** Friedenberger and Tischbein, Ber. 1924, 57 (Bj, 1785) and similar arguments have been advanced with reference to stannic chloride addition compounds of benziloaazones (Hieber and Sonuckalb, Annalen, 1927, **456,** 80). The feet that no absorption in the infra-red spectra of o-hydroxyarylhydrazones can be traced to bydroxyl groups has suggested that chelation normally exists. This can be so only, for example, in **wttoyUldehyde** plienylhydrazone (VI), when the configuration of the aryl and —N H Ph groups about the C = N linkage is *trans,*



VI.

and ihdeed if experience of azo compounds *i$* a guide then this is the normal or more stable configuration of all hydrazones.

Propertied,—Hydrazoncs are usually well crystallised compounds, particularly when derived from arylhydrazines. On warming with mineral acid they are relatively smoothly hydrolysed to the parent earbonyl compounds, but regeneration is more conveniently effected by "double decant position" using pyruvic acid :

$$\mathrm{R,C\text{-}.N\ NHPhH\ CH_3COCO.H}$$
$$\text{-*}\ \mathrm{R_aCO+CH_aC(;NNHPh)CO_aH}$$

(Fischer and Aeh, ***ibid.*** 1889, **253,** 67). Difficutties in regeneration, particularly of ketones, have been recently pverrome by the use of tertiary ammonium iiecthyilrazides, Girard's Reagents *{q.v.).*

Mild catalytic reduction of phony 1 bydrazodbs **by** hylrogen in presence of palladium affords substituted hydrazines whilst more drastic reduction results in rupture of the N-N bond with formation of a mixture of amines:

$$\mathrm{CH_3\text{-}CH_;NNHC,H_6}$$
$$\mathrm{-+CH,CH_)NH_{]1}+C_BH_S\text{-}NH_(}$$

Oxidation of hydrazonee with iodine, amyl nitrite or mercuric oxide (Von Peehmunn, Ber. 1893, 26, 1045) yields tetrazanea (hydrotetrazonea). In some instances (Curtiua, J. pr, Cbem. 1891, [ii], **, 182, 200, 535), however, the products do not contain 4 atoms of nitrogen but are true diazo-com pounds (Forster and Zimmerli, J.C.S. 1910, 97, 2156; Staudinger and Kupfer, Ber. 1911, 44, 2197), this providing a convenient method for their preparation. Thus benzophcnonehydrazone and mercuric oxide yield diphenyldiazometbane, {C $_a$H $_s$)$_a$C N $_a$ (Staudinger, Anthes and Pfenninger, *ibid.* 1916, 49, 1932).

Many hydrazonea lose ammonia when treated with zinc chloride or often -with hot dilute mineral acid to yield indolea *{q.v.),* although normal regeneration takes place in some instances and cold strong hydrochloric acid will normally hydrolyse osazones to the diketonea.

The iroino hydrogen atom of phenylhydrazones reacts with maleic anhydride with the formation of substituted maleiamido-acids; in isolated instances these might be of value as a further means of characterising the hydrazones (Parola, Gazzetta, 1935, 66, 624).

Hydrazones may be oxidised by selerioua acid into diazonium salts which may be detected in amounts as little as 0-04 *y%.* by conversion into azo-colours, the reaction therefore affords a sensitive test for hydrazones (Feigl, Mikrochim. Acta. 1937, 1, 127).

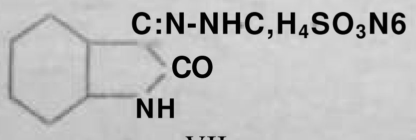
Arylhydrazones of aliphatic aldehydes react with Grignard reagents; the addition compounds may be decomposed to give hydrazines and so provide a useful source of substituted bases (Grammaticakis, Compt. rend. 1937, 204, 1262):

$$R\text{-}CH{:}NNHAr\text{-}yRR'CH\text{-}N(MgBr)NHAr$$
$$\text{-}t\text{-}RR'\text{-}CH\text{-}NH\text{-}NHAr$$

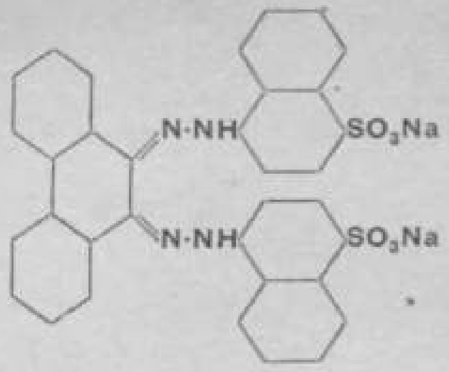
This last reaction is similar to the direct addition of HCN to hvdrazones to form nitrites *{cf.* "Miller Tnd Plothl, Ber. 1892, 25, 2023).

$$R,C{:}N\text{-}NHAr \xrightarrow{HCN} R,C(CN)NH\ NHAr.$$

Application,—Hydrazones havo not found direct extensive industrial application, although the use, for example, of sulphonated arylhydrazones as a source of sulphonated indolea ia the subject of patent claims (B.P. 340619). The derived pyrszoloncs are repreaente'd by isorae drugs (" *untipyrine")* and by an important group of dyestuffs in which tartrazine (t. p. 301a) may be regarded as a hydrazone *(v.* HVOKAZINEH, this Vol., p. 298c). Isatin Yellow (VII), obtained by the action of«phenylhydraziiie-/>-»ulphonic acid on isatin (G.P. 4047Jf), and Phenanthrene Red (VIII) from phenanthraquinone and 1-napbthylhyilrazine-4-nulphonic acid (G.P. 40745) **are** probably true hydrazones.

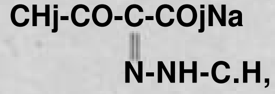


VII.



VIII.

The J)C = N linking in the hydrazones gives rise to considerable absorption of light of A=3,5OO-3,7OOA. and it haa been proposed to utilise this property in more highly substituted hydrazones BUCQ as (IX) in the construction of ultra -violet light filters (U.S. P. 2129132).



$$\begin{array}{l} CHj\text{-}CO\text{-}C\text{-}COjNa \\ \qquad\qquad\ \| \\ \qquad\qquad\ N\text{-}NH\text{-}C.H, \end{array}$$

IX.

In the laboratory hydrazones, usually aryl compounds, provide a ready means of characterising and, in some cases, of estimating carbonyl compounds. Phenyl hydra zone 9 are commonly employed, but *p-aitro-* and p-bromo-phony 1-hydrazone?, /J-naphthyl-. methyl -phenyl-, and aaym, diphenyl-hydrazones are aUo used. The 2:4-dinitrophenylhydrazoncs crystalUw well and aV8 valuable (Brady *el aL,* Analyst, 1920, 51, 77; J.C.S. 1929, 478; 1931, 75«; Allen, J. Amor. Chem. **Soe.** 1930, 52, 2»5fl); owing to the case with which they are obtained in alcoholic aiilphiiric acid or hydrochloric acid solution and their relative insolubility, they can, in some instances, be isolated quantitatively (Iddlcs and Jackson, hid. EngJ Chem. [Anal.], 1934, 6, 454). Instances have been recorded, *t.g.* the complex ketones tetracyclone, acecyclone, etc., whore the commoner hydrazones are unobtainable but where 2:4-dinttrophenylhydrazones have formed normally (Joslen, Ber. * 1938. 71 [B], 2230). Nitroguanyl-hydnjzones (Smith and Shoub, J. Amej. Chem. Soc. 1937, 59, 2077) and m-tolyl-(Sah and Tseu/ Sci. Rep. Nat. Tsing Hua Univ. 1936, 3, 403) have also been recommended for tin* purpose.

Some sugars can lie identified by examining under the microscope the crystalline formof their osazoYies (v. *supra)* with phenyl-, tolyl- and other hydrazines *{see* Sah and Tseu, ***ibid,*** 409 ; Fischer and Paulus, Arch. Pharm. 1935, 273, 83).

A. H. C.

HYDRAZOTOLU EN FS, prepared by suitable reduction of the corresponding nitrotoluene. oo'-Hydrazotolucne, ni.j». **[58**° (Kaasow and Becker, J. pr. Chem. 1911, [ii], 84, 335; G.P. 297019; U.S.P. 1225052). mm'-Hydrazotoluene is **a** yellow oil. pjj'-Hydraxotoluene. ni.p. 134° (Raasow and Rulkc, J. pr. Chem. 1902, [ii], 66, 120, 108).

HYDRIDES. The hydrides, which include a number of the commonest inorganic compounds as well as some of those most difficult to prepare, may be classified as follows :—

(a) Volatile hydrides.
(6) Salt-like hydrides. ^
(c) Solid hydrides of ill-defined composition, which are probably interstitial compounds *(v. infra).*
(d) Certain other hydrides which cannot ra«dily be included in classes *(a)-(c).*

(a) Volatile Hydrides.—The most versatile hydride-forming element is carbon; organic chemistry may be regarded as the chemistry of carbon hydrides and their derivatives, which are, in general, to be assigned to the class of volatile hydrides. Other elements giving hydrides of this type are as follows: boron (Vol. II, 40d); silicon; germanium (Vol. V, 5214); tin (Paneth *et al.*, Ber. 1919, 52 [B], 2020); lead *(idem, ibid.* 1920, 53 [B], 1693); nitrogen *(v.* AMMONIA, HYDRAZINE, AZOIMIDE) ; phosphorus; arsenic (Vol. I, 472(2); antimony ; bismuth (Vol. I, 6996); oxygen *(v.* HYDROGEN PEROXIDE) ; sulphur, selenium, tellurium, polonium ; fluorine (Vol. V, *21Sd),* chlorine (Vol. Ill, 69a), bromine (Vol. II, 117a), and iodine. It will be noted that formation of volatile hydrides is generally characteristic of non-metals, although a few metallic elements also give hydrides of this type. The linkings in volatile hydrides are usually covalent *(v.* COORDINATION COMPOUNDS).

(b) Salt-like Hydrides.—The known salt-like hydrides (viz. LiH, NaH, KH, RbH, CsH (Vol. II, 196c), CaH_2 (Vol. II, *205d),* SrH_2 and BaH_2) are white crystalline solids, generally prepared by heating the metal in hydrogen; for the preparation and properties of barium hydride, *see* Giintz, Compt. rend. 1901, 132, 963; Dafert and Miklauz, Monatsh. 1913, 34, 1685. These hydrides are probably similar in constitution to salts of the metals, since (i) the alkali-metal hydrides have crystal lattices similar to that of sodium chloride; (ii) on electrolysis of the fused hydrides the metal is liberated at the cathode and hydrogen at the anode (Kasarnowsky, Z. anorg. Chem. 1928,170, 311; Peters, *ibid.* 1923, 131, 140);*(iii) the hydrides are exothermic and *denser (cf.* class (c)) than the parent metals (Sieverts and Gotta, *ibid.* 1928, 172, 1; Hagen and.Sievertl, 1930, 185, 239, 254; Proskurnin and Kasarnowsky, *ibid.* 1928, 170, 301). The salt-like hydrides react readily with water, affording hydrogen and the metallic hydroxide, *e.g.*

$$NaH+H_2O=NaOH+H_2.$$

fc) Interstitial Hydrides.—Certain metals absorb relatively large quantities of hydrogen when heated in the gas and give ill-defined solid " hydrides," the exact composition of which varies with the conditions of preparation. Typical products of this type may be represented by the following non-stoichciometric formula*, which merely serve to show the ratio between the numbers of metal and hydrogen atoms in the crystal lattices of the solid hydrides: $LaH_{2\cdot 7fl}$, $CeH_{2\cdot 69}$ (given in Vol. II, 508c, as "CeH_3 (?)"), $PrH_{a\cdot 8V}$ ZrH_{r92}, TiH_{r73}, $ThH_{3\cdot 07}$, $VH_{0\cdot 56f}$ $TaH_{0\cdot 7fl}$ and $PdH_{0\cdot e}$ (Hagen and Sieverts, *ibid.* 1929, 185, 225; Sieverts and Gotta, *ibid.* 1928, 172, 1; 1930, 187, 155; 1931, 199, 384; Z. Elektrochem. 1926, 32, 105; Sieverts and Roell, Z. anorg. Chem. 1926, 153, 289; Huber, Kirschfeld and Sieverts, Ber. 1926, 59 [B], 2891). As in the case of the salt-like hydrides, heat is evolved when these substances are formed from their elements; the interstitial hydrides, however, are *less dense* than the parent elements (Sieverts and Gotta, *II.c).* This fact supports the view that the hydrogen atoms are accommodated in the interstices of the metal lattice, which is expanded by the insertion of these atoms. The interstitial hydrides are powerful reducing agents, probably because the loosely-held hydrogen which they contain is in the atomic condition.

The amount of hydrogen adsorbed by metals such as iron, cobalt, nickel and platinum is insufficient .to indicate formation of interstitial hydrides comparable with those cited above, but the mechanism of the adsorption process is probably^ similar to that of the formation of these hydrides *(cf.* HYDROGEN—Adsorption).

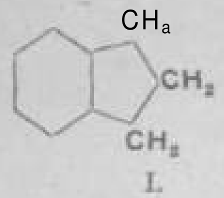
(d) Other Hydrides not Classified Above.—A copper hydride containing rather less hydrogen than is indicated by the formula CuH is precipitated on addition of sodium hypophosphite solution to a solution of cupric sulphate at 65°. Copper hydride is a brown explosive powder when freshly prepared, but it becomes black and more stable on keeping (Neunhoeffer and Nerdel, J. pr. Chem. 1935-36, [ii], 144, 63). It is an endotherjpic compound, the heat of formation being —5-12 kg.-cal. (Sieverts and Gotta, Annalen, 1927, 453, 289). Solid hydrides of nickel, cobalt, iron and chromium, NiH_2, CoH_2, FeH_2 and CrH_2, are precipitated on passing hydrogen through an ethereal solution of phenyl magnesium bromide containing the appropriate anhydrous metal chloride in solution or suspension; another iron hydride prepared by a similar method, FeH_6, is described as a heavy oil (Weichselfelder and Thiede, *ibid.* 1926, 447, 64). There is evidence for the existence of a tungsten compound of a similar type *(idem, ibid.).*

Further details relating to hydrides will be found in articles dealing with the individual elements. For a general review, *see* Emeléus and Anderson, " Modern Aspects of Inorganic Chemistry," London, 1938.

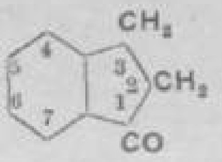
HYDRINDONE, Indanones. From the structure of hydrindene (I) it is evident that it is the parent substance of two cyclic mono-ketones, two di-ketones and one tri-ketone.

a-Hydmndone (Indan-1-one) (II) has been prepared from /9-phenylpropionyl chloride (25 g.) in light petroleum (40 g.) by the action of aluminium chloride (25 g.) with gentle warming for *i* £our (Kipping, J.C.S. 1894, 65, 485). Wcdckind effected the condensation with ferric chloride in carbon disulphide solution (Annalen, 1902, 323, 255). Other modifications of the preparation from 0-phenylpropionyl chloride have been devised (Thiele and Wanacheidt, *ibid.* 1910,

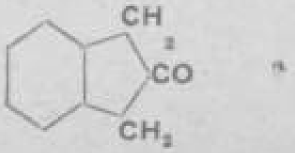
376, 271; Haller and Bauer, Carapt. rend. 1910, 150, 1475; Ingold and Thorpe, J.C.S. 1919,115, 149). It is also formed by dropping acrylyl chloride (20 g.) dissolved in benzene (34 g.) into a mixture of aluminium chloride (20 g.) and carbon disulphide (CO g.) (Moureu, Bull. Soc. chiin. 1893, [iii], 9, 570; Ann. Chim. 1894, [vii], 2, 199; Kohler, Amer. Chein. J. 1909, 42, 375). R. A. Pacaud and C. F. H. Allen (" Organic Syntheses," 1938,18, 47) add hydrogen chloride to freshly distilled indene, the resulting *a*-chloroindene is then oxidised by cbroinie anhydride dissolved in diluted acetic acid (1:1) at 35-40°. After dilution and neutralisation with sodium carbonate, the hydrindone is recovered *by* steam distillation.



I.



II.

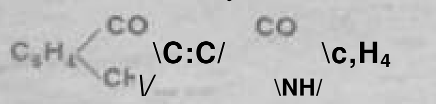


III.

o-Hydrindone is colourless and crystalline, m.p. 39-42° (different observers), b.p. 243-245° (Gabriel and Hausiuann, Ber. 1889, 22, 2018), *d* about 1 1. magnetic rotation (Perkin, J.t'.S. 1894, 65, **489:** 1«M>, 69, 1243).

On halogenation, the hydrogen atoms in position 2 are first replaced, then those in position 3. The *ozime* has m.p. 144°; *cosine,* m.p. 164-165°; *sevuearbazone,* m.p. 239° (or 233°); and •*p-niiropfwnylkydrazQne,* m.p. 234-235°. **The** keto-group ia also capable of reacting with active methylene groups, thus TKorpe and Ingold obtained ethyl indcnyl-3-eyauoacetate *by* condensation with ethyl cyanoacetate in presence of secondary bases (J.C.S. 1919,**115,** 150).

The carbonyl group activates the methylene group in position 2 so that 2 tnol. of a-hydrindone condense to- give an hydro- bis -a-hydrindone (Kipping, *l.c,* p, 495); whilst both methylene groups react with y-nitrpsodimethyl aniline {Ruhemann, J.C.S. 1910, 97, Z445). With isatiii chloride, 2:2'-indoxylindan-l-one,



$$C_6H_4\left\langle\begin{matrix}CO\\CH\end{matrix}\right\rangle C{:}C\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle C_6H_4$$

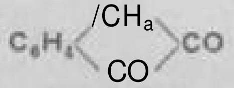
is formed (Felix and Friedla'ander, Monutsli. 1910, 31, 60; Kalle and Co., G.P. 227862).

B-Hythindone. (Indan-2-oneJ (III) has been obtained by distillation of calcium o-phonylenediacetate (Schad, Ber. 1893, 26, 222; Be ledikt, Annalen, 1893, **275,** 353), by **heating** hydrindene glycol with dilute sulphuric acid (Heusier and Schieffer, Ber. 1899, 32, 30) and from 2-nitroindene which ta reduced to /Nhydrindone oxitne (zinc dust and acetic acid) and then hydrolysed by dilute sulphuric acid (Wallaeh and Bewlike, Annulen, l'.)U4. 336, 3). Moore and Thorpe obtained the compound by the action of sulphuric acid on 2-aminoinderie-3-car-boxylie acid which reacts as 2-iinino-hydrindene-3-carboxylic,. acid (J.C.S. 1908, 98, 180; *see also* Proc. C, S., 1911,27, 108).

M.p. 58° or 60°; b.p. 220-225°. *Oxime,* m.p. 155°; *nemicarbazone,* m.p. 218° (decomp.).

l:l:3:3-Tetrachloro-0-hydrindone results from the action of bleaching powder on **l:l:4:4-tetra**chloro-2;3-diketotetrahydronaplithalentt (Zirtcke and Fries, Annalen, 1904, 334, 2.)iij.

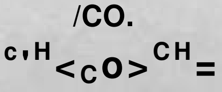
afl-Diketokydrindene (Indaii-l:2-ciione),



$$C_6H_4\left\langle\begin{matrix}CH_2\\CO\end{matrix}\right\rangle CO$$

results when wonitroso-a-hydrindone is hydrolysed bj^ hydrochloric acid in presence of formaldehyde (Perkin, Roberta and Robinson, J.C.S. 1912,101,232; *see* earlier papers. Kipping, ***ibid,*** 1894, 65, 492; Gabriel and Stelzuer, Ber. 1896, 29, 2G04. *Cf. also* Steinkopf and Bessaritsch, ***ibid,*** 1914, 47, 2931).

ay-Diketokydrindzne (Indan-l:3-dione),



$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle CH_2$$

Acetic and phthalic esters are condensed by sodium ethoxide, the resulting diketohydrindene carboxylic ester hydrolysed and carbon dioxide eliminated from the resulting acid. M.p. 129-131° (Gabriel and Neumann, *ibid.* 1893, 26. 954 ; GoPonzio and A. Pichetto, Gaazetta, 1923, 53, 20; W. *O.* Teeters and R. L. Shriner, J. Amer. Chem. Soc. 1933, 55, 3026).

The methylene group is very reactive and anhydrodiketohydrindone is produced by elimination of water between 2 raol. (Wi slit-en us and Kiitzle, Annalen, 1889, 252, 70). According to Hantzsch *(ibid.* 19^, **893,** 322), anhydrodiketo hydrindone is

$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle CH{\cdot}C\left\langle\begin{matrix}CH\\C_6H_4\end{matrix}\right\rangle CO$$

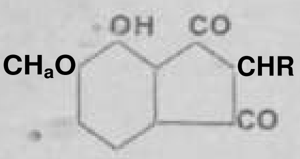
and not

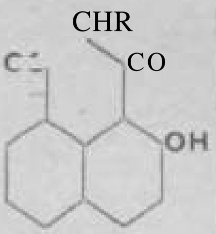
$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C{:}C\left\langle\begin{matrix}CH_2\\C_6H_4\end{matrix}\right\rangle CO$$

Cf. also Fischer and Wanag *(ibid.* 1931, 489 D7)

The reactivity of the methylene group is' also exhibited m the reaction with phenyldiatonimn salts which give triketohydrindetie fl-phenylhydrazone. uy-Diketohydrindene aho condenses with isatin chloride to give 2:2Mndoxyln)duii-l:d-dione, a compound of indigoid type (1'cbx and Friedlander, Monatsh. 1910, 31, 55).

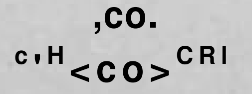
Derivatives of *indan-hZ-dione* have been prepared by Bk<_k, Shaw and T. K. Walker (J.C.S. 1931, 272), iind Walker, Suthers, Boe and Shaw *Ubid., p.* 514). Malonyl chloride and several alkyl substituted malonyl chlorides, $R\text{-}CH(COCI)_a$ (R=H, CH_3, C_aH_s, »-C_3H_7, »-C_4H_B, i*-C,H_u, n-C_aH_{13}, Ti-C_7H_{13}, tJ?o-$C_3H_?$, iso-CiHj, wo-C_5H,,} and $(C_2H_B)_2C(COCI)5$., have been condensed with resoreinol dime thy! ether and with /J-naphthyl methyl ether by aluminium chloride in nitrobenzene solution. Demethylation occurs in tho *ortho-* position to carbonyL and the resulting compounds have the following structures :





The numerous derivatives prepared in this way have been studied with respect to their antiseptic powers, which are selective.

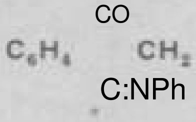
Numerous compounds of the type



$$C_6H_4<\overset{CO}{CO}>CRR'$$

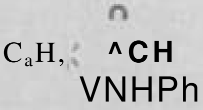
have been synthesised by Freund and Fleischer (Annalen, **1813,** 399, **182; 1913,** 402, 51 ; 1915, 409, 268; 1017, **414,** 1), Das and Ghoeh {J. Amer. Cbeni. Soc. 1911*, 41, 1221), Fleischer (Annalen, 1921, 422, 231, 2t>5, 27:1, 317).

Such disubstituted diketohydrindenes must necessarily possess a diketonic structure, but *enol* ttiutoinerisill is possible in the case of the **parent** substance and certain derivatives. Thus the *ami* (m.p. 208°) is probably



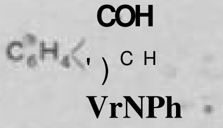
$$C_6H_4\overset{CO}{\underset{C:NPh}{\quad}}CH_2$$

in the free state, whilst the salts with acids and bases are probably derived from the forms



$$C_6H_4\overset{O}{<}CH \quad NHPh$$

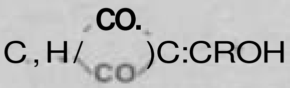
and



$$C_6H_4\overset{COH}{\underset{NPh}{<}}CH$$

respectively.

The enolisation of 2-monoacylindan-l:3-dtones may give compounds of the type

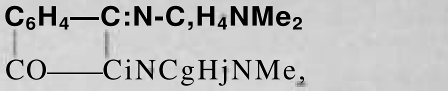


$$C_6H_4<\overset{CO}{\underset{CO}{\quad}}>C:CROH$$

(,• -lieiber and Hopfer, Ber. 192,0, 53 [BJ, 097).

Triketohydrindene, lndanetrione, $C_0H_4O_g$-*Hydrate,* $C_BH_eO_4$. When diplithalylcthane is oxidised with hydrogen peroxide, diphthalyL-ethylene ("indenigo ") is obtained as the chief product of the reaction *(v.* Kaufmann, *ibid.* 1897, 30, 387). A small amount of a by-product was isolated, which was supposed to be tiiketohydrindeno but tbe amount was insufficient for analysis.

Ruhemann subsequently isolated the triketone as its colourless hydrate and cxn.min.erl its reactions (J.C.8. 1910, 97, 143S, 14-tfi, 2025]. For tlie preparation, use is made of the fact that both the methylene groups of a-hydrindone react with p-nitrosodiiuethylanijine. Solutions of 6 g. of the former and 24 g. of **the** latter, each in 50 c.c. alcohol, are mixed, cooled with ice and a small quantity of alcoholic potash added. After a day, the black solid is collected and crystallised from a large quantity of methylated spirit. The product forme green prisms (solution, bluish-black), m.p. 174°, it *U* tiiu hydrate of 2:3-bis (j>-dimethylaminoani)o)-a-hydriiidone:



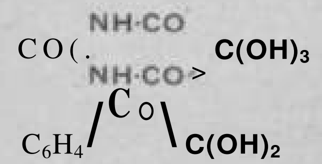
$$\begin{array}{l}C_6H_4—C:N\text{-}C_6H_4NMe_2\\ |\qquad\quad |\\ CO——C:NC_6H_4NMe_2\end{array}$$

By gently warming with diluto sulphuric acid, triketohydrindene hydrate ia liberated *(ibid.).* On crystallisation from hot water, colourless prisms are obtained which turn red at 125°, froth at 139° and decompose at 239-240°. Ruhemann also prepared the hydrate from 1:8-diketohydrindene and from /?-hydrindone using nitroso dime thy laniluio and hydrolysing tho resulting aniLs (J.C.S. 1911, 99, 790; *cf.* PfeiSer and Hesse, J.pr. Chcm. **1W1** [ii], **158,** 315), It is also obtained in 31-35% yiclil from 1:3-dikelohydnnilone and **SeO₂** in aqueous dioxan (W. 0. Teeters and R. L. Shriner, J. Amer. Cbem. Soc. 1933, 55, 3026).

For the absorption spectrum, sec Purvis, J.C.S. 1911, 99, 1953. The alkaline solution ia yellow at first, becoming colourless, at which stage it contains o-hydroiymandelic acid. The aqueous solution reduces Fen ling's and aiomoniacal silver solutions but is itself reduced **tft** 2-hydroxy-l:3-diketohydrmdene by sodium amalgam. The substance is markedly poisonous.

Under the name of *ninhydrbi$_f$* trikctohydrindeoa hydrate has found application as arcagent. ft hud been observed **that the** COXapOOud gave *a.* deep blue coloration with ammo-acids by means of which mere traces of the hydrolytiu products of proteins could be recognised (Ruhemann,J.C.S. **1910,** 97, 2025 ; 1911, 99, 71)3,1486). The presence of free amino- and carboxyl-groups was necessary for a positive result.

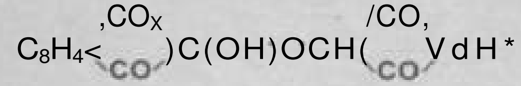
Comparison of the formulas of alluxan and ninhydrin:



$$CO<\overset{NH\cdot CO}{\underset{NH\cdot CO}{\quad}}>C(OH)_2$$

$$C_6H_4<\overset{CO}{\underset{CO}{\quad}}>C(OH)_2$$

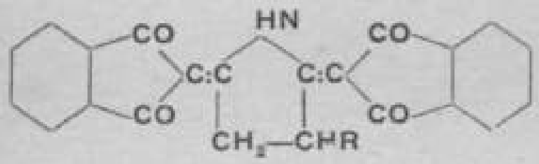
suggests that as alloxan reacts with amino-acids to give an aldehycfe and murexide (Stretker, Annalen, 18C2, 1^, 3b3), so tho triketohydrmdeno may act as an oxidising agent on amino-ncicis giving an aldehyde, carbon dioxide*and ammojiia, the last of those compounds tli.-n rc> acting with the " hytirindantin " formed by the reduction of tho ninhydrin with formation of an ammonium salt of diketohydrindylidenediketohydrindamine. Uydrindantin wast obtained by the reduction of ninhydrin with hydrogen sulphide and gave the expected reactions ; its formula and that suggested for the product from ulnhydrin and ammonia are as follows :



$$C_8H_4<\overset{,CO_X}{\underset{CO}{}})C(OH)OCH(\overset{/CO,}{\underset{CO}{}}VdH*$$

It was found that not only the a-aniino-aeids but also acids with an amino-group in j3-, y-, S-, or e-poBitions respond to the test. Ruhemann states that both amino- and carboxyl-groups must be intact so that the reaction is not given by phenylglycine or hippuric acid or by the esters of the ammo-acids. Ruhemann found that the test was so delicate that when hydrindantin is boiled with alcohol, it gradually dissolves to yield a dark reddish.violet solution. This was attributed to ammonia present in the air of the laboratory, and precautions should therefore be taken (H. Gardner, Lancet, 1930, ii, 525).

Condensation of ninhydrin with proline can be effected in aqueous solution at p_a 7. The products from proline and hydroxyproline have been assigned the constitutions (R = H or OH) (W. Grasamann and *K.* von Amim, Annalen, 1934, 509, 288).



(Numerous references to the use of ninhydrin as a reagent will be found in the biochemical literature.)

Oximes of triketohydrindene :

2-Monoxime, m.p. 200-201° (decomp.). Obtaiacd from l:3-dikctohydrindone'and nitfous actd (W. 0. Teeters and K. L. Sliriner, J. Amer. Chem. Hoc. 1933, 55, 302G).

1:3-Dioxime, m.p. 233° (decomp.). By adding amyl nitrite (10 g.) and HCI (I c.c. 30%) to 2-hydrindone {4-5 g.) in alcohol (15 c.c.) (F. Heualer and H. tSchiuffer, Ber. 1900, 33, 32).

l:2-Dioxirne, m.p. 168" (decomp.). Frota 2-oximino-l:3-diketohydrindone, hydroxylamine hydrocliloride and sodium acetate in alcohol at 60-70°. $(C_9H_6O_3N_2)_aNi$ and other derivatives have been prepared (G. Ponzio and A. Pidictto, Guzzetta, 1923, 53, i, 20).

Jndenone,

Some halogen substituted derivatives have been made (Zincke, Ber. 1687, 20, 1269; Schlossberg, *ibid.* 1900, 33, 2426).

T. m. u.

HYDROCERUSSITE. Until recently this mineral was known only from two localities in Scotland and Sweden as very thin, scaly criiBts with pearly lustre on oxidized lead ores. The Scotch mineral had from its appearance been named " plumbonacrite." Analyses of the very small amount of material had given different results, and the formula

$$2PbCO_3Pb(OH)_s$$

was based on analyses of the artificially prepared crystalline material (L, Bourgeois, 1888). Later it was recognised on specimens from the ancient lead mines in the Mendip Hills in Somersetshire, the best material having been preserved in the mineral collection of John Woodward, which was bequeathed to the University of Cambridge in 1728. In the Mendip lead ores the mineral usually occurs as an intermediate stage in the alteration of mendipite ($2PbO-PbCl_a$) to cerussite ($PbCO_3$). Crystals are rhombohedral with a tabular or lenticular (Oat rhombohedral) habit, and are characterised by a perfect basal cleavage on which the lustre is markedly pearly. On a cross fracture the mineral closely resembles cerussite in appearance, for which it has no doubt often been mistaken. Cleavage flakes are optically uniaxial and negative; sp.gr. 0-80, hardness 3^. Analyses of the Mendip mineral show the presence of a small amount (0-3%) of **oMoiine,** suggesting the presence of a compound $2PbCO_3$-$PbCI_2$ in isomorphous mixture with $2PbCO_3$-$Pb(OH)_2$. Hydrocerussite as minut* scaly crystals lias also been detected in Roman lead slags from Laurion in Greece and from the Mendip Hills (L. J. Spencer, Min. Mag. 1923, 20, 80).

Hydrocerussite is identical in composition with the white lead (Latin, cerussa) of commerce, and the purer flake-white no doubt owts its scaly form to the lamellar habit and the perfect basal cleavage of the crystalline material.

L. J. S.

HYDROCHLORIC ACID *(v.* Vol. III, 69).

HYDROCINCHONIC1NE (v. Vol. III, 163c).

HYDROCINCHONIDINE *(v.* Vol. III, **162a).**

HYDROCINCHONINEftr. Vol. III, ***IGSd).***

HYDROC INCHON I NONE *(v.* Vol. III, **LOW).**

HYDROCINCHOTOXINE (t. Vol. 11.1, 163c).

HYDROCUPRiICINE («. Vol. III, 168a).

HYDROCUPREIDINE *(v.* Vol. III, 165c).

HYDROCUPREINE *(v.* Vol. III, 167c).

HYDROCUPREINOTOXINE *{v.* Vol. III, HiKa).

HYDROCYANIC ACID *(v.* Vol. III, 492c).

HYDROFLUORIC ACID. Use of in etching glass *(v.* Vol. V, 281c).

HYDROFLUOSILICIC ACID *[v.* Vol. V, 2826).

HYDROGEN.

History.—The existence of a gas, which has since been shown to be predominantly hydrogen, was recognised in very early times. Its inilammability was noted by Van Helmont and by Turquet de Mayerne in the seventeenth century. It hence became known as " inflammable air " and was somewhat naturally confused with other inflammable gases such as hydro carbons, carbon monoxide and hydrogen **sulphide.**

Cavendish (Phil. Trans. 1766, 56, 141) showed that in the reaction between dilute sulphuric or hydrochloric acids and iron, zinc or tin the same gas wis liberated. He confirmed its combustibility, and measured its specific gravity and the amount of gas evolved relative to the amount of metal used. During most of the eighteenth century, however^ the ideas on the nature of hydrogm were confused by the phlogiston theory.

Occurrence.—In the free state hydrogen occurs widely but in small quantities. To a viyy slight extent it occurs free in the atmo**jrphflre** (Gautier, Ann. Chiui. Phys. 1901, [vii], 22,5; Liveing and Dewar, *ibid.* p. 482; Rayleigh, Phil. Mag. 1902, fvi], 3, 416; Leduc, Compt. rend. 1902, 135, 860, 1332). According to Claude {*ibid.* 1909, **148,** 1454) there is less'than 1 part^>f hydrogen in 1 million parts of air. It occurs in the upper atmosphere but is virtually absent from certain lay era (Kaplan, Nature, 1935,**136,** 549; Pederson, Kgl. Danske Vidensk. Selsk. Math-fysi. **Medd..** 1U27, 8, No. 4; Amer. Chein, Abstr. 1928, 22, 2873). It occurs in fumarolea in Tuscany and other places. The gases issuing from the Bait beds of Stassfurt (Rcichardt, Arch. Pharm. 1860, 103, 347; Precht, Ber. 1880, 18, 2320) and at Wieliczka {Rose, Pogg. Ann. 1839, **48,** 353) contain hydrogen, arid it also occurs in the gases given off by the oil-wells of Pennsylvania, West Virginia, Ohio and Indiana (Engler, Ber. 1888, 21, 1816; U.S.A. Geol. Sur. 1909, 2, 297). Hydrogen has been found occluded in certain meteorites (Graham, Proc. Roy. Soc. 1867,15, 502; Mallet, ***ibid.*** 1872, 20, 365), and in a large number of minerals (Ramsay and Travers, Proc. Roy. Soc. 1897, 60, 442; Tilden, *ibid.* 1897, 60, 453), and in clays. It occurs in the gaseous mixtures evolved from certain volcanoa (Bunsen, Ann. Chim. Phya. 1853, fin], 38, 259; Deville, Compt. rend. 1862, 55, 75).

Spectroscopic observations have shown that hydrogen completely surrounds the sun, forming an envelope which has received the name of the chromosphere. Hydrogen also occurs in certain stars and nebulae.

In a combined form hydrogen has even a wider distribution onHhe earth's surface than in the free state, and occurs muca more abundantly. In the region comprising the earth's »rust, the ocean and the atmosphere, hydrogen is the ninth most plentiful element from the point of view of weight (0-95%) and the second most plentiful element from the point of view of the number of atoms (16-3%) (Clarke, "The Data of Geocnemistry," Washington, 1916, p. 34). The forms in which combined hydrogen occurs are well known: water and hydrates, acids, alkalis, hydrides, hydrocarbons and virtually all organic compounds.

FOEMATIOS.

(1) Electrolysis.—If a dilute solution of an acid is electrolysed between electrodes which are unattacked by hydrogen, there is an evolution of hydrogen at the cathode as a **primary** decomposition product. Under comparable condittons the electrolysis of a salt or alkaline solution yields hydrogen at the cathode as a secondary decomposition product'. Thus witb Na_zSO_4:

Primary decomposition,

$$Na_3SO_4 -> 2Na^{+}+SO_4=$$

Secondary decomposition at cathode,

$$2Na+2H_aO->2NaOH + H_a$$

In dilute solutions of acids and of alkalis the final products are in both cases H_2 and O_3, and the process is referred to as the electrolysis of water, since the acid or alkali decomposed by electrolysis is reformed by secondary decom-* position and only the elements of water are removed from the reaction medium. The energy required for evolution of equivalent amounts of H_2 and O_2 (apart from over-voltage and the resistance of the solution) is thus independent of the electrolyte. The total energy required with smooth platinum electrodes was determined by Le Blanc (Z. physikal. Chem. 1891, 8, 299; 1893, 12, 333) as about 1-7 volts for *N*-solutions, which is thus the minimum voltage required for the electrolysis of water. Ideally 1 g.-equivalent of hydrogen (for that matter of any element) is liberated by 96,500 coulombs of electricity. In practice the amounts of hydrogen and oxygen evolved are not exactly equivalent to each other or to the amount of current. This is due to the different solubility of H_2 and O_a in water, to recombination of H_a and O_a in solution, and (if a sulphuric acid solution is used) to the formation of persulphuric acid and to other minor causes.

Hydrogen is ako evolved in the electrolysis of certain solutions where oxjpen is not given off at the anode, *e.g.* in the electrolysis of acids such as HCI whose anion does not undergo secondary decomposition. Here the products are H_t and Cl_s and the decomposition voltage ia about 1-31 volts for a Absolution.

In the electrolysis of solutions of certain salts of strong acids and strong bases, *e.g.* $Na_£Sp_4$, $Ca(NO_3)_2$, the final decomposition products are again hydrogen and oxygen. The secondary decomposition, however, results not in the re-formation of the neutral salt but of acid (**H_aSO_4** in the case of Na_2SO_4) at the anode, and alkali (NaOH in the case of $Na_?SO_4$) at the cathode. The anions are thus discharged from an acid solution and the cations from an alkaline solution* The degree of acidity and alkalinity are practically the same for all salta of strong acids and strong bases, and the decomposition potential is about 2-2 volts for *N*-solutions.

In the electrolysis of metal halides, hydrogen is formed by secondary decomposition at the cathode, but there ^ia no corresponding decomposition resulting in oxygen at the anode. The decomposition voltage therefore depends upon the halide. For an Absolution of NaCI"it is 1-98 volts,

(2) Ionic Displacement of Hydrogen from Water.—The action which certain metals exhibit of displacing hydrogen from water depends upon the electropositiveneas of the metal being greater than that of hydrogen.

When an electropositive metal is immersed in a solution of its oun salt it forces eome of its ions into the solution by virtue of its electrolytic solution-pressure. This process continues until t lie osmotic pressure produced by the addition al ions equals the electrolytic dissociation pressure, leaving the metal with *a* negative charge which, for a given **strength** of solution and at a given temperature, is dependent upon the electropositiveness of the metal.

The following are the electroiuetric values for some of the principal elements, measured against normal solutions: Frit z Ephraim, " Inorganic Chemistry," Gurney and Jackson, 1939.

Cs	-2-91	Co^{++}	-02ft
Rb	— L'-7 J	Ni	-0-22
K	**-2-61**	Pb	-012
Na	-2-45	Sn	-0-10
Ba	-2-15	H	000
Ce^{+H}-	-2-10	Sb	+01
Li	**-2-09**	Bi	+0-2
Sr	-2-07	Ce^{++++}	4-0-24
Ca	-1-90	As	+0-3
La	-1-75	Cu^{++}	+0·34
Th	— 1·75	Re	+06
Nd	-1-05	Ag -	+0-80
Mg	-1-55	Hg'+	+0-80
Pr	-1-44	Pd	+0-82
Al	-1-28	Pt	>+0-8G
Mn	-1-04	Air[1].	+1-5
Be	-0-81	Te	-0-84
Zn	-0-76	S	-0-55
Ga	<-0-76	O	+0-39
Cr++	**. -o-c**	I	•; •o-'.-i
Fe++	-0-43	Br	+ 1-08
In	>-0-40	o;	+ 1-3G
Cd	;'V40	F	+ 1-92
Tl	-0-33		

Any of the metals above hydrogen will therefore displace it from a solution containing hydrogen ions. In the case of water where the number of hydrogen ions is low, the rate; of evolution is lower than with acids, but it nevertheless does occur very readily in the cold with **the** alkali **metals,** but decreasing in extent on **deaaendins** the series. The same considerations **which** apply to the liberation of hydrogen from water also govern its displacement from NH_3.

In many cases the hydroxides formed protect the metaf from further action and any method of increasing the solubility of the hydroxide, such as an **increase** in temperature or the application of a mass-action effect, increases the extent **of** the **reaction.**

The effect of metallic couples is to decompose water electrolyticaDy. Metallic **Impurities,** by forming **couples,** h»vo a **marked** effect on the apparent readiness of a metal to replace hydrogen from water (tmd neids).

(3) Displacement of Hydrogen from Acids.—Hydrogen ions can be displaced as hydrogen atoms (and tiience as molecules) from aoid solutions similarly **to** their displacement **from** water. The greater concentration of H ions in this case, and the usually **greater** solubility of the salt compared with the hydroxide, facilitate the reaction. In practice it is found **that** the ease of displacement of hydrogen seldom follows the series given above, since this series refers to normal solutions and the order of the metals varies with concentration. Traces of impurities also have a marked effect on the reaction for reasons which have been mentioned earlier. The reaction is facilitated by any factor **which** increases the number of hydrogen ions {dilution), decreases viscosity of the acid and facilitates replacement of the H ions removed from the sphere of action (increase in temperature), increases the sphere of action (powdering of the metal), or removes a protective gaseous or solid coating from the metal (dilution, etc.). Will known examples of the inhibition of the reaction are Fe an cone. **H_2SO_4** and Pb in H,SO<(in which protective coatings of different types are formed. On exposure to an oxidising agent many metals, particularly iron, form a protective oxide coating, even when the oxidising agent is itself an acid, *e.g.* nitric, chloric, chromic. The passive metal' is then insoluble even in dilute acids until another metal is introduced to set up a couple, or until the coating has been removed by reduction or other means. The Baits of many weak acids are readily hydtolysed to an insoluble hydroxide or to a basic salt, so that weak acids usually have but little action on metals.

(4) Displacement of Hydrogen from Alkalis.—Many elements displace hydrogen from hydroxides, *e.g.*:

React ants.		Products,	
Na	NaOH	Na_2O	H_n
Al	NaOH	Na_3AlO_3	**H,**
Zn	NaOH	Na_2ZnO_2	H,
Sn	NaOH	Na_4SnO_4	H_2
B	NaOH	Na_3BO_3	H_2
Si"-	NaOH	Na_4SiO_4	H
P	NaOH	Na_3PO_4	H,, PH,
Cl	NaOH	NaClO.	HCl->NaCl

The element concerned forms part of the anion in the resulting compound and the reaction is favoured by the metal of the hydroxide being a strong cation. Thus **NaOH** is better than Ca(OH),. Where possible the hydrogen combines with excess of the element ao that the method applies principally to metals and those elements having metallic, nllotropes, *e.g.* PH. as wsll as H, is formed with P, and onlv HCI with Cl.

(5) Reduction of Water.—The ionic dis**pkoemefit** of **H** from water has already been described, but H can also be produced from water by non-ionic reaction with many metals. Th'e reaction of water with the metals other than those at the top of the electrometric series is prolnbly non-ionic, *e.g.* in the high temperature reaction with Fe.

$$H_2O + Fe \rightleftharpoons FeO + H_2$$
$$H_2O + 3FeO \rightleftharpoons Fe_3O_4 + H_2$$
$$4H_2O + 3Fe \rightleftharpoons Fe_3O_4 + 4H_2$$

---

*or the reierenres to the equilibrium coostrnts , hea tS ni111 rates of these M'M ,, reactions, *see.* ucunr, "Comprehensive Treatise on Inorganic an *1* iheoretical Chemistry," 1934, XIII, p. 806.

The vnlues given **btve aince been** motlified (Ciiip. man , J. Amer. Chem. Soc. 1933, 55, 3131; IU34, 56, 2011; Emmett and Shultz, *ibid.* 1933, 55, 1370; Shibata, J. Chem. Soc. Japan, 1935, 56, 736; Tschufarov and Averbuch, Acta Phyaicochim. U.R.S.S. 1936, 4, 617). When no attempt is made to discriminate between ionic and non-ionic reactions, the metals can be divided into groups according to their action on water—a concept which played an important part in early attempts to classify the metals (Thenard, "TraitS de Chiinio Eltmeiitaire," Paris, 1810; Renault, " Ooura elemental re cleChimie," Paris, 1840).

Grqjip.	Metals.	Condition fordecom-poatt Ion of water.
L	Alkali and alkaline earth.	Cold.
2.	Be, Mg. etc., and rare earths.	50-100°C.
3.	*tn,* Cd, Sn, Fe, NI, Co, Cr, Os.	Red heat, *ea.* 550°C.
4.	Cu, Pb, etc.	White heat, *at.* 1,300°C.
5.	Hg, Ag, Au and'Pt family except Os.	No reaction.

Further data, including equilibria, etc., of these reactions, have sinue been obtained, *e.g.*; Cr, Aoyania and Kanda (J. Chem. Soe, Japan, 1934,55, 1174). Co, Shibata and Mori (*ibid.* 1933, 54, 50; Z. anorg. Chem. 1933, 212, 305). Ni, Skapski and Dabrowski (Z. Elektrochem. 1932, 38, 365). Sn, Emmett and Shultz (J. Amer. Chem. Soc. 1933, 55, 1390); Meyer and Scheffer (Rec. trav. chim. 1935,54,294). Mn, Aoyama and Oka (Sci. Rep. T6hoku, 1933, 22, 824; Amer. Chem. Abstr. 1934,28,1915). Me Ala generally, Guertler (Z. Metallic. 1926, 18, 363); Kernbaum (Compt. rend. 1911,152,1668); Pourbaix (Bull. Soc. Beige Ing. Ind. 1934, No. 7-8, 07 pp.). Mo. Chaudron (Compt. rend. 1920, **170,** 182). A I, Scak (Atti. R. Accad. Liacei, 1913, fv], 22, i, 43; Amar. Chera. Abstr. 1913, 7, 1684). Mg, Piccordi (Gazzetta, 1930. 60, **837**j Anier. Chem. Abstr. 1930, 24, 3960); Knapp {Chem. News, 1912, 105, 253); W, Chaudron (Compt. rend. 1920,170. 105U). Ca, Lettermann (Z, physikal, chem. Unterr. 1911, 13. 176). Zn, **Bchacheri** (Gazzetta, 1932, 62, 839). Cu, Gallo (Annali Clrm. Appl. 1937, 27, 269).

Water is also decomposed oy non-metallic elements. The reaction with C is best known.

$$C+H_2O \rightleftharpoons CO+H_2$$
$$C+2H_2O \rightleftharpoons CO_2+2H_2$$

{.it>,i Chemical Reactions, p. 318«, and GAS. WATER).

SI and 8 act similarly. Se and Te liberate H_2 from HgO, Te more readily than Se {Montignic, Bull. Soc. chim. 1934, [v], i, 507). S does not normally liberate H_8 in its reaction with H.O, but at 1,000° H_s begins to appear in the products (Randall and Bichowsky, J, Amer. Chem. **Soc** 1918, 40. **882,** 308; Lewi* **and** Randall, " Thermodynamics," New York, 19U3, p. 047). Similarly, P, under some conditions, yields H_8 (Ipatiev and Freitag, Z. anorg. Chem. 1933, **215,** 388). The halogens do not lilierate H_2 from water.

Besides the elements many compounds react with water to give H_2, *e.g.:*

$$CO + H_2O \rightarrow CO_2+H_2$$
$$CH_4+H_2O \rightarrow CO + 3H_2$$

(*see* C11cmical Reactions, pp. 3ISA, 319a).

Among liquid-phase reactions in which hydrogen is produced are water with nianganous oxide, uranium oxide, chromous oxide, titanoua oxide, potassium cobaltocyunide, raolybdenous chloride, etc. Hydrogen is sometimes evolved during the hydrolysiB of some ra.rbides (**Mn_3C**) (». Vol. II, 281c) and Bilicidea (CaSIj) {». Vol. II, 227c).

(6) Decomposition of Hydrides.—Thesalt-Hko hydrides (NaH, CaHj,, etc.) are readily hydrolysed by water to yield hydrogen,

$$NaH+H_2O \rightarrow NaOH+H_2.$$

This reaction **could** also lie regarded as a decomposition of water to give H_a.

The volatile hydrides behave in various ways with water. The halogen hydridea tend to ionise an acids $HCt \rightarrow H^+ + CI^-$; a tendency which appears less strongly with the VI group hydrides, *e.g.* H_2O, H_2S. The V group hydrides, uuch *as* NH_3, by virtue of the lone pair of electrons on the central atom, co-ordinate with an H of H_aO and ionise as bases, HOH+NH3^HO-++**HNH₃.** With the IV group hydrides on the other hand the O of water tenda to co-ordinate with the central atom, *e.g.* Si, resulting in a hydrolysis which yields H_s, SiH_4+2H_aO ->S\P[5+4'H_2. Similarly with the higher silanes. C is however unable to expand its octet and consequently *CH*± f$ stable to HjO at ordinary temperatures. In the III group a similar hydrolysis ocvurs and the boranes **yield** HJ+HJBO;,. Kilanc, but not methane, yields H_a with HCI, SiH^+HCI ->SiH_3CI+H_r

Thermal decomposition of hydrides is also possible and includes all types of hydrides, *e.g.* NaH, CH_4, NH,, H_2O, H,.S, HBr. Tfte more important of these aro dealt with either under Decomposition of Hydrocarbons (see *below* (7)) or Chemical Reactions, p. 319a.

(7) Decomposition of Hydrocarbons and other Organic Compounds.—Hydrocarbons readily yield hydrogen at elevated temperatures, cither through, rupture of the molecule into smaller fragments jnchiding H_8 (cracking) or by simply splitting off H_2 (dehydrogenation). These reactions are endothcrmic. The development of catalysis in relation to these reactions has made great progress in recent years.

In general the reactions obey certain **principled**

- (i) The decomposition tends to favour the product which involves least rearrangement in the molecule.
- (ii) **The** C—C is more stable than the C—H link in aromatic compounds, and Ifcss stable in aliphatic compounds. Thin is Haber's rule and is of wide but not of universal application.
- (iit) Radicals of low electron-attraction are formed **preferably** to those of high electron - attraction.

See Hurd, " The Pyrolysis of Carbon Compounds," Chem. Cat. Co., 1929, Chap. II; Ellis, " The Chemistry of Petroleum Derivatives," Vol. I, Chem. Cat. Co., 1934; Vol. II, Rheinhold Pub. Corp., 1937, pp. 74-76 ; Egloff, **"The** Reactions of Pure Hydrocarbons," Amer. Chem. Soc. Monograph Series, No. 73, New York, 1937, p. 167; Egloff, Lcvinson and Bolimau, " Thermal Reactions of Aromatic Hydrocarbons," Chicago, 1934; Motovilova, " Catalytic Dehydration and Dehydrogcnation of Alcohols," J. Chem. Ind. U.S.S.H., 1935, 12, 1184, 12t)0.

Preparation of Pure Hydrogen.—The preparation of small amounts of hydrogen raises completely different problems from those of industrial production. For the preparation of hydrogen on a laboratory basis the best sources of information are Gmelin, " Handbuch der anorganischen Chemie," Aun*. 8, Verlag Chemie, Berlin, 1927, System No. 2, p. 18, and Farkas and Melville, " Experimental Methods in Gas Reactions," Macmillan, New York, 1939.

The standard method is by the action of acids (dil. HCI or dil, H_aSOj) on metals {Mg, A I, Zn or Fe), preferably Zn + $\mathbf{H_2SO_l}$ (diluted 1 in 8). Further details are given hv Loftier (Amer. Chem. **Abutr.** 1927, 21, 1071) and Edwards (J. Ind. Eng. Chem. 1919, 11, 961).

The electrolysis of acids can yield reasonably pure hydrogen, *e.g.* 10% $HjSO_4$, with Pt electrodes set wide apart to avoid contamination by O_a, followed by passage of the gas at alight pressure through alkaline pyrogallol and then water.

It is more usual, however, to electrolyse alkaline solutions, *e.g.* pure baryta (Bilker, J.C.S. 1902, 81, 40».or 30% NaOH with pure Ni electrodes (Veaes and Labatut, Z. anorg. Chem. 1902, 32, 4o4: Sivkov. Amer. Chem. Abstr. 1935, 29. 53 ; Kink aud Mantell, Trans. Electrochem. Soc 1927, 52, 109). The procedure given by Farkas and Melville, *op. cit.,* involves purification by passing over CaCL (to remove,most <f the HjjOy, over Pi asbestos or Pd asbestos at 300°C. (to remove O_a), over P_aO_s and through a liquid air trap (to effect complete drying). Sjiwially pure hydrogen is best obtained by allowing the gas to diffuse through a palladium tube into an evaluated reservoir.

Pure water may be electrolysed at 200 volts between Cu electrodes to give pure hydrogen (Saxon, Chem. News, 1931,**142,** 49).

Hydrogen at pressure can[1] be generated in a portable apparatus, depending on the ferrosilicon —NaOH reaction (Lefebvre, Chim. et Ind. 1928,20, 231).

Hydrogen for ordinary use is conveniently purchased in cylinder' at about 100 atm. pressure, '>r *is* generated in"a Kipp*s apparatus. In the latter case the gas cont&iiu $\mathbf{AsH_3}$, PH_3, hydrocarbons, Oj and CO_3 and, according to Farkus and Melville *(op. ciL),* can he purified by being I i.isitedaucc'eKsivelythrough50%KOH, saturated $KMnO_4$ twice over, CaCU over Pt asln-stus ;it 800°C. in a silica, tube, CaCL and P_aO_6. A inore detailed account of individual impurities •*Mid* their method of removal is given in Giuelin, " Handbuch der anorganischen Chemie," Aufl. i$, 19-7. Pure hydrogen may also be obtained by evaporation from liquid hydrogen (U.S.P. 2022165).

When drying is effected either by passing the gas over drying agents or through cooled traps, the weight of H_2O in grams per cubic metre remaining when the systems are in equilibrium is:

Cold traps:	
−193°C.	$0{\cdot}7\times10^{-23}$
−115°C.	2-4x10"*
Drying agents (at 25°C.):	
P_aO_6	<2xIO-»
Mg(CIO<)j,	<5xlO"^{4}
$Mg(ClO_4)_2,3H_2O$	2xlO"^{3}
KOH (fused)	2x10-
$\mathbf{AI_2O_3}$	3xlO"^{3}
$\mathbf{H_2SO_4}$	3x10-*
Ca_ C . ^ . 2. .S . 1	O × $^{-1}$

Estimation of Hydrogen.—On-passinga gas containing hydrogen slowly over palladised asbestos heated to dull redness, hydrogen is removed completely, leaving paraffins unaffected. CO, CO_2, H_2O, benzene, alcohol, HCI or NH_3 interfere. Hg destroys the activity of the Pd. *See* Lunge and Ambler, " Technical Gas Analysis," Guruey and Jackson, 1934,

PHYSICAI. PROPERTIES.

Unless otherwise specified, the following data refer to molecular hydrogen containing the naturally existing ratio of protium and deuterium atoms {about 5,000 to I), the molecules being normal in respect to ortho and para, i.e. 0-7492 ortho and 0-2508 para.

Atomic Weight.—H on the physical scale is 1O081, on the chemical scale thi3 becomes 1-00785; allowance for ^{e}H with the abundance ratio 1:5000 gives 1-00805 for chemical hydrogen, **and** 1*0081 has been adopted (Eighth Report of the Committee on Atomic Weights of tho International Union of Chemistry, in Baxter, HflnigBohmid and LeBeau, J. Amer. Chem. Soc. 1938, 60, 737). A --omplete review on the atomic weight of hydrogen is given by Brescia and Rosenthal (J. Chem. Educ. 1939, 16, 491).

Pressure/Temperature/Volume Relationships, etc. — *{See* table on opposite page.)

The figure for 1 atm. 0°0. is taken from Blanchard and Pickering (U.S. Bureau of Standards Sci. Paper, No. 529, 192B). The remainder are from Deming and Shupe (Physical Rev. 1932, [ii], 40, 848).

The equation of state put forward by Beattie and Bridgeman (J. Amer. Chem. Soc. 1928, 50, 3133; Proc. Amer. Acad. Arts. Sei. 1928, 63, 229) & applicable over a wide range of temp^raturo and pressure. The equation is

p-[KT(I-$_e$)/V*]x[V+B]-A/V«

Mol. wt. adopted 20154.

Where A=A_0[l-(o/V)]
B=B_9[l-(£/V)]
< = c/VT^3
R=0-0820«
V=litres per g.-mol.
jt>=atmiispherea
T^e = K = °c+273·13°

p.	v.	4.	/-	v \dplT	.T (dv) v \dT/p
t = − S0°C.					
25	744-7	2-707	25-41	0-983	09956
100	196-3	10-27	107-1	0-927	0-9R95
1,000	3410	5911	2.252	0-524	0-5592
l=0°C.					
1		008988			
25	910-3	2-214	25-38	0-985	0-9917
100	238 6	8-447	106-4	0-flSfi	0-0617
1,000	38-35	52-56	1,993	0-586	0-6026
(=100°C.					
25	1,240	1-625	25-31	0988	0-9905
100	3220	6-259	105-2	0949	O*0ftl4
i,qpo	46-75	43-12	1,696	0-671	0-6676
f=500°C.					
25	2,554	0-7891	25-16	0-993	0-9938
100	65 \l	3093	102-7	0972	0-9753
1,000	79-91	25-22	1,312	0-814	0-7987

p — pressure In atmospheres.
« \n\wuc. **la** *oil',,*- **oentluwlyM pa** c.-mol.
d~ density in grams per litre.
/ B=fugaclty in atmospheres.

(ir) T = coeffl(;lent of expansion with pressure.
'X.fQ} v\dTJp «anoefTlc!entof expaiiBlon with temiieraturc.

and for H, A_0=01975
a=-000506
B_0=002096
6—004359
c=0-0504 x 10^4

For the compression of mixtures the compressibility of each actual mixture ia required. The compressibility of binary mixtures of hydrogen is treated in general terms by Kleeiuan (J. Franklin Inst. 1930, 209, 229). Mixtures suitable for ammonia synthesis hare been examined over a very wide range of temperature and pressure (Bnrtlett, J. Amcr. 8hem. Soc. 1027,49, **1960;** 1028,50,1275; Demingand Shupe, *ibid.* 1 n:i0, 52, 1382).

Specific Heat. Probably the best values for the specific heat of hydrogen gaa at I5°C are :

rp (cat. **per** g.) *	3-40
C_P (fill, per g.-mol.)	6-86
d, (cal. per g.)	*f* 2-41
C,(cal. perg.-mol.)	4-87
y	141

The **variation** of *Gp* with temperature is given to **within** 1% of theoretical by ***the*** expression :

Cp (cal. per g. mol.)
- 0-88+O-0OO066T+ 0-0000(I0279T*

(Bryant, lnd. **Sng.** Chem. 1933, 25, 820). Similarly the variation of C_p is **ghrsn** I>y

C» (cal. per g. mol.)
= ^$7+ 0-000539T+0-000000146T².

{Kentble and Van Vlctk, Physical Rev. 1923, [ii], 21, 653). *See also* Suhuster **(Wttnne, 1935,** 58, **39); Quna** (FeucruiigBtech. 1935, 23, 85); Chipman and Fontana (J. Amer. Chem. Soc. 1935. 57, 48); Spencer and Justice *(ibid.* 1934, 56, 2311); for high temperatures and pressures, Gelperin and Rips (Khirastroi, 1934, 6, 455) j for high temperatures, Briickner (2, anal. Chem. 1935, 100, 281) anct David and fab. (Phil, Mag. 1934, [viij, 18, 307); for high pressures, Godnev and Sverdlin (Khimstroi, 1934, 8, 8); for low temperatures and high pressure, Gelperin and Rips *(ibid.* 1934, 6, 599); for quantum theory and specific heat, Van Vleek (Physical Rev. 1926, [ü], 28, 980); for *C_P[C_V* ratio, Workman *{ibid.* 1931, [ii], 37, 1345); and fur total h<»t content, Lewis and Elbe (J. Amer. Chem. Soc, 1935, 57, 612), De Witt (Chem. Met. Eng. 1935, 42, 333) and Taylor (lnd. Eng. Chem. 1934, 26, 470). *See also* Partington and Shilling, " The Specific Heats of Gases," Benn Ltd., 1924.

Thermal Conductivity.—The best value of fcT at 00°C. is claimed to be 414x 10^' g.-cal. per cm. pur 1° per sec. There is, however, a certain amount of variation in reported va*luea at 0-0°.

423-8 *x* 10-s	**(Weber,** Ann. Phyaik. 1927, [iv], 82, 479.)
406-0 „	(Hereus and *Laby, Phil. Mag. 1927, fvii],8, **106L)**
4130 „	(Kannrfuik and Martin, Proc. Roy. Soc. 1934, A, 144, **496.)**
4140 „	(Ulsamer, Z. ***Vet.*** deut. Ing. 1936, 80, 537.)
424·5±2·9 X 10'"	(Nothdurft, Ann. Physik. 1937, [v], 28, 137.)

Critical purveys arc given by Ulstiiiier and also by Trautz and **Ztodel** (Z. tech. Phys. 1931, 12, 273).

The temperature coefficient is given by i-£=AT" where A and n are constants. The value at 295-l°K is 459-0 x ICH and at 593-4°x ia7080x10^{-s}.

Mixtures of industrially important gases are considered by lbbs and Hirst (Proc. Hoy. Soc. 1929, A, 123, *134).*

Entropy.—Values in **g.-c&L** per **mol.** per degree:

	-'*Mi*-.	it C.	1000.	500°C.
I iitm. .	29-265	**30-648**	**82-843**	**87-903**
25 „ .		24-24	26-44	31-50
100 „ .	2001	**21-44**	23-66	28-74
1,000 „ .	15-14	16-U7	18-97	2413

[Deming^nd Deming, Physical R«v. **1034,** [H], 46, 109).

Solubility.—The **solubility** of H, in water obeys Henry's law fairly dosely at moderate temperatures and **pressures.** 'i'he **values** at I **atm,** pressure in c.e. H_a (0T., 7 (JO mm.) per c.c. water **are**:

0-C	10°C.	lit) C.	50 D-	' 100°C.
0-02148	**0-01956**	**0-01819**	**0-01608**	O-0I60

(WinHer, Ber. **1891,** 24, 89; Landolt-Bornstem, •• T:ili(l!(.n." **1923,** *1,* **763).**

At higher pressures c.c. H_a (0°C, 700 mm.) per g. water are :

Pros- Mirf **(atin.).**	**O'C.**	**lOTJ.**	20T,	50°C.	**I0O°C.**
t:	**0-3383**	**0-4870**	04498	0-4067	0-4615
100	2130	1932	1-785	1-612	1-805
1,000	18001	16623	15-592	14 • 11.14	15-775

(Wiobe and Gaddy, J. Atner. Chem. Soc, 1934, SB, 76).

For solubility of H, in liquid ammonia, *see* Wiebe and Trcmearne, ***ibid.*** 1934, 56, 2357; for H_2 and N_2 in water at 20°, *see* Wiebo and Uaddy, ***ibid.*** 1935, **57,** 1487; for H_a in individual hydrocarbons, *see* Ipatiev and Levin J. Phys. Chem. U.S.S.R. 1935, 6, 632; for H., in other organic solvents, *see* Frolicli, Tauch, Hogan and Poor, Ind. Eng, Chein. 1931, 23, 548, and **Masted** and Jloon, T^ans. Faraday Soc 1030,32. **769.**

Dielectric Constant.—At 0"C/l atm. the dielectric constant is 1 -0002697 (Michels, Sanders and Si-hipper, Physica, 1935, 2, 753).

Spectrum.—Thj spectrum of hydrogen exlibits four prominent lines: Ha **6662A** (red), ^ 4861A (greenish-blue),**+Hy** 4340A (blue) and H8 4102A (indigo). The hydrogen spectrum is one of the most complicated of all, and for further demiU **and** discussion, *see* Richardson, "Molecular **Hydrogen nnd** Its Spectrum," Yale **University Item, 1934**j Bommerfeld. "Atomic **Strnotaw** *urt* **Spectaal LUIM,"** Dutton & Co. 1935; **Ktonig, "Band Spwrtra Ud Molecular Bteuctow,"** Ma.-nnlhui Co., 19J0; Jevona, " liquid Spectra of Piatoinic Molecules," Cambridge University Presa, 1932; White, " Introduction to Atomic Spectra," New York, 1934 j Condon and Shortley, "Theory of Atomic Spectra," Cambridge University Press, 1935; Tolansky, ^{Li}FineStructureinLioeSpectra and Nuclear Spin," Methuen, 1935; Herzberg, " Atomic Spectra and Atomic Structure," translated by Spinks, New York, 1935; "Molekiil-speetren urni Molekiilstructur," Bd. I, Dresden, 1939.

Adsorption.—The development, particularly over the last two decades, of many catalytic processes m which hydrogen is employed, has given considerable impetus to the study of catalysis and has led, in **its** turn, to the close study of the adsorption of hydrogen and other gases on the various substances used aa catalysts. The substances **which** have received most attention are metals aiic-h as copper and nickel, metal oxides such aa those of zinc, chromium, manganese, together with such well-know.^{1}! general adsorbents as charcoal and silica gel. Developments in this field are summarised in Faraday Society Discussion, Trans. Faraday Soc. 1919, **14,** 173; 1932, 28, 139, by Wansbrough-Jones (Science Progress, 1932, 26, 398) and Gregg (" Adsorption of Gases by Solids," Methuen & Co.. 1984}.

The existence of at least two quite different types of adsorption has been shown by various investigators. Ben ton and White (J. Amer, Chem. Soc. 1930, 52, 2325), in a study of the adsorption of hydrogen on copper and nickel, found that adsorption at low temperatures (below — 190°C) is small but rapid, involving a small heat of adsorption; above — 19U°C., with a maximum at — 100°C-, the amounts adsorbed are gq?:ater, with a high heat of adsorption.

Similar results were obtained by Garner and Kingman (Nature, 1930, 126, 352) for hydrogen and carbon monoxide on zinc-chromium oxides; by Taylor and Williamson (J. Amer. Chem. Soc. 1931, **53,** 2168) for hydrogen on manganese oxides and manganese-chromium oxides; and by Taylor and Sicl^man *{ibid.* 1932, 54, 002) of hydrogen on zinc oxide.

The concept of *activated adsorption* was introduced by Taylor ***{ibid,*** 1930, **52,** 5298; 1931, **53,** 678) to differentiate the high temperature, high-energy type of adsorption from the " molecular " or " Van der WSals " type which occurs at lower Ainperatures and with small energy 'changes. Various other names have been suggested—" chemicaL" " primary," or " activated " adsorption as against " physical," " secondary." or " molecular " adsorption—but in general the conception is the same.

" Activated" adsorption proceeds with a measurable velocity, **u** if a considerable energy of activation is required. As shown by Benton and White, for hydrogen on copper and nickel it begins around liquid-air temperatures; with zinc oxide, niangaTious oxide or their mixtures with chromium oxide, it becomes measurable between 0° and 100°, wliilst with alumina and glass it does not appear until 400°. With charcoal, temperatures ot 4WHKW' are required (Kingman, Trans. Famday Soc. 1932, 28, **269).** In all cases, the heat ot adsorption lies within **the** limits 10-30 kg.-cal. per g.-mol, H, adsorbed.

" Molecular *' adsorption on metal or oxide surfaces shows heats of adsorption of lower order, 1-2 kg.-cal. per g.-mol. These are in close agreement with the values obtained for adsorbents such as charcoal, silica, etc.

"Activated" and **"molecular" adsorption** overlap to a considerable extent, particularly at medium temperatures, Adsorption isotherms being **normally** compounded of two superimposed isotherms corresponding to the two different types of adsorption.

A close correlation is found between adsorption of hydrogen on catalysts such as those cited above and the activities of these catalysts in hydrogenation reactions. Mixed zinc-chromium oxides, for example, adsorb considerably greater quantities of hydrogen than either oxide alone, while the mixed oxides are well known as more active catalysts than the separate components for the synthesis of methanol (V Vol. II, 350a, 425c).

From experiments over a wide range of temperature Bentou *{ibid.* 1932, 28, 202) considers that three different processes occur, physical adsorption, activated adsorption and probably solubility. Ward *(ibid.* 1932, 28, 3119) is of the opinion that solution alone is sufficient to account for all the observed facts.

Palladium " occludes " hydrogen so much more strongly than any other metal that earlier researches on the phenomenon were devoted almost entirely to palladium and in particular to the precise nature of the substance or substances formed after occlusion is complete. Though there is still some uncertainty, considerable evidence has been accumulated indicating that the adsorbed hydrogen is in the atomic form. The equation of Sieverts, according to which adsorption at low pressures is practically proportional to the square root of the pressure, is usually explained by the assumption that hydrogen is in the atomic form. Some objections have been raised to **the interpretation** (c/. Ward, Proe. Hoy. Soc. 1931, A, 133, 531; Tamimum, Z. anorg, Chem,, 1930, **188,** 39(i). But the strong effect of occlusion of hydrogen on the electronic properties of palladium, such as electrical resistance, magnetic susceptibility, colour, photo-electric sensitivity and the thermo-e.m.f. against alloys of palladium with silver and gold, all tend to the conclusion that the adsorbed hydrogen is atomic (c/. Coehn and Specht, Z. Physik, 1930, 62, 1).

The fact that, while palladium adsorbs hydrogen with ease during electrolysis, adsorption in the **gas phase** depends very considerably on the previous history of the metal, is now explained by the assumption that hydrogen can only enter the metal lattice as atoms. In electrolysis hydrogen atoms are produced directly; in adsorption from the gas phase the molecules must first dissociate on the adsorbing surface, and according as the surface is more or less poisoned, so will its catalytic activity in the reaction $H_2 \rightarrow 2H$ be less or greater. Evidence has been brought forward by Smith and Derge (Trans. Electrochem. Soc. 1934, 66, 25) that occlusion occurs in the intergranular fissures, rather than on the grain faces.

The *heat of occlusion* is about 9 kg.-cal. per g.-mol. H, (Gilfespie und Hall, J. Araer. Chera. Soc 19^0,48. 1207).

Liquid Hydrogen.—The boiling-point of hydrogen is 20-37°K. (i.e. -252-81°C.) at **1** atm. (**Blue** and Hicks, J. Amer. Chem. Soc- 1937, 59, ltil>2). The molecular heat of vaporisation =21D'7-0>27(T-16-6)^{i} g.-cal. per g.-mol. (Simon and Lange, Z. Physik. 1923, 15, 312). The vapour pressure of liquid hydrogen is given by

$$\log p_{H_2}(\text{mm.}) = -37\text{-}7882(1/T)+1\text{-}75\log T +0\text{-}0023127T+2\text{-}39078$$

(tiouning, *ibid,* 1927, 40, 775; Henning and Otto, Phyaikal. Z. 1936, 37, 633). The molar heat capacity of liquid hydrogen is 0-33+0-206T (Simon and Lange, i.e.).

The density of the liquid

$$=0\text{-}084404\text{-}223 \times 10^{-fl}T_K\text{-}21\text{-}83 \times 10^{-6}T^2_K.$$

(Int. Crit. Tables), i.e. 007085 at the boiling-point, and 0-07709 at the triple point.

Liquefaction of hydrogen is worked on the Linde principle *{see below),* and liquid hydrogen has been increasingly used recently **in** research work. Simple forms of apparatus for its preparation are described by Ruhetnann (Z. **Physik,** 1930, 65, *til),* Keyes, Gerry and Hir-kri (J. Amur. Chem. Soc. 1937, 59, 1426) and ALL berg, Estermann and Lundberg (Rev. Sci. Instr. 1937, 8, 422).

Solid Hydrogen.—The melting-point of hydrogen is 1413°R. (Henning, Z. Physik, 1927, 40, 775). The triple point is 13-94°K. (Blue and Hicks, J. Amer. Chem. Soc. 1937, **59,** 1962). The critical data are: temperature '33-25°K., pressure 12-80 atm., density 0-3102 g. per c.c. (Woolsey, *ibid.* 1937, 59, 1577).

Solid **hydrogen** has a density of 0-0890 ±0-0004 at 4-2°K. (Megaw and Simon, Nature, 1936,138,**242**; Megaw, Phil. Mag. 1939, [vii], 28, 129); 0-08077 at 11-2°K. and 00763 at 13-3'K. (Int. Crit. Tables).

Solid hydrogen is formed by pumping off liquid hydrogen.

CHEMICAL REACTIONS.

The heats of reaction given refer to kilogram cal. (15°C.) per g. mol. at 0°C. 1 atm. pressure ; a positive sign *is* given to values of ΔH and ΔF to represent endothermic reactions and **a** negative sign to represent exothermic reactions.

Dissociation.—At high temperatures H_2 dissociates into atoms:

$$\log_{10}K = -\frac{21,200}{T} + 1\text{-}765 \log_{10}T\text{-}9\text{-}85\times10^{-"}T$$

$$-0\text{-}266, \text{e.ff.}:$$

The degree of dissociation at 1 atm. is :

2-S6xIO-^{3} «&t300°K.
Mi'Jx10-^{3} at 2,000°K.
0-9469 at 5,000°K.
» 0-9990 at 10,000°K.

(Langmuir, J. Amer. Chem. Soc. 1912, 34, 131U; 1914,36,1708; 1915,37,417; 1916,38.1145; Ind, Eng. Chem. **1927,** IS, 667).

The heat of dissociation is 1O272 according to

Beutler (Z. physikal. Chem. 1935, B, 29, 315), and 103·680 according to Poole (Proc. Roy. Soc, 1937, A, 163.404). The reaction is endothermic.

The following free energy equation was provisionally put forward by Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw Hill Book Co., 1923, p. 471.

$\Delta F = 81{,}000 - 3{\cdot}51\,T\log T + 0{\cdot}00045T^2 + M7T.$

A more recent expression is given by E. N. Erjemin (Acta Physicochim. U.R.S.S. 1935, 3, 147),

$$\Delta H = 102{,}000 - 7{\cdot}185\,T\log T + 0{\cdot}000033T^2 + 0{\cdot}0000000465T^3 - 2{\cdot}332T$$

Halogens.—The affinity of hydrogen for the halogens decreases on passing from F to I, as indicated by the following data.

Heats of Formation :

HF(g.)	ΔH =	—64·45	Von Wartenburg and Schutza (Z. anorg. Chem. 1932, 206, 65).
HCl(g.)	ΔH =	-22·0	International Critical Tables.
HBr(g.)	ΔH =	-8·5	Ditto.
HI(g.)	ΔH =	+ 6·0	Ditto.

Equilibrium Constants.—$2HX \rightleftharpoons H_2 + X_2$.

X=Cl, log K_p=(-9586/T)+0·440 log T-2·16 (Wohl and Kadow, Z. physikal. Chem. 1925, 118, 460).

X=Br, log K_p=(-5223/T)+0·553 log T-2·72 (Nernst, Z. Elektrochem. 1909, 15, 691).

X=I, log K_p=(-540·4/T)+0·503 log T-2·35 (Von Falckenstein, Z. physikal. Chem. 1910, 68, 270; 72, 113).

The heats of activation of the reactions $X+H_2$ and $H+X_2$ are as follows:

$Cl+H_2 \rightarrow HCl+H$	6·0
$Br+H_2 \rightarrow HBr+H$	17·7
$I+H_2 \rightarrow HI+H$	33·0
$H+Cl_2 \rightarrow HCl+Cl$	3·0
$H+Br_2 \rightarrow HBr+Br$	1·0
$H+I_2 \rightarrow HI+I$	0

(Morris and Pease, J. Chem. Physics, 1935, 8, 796), and for the reactions $X_2 + H_2$:

Br_2+H_2 40

(Semenoff, "Chemical Kinetics and Chain Reactions," Clarendon Press, Oxford, 1935, p. 140),

I_2+H_2 40

(Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Clarendon Press, Oxford, 1933, p. 79).

Hydrogen and fluorine combine explosively under all conditions, even in the dark at —252°C. Hydrogen and chlorine readily combine (explosively under some conditions), either light or heat inducing the reaction. Both the thermal and photochemical reactions are also known for hydrogen and bromine (explosive under some conditions). In the reaction between hydrogen and iodine, only the thermal reaction has been observed.

The reaction between hydrogen and chlorine has received exhaustive study, and has played a very important role in the development of the theory of chain reactions. According to Nernst the reaction proceeds through the absorption of a quantum of light by the Cl_2 molecule:

$$Cl_2+h\nu \rightarrow Cl+Cl$$
$$Cl+H_2 \rightarrow HCl+H$$
$$H+Cl_2 \rightarrow HCl+Cl$$
$$Cl+H_2 \rightarrow HCl+H$$

etc.

The reaction is provoked by light or heat; there may be a long induction period, due to the formation of NCl_3 (from nitrogenous impurities) and persisting until this inhibitor disappears; the quantum yield is very high (up to 10^6 molecules HCl per quantum of light); traces of moisture are claimed to be essential. The relationships of rate with light intensity, Cl_2, H_2 and O_2 pressures are given by the formula :

$$\frac{d[HCl]}{dt}=\frac{2k_3I[Cl_2][H_2]}{[O_2](k_4[H_2]+k_5[Cl_2])}$$

I=intensity of the light.

See Semenoff *(op. cit.)* and Hinshelwood *(op. cit.)*. H_2+F_2, Eyring and Kassel (J. Amer. Chem. Soc. 1933, 55, 2976); Bodenstein and Jockusch (Sitzungber. Preues. Akad. Wiss. Berlin, Phys. Math. Klasse, 1934, 27; Amer. Chem. Abstr. 1934, 28, 2978). H_2+Cl_2, Semenov (J. Phys. Chem. U.S.S.R., 1933, 4, 4); Gotsky and Gunther (Z. physikal. Chem. 1934, B, 26, 373); Griffiths and Norrish (Proc. Roy. Soc. 1934, A, 147, 140). H_2+Br_2 and H_2+I_2, Bodenstein (Helv. Chim. Acta, 1935, 18, 743).

Oxygen.—The heat of formation of water measured at 25° and at a constant pressure of 1 atm. is:

$H_2(g.)+\frac{1}{2}O_2(g.) = H_2O(l.)$

ΔH = —68·313 kg.-cal. (15°) per g.-mol.

(Rossini, Bur. Stand. J. Res. 1931, 6, 1; Proc. Nat. Acad. Sci. 1930, 16, 694).

Taking $H_2O(l.)=H_2O(g.)$,

ΔH=+9·721 kg.-cal. (15°) per g.-mol. (Intern. Crit. Tables); $H_2(g.)+\frac{1}{2}O_2(g.)=H_2O$ (g.).

ΔH=—57·592 kg.-cal. (15°) per g.-mol.

The equilibrium for $2H_2O \rightleftharpoons 2H_2+O_2$, is given by

log K_c=(-24900/T)+1·335 log T-9·65 × 10⁻⁴T + 1·37 × 10⁻⁷T² — 6·65 × 10⁻¹¹T³ — 1·08

(Siegel, Z. physikal. Chem. 1914, 87, 659).

Equilibrium constants for the reactions:

$H_2=2H$; $O_2=2O$; $H_2O=H_2+\frac{1}{2}O_2$; $H_2O=H_2+O$; $H_2O=\frac{1}{2}H_2+OH$; $H_2O=H+OH$

are given by Zeise (Z. Elektrochem. 1937, 43, 704).

According to Haber's view the reaction proceeds:

$H_2+O_2 \rightarrow 2OH$ . . 1.

$OH+H_2 \rightarrow H_2O+H$. 2.

$H+O_2+H_2 \rightarrow H_2O+OH$ 3.

etc.

Hinshelwood proposed the initial formation of $H_tO_{£}$. Owing to the equilibrium H_2O_2^2OH, the views may not be irreconcilable.

At temperatures below about £>50°C. the rate of reaction in moderately slow and bears no unusual relationship to pressure. Above this temperature, however, the rate of combination of a given mixture of H_a and O. increases gradually with pressure exhibiting a regular curve, until a pressure is reached at which the reaction proceeds explosively. The explosive reaction occurs over a certain range of presanre, above which the slow reaction reappears and proceeds, with increase in pressure, at rates which are a continuation of the interrupted curve. Finally the rate reaoEes a value comparable with the rate of the explosive reaction.

The explosion is due to the fact that, whereas normally the reaction proceeds according to the chain, branching occurs in the explosive reaction, in particular:

$$H+O_2 \rightarrow OHfO \qquad 4.$$
$$O+H_a \rightarrow OH+H \qquad 5.$$

Thus both products of the first branching (4) are capable of giving rise to fresh chains.

The probability of the branching reaction occurring is given by

$$8=\frac{25x1OVU/BT}{[H_2]}$$

where U is the energy of activation of reaction (4) and is equal to about 27-8 (Semenoif, *I.e. See also* Kontorova and Nalbandyan, Phyaikal Z. Sovietunion, 1933,4, 758).

The lower pressure limit of explosion is determined by the de-activation of the chains at tn% surface of the vessel; the upper limit by the de-activation in the gas phase (v. EXPLOSIONS, GASEOUS).

At 550°C. the lower explosive limit is a few mm. pressure, whilst the upper limit is about 100 mm.

These limits' vary aceording'to many factors. The lower limit, immediately above the minimum temperature, is" decreased by rise in temperature, but subsequently remains independent of temperatjire. The upper limijj is increased regularly Ly increase in temperature.

Riitioa of H_2/O_2 far removec[1] from 2:1 narrow the explosive ranges. The optimum •» ratio requires the oxygen to be in slight excess (Mitschcrlich, Z. anorg. Chem 1916, 88, 145).

Inert gases tend to buffer the ohainB in their approach to the walls where they would be de-activated. They thus lower the lower h'mit and. Jso somewhat lower the upper limit.

A decrease in the size of vessel raises the lower limit but is without effect on the upper limit.

The halogens lower both limits and if present in sufficient quantity prevent the explosion altogether (Hinshelwood and Garstang, Z. physiknl. Chem., Bodenstcin Festbaud, 1931, 656). Trichloroethylene, tin tetramefchyl, dimethyl selenide and telluridi; and ethyl bromide can also be used to suppress the reaction (Tnnnka and Ntvgai Proc. Imp. Acad. Tokyo, 1929, 5, 80, 418, 422 etc.).

The limits of inflammability of H_a are given in the U.S. Dept. Int. Bulletin 279: .

	lower.	Upper.
$H_a$in O_2	4%	111%
Hjinair.	4%	74%

Bibliography.—Hinshelwood, "Kinetics of Chemical Change," Oxford, Clarendon Press, 1940; Hinshelwood and Williamson, "The Reaction between Hydrogen and Oxygen," Jlarjndon Press, Oxford, 1934; SemenofT, "Chemical Kinetics and Chain Reactions," Oxford Clarendon Press, 1935.

Sulphur, Selenium.Tetlurium.—Combination with H_a takes place less readily on passing from S to Te. The heats of reaction (International Critical Tables) are:

$H_2+S \rightarrow H_2S$ (g.); Atf=-5-3 (exothermic)
$H_2+Se \rightarrow H_2Se$(g.); A//=-f15-8 (endothermic)
H_a+Te -»- H_BTe(g.); -A//=+34-6 (endothorzuic)

The equilibrium for the reaction

$$2H,S \rightleftharpoons 2H_2+S_2$$

is:

°CI. . . \	750	830	645	1,065	1,132
KpXlO* .	0-89	3-8	24-5	118	280

(Preuner and Schupp, Z, physikal. Chem. 1909, 68, 157).

The heat of activation is about 43 kg.-cal.

The kinetics of the reaction have been studied *hy* Cook and Robinson (J.C.S. 1936, 464). *8et also* Jones and Sherman (J. Chem. Physics, 1937, 6, 375).

Nitrogen.—The direct reaction between Hj and Ng is of immense industrial importance (t>. AMMONIA, Vol. I, pp. 332-338).

For the reaction $2NH_3$ v^3H_a-f-N_2,

log tfp=(2098-2/T)-2-509 log T-1-006 x 10~*T
+ 1-859x10-'T^l+2*10

(Haber, Z. Elektrochem. 1914, 20, 603). For, high pressures the values determined by Larson (J. Amor. Chem. 1924,46,367) are more accurate.

The heat of the reaction is given by the equation:

JNj(g.)+*/$_8$H((g.)=NH_3(g.)+10-95 **Kg.-oaL**

(Haber, Tamaru and Oeholm, Z. Elektrochem. 1915, 21, 206); for the heat of reaction at higher temperatures, see Haherand Tamaru (*ibid.* p. 191).

The heat of activation of the homogeneous reaction is extremely high and only the heterogeneous reaction is important for the formation of NHj, in which case the heat of activation depends upon the particular catalyst.

The best catalysts are reduced Fe promoted by oxides such as $AI_21>_3$, in addition to K_tO (Laraon, Ind. Eng. Chem. 1924, 16, 1002). S and O compounds poison the catalyst.

The reaction probably proceeds through the foliowing^mechanism : (i) N_z is adsorbed on the catalyst and is activated or even dissociated, (ii) H, is similarly adsorbed and forms NH with the N, (iii) NH is reduced by molecular H. to NH, (Fran ken burger, Z. Elektrochem. 1933, 89, 45, 97, 269).

Since the mechanism is incompletely understood, no kinetic expression is entirely satisfactory but the arbitrary formula, of Benton (Ind. Eng. Chem. 1927, 19. 494) agrees with the experimental data over a. wide range,

$$\frac{X}{t}=\frac{3P^2k_1S}{16ap_{NH_3}}$$

X =volume fraction of NH_3 formed.
(=time of passage over catalyst.
]' =total pressure.
/•j =velocity constant of synthesis reaction.
S =eonstant depending on catalyst.
=constant depending on temperature.
p_{NH_3} — partial pressure of NH_3.

Phosphorus, etc.—Nascent hydrogen reacts with the elements to give PH_3, AsHj, SbH_3 and BiH_3 as veil as lower hydrides. The heat of formation {Kphraim, " **Inorganic** Chemistry," Gumey and **Jackfioa,** 1939),

PH_3, *AII=-$_T$* 11-6 (exothermic)
AsH_3, A//=+3C-7 (endotherniir)
SbH_3. A//=+81-8 (endothermic)

indicate the usual decrense in affinity on passing down the group.

Carbon .—Pure carbon does not react rvadily with H_a, but at hiph temperaturea, especially if catalysed by Co or N(, reaction occurs to an appreciable exifiit

C(amorpb)+SH. -+CH,+2I-7 kg.-cal.

(.«e Itiley, Phil. Mag. 1924, [vi], 48,120).

Tho equilibrium constant A'=[CH^/[H_S]* **may** be calculated from H< **data** of Pring and **PairBe** (J.C.8. liMi'. **101,** !)I).

T (° absolute):				
823	**1,478**	1,548	1,573	l,f>48
K:				
004	0-00244	0-00147	**0-00146**	000100

This equiiiihriuai is discussed fully by Cordon **and** Barnes (J. **Physical,** Cliem. *1932,* 36, **2601).**

Carbon Dioxide.—

(a) **CO_a+H,** →.CO+H_uO
Δ**// + 10**·1 (endothermic).
K **$_{fl}$gV(/)** = −2150 T −1·8×10⁻⁷T²+2·2
(Notiniann and **Kohler,** *7*.. Ele.ktrochem. 1028, 34, 218; *also* Stheibel, **Mouatah.** 1931, 58, 183; Kassel, J. Amer. Chem. Soc. 1934, 56, 1803; *set aUo* GAS, WATER).

(*//*) CO_2+ H_a -v HCOOH (*see* Bredig, Carter ami EnderJi, MonaUh. 192!), 53 54, 1023).

Carbon Moncxide.—Carbon monoxide and hydrogen react under varying conditions of concentration, pressure, temperature, catalyst and purity to give a great variety of products, many of which are of "the greatest importance. Tho following are known reactions, though not necessarily representing the reaction mechanism:

(a) **CO+H,->C+H.O(g.).**
ΔH : —31-4 (exothermic). The reverse of this reaction ia, of course, the basis of water-gas production (*v.* GA8, WATEK).

(t) $2CO+2H_2$-»-CH_4+CO_2.
All: -61-8 (exothermic).
&F: -50,9.50+ lS-OTST/nT−0·01078T² +OO0000031T^3-a0-34T (D. F. Smith, Ind. Eng. Chem. 1927, 19, 801).
K_v: 1/lojj Kj)=(-57,9O3/4J573T)+13S75 (Fischer and Pichler, 1 liennstoflf-Chem., 1931, 12, 36S; Sehmidt and Neumann, Z. Elektroehem. 1932, 38, 925; Ghoah, Chakravarty and Wakshi; Z. anorg. Chem. 1934,217,277),

(c) CO+H_2^HCHO.
All: -2-0 **(exothermic).**
K_p: log *K_P*=(**1,**710/4-573T)-5-431 (Newton and Dodge, J. Amer. Chem. „Soi\ 1033, 56, 4747).

(*d*) CO+2 H_z C_3H(**g**·OH) . .
A//: —33-6 (exothermic).
&F : -20,857+17-88T/WT-0-01423T^2 -64-04T (Smith, *I.e.).*
K_p: log A'j,=(17,030/4-573T)-91293 logT +0'00308T+**13-41**2 (Newton and Dodge, J. Amer. Chem. Soc. 1934, 56, 1287 : FracosHO, L'Ind. chimica, 1934, 9, 293).

(e) $2CO+4H_2$^C_2H_5-OH(g.)+H_iO(g.).
Δff : -708 (exothermic).
Δ*F:* -55,190+ 24-72T/MT + 0-0145T* -O-O00OOO37T^3-0O'74T (Smith, i.e.),

(*f*) $nCO+2nH_2 \rightarrow C_nH_{2n+1}$·OH+(n−1)$H_2$O .

(*g*) **$CO+3H_2$^CH_4+H_2O(g.).**
A II: +51-G (endothermic).
AF: -46,850+13-26riTlnT-0-00033T* -0'00000037T«-3I-60T {Smith, *I.e.).*

Kpi°K	673	703	723	714	7«3
l/-logA";,3-74	3 02	2-5G.	212	1-72-	

(Ghosh, Chakravarty and Bakshi, *'A.* anorg. Chem. 1934, 217, 277; *see also* Kubelkaand Wenzel, Sletallbtirse, 1931, **21.** 1227, 1275, 1372, 1421).

(*h*) 2CO+5H_8->C_2H_a+2$H_!$,O(g.}.
AH -88-1 (exothermic).
AF: - 81,222+ 14-46TtoT+0-018r>.VI - -0-O00O1207T^3+O-7OT (Smith, *!.<•,).*

(t) $nCO+(2n+1)H_2 \rightarrow C_nH_{2n+2}+nH_2O$.

The equilibrium relationships **given have been** determined experimentally and these are more accurate than those calculated from the free energy relationship quoted.

Since nearly all these reactions are exothermic the product depends not eo much on the temperature as on the pi^ssure and particularly on the catalyst. In general, hydrocarbons are formed over VIII group metal catalysts. The products range from methane to liquid hydrocarbons as in the Fischer process (Fischer, Brennatoff-Chcm. 1935,16. 1; Underwood, Ind. **Eng. Chem. 1940,** 32, ^40). or to solid waxes of high molecular weight (Pichler, Brennstoff-Chcm. 1938,19,22li). In most instances the reactions are conducted at atmospheric pressure. For a discussion of the mechanism, *see* Hcrington and Woodward (Trans. Faraday Soc. 1939, 35, 958); Craxford *(ibid.* 1939,35,946).

On the other hand, methanol is usually formed over catalysts such fis Zn, Cr, almost invariably at high pressures (Smith and Hirst, Ind. Eng. Chem. 1930, 22, 1037; Z. angew. Chem. **1827,** 40. Ifi6; Pier, Oel u. Kohle, 1933, 1, 47). By mf Iification of tho catalyst, for instance by the addition of I, VII or VIII group metals, higher primary alcohols are also produced (Graves, Ind. Eng. Chem. 1931, 23, 1381). For the mechanism of these reactions, *see* Frolich and Cryder (*ibid.* 1930, 22, 1051). Morgan, Taylor and Kedley (J.S.C.I. 1928, 47, 117T).

Hydrocarbons.—Reactions of this type including both the forward and the reverse reactions are very numerous and very important. The following simple types serve merely as examples.

(*a*) $C_2H_4 + H_2 \rightarrow C_2H_6$.
ΔH: −21·4 (exothermic).
K_p: $\log K_p = -27{,}798/4{\cdot}573T + 2{\cdot}01 \log T - 0{\cdot}471$ (Frey and Huppke, Ind. Eng. Chem. 1933. 26, 54).

(*b*) $C_3H_6 + H_2 \rightarrow C_3H_8$.
ΔH: = −21·7 (exothermic).
K_p: $\log K_p = -25{,}920/4{\cdot}573T + 2{\cdot}01 \log T + 0{\cdot}047$ (Frey and Huppke, *l.c.*).

(*c*) $C_6H_6 + 3H_2 \rightarrow C_6H_{12}$.
ΔH: = −21·0 (exothermic).
K_p: $\log K_p = 43{,}850/4{\cdot}573T - 9{\cdot}194 \log T + 2{\cdot}285 \times 10^{-3}T + 8{\cdot}505$ (Sharkowa and Frost, Chem. Zentr. 1933, I, 726).

Metals of the VIII group are frequently, though by no means exclusively, used as catalysts). See Egloff, "Reactions of Pure Hydrocarbons," Rheinhold Pub. Corp., 1937, and Hurd, "The Pyrolysis of Carbon Compounds," Chem. Cat. Co., 1929 (see *also* this Vol. HYDROGENATION OF COAL).

Silicon, Boron.—Direct combination,

$$Si + 2H_2 \rightarrow SiH_4,$$

occurs at very high temperatures, though the usual method of formation of silanes is by the acid decomposition of magnesium silicide. The silanes comprise a series SiH_4 to Si_6H_{14}.

Boron and hydrogen do not react, even at high temperatures. The boron hydrides are formed by the action of acid on magnesium boride [*v.* BORON, Vol. II, *40d*).

Alkali Metals, etc.—The alkali metals, the alkaline earth metals (excluding Be and Mg), and many of the rare earth metals react directly with hydrogen, particularly with atomic hydrogen, to give solid salt-like hydrides, in which the hydrogen is the anion.

Metal-Hydrogen Alloys.—The direct reaction of the above type gradually merges into another type in which the hydrogen is held in an atomic state, as an alloy rather than as a compound. "Copper hydride," for instance, is intermediate between the two types, and there has been much discussion as to whether or not it is a true hydride. Most metals take up some hydrogen, but particularly the rare earths (some of which may be regarded as forming salts), Th. U, V, Nb, Ta, Cr, Mn, Fe, Co, Ni, Pt, Cu, and especially Pd. The alloys are metallic in nature; the solubility of H_2 is increased by pressure, but the effect of temperature depends on the metal. For further details, *see* papers by Sieverts, *e.g.* Stahl u. Eisen, 1914, 34, 252; Z. physikal. Chem. 1907, 60, 139, 151, 169, 184; Z. angew. Chem. 1929, 21, 37; Z. physikal. Chem. 1937, 180, 249; B, 38. 4(i,

The hydrides of the elements are classified by Paneth (Ber. 1920, 53 [B], 1710) into (*a*) those in groups I–4 positions before an inert gas in the periodic system and also boron, which form gaseous hydrides. Here the H is normally linked covalently but, in some instances, *e.g.* HCl in solution, it is ionised as a cation, and in the boron hydrides some of the hydrogen atoms are linked by a singlet bond. (*b*) Compounds which are like alloys, *e.g.* hydrogen—palladium. (*c*) Field valency compounds, comprising the compounds with Fe and Ni which are usually classed under (*b*). (*d*) Salt hydrides, *e.g.* KH where the H is negatively ionised.

Metallic Oxides.—Metallic oxides tend to be reduced by H_2 to the metal. The process occurs readily with oxides of metals low in the electrometric series, where the heat of reduction is considerable and where the necessary temperature is low. On ascending the series, however, the reaction becomes more and more strongly endothermic and the requisite temperature increasingly higher.

In the following list, T (the minimum temperature for reduction) refers to reduction to the metal. Reduction of highly oxidised to less

Metal.	T.	ΔH.	
Sr	Electric spark.	+83·2 (SrO)	(endothermic)
Th	1,100°C. 15 atm.	+107·7 (ThO_2)	"
Al	2,800°	+73·9 (Al_2O_3)	"
Mn	1,300°	+33·0 (MnO)	"
Zn	454°	+[illegible]·5 (ZnO)	"
Cr	1,000°	+31·2 (Cr_2O_3)	"
W	1,100°	+6·[illegible] (WO_3)	"
Fe	305°	+6·2 (FeO)	"
Cd	800°	+7·5 (CdO)	"
Co	228°	−0·2 (CoO)	(exothermic)
Ni	270°	(NiO)	—
Pb	235°	−[illegible]·3 (PbO)	(exothermic)
Bi	300–310°	(BiO)	"
Cu	165°	−[illegible] (CuO)	"
Ag	100°	−50·8 (Ag_2O)	"
Hg	80°	−[illegible]·3 (Hg_2O)	"
Pd	Without heating.	−[illegible]·3 (PdO)	"

oxidised oxides occurs at lower temperatures. These data are collected from Gmelin, " Handbuch der anorganishen Chemie," Aufl. 8, System No. 2. The heats of reduction (A//) are calculated from International Critical Tables V, and refer to reduction at 18°, 1 atra., per mol. of H_2O formed.

For further data, *see* references given above for " Reduction of Water."

ACTIVE HYDROGEN.

Many methods have been given in the literature for preparing active modifications of hydrogen, since the original experiments of Wendt and Landauer (J. Amer. Chem. Soc. 1920, 42, 930). In these experiments bombardment with X-rays, high potential electrical discharge, the corona discharge and the ordinary ozoniser were used, all with positive results.

Other authors have found the following methods effective: desorption from platinum or palladium, or diffusion through a closed palladium tube heated at temperatures up to 800°C.; the action of water and heat on metallic hydrides, of acids on metallic magnesium under certain conditions; continuous combustion of oxygen and hydrogen on platinum; electrolyrs; electronic bombardment in a thermionic tube; activation by excited mercury atoms (Venkataramaiah and co-workers, Chem. News, 1922, **124,** 323; J. Amer. Chem. Soc. 1923, 45, 261; Nature, 1923, **112,** 57; Anderson, J.C.S. 1922, **121,** 1153; Grubb, Nature, 1923, HI, 671; Stead and Trevelyan, Brit. Assoc. Rep. 1923, 425; Taylor and Marshall, J. Physical Chem. 1925, 29, 1140; Bonhoeffer and co-workers, Z. physikal. Chem. 1924, 1x3, 199; 1924, **113,** 422; Z. Elekt-ochem. 1925, 31, 521).

Of the methods described, some are not above suspicion. According to Scanavy-Grigoriewa (Z. anorg. Chem. 1926, **159,** 55) positive results with glowing platinum capillaries are probably due to adsorption of H_2S from the air *(cf. also* Paneth and co-workers, Z. EJektrochem. }927, 83, 102;-Copaux, Chim. et. Ind. 1930, 23, 267).

In general, the active hydrogen produced by these various methods reduces S, Se, Te, P and Sb to their hydrides. Most of these reactions have been studied in some detail by Bagdasaryam (J. Phys. Chem. U.S.S.R. 1937, 10, 389, 401). Many metallic oxides, *e.g.* those of W and Cu, are reduced-to the metal (Bagdasaryam, *ibid.* 1935, 16, 1033). Active hydrogen also reduces ethylene, calbon monoxide and oxygen (forming some formaldehyde with carbon monoxide), and reacts with nitrogen to form ammonia. It does not follow, however, that these reactions are general for active hydrogen produced by each uf the various methods given.

The active hydrogen produced by X-ray or electronic bombardment, or by electric discharge, possesses in all cases the properties recorded by Wendt and Landauer (Z.c), *i.e.* its activity is removed by liquid air, and a definite volume contraction is noticeable on its formation (Stead and Trevelyan, *I.e.*; Bonhoeffer and co-workers, *I.e.).* According to Hiedemann, however (Z. physikal. Chem. 1931, 153, 210), the same properties are characteristic of a mixture of bilicon hydrides, and all such " active" or " triatomic" hydrogen may be either **H_2S** or silicon hydrides—or a mixture of both.

For more comprehensive descriptions of the reactions of active hydrogen, *see* Harteck and Roeder (Z. Elektrochem. 1936, 42, 536—reactions in aqueous solution), Bagdasaryam (Uspekhi Khim. 1936, 5, 39) and particularly Geib (Ergebn. exakt. Naturwiss. 1936, 15, 39).

Wendt and Landauer (Z.c.) consider the properties to be those of triatomic hydrogen, but, although the existence of the ion H_3^+ is probably beyond dispute, there is as yet no definite evidence of the existence of neutral H_3 (Paneth and co-workers, Z.c).

It appears probable that hydrogen activated by the electric discharge is monatomic, not "triatomic. If a long, wide discharge tube is used at low pressures, as shown by Wood (Phil. Mag. 1921, [viij, 42,729), the secondary spectrum, characteristic of molecular hydrogen, is confined to the ends of the tube, and the centre of the tube gives only the Balmer series, characteristic of atomic hydrogen. If the hydrogen is dry, the Balmer series is suppressed. Experiments by Boehm and Bonhoeffer *(Lc.)* have demonstrated fairly cbnclusively that this active form is atomic hydrogen.. The bulb of a thermometer moistened with a salt solution, and held in the gas stream, shows a rise in temperature, due to the reformation of molecular hydrogen. The formation of H_aOo with oxygen, and **HCHO** with carbon monoxide, suggest the presence of free atoms, while the immediate destruction of the active form by **HCI, HBr,** etc., is thought to be due to the reaction $H+HCI=H_2+CI$. It has, been shown, however, that hydrogen exposed to electronic bombardment will reduce copper oxide in the cold as soon as the potential applied to the electrons exceeds 11-4 volts. This is exactly the first resonance potential of the hydrogen molecule, and it is therefore possible that " excited " molecules may form a part of" active " hydrogen (Glockner, Baxter and Dalton, J. Amer. Chem. Soc. 1927, 49, 58).

One form of "active" hydrogen is beyond doubt atomic. This form, the discovery of which is due to - Langmuir, is produced by an incandescent tungsten filament heated above 1,300°K. in an atmosphere of hydrogen, or by an electric discharge between tungsten electrodes (Langmuir, *ibid.* 1912,- 34, 1310; 1914, 36,1708; 1915,37,417; 1916,38,1145; Ind. Eng. Caem. 1927,**19,** 667).

The abnormal rate at which heat is conducted from such a filament at temperatures above 1,700°K. (the heat carried away is proportional to $T^{1'}$» for most gases and for hydrogen up to 1,7OO2K., but increases more rapidly above this temperature until at 2,600°K. and above, ic is proportional to T^6) led to the conclusion that strong dissociation of H_2 must take place under such conditions.

Data at higher pressures have demonstrated conclusively that atomic hydrogen H, and not H_3, is responsible for the abnormal conductivity effect.

Atomic hydrogen produced by the Langmuir method reacts rapidly with oxygen at room temperatures and slowly even at liquid-air temperatures. It reduces oxides of tunirstcn, copper, iron (Fe_aO_3) and zinc. No atomic hydrogen, however, passes through a trap cooled in liquid air, Ethylene is decomposed to form acetylene, benzene and other hydroearhons being formed in smaller quantity (Von Wartenberg and ScbulUe, Z. physikal. Chem. 1929, B, 2, 1 ; Bonhoeffer and Hartcck, *ibid.* 1928, **139,** (34). The life of atomic hydrogen is short, the half-period being about 1 second (Bay and Stciner, *ibid.* 1929, B, 2, 146).

THE STRUCTURE OF HYDROGEN ATOMS AND MOLECULES.

The hydrogen (protium) atom consists of a single proton, around which a single electron revolves in an elliptical orbit. Variation can occur in the size of the orbit, but only diw-continuously, *i.e.* there is a finite number of possible orbits. The condition prevailing when the electron is revolving in a given orbit ia a "stationary state "; no energy changes occur and the coulomb force between the electrical charges is balanced by the centrifugal force due to the inertia of the electron.

The stationary states aaay be numbered 1, 2, 3 . . . *n* outwards from tbc nucleus, and are characterised by the fact that in them the electron bears 1, 2, 3 . . . *n* quanta of energy, respectively. Thus the energy of the electron at the nth orbit, E=nftt\

n is an integer denoting the particular orbit.
h=Planck's constant = ti-554 *x* 10~" erg-seconds.
i>=the frequency of rotation.

On transferring from one orbit to another, say from the first to the second, an energy change occurs.

$$E_1-E_2=h\nu$$

Some of the characteristics of the stationary states for hydrogen ate:

Quantum Dumber.	Radius,	Frequency of revolution.	i Work of removal.	Velocity ill orbit.
1	1	1	1	1
2	4	1/8	1/4	1/2
3	**9 i**	1/27	1/9	1/3
4	16	1/64	J/lfi	1/4
n	n?	<*nr**	**ft"²**	

The work of removal of the electron from the nth orbit to infinity is thus proportional to *n*~%, *i.e.*

Eft- $\frac{-}{n}$ *i* ,

where R is "a constant.

The energy radiated when the electron jumps from the nth orbit ia

$$E_n-E_{n_1}=Rh\left(\frac{1}{n^2}-\frac{1}{n_1{}^2}\right)=h\nu$$

or

$$\nu=R\left(\frac{1}{n^2}-\frac{1}{n_1{}^2}\right)$$

When M=1 and »!=2, 3, 4 . . . the resulting series of spectrum lines constitutes .the Lyman Series; when «=2 and 7^=3, 4, 6 . . . the Balmer Series occurs; when n=3 and n_t=4, 5, C . . . the Paschen Series occurs; and when ft=4 and n_1=5, B, 7 . . . the Brackett Series results.

The constant

$$R=\frac{2\pi^2N^2e^4m}{eft^3}=1\text{-}09675\text{x}10^*$$

where m=the mass of the electron
e=the charge on the electron
N=the charge on the nucleus
c=the velocity of light.

Owing to the fact that the orbits are elliptic a , the velocity of the electron varies with its poaition, and hence the energy varies. TIUB results in each of the spectrum lines becoming spread and really consisting of a number of fine spectrum" lines.

The number of atomic and molecular structures, accorded the title of " hydrogen " has greatly increased during recent years. The nomenclature and symbols of these structures are as follows:

Let " hydrogen " be represented by

$$w-{}^y_xH_z$$

In the position of "*w*" the prefix "o" (ortho), "*p*" (para), " e " (equilibrium between *o* and *p*) or "*n*" (normal in relation to "*o*" and "*p*", *t.e.* in equilibrium at ordinary temperatures) given the condition of the molecule in relation to nuclear spin. When omitted, *n* may be assumed. The ButJseript in the position of "*x*" gives the atomic number. This is 1 in the case of hydrogen and is frequently omitted.

The superscript in the position "*y*" gives the atomic weight relative to hydrogen (protium), i.e. \y\ is the hydrogen *(protium)* atom; JH o/ D is the deterium atom f ^H or T is the isotope atom of mass 3, *tritium;* *H* is the isotope atom of mass 4. When omitted it may be assumed that a mixture is meant with the "natural" **amount** of deuterium, *i.e.* 5,000 \\H_t to D, and negligible amounts of higher isotopes.

The subscript in position *x* represents the number of atoms ip the molecule, *i.e.* H (atom), H_a (ordinary diatomic molecule), H_3 (triatomic in-". IF-rule, *hyzone).*

In addition the usual + or — indicates positive or negative ionisation.

Ortho- and Para-Hydrogen.—In the hydrogen atom, both the electron and the proton which comprises the nucleus have two possible directions of spin. The electron spioa of any pair of H atoms may thereforo be parallel or anti-parallel, and similarly with the protdtis. Only those atoms with auti-parallel electron-spins, However, are able to enter into combination, so there occurs in the hydrogen molecule two possible spin isomers—those with parallel nuclear spins (ortho-hydrogen), and those with itnti parallel nuclear spins (para-hydrogen). The existence of these two modifications was experimentally demonstrated by Bonhoeffer and Harteek (Naturwisa, 1929, 17, 182).

A further difference between the isomers is that in the para-molecule only the even rotational levels are occupied, whereas in the orthomclecute it is only the odd levels. Consequently at extremely low temperatures when all the molecules tend to pass into the lowest rotational level (J=0), equilibrium lies entirely on the side of para-. At infinitely high temperature the equilibrium lies at 3 ortho-: I para-. Equilibrium is, however, only reached under favourable conditions and the mixture occurring at normal temperatures {which approximates very closely to 3 ortho-: 1 para-) may be cooled to low temperature without change in composition. Distinction may therefore be drawn between this normal mixture (n-Hj) and the equilibrium mixture (e-H_2), as well as between the pure *o-H_t* and p-H_. The following table taken from Farkaa (" Orthohydrogen, Parahydrogen and Heavy Hydrogen," Cambridge University Press, 1935) shows the rotational levels occupied at different temperatures. The sum of.tho even .1 numbers and the sum of the odd J numbers for e-H_8 indicate also the equilibrium amounts of para- and ortho- respectively.

Temp. *K.	Hydrogen.	J = 0.	J - 1.	J=2,	J - 3.	J = 4.	J = 5.
60	e-H_a	76-88	2311	0-01	—	—	—
	p-H_2	99-98	—	002	—	—	—
	o-Hj,	—	100-0	—	—	—	—
	Tl-Hj	24-995	7500	0005	—	—	—
100	e-H_3	37-36	81-40	ME	002	—	—
	2>-H_2	97-02	—	2-98	—	—	—
	o-H_n	—	99-9.1	—i-	**0-05***	—	—
	n-H_E	24-25	74-97	0-74	003	—	—
200	e-H,	18-65	71-67	7-27	2-38	**0'03**	0-002
	P-H_a	71*82	—	2805	—	**013**	—
	o-H_a	—	96-78	—	3-21	—	**0003**
	n-H_t	L-7-95	**72-59**	701	2-41	0·03	0002
300	e-H,	12-89	65-78	11-78	9·07	0-40	008
	JJ-H-	**61-40**	—	**4700**	—	**1-59**	—
	OM	—	87-80	—	12-10	—	010
	n-H_a	**12-85**	**65-84**	**11-75**	9-08	0-40	0-08

Pure para-hydrogen is prepared by converting n-H_a to e-H_2 (*i.e.* p-H_8) at liquid-air temperatures, using active charcoal or Nikieselguhr catalyst (Bonhoeffer and Harteck, Naturwisa, 1929, 17, 182; Z. physical. Chem. 1929, B, 4,113; B, 5,292; Z. Elektrochcm.1929, 35, (521; Taylor and Sherman, Trans. Faraday Soc. 1932, 28, 247). It is impossible to convert n-H_E into o-Hg, since at no temperature does the equilibrium lie entirely on the o-H_a side, and failing a physical method of separation, pure o-H_{fl} cannot be prepared. For the heat of transformation, *see* Elbe and Simon (Z. physikal. Chem, 1930, B, 6, 79).

The composition of *o-p-H_2* mixtures is conveniently estimated by thermal conductivities (Bonhoeffer and Harteck, *ibid.* 1929, B, 4, 113).

The following properties of *p-H_t* may be compared with those of n- H_t:

	n-H_2.	
Boiling-point °K. • .	20-37 *	20-261
Triple point ᵁK. . .	1^-94 *	13-83 +
Vapour pressure mm.—		
20-18°K. . . .	708-21	732-9*1*
47-18°K. . . .	250-51	261-7 *t*
15-18°K. - . .	108-7 J	103-5 *%*

*Heavy Hydrogen—Deuterium (y.w.).

Other Isotopes of Hydrogen.—In the reaction, jD+fD ~>.»H-t-jH, a hydrogen isotope of mass 3 is formed (Dee, Nature, 1934, 133, 564).

The possibility of the higher isotope of mass 4 has been discussed, by Fltigge (Z. Physik, 1937, 105, 522).

Triatomic Hydrogen (Hyzone).—One of the theories explaining the activity of " artive " hydrogen is that it is triatomic. Actually tho existeno* of a neutral triatomic molecule H_3 is under considerable doubt *(see t.g.* Small wood and L'rey, J. Amer, Cfiem. Soc, 1928, 50, 620). The ion H^" however is known to exist and was first observed by J. J. Thomson in canal rays. He claimed later (Phil. Mag. 1934, [vii],17_t 1025) Lhnt two kinds exist, the one formed by passing the discharge through ordinary hydrogen is very unstabi#, the other, formed by bombarding golid KOH with electrons and passing a discharge through the evolved gases, is fairly permanent. \Vlien_KOD is_U8ed, H_4 is also present (as well as Hj and H_3).

HYDROGEN BIBLIOGRAPHY.—Further details on the properties and reactions of hydrogen can be found in the following sources. Much of the data given there, however, has been amplified or corrected by more recent work :

Mellor, " A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. I, 1922.

• *See above under* **" Physical Properties of Hydrogen."**

t HonhoeffLT and Hiirti>ck, Z. physlkal. Chem. 1S20, B, 4,113; fM Parkas {op. etc.).

% Kecsoui, BIJL and Horst, Proc. K. Acnd, Wctensch. Ams Wrdam, 1931, 34, IS28; *see* Farkas (op. *oil.).*

Newton Friend, " Textbook of Inorganic Chemistry," Vol. II, 1924.
Abegg, " Handbuch der anorgauisehen Chemie/' 1908, Band II, Abt. 1.
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TECHNICAL PRODUCTION.

General Literature.—From 1918-21 a number of ibooks were published dealing with the commercial production and usage of hydrogen, and they form excellent summaries of the state of development of the various processes up to the time they were written. These books are therefore valuable for early history of the subject, including patent references, and the following may be cited:

Martin, " Industrial Gases " (Crosby Lockwood & Son), 1918. .
Teed, " The Chemistry and Manufacture of Hydrogen " (Edward Arnold), 1913.
Greenwood, " Industrial Gases " (Bailliere, Tindall & Cox), 1920.
H, S. Taylor, " Industrial Hydrogen " (Chemical Catalogue Co., U.S.A.), 1921.

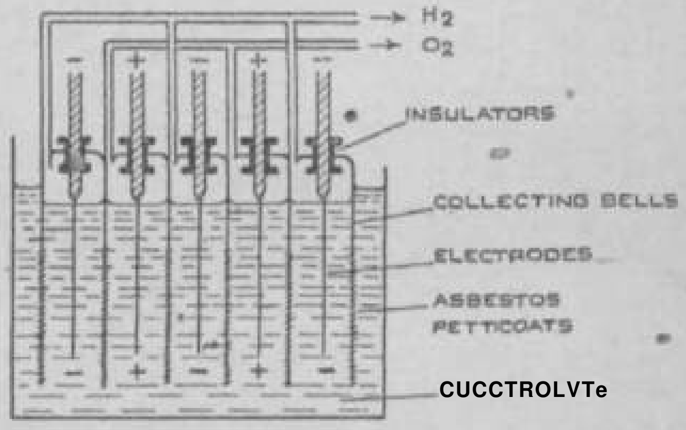
For reference on the subject from the standpoint of ammonia synthesis, *see* AMMONIA, Vol. I, *'S3ld,* and from the standpoint of hydrogenation, *see* Groggins, " Unit Processes in Organic Chemistry" (M.Or&w'-Hill Book Co.), 1935, Chapter VIII, Hydrogenation (Fenskc), Two general articles covering the whole field of commercial hydrogen production are Brownlie, Ind. Eng. Chem. 1938, 30, 1139, and Heinrich, Chcm.-Ztg. Ig33, 57, 933-934, 950-952. Apart from the above, the original references and the patents quoted must be consulted to obtain more information on the processes dealt with below. *

The various processes used commercially for the production of hydrogen may bn classed as follows: i

(1) Electrolytic Decomposition of Water.
(2) Direct Reduction of Steam by Carbon.
(3) Indirect Reduction of Steam by Carbon, Using an Intermediary. ,
(4) Reduction of Steam by Hydrocarbons.
(5) Cracking of Hydrocarbons.
(6) Hydrogen Recovery from Commercial gases (e.ff. Coke-Ovcn Gas) by Partial Liquefaction.
(7) Production of By-product Hydrogen.

(1) ELECTROLYTIC DECOMPOSITION OF WATEB.

Before oxygen and hydrogen can be evolved from the electrodes of an electrolytic cell, the applied E.M.F. must overcome three opposing forces : *(a)* the reversible decomposition voltage of water, which is 1-23 volta, (6) the'sctua) resistance uf the electrolyte, (c) the Og and *H,,* overvoltages at the anode and cathode respectively, both of which rise with increasing current density. The aims of commercial cell design are to reduce *(b)* and (c) to as low a figure as is practicable, to keep separate the hydrogen and oxygen, to avoid corrosion of the electrodes, and to minimise current leakage, electrolytic leakage, and repair requirement*. In commercial practice (n). (6) and (c) total 2 to 4 voltg. To keep *(h)* at a minimum, the electrolyte most commonly used is KOH, sometimes NaOH, at as high a concentration and temperature as possible, consistent with avoiding corrosion. Early type cells *(e.g. Sehoop* cell) employed $HjSO_4$," but these are now almost obsolete. Electrolyte concentration is usually 20% NaOH or 2Q-2S% KOH, and the operating temperature up to 70°C. Since the E.M.F. dissipated in overcoming (ft) and *(c)* above appears as heat, the temperature is maintained without additional heating, and in many cases provision for cooling must be made. A further method of reducing *(b)* is t-i bring anode and cathode as close as possible, but the limit here is set by the necessity of keeping oxygen and hydrogen separate.



Fio. 1.

Electrodes are usually of mild steel, and to reduce (c) above and at the same time to avoid corrosion, the anodca and, in many cases the cathodes also, are nickel plated. In the *Levin* or *Ekctrolabs* cell cobalt plating is used. Other methods of reducing (c) are special treatment of electrode surfaces, and decrease of electrode current density by the provision of subsidiary electrodes held away from the main electrode by small metallic studs *(e.g.* the *Bamag Zdannby* battery). *

Two main types of cell have been developed to ensure the separation of anode ind cathode gases:

(a) The open or bell type, in which gaseff are collected in bells placed above the electrodes. Asbestos " petticoats " are fixed round the bottom of the bells to improve separation (Fig. 1). Examples: *Fauser, Knowles* and *Uolviboe.*
(b] The enclosed or filter press type in which

the walls of the vessel containing the electrolyte themselves serve as electrodes. **In** this case a battery of cells is **formed by** vertical electrodes kept apart from one another by insulating material along **their** edges, with diaphragms alternating with the electrodes for keeping separate the oxygen and hydrogen. The cells are completely filled with electrolyte, and on passing current from one end of the battery to the other, each electrode acts as cathode on one side and anode on the other {Fig. 2). Some of the advantages of this type are that a single battery may contain up to 160 cells in series, permitting the use of high voltages without the necessity of copper conductors to connect a like number of bell-type cells in series. As the electrolyte is not exposed to the atmosphere, CO_t absorption is **avoided,** and the floor space required is **BffuaBy** smaller than with bell-type cells. The diaphragms may be of perforated **nickel** sheet ("*Fechhranz*"), asbestos, or asbestos with steel wire inlay ("*Bamag*"). **Other**

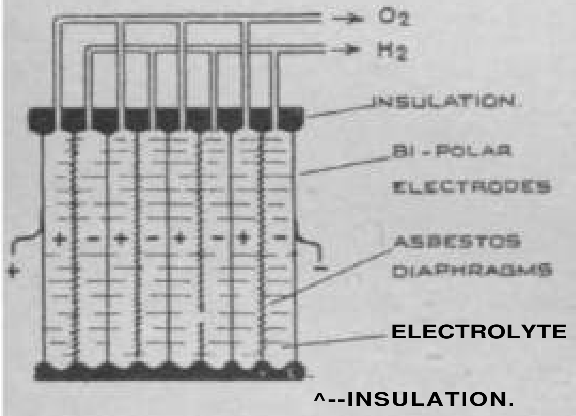


FIG. 2.

examples of the filter press type[p] are Schmidt •*Oerlikon, Siemens, Hoth (1.6.)* and the *National Ettctrolyser.* Metallic diaphragms are permissible unless the **voltage** applied across the cell is so high *(i.e.* about 4 volts) that the potential difference between one electrode **and** the diaphragm exceeds the decomposition voltage of the electrolyte. Then the diaphragm itself will act as an electrode, and impure gases will be obtained. The principal difficulty in the construction **of the** filter press type is to obtain a material suitable for insulation **between** the electrodes which at the same time is not attacked by the electrolyte, and does not allow electrolyte leakage.

The ***Levin or EUctrdabs*** cell is of the enclosed **type,** but in this **case** the electrodes are separate from the walls of the containing vessel, being electrically insulated at the **point** where the **eUbbtode** .connections pass tjirou^h **the electrolyte** 'container. The cathode is a central vertical plate, and **there are** two anodes, one on either side. The anodes are separated from the cathode by vertical diaphragms.

The electro-chemical efficiency of all commercial electrolysers approaches 100%; the slight inefficiency is not due to unwanted chemical reactions, but to the small leakage of current through the insulation. The water supplied to the cells must be very pure. Chloride impurities are particularly undesirable since they may lead to corrosion of the anodes. Any suspended iron in the feed water will deposit on the cathodes and build across to the diaphragm causing this to act as a cathode, resulting in hydrogen impurity in the oxygen.

The purity of the electrolytic gases is normally H_a 99-5-99-8%, O_a 98-5-99-0%. Decrease of purity may be due to the causes given above, or to the rupture of the diaphragms. Where very high-purity gases are required {*e.g.* H_a for ammonia synthesis) they may be obtained by passing the H_a over a catalyst such as platinised asbestos or copper, when the oxygen impurity burns to water and is condensed.

The labour requirement for the electrolytic process is small, and correctly designed cells or batteries may be operated 5 years or longer without need of repair. With open type cells, carbonation of the electrolyte may necessitate installation of a causticistng plant; regulation of the feed water to these cells may also present difficulty, because with variation of the gas pressure inside the bells, overflow of electrolyte may occur. With certain types of cells it is necessary at intervals to remove deposits of spongy iron from the cathodes, clean the diaphragms and replate the anodes. The principal operating cost is power, which may vary from 5-C to 6 0 kw.h. per eti. m. of H_a plus £ cu. m. of O_2. Owing to the fall in overvoltage on lowering the current density, the power consumption per cubic metre of hydrogen of an electrolytic plant will fall with reduction of output. . **Published** figures may therefore be misleading, and for a given output the relative merits of different designs can only be determined by comparison of power requirements at similar capital costs. **Alternatively,** comparison of capital costs should be made with plant of similar efficiencies. It follows also that the economic size of an electrolytic plant will depend on the cost of power, because- for a givftn hydrogen output, capital expended on increasing the number of cells **or** batteries will decrease the power requirement.

Pressure electrolysers have been proposed and developed on a semi-technical scale by *Noegyeruth,* ***NiedtrnUher*** and others, to operate up to 150 atm. pressure. It is* claimed that the increase in pressure reduces the oxygen and hydrojpin overvoltages, with consequent reduction in power requirements. Thus it may be said that **the** electrical energy fed to the cell **appears** partly as compression **energy** in the gases evolved, instead of as heat, **Clearly** one of the major pro Itt* n is a rising **En the design of a** pressure electrolyser will be to avoid *any* marked **difference** of pressure at the cathode and anode. The power required to **compress** oxygen or hydrogen is small compared with that used in the process of electrolysis. Thus in spite of advocacy of the use of pressure cells as a method of storing off-peak electrical power, no large installations have been reported.

The modern tendency of battery design is to obtain a greater output for a given capital cost *by increasing* the operating current density. This necessitates increased provision for cooling. In the *Bamag Zdanshy* battery the electrolyte is circulated by the lifting effect of the bubbles of gas evolved, and the liquor circuit includes, coolers and filters. It is claimed that this system reduces the oxygen and hydrogen overvoltages and prevents iron deposits on the cathodes.

Literature.—AHmand and Eilingham," Applied Electro-chemistry " (Edward Arnold), 1924, pp. 458-464, discuss the following types: *Schoop, Knowhs, Integral Oxygen, Levin* or *ElectrolabB, International Oxygen, Schmidt-Oerlikon, Oeeraard* or *Chnrchill.* Taldmenko, Khimstrol, 1OW.eand 7, describes and gives operating data for the following: *Bamog Zdanaky, Fanaer, Knowles, Pechkranz, Steuxtrd, Kevt, Siri. See also* H. S. Taylor, " Industrial Hydrogen" (Chemical Catalogue Co., U.S.A.), 1921, **Zdansky,** Chem. Fabrik. 1933. 6, .49, describes the *Bamag Zdansky* battery and gives operating data. Diamond, Trans. Inst. Min. Met. 1934, 442^i(10, describes electrolytic hydrogen plant at Trail, B.C., and *Knowks, Father, Stuart* and *Perhkranz* batteries. Noeggerath, Chem. Meting. 1928, 35, 421, and Heinze, Engineering, 1933, 135, 399. Niedcrreither, G.P. 600683 and U.S.P. 1983294.

(2) DIRECT REDUCTION or STEAM BY CABBON.

The commonest industrial reducing agent for obtaining H_2 from steam is. carbon in the form of coke. In the so-called *Water-gas catalytic* process, the reaction takes place in two stages, the first of which involves reaction of a solid, and the second is entirely gaseous.

(a) $C+H_2O \rightleftharpoons CO+H_2$; $\Delta H=+31 \cdot 4$ kg.-cal. per g.-mol. (endothermic).

(b) $CO+H_2O \rightleftharpoons CO_2+H_2$; $\Delta H=-10 \cdot 1$ kg.-cal. per g.-mol. (exothermic).

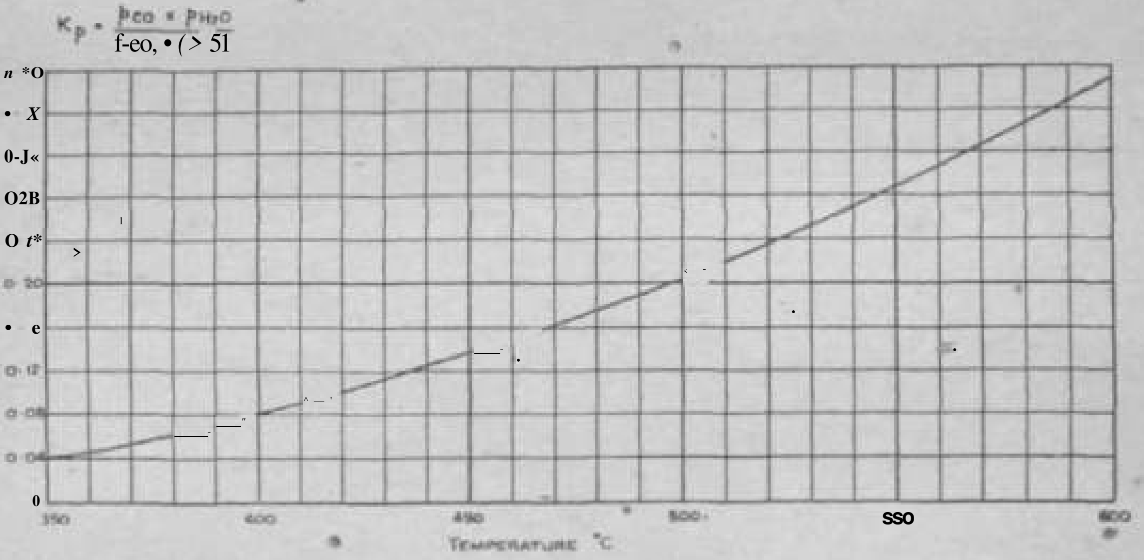


FIG. 3.—EQUIMBBIUM CUBVB (NEUMANN AND KOHLEB) OF THE WATEB-GAS REACTION.

$CO + H_2O \rightleftharpoons CO_2 + H_2$

The first reaction is that which takes place in a standard blue water-gas generator (see GAS, WATER). The second is carried out at a temperature of 400-550°C. over a pelleted catalyst of iron oxide containing promoters. The equilibrium for the so-called water-gas reaction (6) is stated on p. 318c. Fig. 3 gives the **values** of the equilibrium constant over the usual operating range of temperatures. The lower the temperature, the greater the equilibrium hydrogen content. 'Hence it is usual to carry out the reaction in two stages, firstly at 500-nuirC., wlioro the high teni]>crature favours a rapid approach to **equilibrium, and** then at a lower temperature 40G-5U<)°<\, **where,** because of the more favourable equilibrium, the reaction proceeds **further.** The resulting plant is as given in Fig- I. **The catalyst** *in* **bvonght** up **to** operating temperature **by banting** air in water-gas at the top of one or both converters. With adequate heat exchange and insulation the system maintains its own temperature, and in practice some of the heat of reaction and some of the unconverted steam are recovered by **beating** water with the hot converted gas after it leaves the final interchanges This hot water is then used to heat and saturate with water vapour the unconverted water-gas before it pauses to the heat exchanger (t>. Vol. V, 496a). The range of steam : water-gas ratios most commonly employedwis 3:1 to 1:1 by volutiio. The higher the strain ratio, the lower the CO content of the converted gas, which in practice varies from 5 to 1% CO.

The ^action is usually carried out at a pressure of 1-2 atm. absolute, although uuiue plants operate at higher pressures. The equilibrium is no more favourable than at lower pressures, but it is more quickly attained. The catalyst is contained in mild steel vessels and is supported on trays in a manner similar to that used for the catalyst in the contact method of oxidising SO_2. A number of catalysts have been patented which improve the equilibrium by absorbing the CO_2 produced, but no large scale installations operating on this principle are reported. The original Bodische (now the I.G.) units had a capacity of 25,000 cu. ft. per hour although very much larger units are now common.

With most of the catalysts employed industrially, removal of H_2S from the inlet water-gas improves the catalyst activity and lowers the CO content of the exit gas. The standard iron-oxide box process is commonly used for H_2S removal, and a recent development has been the construction of tower purifiers which utilise a very active oxide mass and can be rapidly emptied and refilled. Active carbon can also be employed for oxidising H_2S to S and H_2O, and there are a number of wet processes usually involving gas-scrubbing with iron oxide suspensions or alkaline solutions (examples—*Ferroz, Thylox, Koppers,* etc.). The solution is regenerated by aeration, and the H_2S is oxidised, liberating a sulphur scum which may be recovered from the surface of the solution.

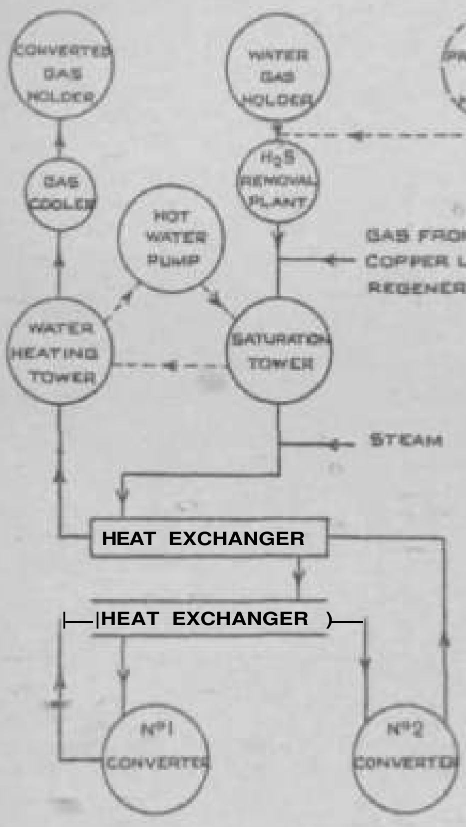


FIG. 4.

To obtain pure hydrogen from the converted gas, CO_2 is removed usually by water-scrubbing at pressures from 10-50 atm. The scrubbing water is freed from CO_2 by air-stripping and is used again. With large plant the energy expended on injecting the water into the scrubbing **tower** is **frequently** partly recovered by passing the water from the tower through a Pelton wheel or other form of water-motor (Fig. 5). As an alternative to water-scrubbing for CO_2 removal, solutions of organic bases may be used which are regenerated by heating (the *Girbotol* and the *Alkacid* (I.G.) processes). The requirements for the absorbing solution are that its volatility should be low to avoid losses, that the CO_2 capacity of the solution should be high, and that the CO_2 partial pressure above a carbonated solution should be low at room temperatures, but to effect easy regeneration should rise rapidly with increase in temperature. These processes for CO_2 removal are to be preferred where the final gas mixture is not required at pressure (*e.g.* the *Fischer-Tropsch* process, *see later*).

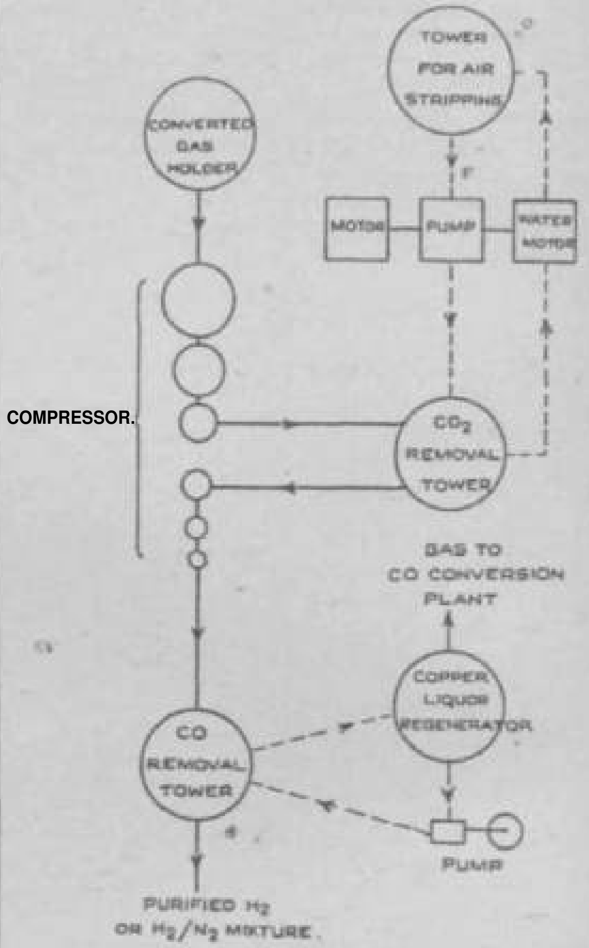
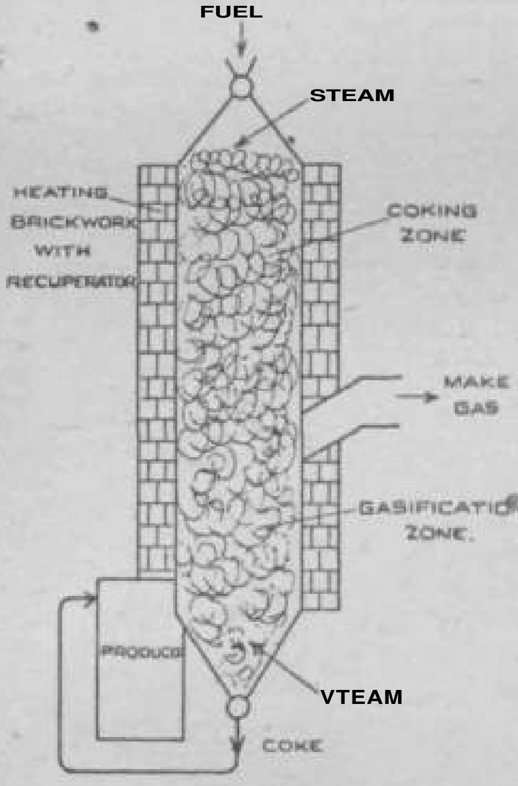


FIG. 5.

The CO not converted in the conversion stage, and any CO_2 still remaining, are removed at still higher pressures by scrubbing with an ammoniacal cuprous salt solution, which is regenerated for further use by heating. The gas given off during regeneration consists largely of CO, and is returned to the inlet of the CO conversion unit. Thus all the CO entering the system is finally oxidised to CO_2, and the ratio of water-gas required to pure hydrogen obtained is very little above 1:1. The impurity remaining in the final gas is nitrogen contained in the **original** water-gas. For ammonia synthesis where a final $H_2:N_2$ ratio of 3:1 is required, producer gas is added before the CO conversion plant or semi-water-gas may be employed.

The most recent developments have been not in the CO conversion or purification **stages** of the process, but in the production of the water-gas. Coal is frequently a cheaper starting material than coke, and may therefore be preferred. Processes utilising coal have the additional advantage that the hydrogen in the coal is also usefully recovered. The disadvantages are the production of tar and the presence of hydrocarbons in the water-gas. For many purposes (*e.g.* the synthesis of ammonia) even small amounts of hydrocarbons are a serious drawback, because they build up in the synthesis system and must be purged therefrom, resulting in the simultaneous loss of considerable quantities of hydrogen. Thus the aim of the coal-gasification processes is to destroy the tar and hydrocarbons given off as the coal is heated, by cracking or decomposition with steam, before they pass to the exit gas. This is achieved by passage of the hydrocarbons through a hot zone, which is frequently the incandescent coke formed after the initial heating of the coal. For processes making gas for the *Fischer-Tropsch* process an additional objective is the production in one stage of a gas containing the required H_2:CO ratio of 2:1.



Fro. 6.

In general, coal-gasification processes are most easily applied to brown coals and lignites, because these produce very active cokes after initial heating. The following are typical examples:*

The *Winkler* Generator is described under GAS, WATER (Vol. V, 501). The hydrocarbon are cracked in the fuel bed itself or in the large hot gaseous zone above the bed, into which secondary air is introduced. For the final production of H_2, or $3H_2+N_2$ for ammonia synthesis, an oxygen-enriched air is used. The oxygen cost is a disadvantage,

The *Bubiag Didier* Retort (Fig. 6).—In this plant the heat necessary for the gasification of coal with steam passes to the fuel bed through the walls of a bench of brickwork retorts very similar to standard gasworks vertical retorts. Steam is added at the top and bottom of each retort, and the gas exit is about one-third of the way from the bottom. Fuel is added at the top, and thus the tar and hydrocarbons given off in the upper or coking zone of the retort must pass through the hot coke in the centre of the retort before they pass to the exit main. They are thereby cracked or decomposed with steam. The unreacted coke from the bottom of the retorts is fed to producers heating the retorts. An exit gas containing <1·0% methane is claimed, and the process is suggested as particularly suitable for *Fischer-Tropsch* gas, owing to the ease of control of the $CO:H_2$ ratio.

The *Viag* Generator (Vergasungs-Industrie A.-G.) (Fig. 7).—This is in effect a twin water-gas generator fed with coal. On the down run the gases given off in the coking or upper zone of the generator pass through the coke bed and are thereby decomposed. On the up run the hydrocarbons pass forward with the make gas, but decomposition is assured by passage down through the incandescent coke bed of the twin generator. Periodically steam is shut off from each generator in turn and a blast of air admitted as in standard water-gas practice. Recuperators are used to improve the heat efficiency of the process.

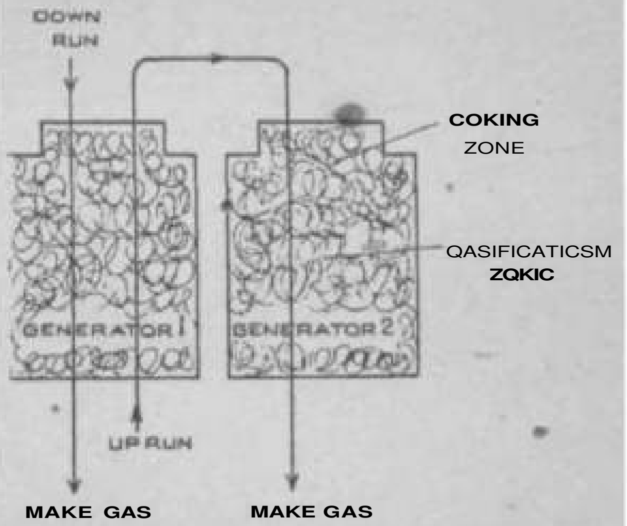


FIG. 7.

The *Pintsch-Hillebrand* Generator is also described under GAS, WATER (Vol. V, 502), but the principles of operation are shown in Fig. 8. In this case the hydrocarbons are decomposed firstly in the recuperator (or regenerator) and then in the fuel bed.

The *Lurgi* Process.—This process utilises oxygen for gasification of brown coal at about 10 atm. pressure. A somewhat similar process has been proposed by Fauser. The advantage claimed for pressure operation is that it enables the fuel bed to be operated at a lower temperature. Thus, for example, for *Fischer* synthesis a gas of suitable composition may be obtained in one stage. As there is no special attempt to crack or decompose hydrocarbons, the methane content of the make gas is higher than with other processes, but it is nevertheless suitable for *Fischer* synthesis. As with, the *Winkier* process the cost of oxygen will be a disadvantage.

Literature. — For general description and operating costs' of stages of process employing coke water-gas, *see* Laupichler, Chem. Met. Eng. 1936, 43, 122. and Gas World, 1930, 105, 71. Held, Petroleum, 1939, 85, 435, discusses production of ammonia-synthesis gas from coal and describes *Pintsch-HillebTand, Didier, Lunji, Witiiershall-Schmalftldt* and *Kcrppcrs* processes. Schultea, Gluekauf, 193U, 72, 273, gives cost estimates for production *of Fischer* synthesis-gas by numerous processes, and describes *Winkier* jjd *Didier* processes; *see also* Giordani, J. Usines Gaz, 1937, 61, 170, 196, 229. Miiller, Chemical Engineering Congress, World Power Conference, 1936, Paper 5E, discusses complete gasification of coal and describes the *Pintsch-Hillebrand* process. For *Didier* process, see Szigeth, 'I. Ungar. Ing. u. Arch. Verein, 1934, 37 and 38, and Thau, Brennatoff-Cliem. 1935, 16. 61. Complete gasification **with** oxygen, Fauser, lltli International Congress Pure and Applied Chemistry, Madrid, 1934; Drawe, Gaa- n. Waaaerfach, 1933, 76, 541, and Blackburn, Williams and Miltett, Inst. Gas Engineers, 1936, Communication No. 141. Van der Werth, Chem.-Ztg. 1935, 59, 276, reviews Gerpinn patents covering CO conversion. Tower purification process, Lenze and Borchardt, Gas- u. Wasserfach, 1333,74, 445. *Alkacid* process, Bii.hr, Proc. Amer. Petroleum Inst. 8th Mid-year Meeting, Sect. Ill, 1938, 19, £7.

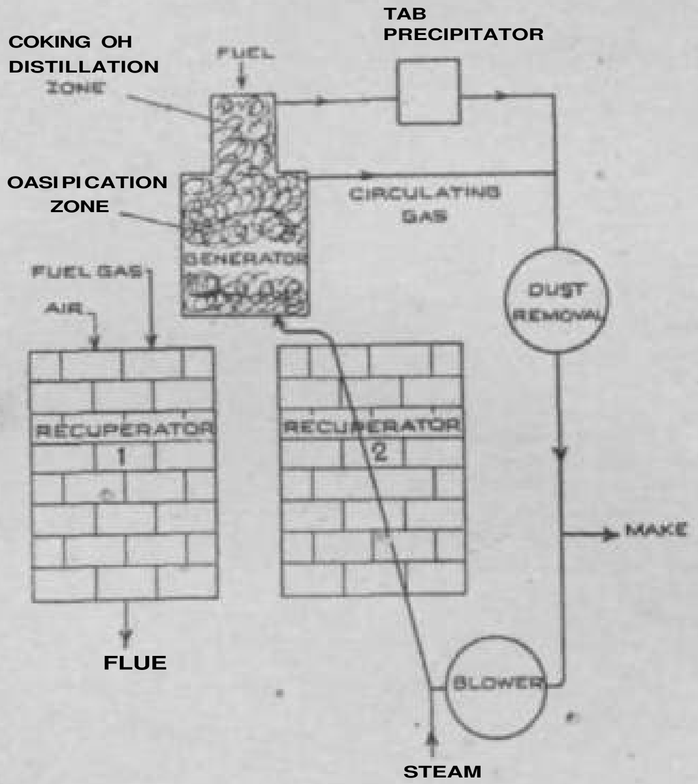


Fig. 8.

(3) IKDIKKCT RBDUcnoar OF STEAM WITH CARBON USING AN INTERMEDIARY.

Tke Iron-SUam Process.—In this process oxides of iron formatho intermediary in reducing titi-cim with carbon. The carbon is first converted into water-gas or^ producer-gas by **the** standard process, and the gas is paed at temperatures varying from 550°C. to 760°C. to reduce oxides of iron, generally in the form of spathic ore, because this is porous and nt the saAe time robust. Silica ia undmrablo in the ore *ta*nce it forms a glaze which prevents reaction. *T\ic* reducing gas is then abut off and steam is passed over the oxide mass, resulting in the oxidation of the mass and the production of hydrogen. The equations can be written :

(a) Reduction $Fe_3O_4+CO \rightleftharpoons 3FeO+CO_2$ or

$Fe_3O_4+H_2 \rightleftharpoons 3FeO+H_2O$

Steaming $3FeO+H_2O \rightleftharpoons H_2+Fe_3O_4$

(b) Reduction $FeO+CO \rightleftharpoons Fe+CO_2$ or

$FeO+H_2 \rightleftharpoons Fe+H_2O$

Steaming $Fe+H_2O \rightleftharpoons FeO+H_2$

The process is thus a cyclic one, the reduction stage being **flndotben&io** and the steaming stage exothermic. When reduction is by CO, the final result is the reaction of strum with CO *w* in the water-gas catalytic process already desc: **ibedj** in id thus there is a net heat evolution. Nevertheless the inevitable heat losses from any industrial **plaaj an roeb** thut heat must be contimidtlv Kupplicii **to** the system, and this is usually obtained by burning spent water-gas obtained during the reducing stage, which from equilibrium considerations still contains a considerable percentage of combustibles. The combustion of producer-gas has been suggested *as* an alternative source of heat, and partly burnt coke-oven gas or even coal dust havo been proposed as alternatives to water-gas for the reducing stage.

Taylor *(op. cit.)* has shown that from published data on iron oxide-H_a-CO equilibria, reaction (o) above will require less water-gas than (6) to produce the same amount of hydrogen, although it is clear from the equations that for a given amount of iron *(b)* would be expected to give the greater hydrogen output. Further, assuming reaction (a) and quite apart from the gas that it is necessary to burn to maintain temperatures, the equilibria involved necessitate that at 750°C. the minimum possible ratio of water-gas consumed to hydrogen produced is 1-0:1. in actual practice this ratio will be 2 to 3:1. A method of overcoming equilibria considerations proposed by Rogers is to circulate the spent water-gas, together with the jtcuni that it contains, back to the water-gas generators where it is used in place of steam. The CO, in the spent gas is reduced to CO and tho steam to hydrogen. A purge from this closed circulating system is necessary to remove CO or CO_a produced from coke gasified in the generator, and also the nitrogen inevitably introduced. Nevertheless an" improvement on the ordinary open cycle is claimed. Other workers suggest the condensation of steam and removal of CO_S from the spont gas before returning it to the retort.

The cycle usually claimed as most efficient is 20 minutes reducing and 10 minutes steaming, and there is a short purge after reducing before the hydrogen ia turned to the collecting main. It ia necessary periodically to burn out deposits of carbon from the^4 iron mass, and if unpurifkd water gas is employed, of sulphur as well. Carbon results from tho decomposition of CO thus:

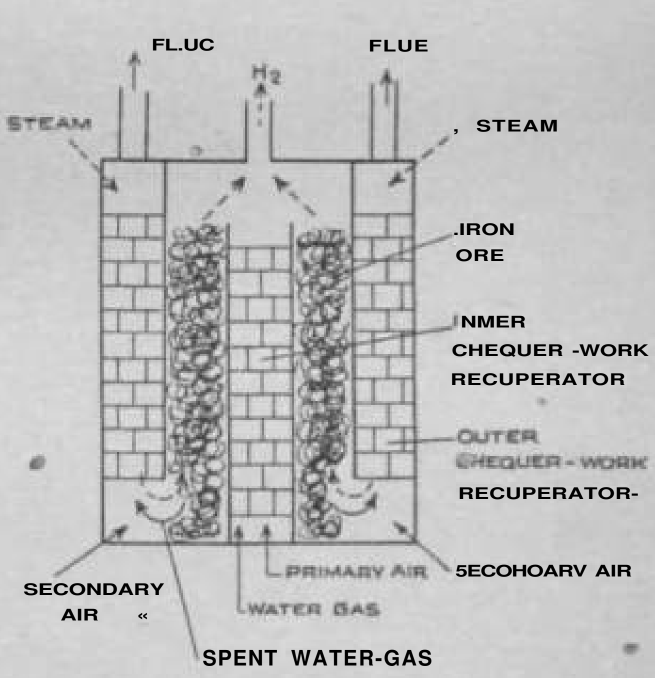
$$2CO \rightleftharpoons C+CO_2$$

and is avoided or minimised ^y a high CO_2 content of the water-gas, driving the above ^reaction from right to left. The same effect may be obtained by the addition of small amounts of steam to the inlet water-gas, which will produce CO, by the "water-gas" reaction. However, since COg and steam are the products of^reductidh of the iron mass, this method of preventing carbon depoaition will slow down the rate of reduction, and its application is therefore limited.

Tho variouB proprietary plants operating the process differ chiefly in the methods of heating the iron maa.s. The simplest is the *Lane* process in which the iron ore is contained in vertical cost iron or mild steel retorts arranged in a heating furnace. A bench of such retorts is usually **bid** out in groups of retorts so that one group may be steaming while one or two groups are reducing. Thus hydrogen production from the bench is continuous. Tho bench is heated by burning producer-gas or spent water-gas.

In the *Bamag* process the iron mass is heated indirectly by means of a recuperator (single-retort process). Water-gas is passed through the iron mass and the spent gas is burned with air before it passes to the recuperator. After reduction, the water-gas is shut off and steam is passed through the recuperator and through the reduced mass. There are suitable purge periods, and air for burning off carbon deposits is admitted every cycle.

The *Messertckmilt Process* (Fig. 9) combines direct heating with the use of a recuperator. Tho iron mass is contained in an annular space between two iron cylinders. Water-gas is burned at the base of the inner cylinder with a quantity of air very much less than that required for complete combustion. The hot gas passes up through the chequer-work, down through the iron mass, and is finally completely burnt in the outer chequer-work. After 20 minutes reducing, the water-gas and air are shut off and steam is passed downwards through the outer recuperator where it is superheated, and upwards through the iron mass, hydrogen »as*ing from the top of the retort. There is a short purge period.



FIO. 9.

The crude hydrogen from an iron-steam plant will contain small quantities of H_aS (greater if the water-gas is unpurified), CO_2, CO and N,, The H,S may be removed by standard methods, and the CO_2 by lime bo3es. Final purities claimed are 99 5-99*75% *(Lane* process) and 98&-99-2% *{MesacrschmiU).*

Both multi- and single-retort processes have. similar efficiencies (2 or 3 vol. water-gas per 1 vol. of^H,). The costs of retort renewal in the multi-retort process may bo heavy, and it has the disadvantage of a largo number of hot joints. In a single-retort plant the volumes requiring purging are greater, and gas purities may bo expected to be less than with a multi-retort plant. This is borne out by the figures quoted above.

This process is not used to anything like the extent of the *Water-gas catalytic, electrolytic* or *Linde* processes. For the specific production of hydrogen for fat hardening it appears to have been **replaced** by electrolytic hydrogen. There **have** been no marked advances in industrial plant for a number of years.

The Liljenrol Process.—In this process, developed largely by the I.G., phosphorus is the intermediary when reducing steam. Thus elemental phosphorus is produced by reduction of pentoxide by **carbon** in the normal manner, and this reacts **with** steam thus:

$$2P+8H_2O=5H_2+2H_3PO_4$$

The **reaction** is carried out in the presence of a catalyst and improvements in the catalyst have enabled operating temperatures to be reduced from 1,000°C. to 350-400°C. Apparently the principal technical difficulty in operating this process is to avoid the production of phosphine and phosphorous acid, and two stages are apparently necessary.

The process was originally developed to allow synthesis of ammonia from the hydrogen obtained. This was to be neutralised with the phosphoric acid to give ammonium phosphate, a dual-purpose fertiliser. No large-scale installations of this process, however, have been reported.

The Silicol Process.—Here the intermediary is silicon or ferro-silicon. The silicon reacts with alkalis according to the following equation :

$$2NaOH+Si+H_2O=Na_2SiO_3+2H_2$$

In practice less than the theoretical quantity of alkali is required. Where ferro-silicon is employed, the hydrogen yield only approaches theoretical when the silicon content is 80-90%. The process is exothermic and maintains itself at operating temperature. Careful control of admission of ferro-silicon is required to give the best results and to avoid carry-over of froth from the reaction vessel.

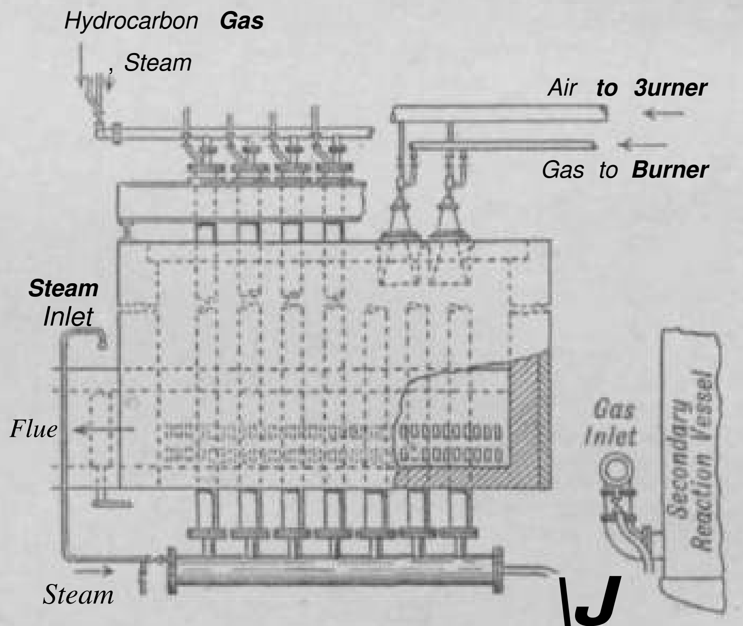


FIG. 10.

The process was originally developed during 1914-18 for producing hydrogen in the field or aboard ship for lighter -than -air craft. For this purpose the disadvantage of expensive raw **materials** was more than counterbalanced by the following advantages; a simple plant with low labour and power requirements, hydrogen rapidly produced and reasonably pure, with raw materials not excessively heavy or bulky. The only recent developments appear to be the generation of hydrogen under pressure by this process, and the development of a dry reaction by introducing water in crystalline compounds as, for example, gypsum.

The Hydrolith Process.—This was developed for the same purposes as the *Silicol* process. Calcium hydride reacts with water, thus:

$$CaH_2+2H_2O \rightarrow Ca(OH)_2+2H_2$$

Commercial calcium hydride yields upwards of 34,000 cu. ft. of hydrogen per ton. The reaction is markedly exothermic. Traces of nitride in the hydride lead to the production of ammonia which must be removed by water-scrubbing. The process is *no* longer used extensively.

Literature.—For reaction equilibria in the iron-steam process, *see* p. 310d, *also* Taylor, " Industrial Hydrogen," Chem. Cat. Co. U.S.A., 1921, p. 25. Recent patents are Rogers, B.P. 249925 and 201124. For the *Silicol* and *Hydrolith* processes, *see* Teed, "Chemistry and Manufacture of Hydrogen," Edward Arnold, 1921, pp. 45, 67; *also* Jaubert, Compt. rend. 17th Congr. Chim. ind. Paris, 1037, 1130. For the *Liljenrol* Process, *see* G.P. 406411, 4093"44, 4S5068; B.P. 324122, 325533.

(4) REDUCTION OF STEAM BY HYDROCARBONS.

Gaseous hydrocarbons here replace coal in the extended form of the water-gas catalytic process already described. The hydrogen m the hydrocarbons is usefully recovered, and the process can be **written** thus :

$$CH_4+2H_BO \rightarrow CO_2+4H_2$$

The reaction is usually carried out in two stages, approximately thus:

(*a*) CH_4+H_sO^$CO+3H_a$;**fiJT—t-M-ftkg.** cal. perg. mol. (endothermic}.
(*b*) CO ;-H_2O^$CO_{fi}+H_a$: a//=-101kg. cal. per g. mol. (exothermic).

Stage (*b*) is exactly similar to the second stage of Vie water-gas catalytic process already described.

Since the total reaction ie endothermic, the higher the temperatures the lower the equilibrium percentage of hydrocarbon. The reaction is therefore carried out at temperatures above about 70^0., over a catalyst which may be contained in tubes of special steel which retains its strength at high temperatures. A typical composition for thia steel is Cr 24, Ni 20, Mn 0-7, Si 1-0, C 0-22%. Th» tubes are contained in a brickwork furnace and are externally heated by combustion of Fuel gas. There is a very extensive patent literature covering catalysts for this process. Fe, Ni, Ca promoted with Cr, V, Ce and K, Mg; or At have all been proposed.

The Standard Oil Company's plant at Bayway, N. J., U.S.A., has a capacity of 300,000 cu. ft. per hr. of hydrogen, and operates on refinery gases at atmospheric pressures and temperatures up to 1.000°C. There is less than 1% unconverted hydrocarbons in the exit gas.

Literature.—Ind, Eng. Chem. News Edition, 1932, 10, 205, describes the Bayway plant. Petroleum Zeitsohrift, 1932, 28, 10 (Standard I.G.J describes an improved type of apparatus from which Figs. 10 and 11 are taken.

(5) CRACKING OP HYDROCARBONS.

Previous to the development of steam reduction by hydrocarbons, there* was considerable activity in the development of processes for the production of hydrogen by the cracking of hydrocarbons thus:

$$CH_4 \rightarrow C+2H_2$$

The commercial success of any such process appears to depend largely on tfye valu» of the carbon black produced. There is only one large plant reported as operating on hydrogen obtained in this manner, that of the Shell Company in California. The methane-steam process has now clearly superseded cracking where hydrogen production is the solo consideration. It should be noted, however, that there is very considerable development now taking placo in the petroleum industry in the direction of catalytic dchydrogenation of hydrocarbons. These promise to yield substantial quantities of fairly pure by-product hydrogen, and although no extensive use has yet **bora** made of this source, it may become of considerable commercial importance.

During 1914-18 the Carbonian Gesellschaft developed a proccsB for hydrogen production from acetylene by decomposing with an electric spark at 2 atm. pressure. A number of Zeppelins were actually filled with gnjf thus produced, but the process is now no Ionizer uspd.

Lilfrohirr.—The. Plant of the Shell Chomionl Co.! California, has been described by Rosen-*ti in. Ohem. Met. Eng. 1931. 38, 030,

(6) RECOVERY FROM COMMERCIAL GASES BY PARTIAL LIQUEFACTION.

Gases such as coke-oven gas and water-gas contain considerable quantities of H_a which may be separated from the remaining constituents by the physical process of partial liquefaction. Two main processes were developed from about 1912 onwards, by George Claude in France, and by Linde and Bronn in Germany. The original main difference between these processes was the method adopted for obtaining the neceasary low temperature. Claude used expansion of a compressed gas through a specially developed «ngine, which because of the low temperatures employed was lubricated with liquid nitrogen. Linde and Bronn uaed the Joule-Thomson effect by expansion throHgb a porous plug, in actual practice an expansion valve. The following is a description of the Linde process as applied to coke-oven gas, which is the commonest case found industrially. It is significant that a number of plants originally obtaining hydrogen by the partial liquefaction

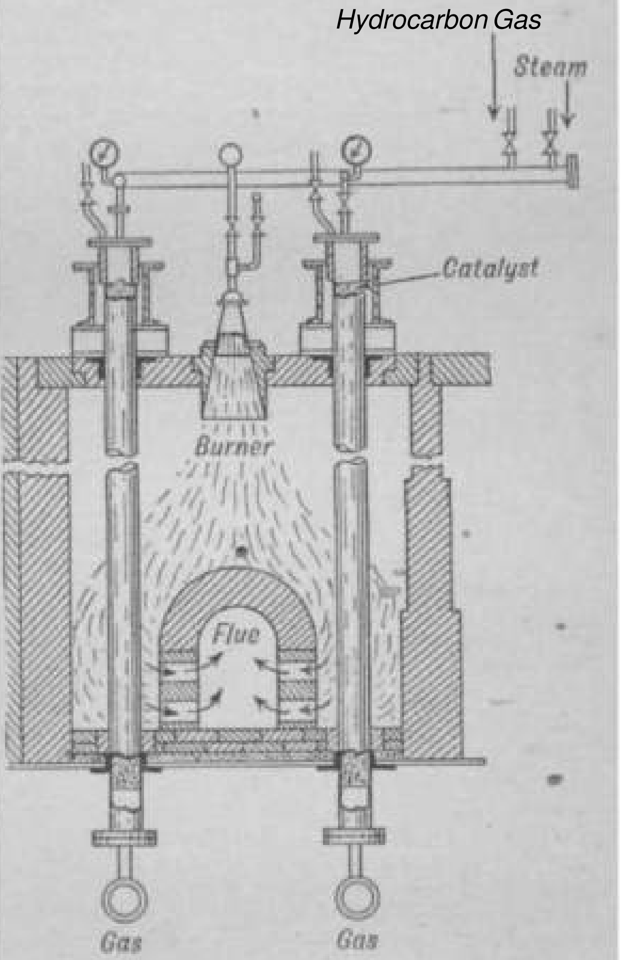


FIG. 11.

of water-gas have changed over to the *Badische* process.

The coke-oven gas is first purified from H_2S, usually by passage through iron-oxide boxes in the standard manner. It is then compressed to 10-12 atm. and is cooled with anhydrous ammonia to about —45°C, a suitable cold exchanger being provided to economise power. This preliminary cooling effects the separation of water, followed by benzol and relatively high boiling substances. After warming in the cold-exchanger of the benzol removal plant, the compressed gas is scrubbed with water to remove CO_2 and acetylene, and finally complete removal of CO_2 is obtained by scrubbing with caustic soda solution. The compressed gas is then cooled by cold exchange with gases coming from a colder part of the system, then by anhydrous ammonia, and by further cold exchange until at a temperature of —145°C. a fraction condenses out which contains practically all the C_2H_4 and some CH_4. The ethylene in this fraction may be separated from the methane by further rectification, should it be required for other chemical processes. The temperature of the gas thus freed from C_2H_4 is further reduced by cold exchange, and final cooling is by liquid N_2 at —193°C. when practically all the methane condenses out. In the last stage of purification the gas is washed counter-currently at 10 atm. pressure and —190°C with liquid nitrogen, which dissolves out the CO and at the same time partly evaporates to give the $3H_2+N_2$ mixture required for ammonia synthesis. To obtain the liquid N_2, pure compressed N_2 from an air fractionation plant is supplied at about 110 atm. pressure. This is cooled by anhydrous ammonia and then by cold exchange to about — 150°C. Finally it is let down through an expansion valve when cooling by the Joule-Thomson effect causes liquefaction at -19.TC. The N_2 which evaporates is warmed by cooling the inlet gases and passes from the system for recompression. That portion of the liquid N_2 required to scrub out CO is let down to 10 atm. only and cooled to — 190°C. with the liquid which has been expanded to a lower pressure (Fig. 12).

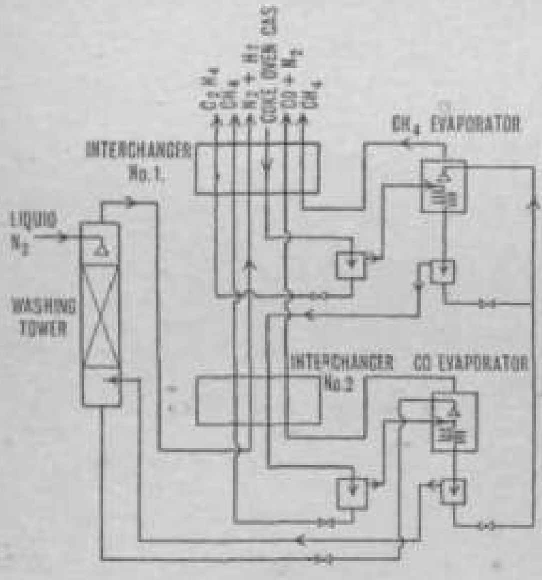


FIG. 12.

The very greatest care is taken to utilise all available cold and the latent heat of the condensed fractions, etc., so that all gases pass from the system at substantially room temperature. The $3H_2+N_2$ mixture, which is very pure, leaves at about 10 atm. pressure. Thus all the energy required for supplying cold to the system is provided by the evaporation of anhydrous ammonia, and the Joule-Thomson expansion of compressed cooled N_2. It is usual to mix the C_2H_4, the CH_4 and the CO fractions (the latter containing considerable quantities of N_2), and to return them as a heating gas of high calorific value to the coke ovens whence the original supply of coke-oven gas was obtained.

Plants for the partial liquefaction of coke-oven gas have also been built by *Messer,* and are apparently somewhat similar in operation to *Linde* plants.

Literature.—Borchardt, Gas- u. Wasser-fach, 1927, 70, 502, gives description of *Linde* process, analyses of gas fractions and estimated operating costs. *See also* Borchardt, Chem.-Ztg. 1930, 54, 649. For *Claude* process, U.S.P. 1135355, 11U2455; Claude, Z. angew. Chem. 1930, 43, 417. For *Messer* plant, Van Iterson, Ingenieur (Holland), 1932, A, 47, 427, *also* Berthelot, Genie Civil, **1936,** 108, 573.

(7) PRODUCTION OF BY-PRODUCT HYDROGEN.

In the process of electrolysis of brine to produce caustic soda, a substantial quantity of hydrogen is obtained as a by-product, and in many cases this is recovered and utilised.

In the *Fernbach* or *Weizmann* process for the production of acetone and butyl alcohol by the fermentation of maize, a gas is given off which contains about 40% H_2 and 60% CO_2. At one plant in the U.S.A. this gas is freed from alcohol vapour by active charcoal, and compressed and scrubbed with water until the CO_2 content is 26%. The gas is then used to synthesise methanol

$$CO_2+3H_2 \rightleftharpoons CH_3\cdot OH+H_2O$$

The *IHag* process, which is used fairly extensively for the production of acetone from alcohol, gives by-product hydrogen by the following reaction :

$$2C_2H_5\cdot OH+H_2O \rightarrow CH_3COCH_3+CO_2+4H_2$$

Literature.—By-product hydrogen from *Fernbach* process, Anon., Chem. Met. Eng. 1930, 37, **548.** Uukonyi, Chem.-Ztg. 1926, 50, 357. Woodruff, Ind. Eng. Chem. 1927, **19,** 1147. *See also* Vol. V, 44a.

COSTS OF COMMERCIAL PRODUCTION.

It is difficult to give generalisations on the relative costs of hydrogen by the processes already described, because the cheapest process for any particular requirement will depend on a number of circumstances, and each individual case must be considered on its merits. This is clear from the fact that the various processes already described do actually operate in commercial competition. If any one process were overwhelmingly cheaper under all conditions, it would supplant all others. Clearly the main factors affecting the choice of process will be (a) the raw materials available, (6) the cost of power, (c) the purpose for which the hydrogen is to be used, *(d)* the quantity required. Taking these factors in turn, the following examples are illustrative:

(a) Where brown coals or lignite are available and coke is expensive, one of the coal-gasification processes worked in conjunction with the *Badische* process, as described above, is likely to be favoured. Thus in Germany, the I.G. use the *Yfinkier* process extensively, and there are *Didier* plants producing *Fischer* synthesis-gas *(see later).* In Hungary the ammonia plant at Petfurdo has a *Didier* plant operating on lignite. Where large quantities of surplus coke-oven gas are available, *e.g.* in Belgium and Holland, the partial liquefaction processes *(Claude, Linde* or *Messer)* are widely employed. At oil wells, refineries, and coal- or oil-hydrogenation plants the availability of surplus hydrocarbon gases has favoured reduction of steam with these gases to produce all or part of the hydrogen required for hydrogenation.

(b) Ample and cheap electric power will favour the *electrolytic* process. Thus Norway has a large synthetic ammonia plant operating on electrolytic hydrogen from hydro-electric power, and this method was proposed in recent schemes for harnessing the Aswan Dam in Egypt. However, to be economically attractive in competition **with the *water-gas catalytic or partial liquefaction*** processes, the power must be very cheap indeed. Pollitt has shown that with power at 0·07d. per kw.h., electrolytic hydrogen will compete with other processes. The high capital cost of electrolytic and ammonia-synthesis plant precludes the erection of plant operating only on off-peak or seasonal power.

(c) For reasons already given, CH_4 is objectionable in gases to be used for ammonia synthesis. This consideration will militate against the use of the coal-garification processes, or steam reduction with hydrocarbons, except in cases where the decomposition of CH_4 is very complete. For *Fischer* synthesis the necessity for a very low CH_4 content does not hold, and thus coal-gasification processes are frequently employed. For fat-hydrogenation extreme purity is essential, hence electrolytic hydrogen is favoured.

(d) The largest synthetic-ammonia plants operate on coke by some form of the water-gas catalytic process. Two factors can explain this: (1) Coke is usually available in larger quantities than say coke-oven gas. Where the latter is used, the amount of hydrogen which can be made is regulated by the output of the coke ovens, in its turn depending on the market for coke. Thus an absolutely assured supply of gas may be difficult to obtain. (2) The water-gas catalytic process is more easily adapted for large-scale production than most of the other processes. A large number of the smaller synthetic-ammonia plants use partial liquefaction of coke-oven gas to supply hydrogen, but the major factor in deciding this is probably (a) above. There is no reason to suppose that this process is particularly adapted to small and intermediate hydrogen outputs. For very small outputs such as those required for the hydrogenation of fats, and where the hydrogen cost is not a big factor in the total cost of the product, **the *electrolytic* or *iron-steam* processes may be** employed in spite of their high operating costs.

One estimate of the relative importance of the various processes gives the percentages of the world's total hydrogen production as follows: *Water-gas catalytic* and related processes **55%, *partial liquefaction* 26%, *electrolysis* 16%,** all other methods 3%.

Literature.—For a comparison of electrolytic and water-gas catalytic processes, *see* Pollitt, Trans. 2nd World Power Conference, Berlin, 1931,2,145. For estimated cost of stages of the water-gas catalytic process, *see* Laupichler, Chem. Met. Eng. 1936,43,122, and Gas World, 1936,**105,** 71. For cost of electrolytic hydrogen, Zdansky, Chem. Fabrik. 1933, 49, and of *Linde* process, Borchardt, Gas- u. Wasserfach. 1927,23, 1, and Metallbörse, 1930, 20, 1856. For cost of *Fischer* synthesis gas by a number of processes, *see* Schulfes, Glückauf, 1936, 72, 273.

TECHNICAL USES.

The relative importance of the various commercial uses for hydrogen may be illustrated by the following figures applying to the U.S.A. for 1938. Of a total consumption of about 25 x 10^9 cu. ft., approximately 66% went to ammonia synthesis, 19% to synthetic methanol, 9% to technical *isooctane,* and 6% to petroleum hydrogenation. No data, are available for Europe, but the relative orders of importance would probably be (1) Ammonia production, (2) Motor, fuel production including hydrogenation, (3) Synthetic alcohols production, (4) Other uses.

(1) Synthetic Ammonia *(see* AMMONIA, Vol. I, *331 d).*—The sources of the hydrogen used in world, production of synthetic ammonia are approximately as follows: *Water-gas catalytic* **52-4%; *partial liquefaction* coke-oven gas** 21-1%; electrolysis of water 17-0%; other processes 1-5%.

(2) Motor Fuels *(see* HYDROGENATION OF COAL).—This represents one of the most recent developments in the commercial use of hydrogen. It includes hydrogenation of bituminous and brown coals, coal distillation products, petroleum and petroleum residues, and hydrocarbon synthesis by the *Fischer-Tropsch* process which may be represented:

$$nCO+2nH_2 \rightarrow (CH_2)_n+nH_2O.$$

There are a number of *Fischer-Tropsch* and brown coal hydrogenation plants in Germany. In England the I.C.I.-plant at Billingham, Co. Durham, hydrogenates bituminous coal and creosote oil. In Italy there are plants hydrogenating Albanian crude oil and petroleum residues. In America plants at Baton Rouge (Louisiana) and Bayway (N.J.) have been used for hydrogenation of gas oils and for the production of special types of lubricants by hydrogenation. A recent development is the production of the high-efficiency aviation fuel *iso-*

octane by the hydrogenation of *isooctene.* Since in petroleum refineries there are usually available considerable quantities' of surplus hydrocarbon gases, these are generally used to reduce steam for the production of hydrogen.

(3) Synthetic Organic Chemicals (*see* CATALYSIS, Vol. II, 425c).—The most important product in this class is undoubtedly methyl alcohol or methanol produced by the reaction:

$$CO+2H_a \wedge CH_3OH$$

Recently there has been considerable expansion in the synthesis of higher alcohols by analogous processes. Water-gas partly converted with steam to give the required H_a:CO ratio is the commonest starting material, but coke-oven gas partly burnt with air has also been proposed. The gases remaining after passage through a methanol converter are then used for the synthesis of ammonia.

(4) Fat Hardening (*see* HARDENED OR HYDROGENATED FATTY OILS).

(5) Lighter-than-Air Craft.—The development of the airship has been impeded by a number of serious accidents and by the perfection of the aeroplane. Nevertheless for a number of specialised purposes lighter-than-air craft are still used. For instance, protection of objectives from attacking aircraft is secured by a number of balloons moored by cables (the balloon barrage). The hydrogen is then required in comparatively small quantities over widely distributed areas, and the development of relatively light-alloy steel cylinders has clearly helped considerably in the solution of this problem. The Graf Zeppelin Co. used small electrolytic hydrogen plants at its various bases for replacement of the hydrogen losses.

(6) Heating and Welding.—The intense heat of the oxygen-hydrogen flame enables it to be used for autogenous welding and the flame-cutting of steel plate. For this reason also, it was once employed for producing an intense light for cinema lanterns, etc., by heating lime to incandescence. The development of the electric arc and special forms of filament lamp has completely superseded "limelight," and for welding, acetylene is generally preferred because it is easier to generate in small quantities, is easily stored under pressure in acetone (dissolved acetylene) and the oxy-acetylene flame is hotter (*see* ACETYLENE, ITS USE IN INDUSTRY, Vol. I, 111). For some purposes, however, the carbon in acetylene is objectionable, and for welding of aluminium on platinum, for the fusion of quartz to give artificial gems, and for certain cutting operations the oxy-hydrogen flame is still employed (*see* GEMS, ARTIFICIAL).

In welding with the electric arc, hydrogen has two uses. It can be used to shield the arc, thus preventing the formation of oxides or nitrides of iron, or by passing hydrogen through an arc formed between two tungsten electrodes, it can be dissociated to atomic hydrogen. Molecular hydrogen re-forms 6-10 mm. from the arc with evolution of intense heat. An alternating- current arc is usually employed, and the temperature thus obtained is probably above 3,760°C. The development of covered electrodes for ordinary electric-arc welding has prevented any great extension of the use of hydrogen for shielding welding work from atmospheric attack, but for certain specialised purposes, *e.g.* the welding of thin sections, atomic-hydrogen welding is still fairly extensively employed.

(7) Bright Annealing.—Metallic objects may be annealed in an atmosphere of nitrogen or hydrogen or mixtures of these gases, when it is desired to avoid the formation of an oxide scale which must otherwise be removed by "pickling" in the usual manner. This process is termed "bright annealing" and it may actually be extended to de-scaling, but in such cases the finely divided metal on the surface of the object treated gives a matt and not a burnished finish. A good example of bright annealing is in the production of motor-car lamp reflectors. The brass pressing is so deep that it must be done in stages, and bright annealing is carried out between each stage. When using hydrogen for the bright annealing of steel parts, decarburisation of the surface may result. If this is objectionable it can be prevented by the introduction of a suitable quantity of hydrocarbons into the reducing atmosphere.

(8) The Production of Metals.—Hydrogen is extensively used for the reduction of metallic oxides, *e.g.* in the production and working of tungsten and molybdenum. It can also be used in the production of metallic magnesium by reduction of the oxide with carbon. If the CO and magnesium vapours issuing from the reduction furnace are cooled slowly, the reverse reaction to that taking place in the furnace will occur, resulting in the production of carbon and magnesium oxide. This can be prevented by rapidly chilling the gases issuing from the furnace with a blast of cold hydrogen.

Literature.—Synthesis of alcohols, Natta, Osterr. Chem.-Ztg. 1937, 40, 162. Atomic hydrogen welding, Weinman and Langmuir, Gen. Electric Review, 1926, 29, 160; Miller and Deglon, Sheet Metal Industries, 1934, 8, 131,189, 252; Guest, Metal Treatment, 1936, 2, 17.

TECHNIQUE AND TRANSPORT.

Hydrogen Attack on Steel.—Compressed hydrogen can cause fissuring and a severe reduction of the tensile strength and impact value of steel. Under some conditions this may occur at relatively low temperatures, *e.g.* 150-200°C. The effect is due mainly to decarburisation, but in some cases deterioration of the properties of the steel takes place before decarburisation and the effect is then due to hydrogen adsorption. In general nickel-chromium-molybdenum steel alloys are more resistant to attack than mild steel, but in all cases careful heat treatment is required to obtain the best service.

Literature.—Inglis and Andrews, J. Iron and Steel Inst. 1933, 127, 2, 383. Baukloh and Guthmann, Z. Metallk. 1936, 28, 34, describes also the effect of hydrogen on Cu, Ni and A I.

Hydrogen Transport.—During the last few years the difficulties of transport of all compressed gases, including hydrogen, have been to some extent reduced by the development of relatively light cylinders of special alloy steels. One very convenient form in which hydrogen may be transported is as liquid ammonia Passage of ammonia gas at low pressures ovei catalysts similar in type to those used for the ammonia-synthesis reaction and operating at about 600°C. results in practically complete (99·5%) decomposition to IM_2+3H_2. The space velocity employed is about 500 cubic metres of gas per hour per cubic metre of catalyst. A 100 lb. cylinder of anhydrous ammonia contains the equivalent of 3,400 cu. ft. of hydrogen, and for a large number of purposes, *e.g.* bright annealing, the presence of 25% nitrogen in the hydrogen obtained is of no serious consequence. The apparatus for decomposing the ammonia is usually termed an "ammonia cracker." "Cracked" methanol, which is a 2:1 mixture of hydrogen and carbon monoxide, can also be used for a number of purposes, although the presence of carbon monoxide limits its applications as compared with "cracked" ammonia.

Suggestions have been made to transport hydrogen as a liquid at 1 atm. absolute pressure in heat-insulated containers. Liquid oxygen is transported by such methods, but liquid hydrogen in comparison has a number of very serious disadvantages. The temperature is -253°C, the specific gravity only 0·07, and problems of transport are complicated by the continuous evolution of an inflammable gas, due to heat leaks into the container, and the exothermic change from ortho- to para-hydrogen which takes place at low temperatures.

Literature.—Ammonia Crackers, B.P.473696.

H. S. C. and P. H. S.

HYDROGEN ION DETERMINATION. The relative acidity of an aqueous solution is the most important single factor determining its properties and reactions. This "acidity" is measured by the concentration of hydrogen ions in the solution and, since this quantity may vary over a very wide range, it is convenient to express it on a logarithmic scale. The convention, that is now always followed, was introduced by Sorensen (1909) who used the term p_R and defined it by thj following expression:

$$p_H = \log_{10}\frac{1}{[H^+]} \quad \text{or} \quad p_H = -\log_{10}[H^+]$$

where $[H^+]$ is the hydrogen ion concentration of the solution. It fc now known that these ions are hydrated and they wouk[1] be written more correctly as H_3O^+, but as it is jjtill customary to represent them as H^+ this simpler practice will be followed.

A perfectly pure sample of water will be neutral but it still has some electrical conductivity indicating that there are charged particlesjjions) in solution. In this case they are hydrogen and hydroxyl ions, formed by the dissociation of the water,

$$H_2O \rightleftharpoons H^+ + OH^-$$

and they must be present in equal concentrations. If by any means the hydrogen ion concentration is made larger than that of the hydroxyl the solution is said to be acid while, if the converse is the case, the solution becomes more alkaline us the excess of hydroxyl ions increases. The electrolytic dissociation theory indicates that the product of the concentrations of these two ions is a constant whicji is known as the ionic product for water. This quantity has been measured and at 25°C. is equal to

$$1{\cdot}42 \times 10^{-14}$$

when concentrations are given in gram ions per litre. The quantity changes with temperature and at 22°C. is equal to

1·01 x 10-''

and at room temperature the following expression is nearly correct:

$$[H^+][OH^-] = 10^{-14}$$

If the hydroxyl ion concentration is measured on the logarithmic scale, defining p_O*i&* in a fashion analogous to p_H, one can write

$$\log_{10}[H^+]+\log_{10}[OH^-]=-14\log_{10}10=-14$$

or

$$p_H + p_{OH} = -14$$

Hence the acidity or alkalinity of any aqueous solution can be expressed in terms of either p_a *orpon*; if the p_a is greater than seven the solution is alkaline and if smaller it is acid. The measurement and control of the above quantities are important whenever an aqueous solution is used and it is therefore not surprising that j>H measurements are employed in the most diverse types of industrial processes, among which are the refining of sugar, the manufacture of sweets, the tanning industry, brewing, medicine, bacteriology and the preparation of pharmaceutical products.

The Hydrogen Electrode is the ultimate standard to which all determinations of p_a are referred. Finely divided platinum or indium is, able to act as a catalyst by*means of which hydrogen gas can be converted reversibly inta*hydrogen ions, according to the equation

$$H_{2\,(gas)} \rightleftharpoons 2H^+ + 2\ominus$$

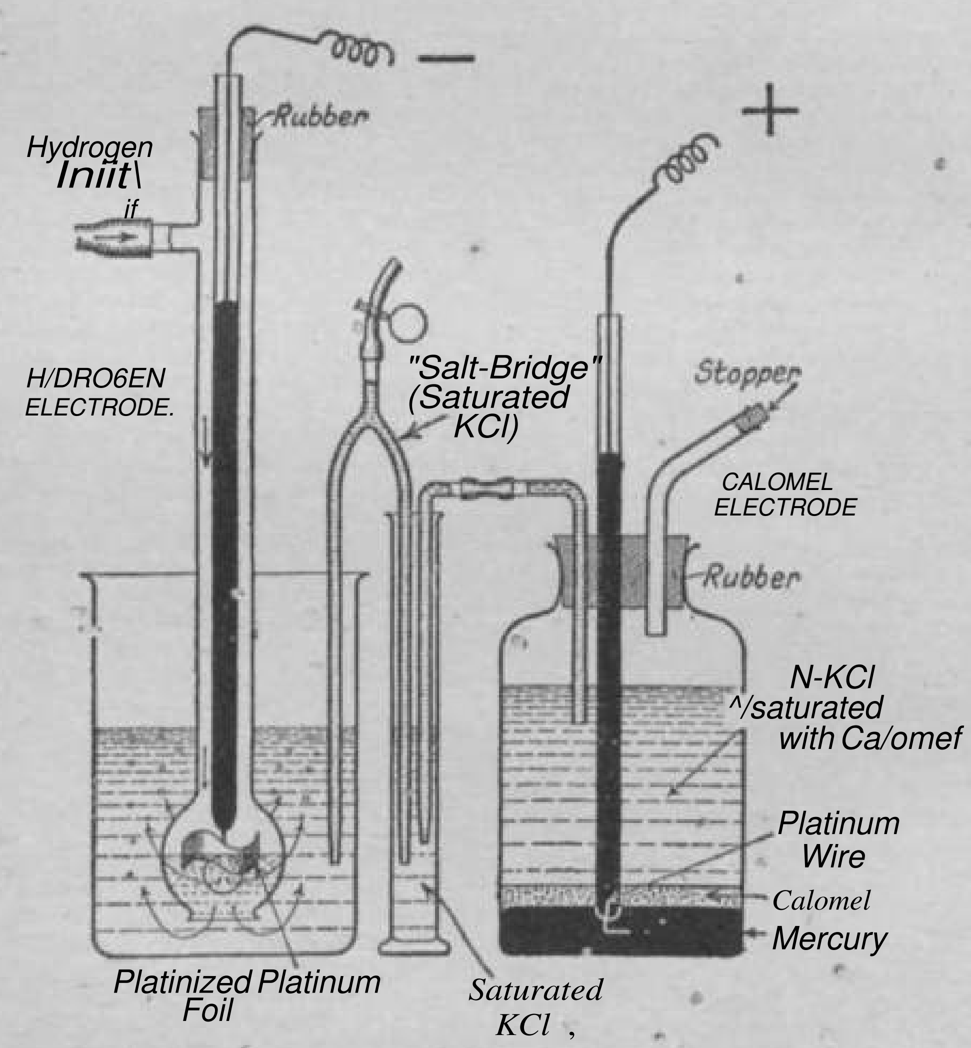
and when a plate, covered with platinum black, is lowered into a solution that has hydrogen* gas above it the above reaction will tend to take place: The metal plate will take up the free charge, indicated by 0, until the electric potential between the plate and the solution has built up so as to prevent further change. This potential is a measure of the tendency of the hydrogen gas to split up into ions and pass into the given solution, and any practical apparatus for this measurement can be called a hydrogen electrode. It can be shown that, if the hydrogen gas is at one atmosphere and the potential of the electrode is E volts, the following relationship holds:

$$E = -\frac{RT}{F}\log_e[H^+]$$

where T is the absolute temperature, F.the Faraday and B the gas constant. Or at 18°C.

$$E=-0{\cdot}058\log_{10}[H^+], \quad i.e.\ p_a = \wedge$$

In order to measure the potential between the platinum plate and the solution the latter must be connected to the measuring instrument. This is done by means of another electrode system where there ip a solid conductor in contact with a solution. A second potential difference is thus involved which must be as constant and reproducible as possible in different apparatus. The calomel half-element is the device that is normally used, it consists of a layer of pure mercury connected with the potentiometer by a platinum wire fused through the bottofli of the vessel. The mercury is covered with a solution of normal potassium chloride that has been saturated with mercuroua chloride, the excess of which forms a thin layer on the surface of the metal. Provided that the calomel half-element has been set up with pure chemicals the E.M.F. between solution and mercury is+0-2816 volts at 25°C. with a temperature coefficient of -0-00024 volts per °C, It is possible to make tip standard cells in a similar fashion with solutions that are respectively *NjlQ* or saturated with potassium chloride; the E.M.F.'s of these cells at 26°C. are +0-3341 and 0-2426 volts respectively and their temperature coefficients —000070 and -0-00076 volta per °C. *(see* Lewis, Brighton and Sebastian, J. Araer. Chem. Soc. 1917, 39, 2245; Randall and Young, ***ibid.*** 1928, 50, 989 j D. A. MacInneS) " The Principles of Electrochemistry," Reinbold, New York, 1939, p. 247).



Fin. 1.

Contact between the potassium chloride solution and that around the hydrogen electrode is normally made through a 0-shaped capillary or quill tubing " salt bridge " that is filled with either saturated potassium nitrate or saturated potassium chloride solution. A typical set up of a'hydrogen elecSrode and calomel nalf-elcment is shown in fig. 1. The E.3I.F. of the complete cell is measured with a potentiometer and a high resistance galvanometer using the usual P<rjgendorS method; the p_H of the solution around the hydrogen electrode is calculated from the following expression;

$$-\log_{10}[\mathrm{H}^+]=p_H=\frac{\underset{\text{observed}}{\text{E.M.F.}}\ —\ \underset{\text{calomel electrode}}{\text{E.M.F.}}}{0{\cdot}058}$$

The hydrogen electrode has certain limitations which restrict its use and may introduce errors. One Cf the most serious of these is the ease with which the platinum black adsorbs " poisons " which prevent it acting efficiently as a catalyst for the interchange of hydrogen ions-and hydrogen gas. Arsenic, hydrogen sulphide, mercury and certain organic dyes are common materials producing this trouble, which manifests itself by abnormal values and by a tendency for the measured p_u to change erratically with time. A further difficulty is introduced by the possible interaction of the hydrogen, which ia in an active condition on the platinum surface, with any reducible substance in the surrounding solutior. Strong oxidising agents, salts of easily reduce* metals, or organic compounds will consequentlj interfere with the functioning of the electrode, and it should never be used in their presence. The p_s of such solutions may be found by one of the secondary methods : *i.e.*. by a comparisoi of the unknown solution with one whoso p_a is known from hydrogen electrode measure-meats.

ColorinMric Methods provide a very simple and convenient way of effecting this comparison. A suitable indicator is added to the solution ant the colour compared with the shade that it assumes in a series of solutions whose p_a values are known. The simplest form of apparatus for this purpose is shown in fig. 2. It consists of a block of wood, or other suitable material, *e..g.* bakelite, in which six holea are bored so that test-tube^ can be slipped into them. Slits are cut in the block through which the colour of the l^ht that passes through each of the three paira of tubes in the direction of the arrow can be compared.

The middle pair of tub^b contain the solution to be tested with a little of the indicator added and plain water respectively. Each of the outer pairs of tubes contain respectively the test solution without indicator and a solution of known *PH* containing an equal concentration of indicator. The tubes of known p_n are changed until the colours observed through the slots match, or if that is impossible, a slightly lighter colour i^ observed on one side of the test solution and a darker colour on the other. The p^ of the solution can then be said to be between those of the two standards and a visual estimate of its value can be made. The procedure d&cribed compensates for any colour in the test solution unless **this** is very strong, in which case the colorimetric method is not applicable.

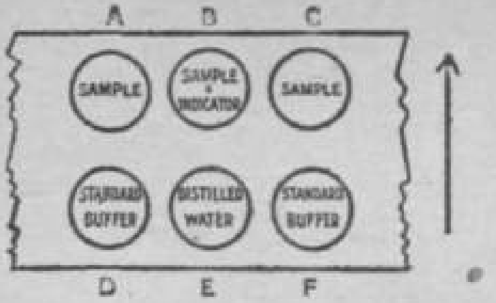


FIG. 2.

Provided that the **indicator** and conditions are standardised it is possible to replace the tubes containing the indicator and standard solutions with coloured glass which is not subjeci to change and deterioration. A number of convenient types of apparatus, " comparators," are now on the market in which a series of glass discs are suitably mounted—generally in a ring so that one after the other is compared with the unknown solution until a match is obtained.

When solutions of known p_H have to be made up it is obviously desirable that their hydrogen ion concentrations shall be practically unchanged by the addition of other substances. For example, they must change as little as possible owing to the absorption of alkali from a glass vessel, or carbon dioxide from the air. Solutions that have a reserve acidity or alkalinity so that the hydrogen ion concentration changes but slightly on dilution and on the addition of acids and alkalis are called " buffer solutions." They are generally made by mixing a weak acid or base with a solution of one of its salts, the effect of which is illustrated by the following figures. If I c.c. of normal hydrochloric acid is added to 100 c.c. of water the p_H changes from 7 to 2, i.e. 5 units. A 0-01356 molar potassium dihydrogen phosphate solution which is also **0-0411** molar with respect to disodium hydrogen phosphate also has a p_H of 7, but when 1 c,c. of normal acid is added to a corresponding volume the p_H is only reduced to 6-75.

A large number of buffer solutions are available, most of them covering a range of 2-3 PH units. Britton and Robinson {J.C.S, 1931. 1456), however, have described a " universal buffer solution " which works from p_a 3'5 to 9. It is prepared by taking a iV/35 solution of hydrochloric acid and adding sufficient potassium dihydrogen phosphate, citric acid, boric acid anC vortmal so that when they are dissolved the solution ia iV/35 with respect to the replaceable hydrogen of each of them. Then if a; c.c. of pure carbon-dioxide-free *NfZ* caustic soda solution is added to each 100 c.c. of the above solution the p_n of the resulting mixture is given by the expression p_a=2-686+O*US53a:, Provided the **chemicals** aro pure these figures should be correct to 0'02 of a unit of p_a.

The colorimetric method has many advantages ; it is rapid" in action, uses only simple apparatus and can be readily adapted to specialised needs. For example, it can be used with very small quantities if the liquids to be compared are contained in capillary tubes. These advantages should not cause errors to which the method is subject to be overlooked. The .indicator uaed has its own acidic properties and if the solution to be tested is not buffered its PH may be changed appreciably when the indicator is added. This effect is called " the acid error "; and it may be eliminated by flrat making a rough determination and then buffering the indicator so that it is approximately aoelectric with the test solution. This mixture is then uaed for a more accurate determination of the p_u- Errors may also "be introduced when certain other materials are present in the solution ; these are commonly known as " salt" or ' protein errors " and they may become very urge indeed under unfavourable conditions. Lhus a 0-01 ^-hydrochloric acid and *Q-2&N*-»otas«ium chloride solution has a p_H of 2-05, >ut the value determined with Methyl Violet ia •91, with Methyl Cfeeen it is 1-82, wh with fropujoline OO it ia 202, Similarly a dilute sulphuric acid solution containing egg albumin gave a $p_{\&}$ value of 249 with the hydrogen •lectrode, but cotorimetrically it was 2*53 using -lethyl Violet and of the order of 50 using Congo led. The indicators recommended by the manufacturers to cover & given p_a range are normally those which give as small a salt and irotein error aa possible.

The Quinhydrone Electrode is the most common method of measuring p_a by a potentiometric procedure. The conditions for the use of the electrode were first worked out by E. Biilmann (Ann, Chim. 1921, [ix], 15, 109; 1921, [ix], 16, 321)* Later the electrode was studiet in detail by Livingstone, Morgan and P til laborators (J. Amer. Chem. Soc. 1931, 63, 464, 597 and 2154; *idem., ibid.* 1932, 54, 910) who confirmed the earlier work showing that the electrode is quickly and easily prepared, develops its potential very quickly, is not affected by atmospheric pressure and, since it does noi require a gas to be bubbled through the solution, can be used for work on body fluids containing carbon dioxide. To set up an electrode it is only necessary to immerse a bright platinum plate in the test solution, to which a little quinhydrone haa been added, and then measure the E.M.F. between the plate and solution, employing a standard calomel half-element in an identical fashion to that used for the hydrogen electrode. It is best to have the platinum plate on a long length of platinum wire; if this is impossible and the wire is sealed through glass which is in contact with the solution great care must be taken that the seal is a perfect one or considerable error may be introduced. The electrode should be cleaned in boiling cleaning mixture, allowed to cool, washed in a stream of tap water, then in distilled water and after rinsing in alcohol allowed to dry. With ordinary laboratory apparatus satisfactory results are obtained with an electrode that is 1 cm. square or larger. The electromotive force E taken up by the platinum with respect to the solution will be determined by the fdilowing equation:

$$C,H_4O_|+2H++29_?\pm C_tH_4<OH)_|.$$

The concentrations of quinone and **hydro**quinone are the same, since they are introduced as the molecular compound quinhydrone and the only other variables are the hydrogen, ion concentration and the tendency of the solution to give up electrons. Consequently E should be a function of the hydrogen ion concentration and it is found that

at20°C. $E=0\text{-}7044+0\text{-}0581Iog_{10}[H^{!}]$

and at 25°C. $E=0{*}6994+0\text{-}0591\ \log_{10}[H+]$

For precision work a saturated solution of the quinbydrone is employed but in works control, where there is a continuous recording of p_H and costs become important, it is possible to reduce the concentration to 1 part in 10,000 and still obtain an accuracy of ±005 p_H units (C. C. Coons, Ind. Eng. Cfiem. [Anal.], 1931, 3, 402).

The chief disadvantage «>f the quinbydronc electrode is that it is unsuitable for use above p_H 8-5, where the acid character of the *hydro*quirOne begins to manifest itself and hence there is a tendency for it to react with the solution ; the atmospheric oxygen also begins to attack the quinhydrone at about this p_{tt} value.

The errors introduced by salts have been studied by Biilmann *(I.e.)* and also by Hovorka and Dearing (J. Amer. Chem. Soc. 1935, 67, 446). The magnitude of the errors to bo anticipated aie shown by the following figures:

Salt concentiation.		Error In *v-a* measured by the quinhydrone electrode.
	B.	unit of p_K.
NaCI . . .	0-4	-002
KCI . . .	2-0	-0-09
$MgSO_4$ . . .	10	+0-02
$\{NH_4)_2SO$, .	0-5	+00i9
" .	10	+0-038
" .	20	+0078

It will be seen that the results for ammonium sulphate indicate that the error is nearly proportional to the salt concentration. This relationship was also found with the errors introduced by other salts. If the concentration is not large the salt and protein error can bo neglected for most practical purposes.

The Glass Electrode has in recent years found increasing use, especially in physiology and biochemistry. Its popularity is due to the production of suitable electrodes and measuring instruments as standard commercial articles. Earlier work was hampered by the difficulty of E.M.F. measurements through the high resistance of a glass diaphragm, but this has been overcome by the use of special glasses that have a minimum electrical resistance and by the cheap production of wireless valves that can be made to work as voltmeters even when the external resistance is high—a hundred megohms or more. It must be realised that there is no satisfactory theoretical relationship between a gla<* electrode and a solution of given jt>$_H$, but that it does serve as an method *of comparing* a series of solutions. In practice the electrode is standardised against a known buffer whose p_u is as near aa possible to that of the unknown solution.

The most common form of glass electrode is a thin-walled bulb a "few centimetres in diameter which contains an acid tolution saturated with qninhydrone into "which a platinum wire is dipping. The tube is generally sealed off and consequently the external lead is connected to one side of the gloss diaphragr' under constant londitions. This hulb is then dipped into the test solution and the, circuit completed with a calomel half element in the usual manner. It is then found that the E.M.F. of the bulb with reference to the solution varies with its hydrogen ion concentration in the p_H range of 2-8 unite and can be represented by the familiar type of "brmuhi in which E_o is the E.M.F, that Ao rlectrode would take up in a solution that is normal with respect to hydrogen ions and it is a constant.

$$E=E_0-k\log_{10}[H^+]$$

i.e. $$p_H=\frac{E-E_0}{k}$$

The most suitable glass available for the c™ atruction of electrodes contains 72% SiO,, 22% Na_aO and 6% CaO and is known commercially as Corning 015 glass (we Hughe* J.C.S.

1928,491; Dole *et al.,* J. Amer. Chem. Soc. 1930, 52, 29; Trans. Electrochem. Soc. 1937, 72, 129, Gardiner and Sanders, Ind. Eng. Chem. [Anal.], 1937, 9, 274).

Even when the glass electrode is properly made it is necessary to watch for irregularities that may be introduced by dissolved salts and organic materials. Considerable work has been carried out to find the conditions under which these errors become pronounced. In general it may be said that the greater the salt concentration the lower the p_E at which the electrode will function satisfactorily. For example, in the presence of (MAT-sodium chloride the electrode is satisfactory up to p_E 10*5, but with a normal solution the errors become serious at above j?$_H$ 8*5. *See* Gardiner and Sanders *(I.e.).*

As the temperature is increased the difficulties in using a glass electrode are greatly increased. The deviations become very much larger, also the readings obtained are not consistent and consequently, unless special precautions are taken, the glass electrode should not be used above 30°C. A further difficulty is that the glass used is of the soft variety and, if the test solution is unbuffered, sufficient alkali may be taken from the glass to effect a considerable change in the p_H *{see* Humphreys, Chem. and Ind. 1939, 58, 281). In spite of its errors the glass electrode provides a very convenient mechanism for investigating the p_H of solutions where other methods are impossible. It is not affected by oxidising or reducing agents, it does not introduce salts or other obnoxious materials into the specimen to be tested and the electrode does not deteriorate with time; moreover the p_n range 5-7 in which the electrode functions best is the one which includes most biological fluids. Hence it is not surprising that the electrode is much used especially where speed rather than extreme accuracy is required.

The Antimony Electrode is sometimes used when a rough comparison of the p_H of similar solutions is required. It consists of a rod of antimony covered with a superficial layer of oxide by atmospheric oxidation. It is claimed that greater uniformity is obtained if the metal is covered with a layer of sulphide (Ball, Schmidt and Bergstresser, Ind. Eng. Chem. 1934, 6, [Anal.], 60; Bajl, Trans. Electroch&n. Soc. 1937, 72, 235); the general conditions for its use have not been sufficiently worked out, and it is not recommended except when cheapness and simplicity are the all important factors.

Bibliography.—Britton, " Hydrogen Ions," Chapman and Hall, 1932; Clarke, " The Determination of Hydrogen Ions," 3rd ed., Williams and Wilkins, 1928; Jørgensen, " Die Btsiimmung der Wasserstoffionen-konzentration und deren Bedeutung für Technik und Landwirtscbaft," Theodor Steinkopff, Dresden, 1935; MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corporation, New. York, 1939.

R. H. P.

HYDROGEN OVERPOTENTIAL *(v.* Vol. Ill, 3766).

HYDROGEN PEROXIDE. *History.*—Hydrogen peroxide, H_2O_2, was discovered in 1818 by Thenard (Ann. Chim. Phys. 1818, [ii], 8, 306; 9, *51,* 94, 314, 441) who obtained it by the action of acids on barium peroxide. Thenard found that the new substance behaved as " oxygenated water," and established its formula as H_2O_2. He also described many of its characteristic properties, including the decomposition by solid catalysts and by heat, and showed that as one of the oxygen atoms is only very loosely bound the compound is a powerful oxidising agent. At first hydrogen peroxide was obtained only in dilute aqueous solution, but it was later found possible to concentrate it by evaporation under reduced pressure, and in 1904 the firm of E. Merck (G.P. 152173) produced a concentrated solution free from solid residue by direct distillation of the solution resulting from the action of sulphuric acid on sodium peroxide. The important electrochemical method of preparation, based on the formation of persulphuric acid, was patented in 1907 (G.P. 217539). Substantially pure H_2O_2 was first obtained by Wolffenstein in 1894 (Ber. 1894, 27, 3307), and in 1920 Maass and Hatcher (J. Amcr. Chem. Soc. 1920, 42, 2548) starting with a 3% solution prepared pure hydrogen peroxide by fractional distillation and evaporation and finally by crystallisation.

Natural Occurrence.—Extremely minute quantities of H_2O_2 are said to occur in the atmosphere and in natural waters. E. Schöne (Ber. 1874, 7, 1693; 1878,11, 483, 561, 874, 1028) reported up to 1 mg. H_2O_2 per litre in rain water, but only 0*05 mg. per litre in dew and hoar frost. The atmosphere was said to contain about 4 x 10"^{10} g. H_2O_2 per litre. Schöne and others concluded that it is formed in the atmosphere by the action of sunlight. However, much of the early work on the natural occurrence of traces of H_2O_2 is untrustworthy and lacks modern confirmation.

Similarly, early reports of the occurrence of H_2O_2 in animal and vegetable tissues are unreliable. However, recent work has established beyond doubt the presence of H_2O_2 in various biological systems. Working with lactic fermentation bacteria (which contain no catalase *(q.v.)* —the common enzyme which decomposes H_2O_2) Bertho and Glück (Naturwiss. 1931, 19, 88) claimed to have made quantitative estimations of the hydrogen peroxide produced. Tanaka (Biochem. Z. 1925, 157, 425) identified H_2O_2 as a primary product of respiration when *Chlorella* was illuminated. It is generally held that hydrogen peroxide is an intermediate product in biological oxidations, although usually so rapidly decomposed that detectable concentrations are not formed. According to Avery and Morgan (J. Exp. Med. 1924, 39, 275) appreciable amounts accumulate in a broth culture of *Pneumococci* or of *Staphylococci* provided air is present and catalase, peroxydase and other enzymes which decompose H_2O_2 are absent. Fromageot and Roux (Biochem. Z. 1933, *9&I,* 202) found that the fermentation of sugar by *B. bultftricua* is inhibited because of the accumulation of H_2O_2.

Hydrogen peroxide has also been found in the fermentation of tea (Biochem. J. 1939, 38, 836); in leaves of sugar cane (So and Nisioeda, Rept. Govt. Sugar Expt. Sta. Tainan, Formosa, 1939, No. 6, 62); and in cultures of various bacteria such as *Pneumococci* (Johnstonc, J. Path. Bact. 1940,**51,**59)andhffimolytic *Streptococci* (Hadley and Hadley, J. Bact. 1940, 39, 21; Proc. Soc. Exp. Biol. Med. 1940, 43, 102).

FORMATION,

From the Ekmenls or Water.—Small amounts of hydrogen peroxide have been detected in the water formed by the combustion of hydrogen in oxygen. Traube (Ber. 1883, **18,** 1800, 1894) and Engler *(ibid.* 1000, 33, 1109) concluded thai H_2O_2 is the primary product of combustion: normally, it is decomposed at the high temperature, but appreciable quantities can be observed if the flame is cooled, Lewis and Randall, "Thermodynamics," 1923, however, calculated the theoretical amount of **HjO„** in the oxy-hydrogen flame _at 2,000-3,000°k. from the thermodynamics of the reaction :

$$2H_2O+O_a=2H_2O_2$$

and found that the concentration nuist bo infinitesimal at that temperature, and, hence, the considerable amounts detected by Traube must be formed in the cooler parts of the Same, probably at 500-1,000°C.

Hydrogen peroxide is also formed in the explosion of hydrogen with excess oxygen ; in a spark discharge under water; in a silent electric discharge through a mixture of water vapour and oxygen; in a Testa discharge in moist air and in other similar circumstances. Fischer and-Wolf (Ber. 1911, 44, 2956) succeeded in preparing a solution of hydrogen peroxide containiDg 86-9%.,$H*O_s$ by "passing a silent electric discharge thror^n a non-explosive mixture of oxygen and hydrogen (97% H_2, 3% O_2) at the temperature of liquid air.

In all these modes of formation, the H_2Oj is protjably derived from short-lived atoiUB, ions or free radicals {*e.g.* OH and HO_3) by such reactions ae: <

$$HO_2+H_2=H_2O_2+H$$

(For the theory of combustion of hydrogen, *see* Hinshelwood and Williamson, " The Reaction between Oxygen and Hydrogen," Oxford University Press, 1934.) Atomic hydrogen has been used to study the mechanism of formation of hydrogen peroxide (Taylor and Marshall, J. Physical Chem. 1925, 29, 842; Bonhoeifer and Loeb, Z. physikal. Cbem. 1926, **119> 3Bf>,** 474). More recently, Rodebush and his collaborators (J. Chem. Physics, 1933, 1, **696;** *ibid.* 1936, 4, 293; J. Amer. Chem. Soc. 1937, **59,** 1924) anil others have investigated its production in an eleetrodeiess discharge in water vapour.

Hydrogen peroxide is formed in the electrolysis of certain dilute aqueous solutions, but in mo^t cases *(e.g.* with dilute sulphuric acid) this is not strictly formation from the elements but is rnther a secondary product from the decomposition of per-compounds *(see below).* However, dissolved oxygen is reduced to **H_SO_2** by nas.(•nt **electrolytic** hydrogen at a mercury cathode (Foerster, " Elektrochemic wassertger LOsungen," 1922, p. 608). A glassy solid formed by the action ot atomic hydrogen on Oxygen at —115° may be the isomer

(Geib and Harteck, Ber. 1032, 65 [BJ, **1551).**

Detectable amounts of H_2O_2 are formed by irradiating pure water containing dissolved oxygen with *X-rays* or o-, £- or y-rays (Fricke, J. Chem. Physics, 1934, 2, 349, 55C; Nurnberger, *ibid.* 193C, 4, 697). Ultra-violet light acts similarly in the presence of zinc oxide, which behaves as a photosensitiser (Baur and Neuweiler, Helv. Cnim. Acta, 1927, 10, **901);** otherwise very short ultra-violet is needed to produce any photochemical reaction. Sonic vibrations of frequency 9,000 (Flosdorf, Chambers and **Mahsoff,** J. Amer. Chem. Soc. 1936, 58, 10(i9) and ultrasonic waves of frequency 540,000 Hz. (Schultes and Gohr, Angew. Chem. **1838,** 49,. 420) are said to produce traces of H_aO_3 in water saturated with O_3.

In Oxidation Reactions.—According to Lenher (J. Amer. Chem. Soc. 1931, 53, 2420, 3737, 3752) hydrogen peroxide is a secondary product of the combustion of hydrocarbons, and it has also been found in the condensate from flames impinging on ice of hydrogen, alcohol, coal gas, ether and carbon disulphide (Engler, Ber. 1900, 33, 1109) and methane (Riesenfeld and Gurian, Z. physikal. Chem. 1928,**139,** 109).

Hydrogen peroxide is formed in certain so-called " autoxidation " reactions, including the slow oxidation of various organic materials such *ixa* **turpentine** in the presence of air and water (Kingzett, Chem. News. 1878,38,224), and when finely divided Zn, Mg or Al is shaken with water containing oxygen, or with dilute acids in the presence of air (Traube, Ber, 1893, 26, 1471; Fryiing and Tooley, J. Amer. Chem. Soc. 1930, **58,** 826; Miiller and Barchmann, Z. Elektrochem. 1934, 40, 188). Furman and Murray (J. Amer. Chera. Soc. **1986,** 58, 429) suggested that tlsp formation of H_2O_2 when mercury dissolves in dilute **HCI** saturated with oxygen probably occurs by way of HO_a produced from atomic hydrogen and molecular oxygen at the mercury surface. Similar views were expressed by Churchill (Trans. Eleetrbchem. Soc. 1939, 76, 341) with regard to the corrosion of Al.

Certain auUxidation reactions in whit-h hydrogen **peroxide** is formed have been proposed for its technical preparation. These include tho oxidation of antlrraquinone and similar substances by air or oxygen to cjuinonoid compounds, and of hydrazo- to azo-compounds (*.». B.P. 489978-9). The formation of **hydwjg**en peroxide in the enzymic oxidation of amino-adda *in vitro* (Bemheim *el al,* J. JJiol. C'hem. 1936, **114,** 657) and in other biological processes may be analogous. It is also said to be formed in catalytic dehydrogenations of MeOH and EtOH (Macrae, Biochem. J. 1933, 27, 1248).

From Peroxide^.—Hydrogen peroxide is produced in good yield ***vtbm*** metallic peroxides of the **typea** M'$_E$O$_2$, M"O$_a$ are dissolved in dilute acids m **the ooW.** The pproxides used are those of Ba, Na or K; the acids recommended include

HLSO,, HF, H_3PO_4, H,SiF_9, HNO_3. HCI, tartaric and carbonic, and the method is, convenient if the salt formed is sparingly soluble The moat common method of preparation in the laboratory is by the addition of barium peroxide to the calculated quantity of cold (ca. 10°C.) dilute **H_2SO_4** (1 vol. acid to 5 vol. ater):

.

$$BaO_a+H_2SO_t=BaS0_4+H_2O_{!1}.$$

The filtrate, after removal of the precipitated barium sulphate, is a practically pure solution of H_aOjj of about " 8-volume " strength (8 vol. of oxygen liberated from 1 vol. of solution by boiling with a catalyHt}. Carbon dioxide can be used instead of sulphuric acid:

$$BaO_a+CO_2+H_aO=BaCO_a+H_aO_a.$$

0'ombinations of other peroxides and other acids have be#n recommended *(e.g.* K_2O_E with tartaric acid), and the usual methods may be applied to precipitate excesB salts or, alternatively, the hydrogen peroxide can be separated by distillation under reduced pressure.

From Per-Acid$ and dlteir Sails.—Hydrogen peroxide ia obtained very efficiently by the hydro!yaia of pennonosulphuric acid {Caro's acid):

$$H_2SO_5+H_2O=H_2SO_4+H_2O_2.$$

In technical practice persulphuric acid (prepared by electrolysis) is distilled under reduced pressure, Caro's acid being formed as intermediate :

$$H_2S_2O_8+H_2O=H_2SO_5+H_2SO_4.$$

The hydrogen peroxide formed distils off and is obtained as a p\ire solution. Persulphates^i ve hydrogen peroxide when warmed with acids:

$$K_aS_{,,}O_8+H_aSO_{.,}=K_2S\,,O_7+HSOj$$
$$''\ HJSOB\text{-}I\text{-}\ H_2O=H_aSb_4+H_2O_2$$
$$K_1.S_2O_rhH_aO=2KHSO_1\ (solid).$$

Concentrated H_2O_2 can thyefore be **produced** by direct distillation from potassium or ammonium persulphate, provided a small amount of HjSOfl is present.

Perearbonates similarly give H_aO_2 by hydrolysis, even in the^cold: *

$$K_2C_sO_a+2H_2O=2KHCO_3+H_{\pounds}O_{,,}.$$

Perphosphates *[e.g.* potassium perdiphoaphate, $K_4P_SO_S$) and numerous other per-coiupounds may give rise to H_2O_a, although in practice many of them are prepared from it.

See also B.P. 297880, 316919; G.P. 528461, **330111;** Lowenstein, Z. Elektroc hem? 1928, 34, 784; Walton and Filson, J. Amcr. Chem. Soc, 1932, 54, 3228.

TECHNICAL PREPARATION.

The Persulphate Process.—The electrolytic preparation of persulphates (see *above),* followed by their hydrolysis, has now become the chief method in use for the technical manufacture of hydrogen peroxide. (For a comprehensive account; and list of patents, *see* Maehu, " Das Was•eretoffperoxyd und die Perverbindungen," J. Springer, Vienna, 1937). The process has developed in three stages :

(1) Originally, persulphuric acid was made by the electrolysis of sulphuric acid, und hydrogen peroxide was separated by warming and vacuum distillation of the solution.

(2) Later, in place of sulphuric acid, ammonium sulphate dissolved in sulphuric acid was used as electrolyte, and the resulting ammonium persulphate was converted to the sparingly soluble potassium salt by adding $KHSO_4$. The potassium persulphate which separated was subjected to vacuum distillation with sulphuric acid and steam.

(3) More recently, ammonium persulphate solution has been vacuum-distilled directly without conversion to the potassium salt.

All three are cyclic processes as the residue from distillation is used again.

. For a discussion of the theoretical principles which determine the efficiency obtained in the electrolytic preparation of persulphuric acid and persulphatea, *see* Machu, *op. cit.,* Ch. XI; Esain *ei al., Z.* Elektroehem. 1927, 33, 107; 1933.39, 891 ; 1935, 41,261; *Z.* physikal. Chem. 1932, **162,** 44; Riesenfeld and Solowjan, *ibid.* 1931, BoUcnstein-Festband, 405.

The following general conditions have been found desirable in practice. The anolyte must bo very pure owing to the catalytic action of impurities such as heavy metal ions; it is necessary to repurify it at intervals by distilling the sulphuric acid in quartz vessels or by recrystallising the sulphate. For the same reason, all parts of the cell must be freo from injurious impurities. For instance, the copper conductors must be lead-coaftd, or alternatively, lead or aluminium connections can b^ used. Smooth platinum is the best material for the anode, and since only a small surface area is required this may take the form of a thin strip of platinum foil on the surface of conducting bars of tantalum {G.P. 386514) or on aluminium (G.P. 591263) which has been previously anodically oxidised.

Various methods have been devised to av<jid the use of a diaphragm to separate the anode and cathode compartments *(e.g.* G.P. 195811, 267276, 271642), but more often a thin diaphragm of unglazed porcelain, kieselguhr or synthetic resin is used, and in this case the cathode can be of lead. It is usually in the form of a coiled pipe through which cooling water is passed.

In general, the*efficiency of persulphate formation increases with the anodic current density. With sulphuric acid as anolyte there is an optimum acid concentration (sp.gr. 1*60-1 *-45,* depending on the current density). Replacement of some of the H_2SO^by ammonium sulphate increases the efficiency considerably and, in fact, a recent prcbesa uses ammonium bisulphate alone. The volume of anolyte between the anode and diaphragm should be small; one arrangement (G.P. 567542) employs a thin^film of liqind flowing rapidly over the electrode at *A* temperature of I0-I5°C.

An example of a persulphate unit cell is shown in figs. 1 and 2, tivken from G.P. 567542.

The anolyte flows into the cell through a glass tube (6) and then upwards through a narrow space between the cylindrical porous pot (3) and a close-fitting glass vessel (5) and finally leaves the cell at the over-flow (4). Between (3) and (5) is the anode (12) which consists of a number of vertical Pt-Ta strips connected at the top (9). The cathode is a spiral lead pipe (14) through which cold water circulates, eventually passing into the inner vessel (5) and out at the top. When a number of cells are worked in series the catholyte and anolyte are fed into the first cell (which is highest) and then flow from cell to cell by gravity. With sulphuric acid as electrolyte an anodic current density of 0·6-0·8 amp. per sq. cm. is used. If the anode compartment is 5 cm. in diameter, 50 cm. high and 0·2-0·3 cm. thick the capacity is 180-230 c.c.

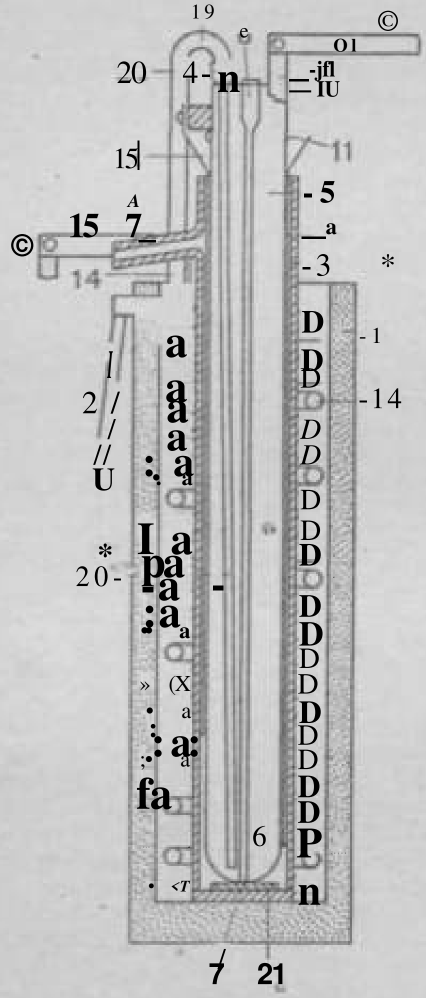


FIG. 1.—DIAGRAM OF THE WEISSENSTEINER PERSULPHATE CELL (Machu, *op. cit.*, Fig. 13).

The rate of flow of anolyte is about 3-25 c.c. per **amp.** JUT miiit,ut% and a current of 80-100 iiriin. is used. This requires fi-6 volts per cell. Under these conditions persulphuric acid of concentration 21-30% is produced from H_2SO_4 of sp.gr. 1·285 with a current efficiency of more than 70%. Using ammonium bisulphate as electrolyte an efficiency of 85% can be obtained.

Hydrogen peroxide is prepared from the persulphate solution by hydrolysis and vacuum distillation. In one method (Fig. 3) (F.P. 733201) the solution is heated to 50-60°C. and then atomised into an evacuated, heated column (in some cases with the addition of steam). The acid mist passes into a separator whence the water and H_2O_2 vapour are removed and condensed while the residual liquid (*e.g.* ammonium bisulphate) runs back to a cooler and pump to the electrolytic cell. The distillation can be carried out with an efficiency of about 95%. The flow diagram of a typical continuous flow process is shown in fig. 3.

The energy required to produce 1 kg. of 30% hydrogen peroxide by any of the three continuous persulphate processes is about 4-5 kilowatt-hours.

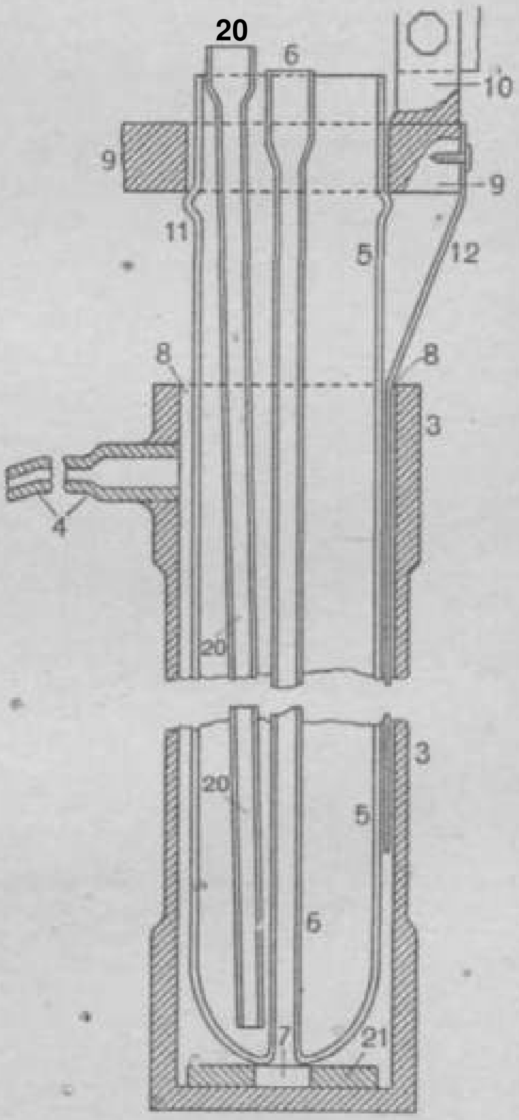


FIG. 2.—DETAILS OF THE ANODE COMPARTMENT (Machu, *op. cit.*, Fig. 15).

The Barium Peroxide Process.—This method of preparing H_2O_2, although the oldest known, is still in use to some extent, largely owing to the fact that the fine white pigment " blanc fixe " is obtained at the same time. The chief difficulties are that a very pure BaO_2 must be used, and that the H_2O_2 is obtained only as a dilute solution. The first difficulty necessitates a long method of preparation from barytes; the second is less serious now that efficient vacuum distillation is available. The usual method for the preparation of pure BaO_2 involve* the followirg steps:

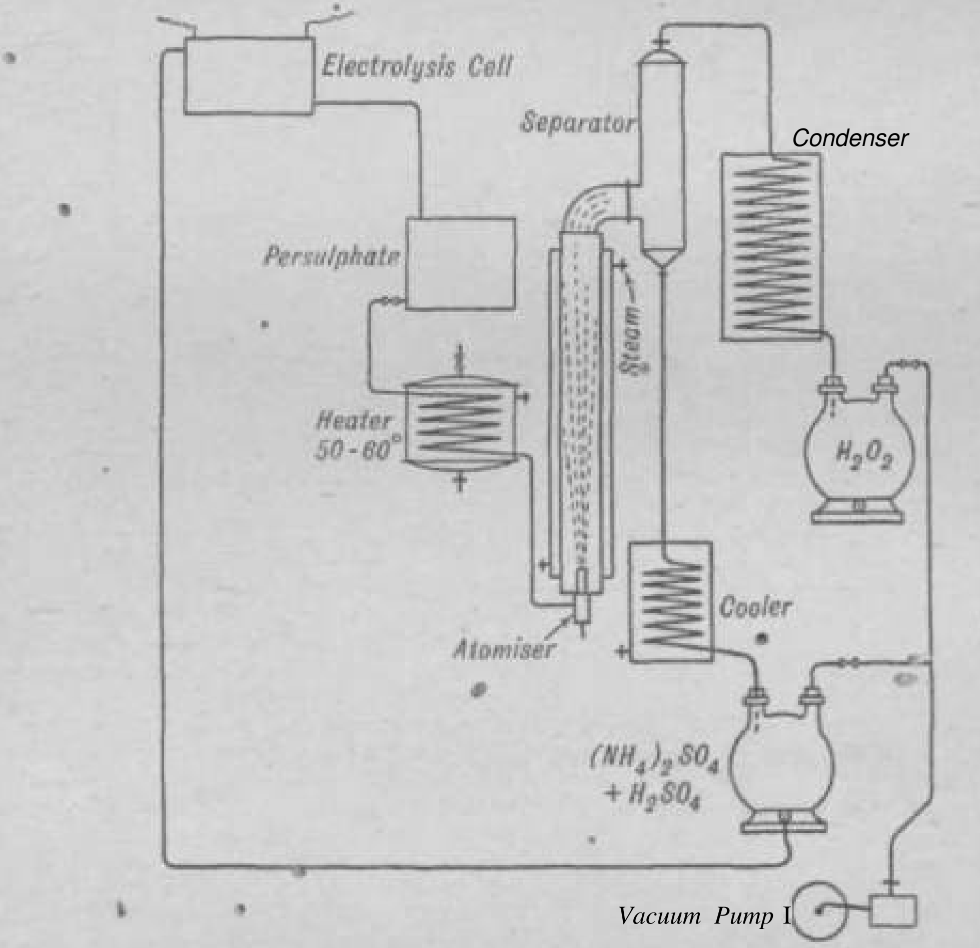
(1) Ground barytea mixed with coke is heatel in a rotary kiln to give barium sulphide (BaS).

(2) The kiln clinker (BaS) is lixiviated -with •water, and barium carbonate IB precipitated by the addition of soda ash.

(3) The barium carbonate is mixed with carbon and heated to 1,200° in a furnace to form barium monoxide (BaO).

(4) This BaO when heated in a stream of purified air at 540°C. is oxidised to barium peroxide, which is the immediate starting-point in the chemical preparation of hydrogen peroxide.

The barium peroxide is decomposed in the cold with either dilute sulphuric or phosphoric acid; more concentrated H_2O_a can be made by use of the latter (15% as against 3-6% with HjSOJ and the precipitated barium phosphate is easily filterable and carries down with it impurities like iron, manganese, etc., leaving a pure eolation of H_BO_a of good stability. In technical practice the decomposition of BaO. givea a 95% yield. (Phosphoric acid is recovered by adding H_ESO4 to the barium phosphate, and the precipitated $BaSO_4$ is used as a pigment (" blano fixe "). A convenient way of removing impurities from the regenerated phosphoric acid haa been patented . (G.P. 435900).) *



Fio. 3.—DIAGRAM OF PLANT *YOB.* THB CONTINUOUS DISTILLATION OF HVDROGEH PEROXIDE FHOM AHMONIDM PEF9ci.paATE SOLUTIOW (Machu, *op. cit.,* Fig. 35).

The dilute $H\text{-}O_s$ obtained in tho BaOj process is commonly concentrated to 30—40% by distillation and rectification. Table I showa, for example, that the distillate from 14-2% H_2O_a boiling at 3O-8°C./17 mm. contains only 0-58% Hj,O|; *hence,* the residue becomes more concentrated. (For examples of rectification plant, see P.P. 563908, G.P. 525923.)

PHYSICAL PROPERTIES.

Solid H.Oj (Stacde), Z. angew. Chem. 1902, 15, 642), large prisms from 95% H_8O, cooled

TABLE I.—(Machu, *op. cit.,* Table 14, p. 152.)
•17 mm. Hg.

Boiling-point °C.	Concentration of residue ID weight, %.	Concentration of distillate In weight, %.
210	5-5 *	0-21
230	• 5-7	022
25-5	6-85	0-23
LY.H	8-0	034
28 5	9-8	0-4ff
80-8	14-2	0-58
33-3	19-2	105
35-5	24-5	1-3
38-2	320	2-9
40-fi	48-8	10-4

with ether-carbon dioxide. M.p. —0-89°C. (Cuthberteon *et* oi., J. Amer. Chem. Soc. 1928, 50, 1120).

Pure HjO, is a colourless liquid, the physical properties of which are very sensitive to the addition of traces of water. Published data are rather discordant, but the following list gives probable values. Much of the recent work ia due to Maass and co-workers *(ibid.* 1920, 42, 2548, 2569; 1922, 44, 2472; 1924, 46, 2693; 1929, 51, 674 ; 1930, 52, 489).

Density (liq.) d_4°=l-4649; b.p. 151-4°C./760 mm.; latent heat of vaporisation 11,610 cal-per g.-mol.; Trouton'a constant 27-3; surface tension at 18-2°C. 75-94 dynes/cm.; magnetic susceptibility (diamagnetic) 8-8 x 10^{-7} e.m.u.; specific conductivity 2 x 10^{-6} ohm^{-1}; specific conductivity of 4-5% solution 2-89 X 10^{-8} •ohm^{-1}; dissociation constant

$$(H_2O_2 = H^{\cdot} + OOH')$$

at 25° 2-4xHh$^{1!}$; heat of ionisation 8-6 x$1O^3$ cal. per g.-mol.; oxidation potential of H_aO_n -1-81 ±0 03 volts; reduction potential -0-G6 ±0-03 volt; dielectric constant of pure H_aO_2 93-7, of 20-8% H_3O_3 113-5; mean coefficient of expansion —10° to +20°, 0-00107; latent heat of fusion 74 cal. per g.; specific heat (liq.) 0-579, (solid) 0-470; viscosity at 18° 0-0130 poises; w^ =1-4139; heat of formation (H_2+Oa=H5,O,(iiq.)) 45,320 cal. per g.-mol.; heat evolved in decomposition ($H_2O_a=H_2O+O$) 23,450 cal. per g.-mol,; heat of solution in water 460 cal.; vapour pressure is given by the equation:

$$\log_{10} p_{mm} = 8{\cdot}853 - \frac{(6\text{-}05223x48530)}{T}$$

Dipole moment 2-1 D.; mol. wt, {from v.d.) 34; partition coefficient of H_sO_a between water and ether 0043.

Hydrogen peroxide is miscible with water in all proportions; Table II gives the relation between the density at 18°, the composition by weight (g. H_aO_a in 100 g. solution), the composition by volume per cent, and the number of volumes of oxygen gas evolved when the solution is decomposed.

Hydrogen peroxide is soluble in alcohol, ether and quinoline, but not in dry benzene or petroleum spirit.

The infra-red absorption spectrum of liquid and gaseous H_SO_S has been studied by Baly and Gordon (Trans. Faraday Soc. 1938, 34, 1133).

CHEMICAL PROPERTIES.

The structure of hydrogen peroxide is H—O—O—H. Tae majority of its reactions depend on the ease with wfcich one oxygen atom is given off:

$$H_3O_3 \rightarrow H_2O+O \quad (+23,450 \text{ cal.})$$

This leads to both oxidising and reducing properties. In addition, H_SO_2 acts as an extremely weak acid and gives rise to many per-compounds contaiuing the ---O—O— bridge. Finally, it forms numerous addition compounds.

Oxidation.—Hydrogen peroxide is a powerful oxidising agent. It reacts with sulphites, sulphides, thioaulphates, tetrathionates, etc., to give sulphates. Nitrous aeid is oxidised to nitric as is a)so hydroxylamine sulphate at 60°. Aqueous ammonia gives ammonium nitrite and nitrate, but at -48° in ether thB crystalline compoiLid (NH4),jOa-H_2O is deposited. Stannoua salts give stannic, ferrous give ferric, etc. Concentrated H_2O_K oxidises As, Se and Te to arsenic, selenic and telluric acids, while yellow phosphorus reacts at 60° to form phosphino and phosphorous and phosphoric acids.

TABLE II.—(Machu, *op. ciL,* Table 7, p. 37.)

Density, d_{4}^{18}.	Weight, %.	Volume, %.	Volumes of oxygen.
0-9986	**0**	0	0
1-0018	1-0	1·0	3-3
1-0034	1-5	1-5	5
1-0050	2-0	2-0	6-6
1-0083	3·0	3-0	10
1-0134	4-55	4-55	**• 1 5**
1-0151	5-0	5·1	17
10187	6·0	6·15	20
1-0241	7-5	7-7	25
10336	**100**	10-35	34
10526	15·0	15-8	52
10717	20-0	21-45	**70**
10911	25-0	27-3	90
1-1023	27-2	30·0	100
Mill	30-0	33-33	.110
1· 1331	35·0	39-7	132
1-1561	40·0	46-25	153
1•1796	45·0	53·1	175
1-2031	50-0	63-15	208
l[-2505	60-0 '	75-05	248
][-2080	70-0	90-85	300
1•3456	80-0	107-65	355
1•3936	90-0	125-4	415
l[•4442	1000	144-4	475

Hydrogen peroxide reacts with HCI, HBr and HI, but it is stabilised by HF (Maass and Hiebert, J. Amer. CheLi. Soc. 1924, 46, 290). The reaction with HCI is slow, the products being HOCI, Cl^ and oxygen; HBr reacts much mq,^{1}^ rapidly.

Al and Mg dissolve slowly'in concentrated H_2O, forming hydroxides. Sodium amalgam reacts jore strongly with H_2O,j than with water. Cu, Ag, Hg, Ni and Bi dissolve in dilute HJJSO,, in the presence of H_BO_a, but Sn, Pb, Au, Pt and Sb do not. The decomposition of H_aO» by Hg is a periodic phenomenon (Okaya, Proc. Phys.-AIath. Soc. Japan, 1919,, 1, 283).

A large number of organic substances are oxidised by H_aOj, the extent of oxidation depending on conditions such as concentration and the presence of promoters *{see below).* Polyalcohols give aldehydes; oxalic acid is broken down into CO. and water; tartaric a. i,l gives dihydroxymaleic acid; sugars form ozonides; benzene is oxidised to phenol. In alkaline solution H_2O_a oxid^es RCS-NHR' to RCO-NHR'. Alkaloids give new crystalline bases which arc often highly coloured. Indigo is slowly decolorised. An unusual reaction occurs between H_2O_2 and formaldehyde in alkaline solution, hydrogen gas being evolved:.

$$2HCHO+H_2O_2+2KOH$$
$$=2HCOOK+2H_2O+H_2$$

The oxidation of organic materials by H_2O_2 is catalysed by some substances which themselves accelerate its decomposition. For instance, in the presence of ferric salts H_2O_2 oxidises alcohol to acetic acid. Walton and Graham (J. Amer. Chem. Soc. 1928, 50, 1641) studied the catalysed oxidation by H_2O_2 of organic acids such as succinic, lactic, etc., and also of ethylene glycol and glycerol to CO_2 and water with ferric chloride, CuO and $CuSO_4$ as catalysts. The addition of H_2O_2 to a]8- unsaturated ketones (in ether or benzene) to give the dihydroxyketones is catalysed by OsO_4 (Butenandt and Wolz, Ber. 1938, 71 [B], 1483). The oxidation of dienes by H_2O_2 is catalysed by ferric hydroxide.

Organic materials such as paper inflame when treated with highly concentrated H_2O_2.

Reduction.—Besides producing oxidation, the nascent oxygen atom from H_2O_2 can attach itself to a similar oxygen atom of other oxidising agents, and thus apparently cause reduction with the evolution of oxygen gas. For example, potassium permanganate is reduced to MnO_2 in alkaline solution or to $MnSO_4$ in the presence of H_2SO_4:

$$2KMnO_4+5H_2O_2+3H_2SO_4$$
$$=K_2SO_4+2MnSO_4+8H_2O+5O_2$$

Ferricyanides are reduced to ferrocyanides in alkaline solution, but in acid or neutral solution the reverse reaction occurs. Silver oxide is reduced to metallic silver; NaOl gives Nal; $Ca(OCI)_2$ gives $CaCI_2$.

Formation of Per-Compounds.—The true per-compounds contain the —O—O— bridge; a large number are known to exist, but many are unstable. Many per-compounds are formed directly from H_2O_2 which can be regarded as a very weak acid. The addition of H_2O_2 to an aqueous solution of Nat)H gives sodium peroxide, Na_2O_2. Unstable peroxides of Zn, Mg, Cd are formed by the action of H_2O_2 on the metal hydroxides; those of Zr, Ce, Th, Y, La, Sm are obtained from the oxides. The addition of ammonia to a solution of $CaCI_2$ and H,O_2 precipitates CaO_2.

Sulphuric acid reacts with H_2O_3 to give Caro's acid, permonosulphuric acid, $HO{-}OSO_2{-}OH$; similarly acetic acid yields peracetic acid. Permonophosphoric acid is not formed in this way from orthophosphoric acid, but can be made by the reaction: $2H_2O_2+P_2O_6+H_2O=2H_3PO_5$. The true percarbonates ($K_2C_2O_6$, Na_2CO_4) are not obtainable directly from H_2O_2, only the carbonate perhydrates being formed *(v.i.)*. Many per-compounds are strongly coloured; for example, the addition of H_2O_2 to solutions of TiO_2 gives the intense yellow of pertitanic acid (hydrated Ti O_3). Perchromates are formed by adding H_2O_2 to soluble chromates *(v.* Vol. III, U4a). Salts of Mo, Ce, Va, Nb, U and W also give coloured (mostly yellow) solutions of unstable per-compounds. For example, uranyl nitrate and H_2O_2 form UO_4*2H«O_2. Pertantalates are white powders (*see* Emeleus and Anderson, " Modern Aspects of Inorganic Chemistry," G. Routledge, London, 1938, p. 356).

Addition Reactions.—A number of stable compounds can be prepared from H_2O_2 by simple addition. H_2O_2 combines with ammonium sulphate, sodium sulphate, borate, phosphate, acetate and arsenate as " hydrogen peroxide of crystallisation." It forms crystalline compounds such as $Na_2O_2{-}2H_2O_2$ with the alkali and alkaline earth peroxides.

The " sodium perborate " (" *Perborax,*" " *Peroxydol*") of industry is $NaBO_2{\cdot}H_2O_2{,}3H_2O$ and can be made by mixing sodium borate solution, with hydrogen peroxide in the cold *(v.* Vol. II, *51d-52b).* When dry, it is completely stable, while its solutions possess oxidising powers like H_2O_2. It is used extensively in washing powders and for bleaching. A large number of sodium carbonate perhydrates such as $2Na_2CO_3{-}3H_2O_2$ and a series

$$(Na_2CO_3{-}H_2O){\cdot}xH_2O_2$$

where z=*i, 1, H, 2, 2£ are known. They can be prepared by adding anhydrous sodium carbonate to a suitable amount of H_2O_2 solution. The carbonate perhydrates are more stable (and therefore of greater technical importance) than the true percarbonates. Many phosphate perhydrates and silicate perhydrates can be obtained similarly.

Hydrogen peroxide forms addition compounds with acetamide, urethane, succinimide, asparagine, pinacol,' stryofenine, erythrose and mannose. Addition compounds 'cti H_2O_2 with ammonia, ethylamine, propylamine, butylamine and pyridine have been obtained from ethereal solution.

Of special interest is the compound

$$CO(NH_2)_2{\cdot}H_2O_2$$

(*"Hyperol," " Perhydrite," "Ortizon"*) which is prepared by cooling a solution of urea dissolved in 30% H_2O_2 to -5°. It is a stable white powder, soluble in 2£ parts of water. It provides a convenient form of " solid " H_2O_2 for pharmaceutical and analytical purposes (Booer, Chem. and Ind. 1925, 44, 1137).

DECOMPOSITION.

Hydrogen peroxide is thermochemically unstable ; its decomposition into water and oxygen is exothermic to the extent of 23,450 cal. per g.-mol. However, pure H_2O_2 and its pure solutions keep well at ordinary temperatures and decompose only comparatively slowly when heated, with the exception that the pure liquid explodes at about l£l°C. Apparently the true homogeneous decomposition of liquid or vapour requires a high energy of activation, and even the slow reaction of H_2O_2 vapour in a quartz flask at 85° occurs heterogeneously on the walls, but the decomposition is greatly accelerated by the catalytic action of solid surfaces (particularly carbon, platinum and manganese dioxide); by heavy metal ions (notably Fe and Cu, but also salts and oxides of Pb, Hg, Co, Ni and Mn, etc.);

by natural enzymes; or by irradiation with ultra-violet light or JT-rays.

Very concentrated H_aO_2 explodes when brought into contact with an effective catalyst such as MnO_2.

Catalysis at the surfaces of dispersed solids has been the subject of many investigations. The most effective material known is an osmium sol which still exerts a strong catalytic action at dilutions as great as 10~^{9} g. per c.c. Other metals in colloidal form (particularly Pd, Pt, Ir, Au and Ag) are also very effective, as are MnO_2, Co_2O_3, PbO_2 and copper peroxide. High surface area naturally enhances the effect of a solid (sugar charcoal, for instance, is very active)* but the nature of the solid is particularly important. According to Wright and Rideal (Trans. Faraday Soc. 1928, 24, 530) the velocity of catalytic decomposition of H_2O_2 by sugar charcoal, iron oxide, $Mg(OH)_2$, kaolin, WO_8, glass, CrCI,, ZnO and silica gel is very dependent on traces of acids, alkalis or heavy metals, and it reaches a maximum at a p_E corresponding to the isoelectric point of the surface. On the other hand, haemin and the chemically related iron compounds of the porphyrin group exert an enormous and virtually specific* catalytic effect on the decomposition of H_2O_2. Natural enzymes possessing the specific property of destroying hydrogen peroxide occur widely in animal and vegetable tissues and are known collectively as " catalases " *(q.v.).*

The metal-sol catalysts (Pt, Ag, etc.) are very susceptible to " poisoning " by minute quantities of sulphides, arsine, HCN, CO, $HgCl_a$, phosphine, phosphorus, CS_2, phenol, strychnine, iodine, etc., thereby their catalytic activity is largely reduced:, or destroyed *(see,* for example, Bredig and Ikeda, Z. physikal. Chem. 1901, 37, 1). The effectiveness of positive catalysts is also impaired to a greater or less extent by many capillary-active substances which are probably preferentially adsorbed on the surface of J)he solid; among these are alcohols, ketones, :ric acid, barbituric acid, etc.

Stabilisers.—Solution of H_aO_2 are slowly decomposed by alkalis (as, for example, from soda-glass bottles), and hence their stability is improved by acids *(e.g.* 0*1% of H_2SO_4 or H_3PO_4). In addition, a very large number of substances have been proposed as general stabilisers; phenacetin and salicylic acid (0-1-0*5 g. per litre) are suitable for pure H_2O_2 solutions; other substances claimed include: pyro- and meta-phosphates of Na, Mg, Ca, Sn, magnesium and sodium silicates, sodium benzoate, acetanilide, methyl p-hydroxybenzoate (" *nipagin*"), hexamine, tannin, a-naphthylamine, numerous alcohols, ketones, aldehydes, amides, ether, glycerol, pyrogallol, oxalic acid and many other diverse organic compounds. Sodium and calcium chlorides are appreciably preservative if used in large amount. Modern pure preparations of H«O_2 scarcely need stabilising, but in technical use-, as in bleaching baths, destructive impurities may be introduced, and a suitable stabiliser may reduce loss of peroxide.

Storage.—Stabilised H_2O_2 solutions can be stored in glass, porcelain or stoneware vessels, while small quantities of pure 30% H_2O_2 are commonly kept in paraffin wax bottles. There is some fire danger in the transport of 30% H_2O_a owing to its powerful oxidising action on organic materials, but it has been found possible to store large quantities in tanks of treated aluminium or of certain aluminium and other alloys, provided suitable stabilisers are added. The addition of ammonium nitrate or nitric acid to H_2O_2 is said to retard the corrosion of aluminium.

TECHNICAL APPLICATIONS.

Hydrogen peroxide is extensively used as a bleaching agent, antiseptic and preservative on account of its powerful oxidising properties.

Bleaching is carried out with warm, mildly alkaline solutions containing suitable stabilising agents such as water-glass. Injurious impurities *(e.g.* traces of Fe and Cu) must be carefully excluded from the bleaching bath to avoid waste of H_2O_2, and when not in use the bath may be acidified to improve its stability. For mild bleaching a concentration of about 0*2% H_2O_2 is used at 40-45°C, while more powerful action can be obtained by using stronger solutions and higher temperatures *(e.g.* 3% H_2O_2 at 80°C). Hydrogen peroxide can be used to bleach practically any material; among those mentioned in the literature are all forms of cotton, wool, silk, linen *(v.* Vol. II, 10c, 17a, 18c), furs, skins, wood, horse hair, parchment, feathers, hoof, horn, bones, ivory, fats and oils. For many purposes H_2O_2 may be replaced by its stable solid derivates, the carbonate and borate perhydrates. Sodium perborate may be incorporated in soaps and is extensively used in laundering.

As a Disinfectant and Preservative.—Bacteria are rapidly destroyed by dilute solutions of H,O_2: *Staphylococci* and diptheria bacilli are killed by 1-75% H_2O_2 within 5 minutes *(v.* Vol. IV, *19a).* A 3% H_2O_2 solution has an antiseptic power equivalent to 1 in 1,000 $HgCI_2$ and has the advantage of being non-poisonous (although concentrated. H_2O_2 blisters the skin). Dilute H_2O_2 was formerly used as a preservative for milk, meat, gelatin, glue and cocoa-milk beverages but its use in food is not now permitted (V FOOD PRESERVATIVES) ; fish has been packed in ice containing H_2O_2. Cut flowers are said to last much longer in very dilute H_2O_2. It has also been suggested for disinfecting seeds and as a leavening agent in place of yeast.

For pharmaceutical purposes the " 10-volume " and " 20-volume " solutions with sodium pyrophosphate or urea as stabiliser are generally used; and are further diluted a number of times. The very dilute solution is useful for cleaning or sterilising new or septic wounds and to stop bleeding; as an eye lotion, gargle or mouth wash; for external application in skin diseases; for burns and scalds, and to whiten the teeth. The solutions have a somewhat metallic taste.

DETECTION AND ESTIMATION.

Qualitative Identification.—The following are probably the most sensitive and characteristic of the numerous tests which are available for hydrogen peroxide. (1) The orange-coloured pertitanic acid is formed when HgOg is added to a solution of TiO_2 in sulphuric acid (detects, 1 part H_2O_2 in 1-8 x 10^8 parts of water). (2) A solution of H_aO_2 is treated with 1 drop of dilute H_2SO_4, 2 c.c. of ether, and 1 drop of 1% potassium dichromate, and shaken, the characteristic blue colour of perchromic acid is formed in the ether layer (limit 0-2 mg. in 20 c.c). (3) The guaiacum test is the most sensitive for H_2O_2. The solution to be tested is mixed with a fresh 1-2% solution of guaiacum resin in 90-98% alcohol until a slight turbtfity develops; then one drop of an extract of malt is added, a blueacolour is produced which serves to detect 1 part of H_2O_2 in 5 x 10^7 parts of water. (4) The solution containing H_2O_2 is added to a reagent containing tartaric acid, potassium iodide and ferrous sulphate; after mixing, 5 or 6 drops of NaOH solution are added, a violet colour is formed (detects 1 in 25 xlO^6). (5) Several sensitive spot tests are available, such as the bleaching of lead sulphide paper, the formation of Prussian Blue from a solution containing ferric chloride and potassium ferricyanide, or the formation of a red or blue gold colloid by reduction of gold salts. *(See also* Vol. II, 574a.)

Quantitative Determination.—(1) By titration with potassium permanganate solution in the presence of a large excess of sulphuric acid,

$$2KMnO_4+5H_2O_2+3H_2SO_4$$
$$= K_2SO_4+2MnSO_4+8H_2O+5O_2$$

1 c.c. of tf/10 $KMnO_4$=0-001701 g. of H_2O_2.

This method cannot be used if organic preservatives are present.

(2) The reaction with *N/10* iodine and alkali subsequently acidified gives in effect:

$$H_2O_2+2KI+H_2SO_4=I_2+K_aSO_4+2H_20$$

the liberated iodine being titrated with sodium thiosulphate using starch at the end-point in the usual way.

(3) With titanous chloride. On treating H_2O_2 with a dilute solution of Ti_2Q_3 in the presence of acid the deep orange colour of pertitanic acid develops. This may be lised to estimate H_2O_2 directly by colorimetry, or alternatively, further Ti_2O_3 may be added until the colour is just bleached; the end-point is sharp.

$$Ti_2O_3+3H_2O_2=2TiO_3+3H_2O$$
$$2TiO_3+2Ti_2O_3=6TiO_2$$

The titanous chloride is standardised in an inert atmosphere with iron alum; when the Fe:'' colour has practically disappeared a drop of potassium thiocyanate solution is added and the titration continued to complete decoloration (Knecht and Hibbert, Ber. 1905, 38, 3324). This method of determining H_2O_2 is particularly useful whea organic substances are present.

(4) Another method of determining H_2O_2 is by measurement of the volume of oxygen evolved when the solution is decomposed by catalysts, by hypobromite or by potassium permanganate.

(5) Other methods based on potassium iodate, eerie sulphate, sodium arsenite, or manganic sulphate are also applicable.

M. C. and J. A. K.

HYDROGEN SWELLS *(v.* Vol. V, 291a).

HYDROGENATION has come to be regarded as the combination of organic substances with hydrogen under the influence of a catalyst; the present article is concerned with the laboratory aspects of the subject. Articles on hydrogenation reactions of special importance in industry will be found in the appropriate places in the Dictionary.

Historically the first example of a catalytic hydrogenation was the production of methylamine by passing a mixture of hydrogen and hydrogen cyanide over platinum black (Debus, Annalen, 1863, 128, 200). The development of this vapour-phase method of hydrogenation is due mainly to Sabatier and Senderens and their co-workers (1897-1914). Since 1905 development has been mainly along the lines of using finely divided metals in the liquid phase (Willstätter, Paal, Skita, Adams, Adkins). This method of liquid-phase hydrogenation has, for the most part, ousted the vapour-phase method in laboratory, and largely in industrial, practice.

GENERAL.

VAPOUR-PHASE HYDROGENATION.

The apparatus in its simplest form consists of a hard-glass combustion tube, packed with a suitable catalyst and heated in a furnace (preferably electric). Hydrogen is passed through the tube and the substance is most conveniently introduced by bubbling the hydrogen through the liquid material heated to a suitable temperature. Such an apparatus, was used by Sabatier and Senderens in their classical series of investigations (for summaries, *see* Ann. Chim. Phys. 1905, [viii], 4, 319; Sabatie/f transl. Reid, " Catalysis in Organic Chemistry," 1923). The following are two typical catalysts used in these experiments:

(1) Pumice, broken up into small piecej, is boiled with nitric acid, washed with water and then ^saturated with a concentrated solution of sufficient nickel nitrate to give a catalyst of tip desired nickel content. The product is then evaporated to dryness with good stirring and finally heated in a nickel dish over a free flame until the nickel nitrate is completely decomposed. The product is packed into the hydrogenation tube and, after sweeping out with hydrogen, reduced by heating to 300-400° in a stream of hydrogen. After cooling in hydrogen the tube is ready for use.

(2) Sixty grams of kieselguhr, purified by boiling with nitric acid and with water, are made into a paste with an aqueous solution of nickel nitrate. An excess of sodium carbonate solution is added and the mixture is boiled fqr a few minutes. After washing several times with hot water by decantation, the precipitate is filtered off, dried and then reduced as described for the pumice catalyst.

Such catalysts may be used for the reduction of ethtfenic linkages (at about 100-150°), aromatic nuclei (about 200°), carbonyl- and nitro-groups.

A somewhat analogous but much more convenient vertical apparatus has been devised by Lush (J.S.C.I. 1923, 42, 219T; c/. Pelly, *ibid.*

1927, 46, 449T). In this apparatus the catalyst consists of nickel turnings which, before use, are first coated with an oxide film by anodic oxidation and then reduced in hydrogen. The apparatus may be used under pressure and has found application on a semi-technical scale and in laboratory operations; it is marketed by Messrs. Technical Research Works, Ltd. The apparatus is particularly suitable for routine laboratory hydrogenations on a fairly large scale; it has the advantage of being simple to operate and requires no expensive catalyst.

LIQUID-PHASE HYDROGENATION.

Apparatus.—The simplest form of apparatus may easily be assembled from ordinary laboratory equipment; it consists of a calibrated hydrogen-reservoir connected to a hydrogenation flask which is mounted for mechanical shaking. An arrangement for evacuating the flask is necessary and it is an advantage to arrange also for heating. To carry out a hydrogenation the substance to be hydrogenated, dissolved or suspended in a suitable solvent, is introduced into the hydrogenation vessel together with the catalyst. After evacuation, hydrogen is admitted and the flask is shaken until the required amount of hydrogen has been taken up; the flask is then once more evacuated, air is admitted, the catalyst is filtered off and the product isolated in an appropriate manner. Many forms of apparatus of this type have been described in detail in the literature (Paal and Gerum, Ber. 1908, 41, 813; Willstätter and Hatt, *ibid.* 1912, 45, 1472; Skita and Meyer, *ibid.* 1912, 45, 3594; Stark, *ibid.* 1913, 46, 2335). A similar apparatus adapted for working at pressures up to 3-5 atm. has been described by Adams and Voorhees (Organic Syntheses, 1928, 8, 10) and compact modifications are marketed by several firms; the hydrogen reservoir is a stout metal tank and the hydrogen-uptake is followed by the fall in hydrogen pressure during the reaction. This type of apparatus is well suited for general laboratory use.

It is frequently necessary, or at any rate desirable, to carry out hydrogenations at comparatively high temperatures and pressures. Adkins (J. Amer. Chem. Soc. 1933, 55, 4272) has designed an apparatus suitable for hydrogenations at temperatures up to 400° and pressures up to 300 atm. It consists essentially of a specially designed autoclave mounted on a shaker and fitted with an electrical heater. A modification of this apparatus is marketed by the Burgess-Parr Company.

The development of modern micro-methods has led to the devising of a number of pieces of apparatus for the determination of the number of double bonds in the molecule of a substance by the hydrogenation of a few milligrams of material. Smith (J. Biol. Chem. 1932, 96, 35) devised an apparatus in which the uptake of hydrogen was measured directly by the diminution in volume under constant pressure; an improvement of this apparatus by Jackson and Jones (J.C.S. 1936, 895; *cf.* Jackson, Chem. and Ind. 1938, 57, 1076) is extensively used to-day. The other widely used apparatus is that of Kuhn and Müller (Angew. Chem. 1934, 47, 145) in which the difference in volume between the hydrogen taken up by the substance and that taken up by a control substance is measured. Adams' platinum oxide catalyst *(see below)* is the catalyst generally employed in these experiments, the solvent being, usually, acetic acid, decalin or methylcyclohexane.

Catalysts.—(1) *Platinum Catalysts.—Of* the platinum catalysts in use to-day by far the most popular is platinum black produced by reduction, in the hydrogenation vessel, of platinum oxide prepared by the method of Adams, Voorhees and Shriner (Organic Syntheses, 1928, 8, 92) This "Adams' catalyst" is prepared by fusing chloroplatinic acid with sodium nitrate at 500-550°. After use it may be re-worked by solution in *aqua regia* followed by evaporation and fusion with sodium nitrate; if extensively poisoned it may be necessary to purify it by conversion into ammonium chloroplatinate (Baldeschweiler and Mikeska, J. Amer. Chem. Soc 1935, 57, 977) which can then be used directly for the fusion with sodium nitrate (Bruce Organic Syntheses, 1937, 17, 98; J. Amer. Chem. Soc. 1936, 58, 687). Cook and Linstead (J.C.S. 1934, 952) recommend the use of potassium, instead of sodium, nitrate in the fusion and consider that a more active catalyst is obtained in this way. Short (J.S.C.I. 1936, 55 14T) describes a special apparatus for carrying out the fusion. The following simplified procedure has been found to give consistently good results:

One gram of commercial chloroplatinic acid is dissolved in 3 c.c. of water in a porcelain crucible and to the solution is added 10 g. of pure sodium nitrate. The mixture is evaporated to dryness over a small flame with stirring The full heat of the Bunsen flame is then applied to the crucible and vigorous stirring is continued until the mass is completely molten and the initial vigorous decomposition, which is accompanied by frothing, has abated. The flame is then regulated so that the base of the crucible is at a dull red heat and this temperature is maintained, without stirring, for 30 minutes. The cooled product is extracted with hot water, filtered and the brown oxide washed well with hot water and dried in a vacuum desiccator. The yield is almost theoretical.

Loew (Ber. 1890, 23, 289) prepared platinum black by the reduction of platinum chloride with formaldehyde in the presence of sodium hydroxide. Many modifications of this method have been described of which the following (Willstätter and Waldschmidt-Leitz, *ibid.* 1921, 54 [B], 121) seems to give a very active catalyst:

Eight c.c. of a solution of chloroplatinic acid, prepared from 2 g. of platinum and containing some hydrochloric acid, are mixed with 13 c.c. of formalin. After cooling to -10°, 42 g. of 50% potassium hydroxide solution are added dropwise with stirring, the temperature being kept below 5°. When the addition is complete the product is stirred at 55-60° for 30 minutes. The platinum black is then washed by decantation (best in a cylinder), until the washings are neutral and free from chloride. It is then filtered off, care being taken to keep it covered with water, lightly pressed between filter papers and dried in a vacuum desiccator. Access of air to the catalyst must be avoided.

(2) *Palladium Catalysts.*—Palladium black, may be prepared by methods analogous to those described above for platinum black; thus Shriner and Adams (J. Amer. Chem. Soc. 1927, 49, 1093) fuse palladous chloride with sodium nitrate and Zelinsky and Glinka (Ber. 1911, 44, 2309) reduce palladous chloride with potassium formate.

Usually, however, palladium is deposited on an inert carrier. For this purpose charcoal (Mannich and Thiele, Arch. Phajm. 1915, 253, 183), barium sulphate (Schmidt, Ber. 1919, 52 §B], 409) and alkaline-earth carbonates (Busch and Stöve, *ibid.* 1916, 49, 1064) have found extensive application. For the preparation of palladised charcoal, palladous chloride is dissolved in warm concentrated hydrochloric acid; the requisite amount of active charcoal (previousfy purified by boiling with hydrochloric acid) is added to the diluted solution and the whole is stirred or shaken in hydrogen with the addition of some sodium acetate. The palladised charcoal may dither be filtered off and stored in a desiccator or used directly. Zelinski,, Packendorff and Leder-Packendorff *{ibid.* 1933, **66** [B], 872; *cf.* Robinson and Koebner, J.C.S. 1938, 1996) prepare a selective catalyst by depositing both platinum and palladium on active charcoal. -Of the other carriers strontium carbonate gives an excellent robust catalyst suitable for general use. For the preparation of 2% palladised strontium carbonate, 30 g. of strontium carbonate are suspended in 500 c.c. of water at 70°. A solution of 1 g. of palladous chloride in a little warm concentrated hydrochloric acid is stirred in. After stirring at 70° for a few minutes fhe catalyst is filtered off, washed, dried in the steam-oven and stored; it is reduced, as required, in the hydrogenation vessel.

(3) ***Colloidal Platinum and Palladium Catalysts.***—Paal and his co-workers (Ber. 1904, 37, 124; 1905, 38, 1401; 1908, 41, £05) developed a catalyst which consists of a colloidal solution of platinum or palladium protected by " sodium lysalbate," a product of the alkaline hydrolysis of egg albumen; this catalyst can only be used in neutral or alkaline solution, since ihe protective colloid is sensitive to acid.

Skita and his co-workers *(ibid.* 1909, 42,1627; 1911, 44, 28C2; 1912, 45, 3579,3589) u3e gum arabic as the protective colloid. A solution of palladous chloride containing gum arabic is added to a solution of the substance to be hydrogenatcd in alcohol or acetic acid. The c*at#lyst is formed by shaking in hydrogen, after which the hydrogenation proceeds in the usual way. Recently these colloidal catalysts have fallen* into disfavour owing to the greater robustness of such non-colloidal catalysts as Adams' platinum oxide and palladised charcoal or strontium carbonate.

(4) *Nickel Catalysts.*—The outstanding nickel catalyst for hydrogenation in the liquid phase is Raney nickel, which has no serious rival among nickel catalysts for this purpose. Raney (U.S.P. 1628190) prepared his, catalyst by the action of sodium hydroxide <5n a .nickel-aluminium alloy of the composition **Al_2Ni.** This catalyst has been much used by Adkins and his co-workers in connection with the high-pressure hydrogenator mentioned above; the following more active preparation is due to Covert and Adkins (J. Amer. Chem. Soc. 1932, 54, 4116).

Finely-ground nickel-aluminium alloy (300 g.) is added over 2-3 hours to 300 g. of sodium hydroxide in 1,200 c.c. of distilled water in a 4 litre beaker surrounded b/ ice. The mixture is then heated for 4 hours to 115-120° with occasional stirring. A further 400 c.c. of 19% sodium hydroxide solution is then added and the mixture kept at 115-120° until no more hydrogen is evolved (about 3 hours). After dilution to 3 litres the nickel is washed 6 times with water by decantation and then alternately by Suspension and by washing on a Buchner funnel until the filtrate is neutral to litmus. The nickel (which is pyrophoric when dry) is then washed 3 times with 95% alcohol and stored under alcohol in glass-stoppered bottles. Raney nickel may retain about 17% of alcohol, which may lead to ester formation in the hydrogenation of acids, but it may be removed by storage for some hours under ether or methyl*cyclohemne* (McClellan and Connor, *ibid.* 1941,63, 484). The outstanding characteristic of Raney nickel is its activity as compared with other nickel catalysts. Lieber and Smith *(ibid.* 1936, 58, 1417) enhance its activity by adding a small amount of platinum chloride at the commencement of the hydrogenation. Paul and Hilly (Compt. rend. 1938, **206,** 608) prepared an iron catalyst, said to be specific for tjie semi-hydrogenation of %cetylenic linkages, by a similar process with an iron-aluminium alloy; they have also described a modified process for the preparation of Raney nickel (Bull. Soc. chim. 1936, [v], 3, 2330).

Adkins has also used a nickel-kieselguhr catalyst produced by treatment of kieselguhr with-.nickel nitrate and ammonium carbonate followed by reduction at 450° (Covert, Connty and Adkins, J. Amer. Chem. Soc. 1932,54,1651); this catalyst is less active than Raney nickel. Sully (Chem. and Ind. 1939, 58, 282) prepares an active catalyst by precipitation of nickel carbonate from nickel sulphate by means of sodium catbonate; the precipitate is washed carefully and reduced in hydrogen. It is claimed that this catalyst (5%) will hydrogenate crotonaldehyde to butyl alcohol in 5 hours at 80°/200 lbs.

(5) *Other Catalysts.*—Among the many other catalysts described in the literature the only one whose action has been generally studied is " copper chromite" (Connpr, Folkers and Adkins, *ibid.* 1931, 53, 2012; 1932, 54, 1138). In these two papers procedures for the preparation of a wide range of copper chromite catalysts are described; the most active are made by adding ammonia to a mixture of copper nitrite, bariuminitrate and ammonium dichromate and igniting the precipitate. Adkins and Connor *(ibid.* 1931,53,1091) specially recommend copper chromite for the hydrogenation of carbonyl compounds to alcohols, of benzyl alcohols to hydrocarbons, nitro-groups to amines and for

the selective hydrogenation of double bonds. Pyridine nuclei are readily hydrogenated but the catalyst is inactive towards cyano-groups and benzene nuclei. It is not so easily poisoned as nickel and is best used at high pressures.

Faucounau (Bull. Soc. chim. 1937, [v], 4, 58, 63) has prepared active copper and cobalt catalysts by the action of sodium hydroxide on Devarda's alloy and the alloy Co_2AI_5, respectively.

Solvents.—The' most widely used hydrogenation solvents are ethyl alcohol, acetic acid, ethyl acetate, ether, and saturated hydrocarbons such as n-hexane, decalin and cycZohexane. It is generally considered that acetic acid is the most useful solvent from the point of view of rapidity of hydrogenation (Willstatter and Hatt, Ber. 1912, **45,** 1471; Skita and Meyer, *ibid.* 1912, 45, 3590); it is specially useful for the hydrogenation of aromatic nuclei (Adams and Marshall, J. Ainer. Chem. Soc. 1928, **50,** 1970). Carothers and Adams *(ibid.* 1924, 46, 1675) investigated the hydrogenation of aldehydes in a variety of solvents but came to no very definite conclusions. Maxted and Stone (J.C.S. 1938, 454), working with crotonic acid and platinum, were unable to correlate the rate of hydrogenation (corrected for the vapour pressure of the solvent) with any other property of the solvent.

Experimental Conditions.—In general, increase of temperature leads to an increase in the rate of hydrogenation, but this effect is masked by the lowering of the partial pressure of hydrogen in the reaction vessel consequent on the rise in the vapour pressure of the solvent; it is thus necessary to determine the optimum temperature for'each case experimentally. The^ate of hydrogenation usually increases with increasing pressure, but here again no general rule as to the magnitude of the pressure effect can be given. The effect of pressure is particularly marked with nickel catalysts, with which there seems to be an optimum pressure for many hydrogenatioMB *(cf.* Adkins, Cramer and Connor, J. Amer. Chem. Soc. 1931, 53, 1402). In many cases increase of pressure has been shown to give rise to the formation of a different product (Skita, Ber. 1915, 48, 1486; Skita and Ritter, *ibid.* 1910, 43, 3393). The amount of catalyst used has also an important effect. Within limits the rate of hydrogedation increases with an increase in the amount of catalyst added *(cf.* Paal and Schwartz, *ibid.* 1915, 48, 994; Bourguel, Gredy and Roubach, Bull. Soc. chim. 1931, [iv], **49,** 897). Another factor influencing the rate of hydrogenation is the vigour of the shaking or stirring.

It frequently happens that a catalytic hydrogenation comes to a standstill short of completion ; in such cases the catalyst may often be re-activated by shaking or stirring with air or oxygen. In specially difficult cases hydrogeiwtion may be effected by boiling the substance with an excess of tetralin in the presence of palladium black or palladised charcoal, the tetralin being dehydrogenated to naphthalene (Kindler and Peschke, Annalen, 1932, **497,** 193; 1933, **501,** 191).

Poisons and Promoters.—The literature on catalyst poisons is both large and chaotic. In general, mercury compounds are regarded as poisons (Paal and Hartmann, Ber. 1918, 51, 711); nevertheless the presence of a small amount of metallic mercury in the hydrogenation vessel seems to have little adverse effect, at any rate with palladised charcoal and Adams' catalyst. Compounds of sulphur (including vulcanised rubber), arsenic compounds and hydrogen cyanide are also stated to be poisons (Hinrichsen and Kempf, *ibid.* 1912, 45, 2107; Busch and Stove, *ibid.* 1916, 49, 1070; Kelber, *ibid.* 1916, 49, 1868); for this reason Adams and Voorhces (Organic Syntheses, 1928, 8, 14) recommend that rubber tubing and stoppers used in apparatus for catalytic hydrogenation should be boiled out with 20% sodium hydroxide and then with water. However, Truffault, in a study of poisoning in catalytic hydrogenation (Bull. Soc. chim. 1935, [v], 2, 244), found vulcanised rubber to be ineffective as a poison. Unsaturated substances obtained by dehydration by means of thionyl chloride are frequently resistant to hydrogenation owing to the presence of small amounts of sulphur compounds; treatment with a little ahlminium amalgam in moist ether frequently brings about the removal of these impurities *(cf.* Gaubert, Linstead and Rydon, J.C.S. 1937, 1977). Partial poisoning of the catalyst may be of value in increasing its selectivity; thus a partially poisoned catalyst is used in the Rosenmund hydrogenation of acid chlorides to aldehydes (p. 359a). Maxted and Morrish *(ibid.* 1940, 252) find that, in the case of elements such as sulphur, selenium, tellurium and phosphorus, the catalytic toxicity generally disappears if the normally poisonous atom is associated with a completely shared octet of electrons.

Adams and his co-workers (J. Amer. Chem. Soc. 1923,45,1071, 3029; 1924,46,1675; 1925, 47, 1047, 1098, 1147, 3061; 1926, 48, 477) found that the addition of certain inorganic salts affected the rate of hydrogenation; iron salts, especially, markedly increase the rate of hydrogenation of Idehydes.

Many authors have noted the effect of mineral acids in small amount in speeding up hydrogenation (Kindler, Brandt and Gehlhaar, Annalen, 1934, **511,** 209; Kindler and Peschke, *ibid.* 1925, **519,** 291; Brown, Durand and Marvel, J. Amer. Chem. Soc. 1936, 58,1594), and a recent study shows that the hydrogenation of benzene with platinum black is markedly dependent on p_{Hy} being fastest in acid, and almost stopped in alkaline, solution (Foresti, Gazzetta, 1936, 66, 455, 464). Peroxides, such as benzoyl peroxide and perbenzoic acid, have also been found to increase the velocity of catalytic hydrogenations (Thomson, J. Amer. Chem. Soc. 1934, 56, 2744).

General Considerations.—Owing to the vastly different characters of the available catalysts it is not possible to place them in any definite order of effectiveness. For laboratory hydrogenation the catalysts in greatest favour are Adams[1] platinum oxide catalyst, palladised strontium carbonate or charcoal, and Raney nickel. The most favoured solvents are ethyl alcohol and acetic acid.

The effect of constitution on ease of hydrogenafcion follows no very general rules, but the hydrogenation of aromatic nuclei is more difficult than that of ethyienic and acetylenic linkages and carbonyl groups. Among ethylenic compounds it has been observed by many workers that the rate of hydrogenation decreases with the accumulation of alkyl groups on the uneaturated carbon atoms *(cf.* Vavon *et* a/., Compt. rend. 1923, 176, 898; **177,** 401, 453; Lebedev, Kobliansky and Yakubehik, J.C.S. 1925, **127,** 417). It has been observed that the *cydo*-pentane ring is sometimes opened in hydrogenations at high temperatures (Zelinski, Kazanski and Plate, Ber. 1933, (J6 [B], 1415; 1935, 08 [B], 1869; Denisenko, *ibid.* 1936, 69 [B], 1553, 1668, 2183).

Paal and Schiedewitz. *(ibid.* 1B27,60 [B], 1221; 1930, 63 [B], 766 ; Paal, Schiedewitz and Rauscher, ***ibid,*** 1931, 64 [B], 1521) state that, in general, the c is-forms of ethylenic compounds are more fepidly hydrogenated than the *trans*; Weygand, Werner and Lanzeudorf (J. pr. Chem. '1938, [ii], **151,** 231), however, find that this conclusion is not universally valid. According to Bourguel and Yvon (Compt. rend. 192fi, 182, 224) the partial hydrogenation of acetylenic compounds yields cis-ethylonie compounds, A stereochemical conclusion which ia much more general ia the now classical Auwers-Skita rule (Skita, Ber. 1920, 53 [B], 1792; von An were, Annalen, 1920, 420, 84) which, states that hydrogenation in neutral or alkaline solution favours the formation of *trans-* compounds, whereas hydrogenation in acid media leads to eta- com pounds. This rule has proved of great value in the assignment of configurations to many products but its interpretation is, in certain cases, rather doubtful {Ruzicka, Briingger, Eichenberger and Meyer, Helv. Chim. Acfh, 1934,17, 1407).

Iu a recent review {Chem, Soc. Annual Rep, 1937, 34, 221) Linstead remarks that " Hydrogenation of unaaturated compounds over platinum or palladium catalysts is now part ol standard technique. By the improvement in the activity of catalyst9 . .' it has become possible to hydrogenate almost any description of double bond, the operation being carried out in the liquid phase or in solution at the ordinary temperature and at the ordinary or very $ lightly raised pressure. . "*. . Complete hydrogenation has thus largely become a m attar of routine, anc the main developments ***mitt*** *nqw* be ai the improvement of selectivity." Several example! of selective hydrogenation will be discussec later, but certain results may be mentioned -here. Dupont (Bull, Soc. cbim. 1936, [v], 3 1021,1030) found that Raney nickel was gene/all v mcrd selective in its action than Adams' catalyst in the hydrogenation of polyenes with this catalyst step.wise reduction was the rule as it was in the case of acetylenes. Similar results were however, obtained by Bourguel {Bull. Soc. chim 1927, [iv], 41, 1446) with a platinum catalyst The work of Adkins on high pressure hydrogenation with Raney nickel and copper chromiU has led to the possibility of achieving remarkably selective hydrogenation. Thus, since coppe chromite is inactive to benzene nuclei, whereas Raney nickel is inert towards eater groups, i t i)os8ible to hydrogenate one and the same rom&tic eater to an aromatic alcohol, with jopper chromite, or to a cyc/ohexane ester, with laney nickel. A moat remarkable selective lydrogenation is the reduction of butyl oleate o the corresponding unsaturafred octadecenol using a zinc-chromium oxide catalyst (Sauer and Adkins, J. Amer. Chem. Soc. 1937, 59, 1).

SPECIAL.,

The remainder of this article deals, in detail, with the hydrogenation of various important classes of compound.

Ethylenic Compounds.—In general carbon-carbon double bonds are readily hydrogenated even with comparatively inert catalysts; carjoxyl groups do not interfere and it is generally possible, by correctly choosing the experimental ;onditions, to hydrogenate the ethylenic linkage n an unsaturatcd carbonyl compound without affecting the carbonyl groups *(cf.* Skita, Ber. 1908, 41, 2938; Skita and Ritter, *ibid.* 1910, 43, J393; Paal, *ibid.* 1912, 45, 2221; Vavon, Ami. cbim. 1914, [ix], i, 193). A useful table showing ihe relative ease of hydrogenation (Adams' catalyst) cf a wide range of ethylenic compounds is given by Kern, Shriner and Adams [J. Araer. Chem. Soc. 1925, 47,1147); attention lias already been drawn to the fact that the rate of hydrogenation of an ethylenic linkage is reduced by the accumulation of substituents (*cf.* Zartman and Adkins, *ibid.* 1932, **54,** 1668); Lebedev and Flatonov, J.C.S. 1930, 321). Poal (Ber. 1912, 45, 2221) studied the stepwiae hydrogenation of a series of dienic compounds; he concluded that stepwise hydrogenation only occurred when the double bonds^ere separated by at least 1 carbon atom, thus:

m

PhCH:CHCH:CHCOMe

+ 2H, PhCHg-CHj-CHj-CHj-COifle

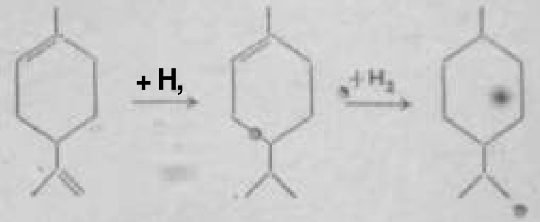
but

PhCH:CHCOCH:CHPh

_J ^. PhCH,-CH$_s$-CO-CH:CHPh

$\xrightarrow{+H_2}$ PhCH$_2$·CH$_2$·CO·CH$_2$·CH$_2$Ph

Similar phenomena are observed with terpene derivatives *(cf.* Waltach, Annalen, 1911,381, 51), *e.g.* limonene:



If a relatively inactive catalyst is used it is frequently possible to obtain good yieldB of the pure mo no-unsaturatcd compound in this way *(e.g,* caryophyllene -> dihydrocaryophyllene; Deuasen, *ibid.* 1912,388, 156; J. pr. Chem. 1926, [iij, **114,** 83).

Acetylenic Compounds are usually very rriidily hydrogenated under mild conditions. Two-stage hydrogenation:

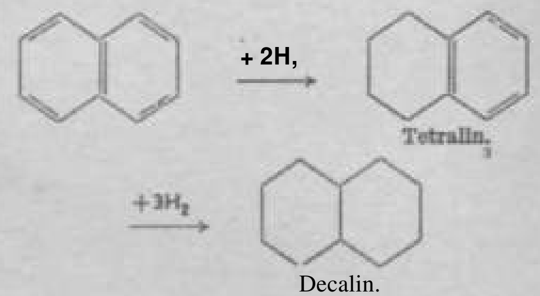
$$RC;CR' \xrightarrow{-I\ H>} RCH:CHR' \xrightarrow{+\ hU} RCH_2\cdot CH_2R'$$

has frequently been observed, especially with palladium catalysts (*cf.* Paal *et al.,r* Ber. 1909, 42,3930; 1915,48,1202; Kelber and Schwartz, ***ibid.*** **1012,** 45, 1946; Bourguel, Bull. Soc. chim. 1927, *[iv~\,* 41, 1475}. Platinum catalysts are not so effective in bringing about this partial hydrogenation, mixtures of saturated and ethylenic compounds being produced (Paal and Schwartz, Ber. 1918, 51, 640; Salkind *et al.,* J. RUM. Phys. Chem. Soc. 1914, 45, 1875; 1917, 49. 130; Ber. 1933, 66 [BJ, 321; J. Gen. Chem. U.S.S.R. 1933,3,91; 1936,6,1085; 1937,7, 740, 1235). Raney nickel (Dupont, Bull. Soc. chim. 1936, [v], 3, 1030; Campbell and O'Connor, J. Amer. Chem. Soc. 1939, 61, 2897) and the'iron catalyst prepared similarly (Paul and Hilly, Compt. rend. 1938, 206, 608; Thompson and Watt, J. Amer. Chem. Soc. 1940, 62, 2555) are effective catalysts for the semi-hydrogenation of acetylenes. U.S.P. 1920242 describes the partial hydrogenation of vinylacvtylene to butadiene. Bourguel (Compt. rend. 1925, 180, 1753) finds that the hydrogenation of acetylenic compounds with colloidal palladium at low temperatures usually yields the eis-form of the ethylenie product.

Aromatic Nuclei.—The hydrogenation of the benzene nucleus is a more difficult process than that of the ethylenic double-bond; it is beat brought about with a platinum catalyst in acetic acid solution (Willstatter and Hatt, Ber. 1912, 45V 1471; Skita and Meyer, *ibid.* 1912, 45, 3589)7 Adams and Marshall (J. Amer. Chem. Soc. 1928, 50, 1972) give a useful table of the relative rates of hydrogenation of a range of aromatic compounds with Adams' catalyst in iicetic acid. Copper chromite is not effective for the hydrogenation of aromatic nuelej, but benzene and its homologues are hydrogenated over Raney nickel at 120-1757100 atm.;.. the accumulation of phenyl groups renders hydrogenation more difficult (Adkins, Zartman and Cramer, *ibid.* 193), 53, 1425; Zartman and Adkins, *ibid.* 1932, 54, 1668). Benzenoid compounds are also fairly readily hydrogenated by the method of Sabatier and Senderens (Compt. rend. 1901, 132, 210, 566, 1254); in the ease of compounds containing several isolated benzene nuclei it is possible to hydrogenate these successively (Sabatier and Murat, *ibid.* 1912, 154, 1390,1771; 155,385; Godchot, *ibid.* 1908,**147,** 1057). It is interesting to' note that, whereas most diphenyl derivatives can be hydrogenated norfially, certain compounds which are optically active owing to restrict rotation are very resistant to hydrogenation (Waldeland, Zartman and Adkins, J. Amer. Chem. Soc. 1933,55,4234). Wilatatter and King (Ber. 1913, 46, 527), using platinum black, brought about the **hyflrogsnation** of styrene in two stages :

$$PhCH:CH_2 \xrightarrow{+H_2} PhCrVCH_3 \xrightarrow{+3H_2} C_6H_{11}\cdot CH_2\cdot CH_3$$

Sabatier and Senderens (Compt. rend. 1901, 132, 1257) succeeded in hydrogenating naphthalene to tet.rahydronaphthalene (tetralin); Leroui (*ibid.* 1904, **139,** 672), using more drastic conditions, converted this into decahydronaphthaleno (decalin). Using a nickel catalyst at 250°/I20 atm., Ipatiev (Ber. 1907, 40, 1281) brought about the two-stage hydrogenation of naphthalene:

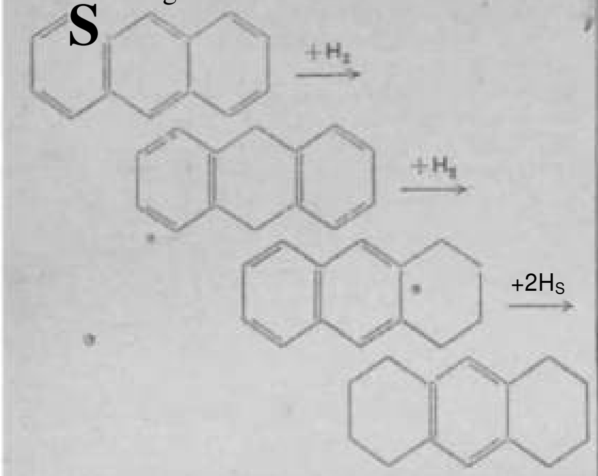


Decalin.

Willstatter and his co-workers made a careful study of the hydrogenation of naphthalene over platinum black in acetic acid; they were able to demonstrate the successive formation of the dihydro-, tetrahydxo- and decahydro-compounds (*ibid.* 1912, 45, 1471; 1913, **46,** 527). Willstatter and Seitz (*ibid.* 1924, 57 [B], 683) showed that the decalin 80 obtained was the pure ciVcompound, whereas nickel at 160° yields chiefly *trans*-decalin. The most important work on the hydrogenation of naphthalene is probably that of Schroeter (Annalen, 1922, **426,** 1) who worked out a method, using a nickel catalyst at 200°/12-15 atm., for the production of tetralin in large quantities. Since naphthalene ie produced as a by-product in quantities greatly in excess of requirements, its hj Irogenation to useful solvents ha3 become of great technical importance (B.P. 147474,147476, 147580, 147747, 172688, 322445; U.S.P. 1733908,1733909; G.P. 299012,324861, 324862, 324863; *cf.* B.P. 304403). Musser and Adkins (J. Amer. Chem. Soc. 1938, 60, 664) find that naphthalene majj be hydrogenated to tetralin over Raney nickel at 100°; with copper chromite a higher temperature (200°) is required, but the reaction stops completely at the tetralin stage. Lush (J.S.C.1.1927,46, 454T) finds that, with a nickel catalyst, valour-phase hydrogenation of naphthalene yields exclusively tetralin, while uecalin is produced in liquid-phase hydrogenation; he suggests that this is due to a difference in orientation at the catalytic surface in the two phases. On the other hand, MaiJlard (Compt. rend. 1933, **197,** 1422) Snds that, in the liquid phase, decalin is produced directly at 20°, whereas tetralin forma an intermediate product at all temperatures above 90*

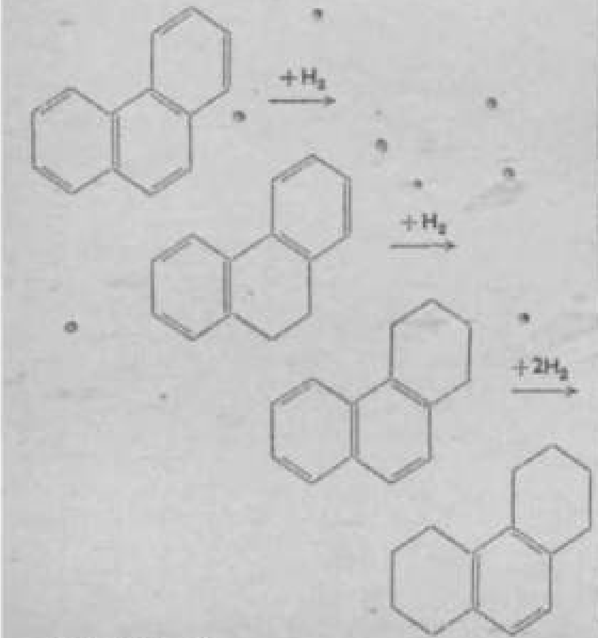
Godchot {Ann. Chim. Phys. 1907, [viii], 12, 468; Bull. Soc. chim. 1907, [iv], 1,724) observed stepwise hydrogenation of anthracene to tctrahjdro-, octahydro- and perhydro-anthracenea in the vapour phase over an active nickel catalyst, and similar results were obtained by pressure hydrogenation (Ipatiev, Jakovlev and Rakitin, Ber. 1908, 41, <mii). s.-liroeter (***ibid,*** 1924, 57 [B], 2003) found that anthracene undergoes hydrogenation with a nickel catalyst at 120-

100°/10-20 atm., to the octahydro-compound in three stages:



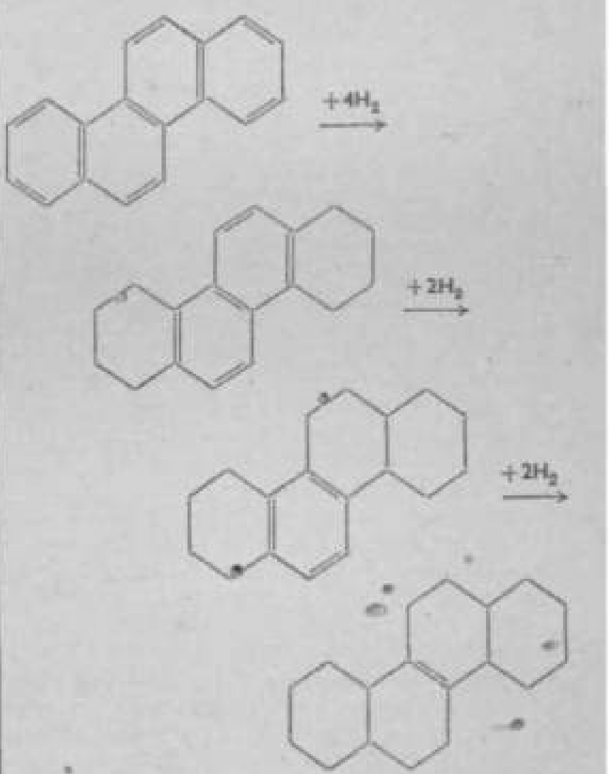
Fries, Schilling and Littmann (*ibid.* 1932, 65 [B], 1494) state that the 1:2:3:4-tetrahydro-compound is formed by two simultaneous reactions, viz. a slow reaction through the 9:10-dihydride and a fast direct reaction. Further hydrogenation yields perhydroanthracene, which is obtained in different stereoisomeric forms according to the catalyst and solvent used. Martin and Hugtsl (Bull. Soc. chim. 1933, [iv], 53, 1500) have, however, brought forward evidence in support of Schroeter's view of the course of the reaction. According to Waterman, Leendertse and Cranendonk (Rec. trav. chim. 1939, **58**, 83) hydrogenation of anthracene over a nickel-kieselguhr catalyst yields first octahydroanthracene and then a mixture of perhydroanthracenes.

The earlier results on the hydrogenation of phenanthrene (Breteau, Compt. rend. 1905, **140**, 942; Schmidt and Metzger, Ber. 1907, 40, 4240; Ipatiev, Jakovlev and Rakitin, *ibid.* 1908, 41, 996; Schmidt and Fischer, *ibid.* 1908, 41, 4252; Padoa and Fabris, Gazzetta, 1909, 39, 333) are somewhat conflicting. It was shown, however, by Schroeter (Ber. 1924, 57 [B], 2025; Schroeter, Müller and Huang, *ibid,* 1929, 62 [B], 645) that the reaction took the following course:



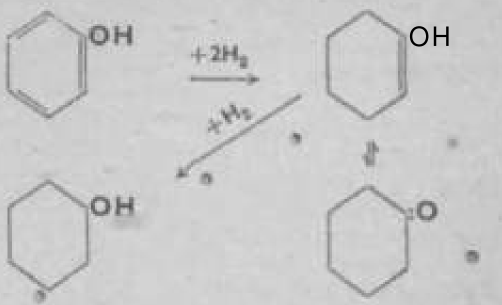
The symmetrical octahydride can be prepared in good yield by this method (van de Kamp and Mosettig, J. Amer. Chem. Soc. 1935, 57, 1107); recently Durland and Adkins (*ibid.* 1937, 59, 135) working with Raney nickel and copper chromite, have shown that, by varying the experimental conditions, considerable amounts of the unsymmetrical octahydride may be obtained. The pure 9:10-dihydride may be prepared in quantity by selective hydrogenation using a special copper chromite catalyst (Burger and Mosettig, *ibid.* 1935, 57, 2731; 1936, 58, 1857).

J. von Braun and Irmisch (Ber. 1932, 65 [B], 883) found that chrysene is hydrogenated over a nickel catalyst in three stages;



These workers were unable to obtain the perhydro-compound, but Spilker (Angew. Chem. 1935, 48, 368) succeeded in preparing this by using specially pure chrysene in decalin solution.

Benzene Derivatives.—According to the conditions, a phenol may be hydrogenated either to the corresponding cyclohexanol or to the cyclohexanone:



The initial formation of the enolic form of the *cyclohexanone* postulated in the above scheme has been substantiated by the work of Grignard and Mingasson (Compt. rend. 1927, **185,** 1552).

In the vapour-phase hydrogenation of pheno over nickel, Sabatier and Senderens {ibid. 1903, 137, 1027) found that the amount of *cyclo*hexanone formed increased with rise of temperature. The mixture formed from phenol by hydrogen&tion at 180° may be converted into pure cycfohexanol by rehydrogenation wit! nickel at 150-170° and into pure cyciohexanon* by dehydrogenation over copper at 330°; homologues behave similarly (Sabatier ant Mailhe, ***ibid.*** I905/-140, 350;' 1000, 142, 553). Willstatter and Hatt (Ber. 1912, 45, 1471), using platinum black in acetic acid, obtained a mixture of ct/dohexanol and cyciohexanone from phenol; however, a convenient laboratory method for the hydrogenation of phenol to cydohexnnol with Adams' catalyst in acetic acic has been described (Adams and Voorhccs, J. Amer. Cheni. Soc. 1922, 44, 1404). Brochet (Compt. rend. 1922, **175,** 583; Bull. Soc. chim. 1922, [ivj, 31, 1270) studied tic pressure hydrogenation of a number of phenols to the corresponding *cyclohex&nols* over nickel. In recenl years cyc/ohexanone (q.t.) ("*Seztone*") and *cyclo*hexanol *(q.v.) ("Sextol*"; "*Hexalin*") and their homologues have become technically important as inexpensive solvents and large quantities are produced by the hydrogenation of phenol and the cresola (UJB.P. 1247629, 1643619; G.P. 444665, 473900). The hydrogenation of polyphenols is not generally very satisfactory (Sabatier and Sendorens, Ann. Chim. Phys. 1905, [viii], 4, 428; Sabatier and Mailhe, Compt. rend. 1908, 146, 1193; Ipatiev and Lougovoy, J. Russ. Phys. Chem. Soc. 1914, 46, 470; Wieland and Wishart, Bur. 1914, 47, 2082; Von Braun, Haensel and Zobel, ,^nnalen, 1928, **462,** 2S3).

a- and /J-NapA'thols on reduction over nickel *«L* 130^e give 85% and 75% respectively of the 1:2:3:4-tctniln uro-derivative and 15% and 25% respectively of the 5:6:7:8-tetrahydro-dfcrivative (Brtichet and Cornubert, Compt, rend. 1921, 172, 1499; Bull. Soc. chim. 1922, [iv], 31, 1280). Schroeter (Annalen, 1922, 426, 83) obtained large amounts of a-tetralone anil of tetralin in the hydrogenation of a-naphthol at 200*; at lower temperatures n-tetralone was the chief product. With j3-naphthol less de-oxygenation was observed (c/. HiickeU *ibid.* 1927, 451, 109). Complete hydrogenation of tho naphthols ields a- and 0-deealols (Leroux, Compt. rend. 1905,141, 953; Ann. Chim. Phys. 1910, JViii], 21, 483; Ipatiiv, Ber. 1907, 40, 1281; G.P. 444665).

Sabatier and Murat (Compt. rend. 1912, 154, 923) wero unable to hydrogenate benzoic acid with nickel at 170-180" but found that benzoic esters were readily converted into the *cyclo*hexane derivative^r. Ipatiev and his co-workers (Ber. 1908, **41,** 1001 ; **19S6,** 59 [B], 306) were able to bring about the smooth hydrogenation of the alkali salts of aromatic acids by using nickel **ondar** pressure. This method *is* to be preferred when the vapour-phase hydrogenation of the ester is accompanied by decarboxylatiorf'; thus, die I hyl phthalate yields carbon dioxide and the esters of phthalie and beuzoic acids, whereas potassium phthalate gives potassium *cych*nex&ne-1:2-dicarboxylatu in good yield (Ipatiev and Philipev, *ibid.* 1908, 41, 1001). Skita and Meyer *(ibid.* 1912, 45, 3589) were able to hydrogenate benzoic acid successfully with colloidal ^alJadium in acetic acid, and Willatatter and Jaquet *(ibid.* 1918, 51, 707) studied the hydrogenation of several aromatic acids with platinum black in acetic acid; the latter authors noticed the interesting fact that hydrogenation was rendered very much more difficult by the presence of even small traces of the acid anhydride. The hydrogenation of ethyl benzoate with Adams' catalyst in efch'yl alcohol has been described by Gray and Marvel (J. Amer. Chem. Soc. 1925, 47, 2799). The presence of a hydroxyl group appears to facilitate the hydrogenation of aromatic acids; thua, Balai, and Srol (Coll. Czech Chem. Comm. 1929, 1, 685; *cf.* Edson, J.S.C.1. 1934, 53, 138T) were able to hydrogenate hydro xy ben zoic acids under very mild conditions.

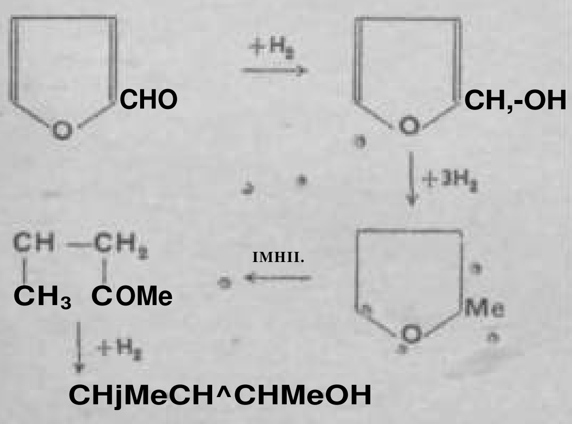
The hydrogenation of aromatic ".mines is complicated by the formation of by-products. Thus Sa bit tier and Senderena .(Compt. rend. 1904, 138, 457, 1257) found that, in the vapour-phase hydrogenation of aniline over nickel, not only was eyc/ohexylamine formed by the normal reaction, but the secondary amines dicyefohexyiamine and cye/ohexylanibne were also produced, ammonia being eliminated. The same side-reactions are observed with other catalysts, *e.g.* nickel under pressure (Ipatiev, Ber. 1908, 41,'991), Wills tatter's platinum black (Willstatter and Hatt, *ibid.* 1912, 45, 1471). This type of side-reaction does not occur **with** *sec-* and (erf-aromatic amines (Sabatier and Senderens, *ibid.* 1904, 138, 1257; Darzens, *ibid.* 1909, 149, 1001). Adam's catalyst has been used successfully in the hydrogenation of anrjnatie amines (Hiers and Adams, *ibid,* 1926, 59 [B], 1B2).

HeterocycMc Compounds.—The hydrogenation of many hetcrocyclic compounds by tho Sabatier-Senderens technique i« unsatisfactory owing to ring-fission, but Darzens (Compt. rend. **1909, 149,** 1001) successfully hydrogenated quinoline over nickel at 160-180° to the 1:2:3:4-tetrahydro-derivative:,

Pressure hydrogenation has also been employed successfully (Von Braun, Petzold and Seemann, Bor. 1922, 65 [B], 3779; Sadikov and Mikhailov, *ibid.* 1928, 61 [B], 421, 1797; **J.O.S.** 1928*438); the nature of the product is de"endent on the nature and position of the aubsti;uents (Von Braun e(ai., Ber. 1923, 56 [B], 1338, 347). Platinised asbestos appears to be a perially useful catalyst for the hydrogenation of pyridine to pipcridinc (Zelinsky and Borisoff, bid. 1924, 57 [B], 150). The hydrogenation of a arge number of pyridine and qitinoline derivaives with colloidal palladium was studied by SkiU and **bit** co-workers ***(ibid.*** 1912, 45, S312, 3579; 1916, 49, 1597; 1924, 57 [B], 977); gum arabic was used as the protective colloid and the presence of acetic acid was advantageous except in the case of pyridine which was best hydrogenated in the presence of hydrochloric acid. Adams' platinum oxide* catalyst is not effective for the hydrogenation of free pyridine, but the hydrochloride is readily hydrogenated in alcoholic solution (Hamilton and Adams, J. Amer. Chem, Soc. 1928, 50, 2260). Using colloidal platinum, quinoline has been hydrogenated to a mixture of stereoisomeric decahydro-compounds :

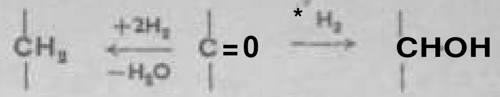
(Hückel and Stepf, Annalen, 1927, **468,** 163; Lehmstedt, Ber. 1927, 60 [B], 1370). Recently, Raney nickel has been found to be an excellent catalyst for the hydrogenation of pyridine and its derivatives (Adkins and Connor, J. Amer. Chem. Soc. 1931, 53, 1091; Adkins Kuick, Farlow and Wojcik, *ibid.* 1934, 56, 2425), substituents in the 2- and 6-positions facilitating the hydrogenation; a special palladised nickel catalyst has also been recommended (Ushakov, Livshitz and Zhdanova, Bull. Soc. chim. 1935, [v], 2, 573). M. De Jong and Wibaut (Rec. trav. chim. 1930, 49, 237) used Adams' catalyst in acetic acid for the hydrogenation of pyrroles to pyrrolidines and observed that substitution facilitated hydrogenation; a similar observation has been made with Raney nickel (Signaigo and Adkins, J. Amer. Chem. Soc. 1936, 58, 709; Rainey and Adkins. *ibid.* 1939, 61, 1104).

The hydrogenation of furfural in the vapour-phase over nickel is a complicated process, the following reactions taking place:



(Padoa and Ponti, Atti R. Accad. Lincei, 1906, 15, (ii), 610; *cf.* F.P. 639756). Scheibler, Hotschick and Friese (Ber. 1924, 57, 1443) attempted to hydrogenate furfural to tetrahydrofurfural; in order to protect the aldehyde group they employed the diethylacetal and the diacetate, of which only the latter gave satisfactory results. Kaufmann and Adams (J. Amer. Chem. Soc. 1923, 45, 3029) found that tetrahydrofurfuryl alcohol was the main product of the hydrogenation of furfural with Adams' catalyst in alcoholic solution; ferric chloride is a marked promoter for this reaction. Tetrahydrofurfuryl alcohol is now made on a large scale for use as a solvent (U.S.P. 1703697). Wienhaus (Ber. 1913, 46, 1927; 1920, 53 [B], 1656) has successfully hydrogenated furan rings with a colloidal palladium catalyst. Pyrones may be smoothly hydrogenated in the nucleus with colloidal palladium or with platinum black (Borsche et al., *ibid.* 1915, 48, 682; 1926, 59 [B], 237).

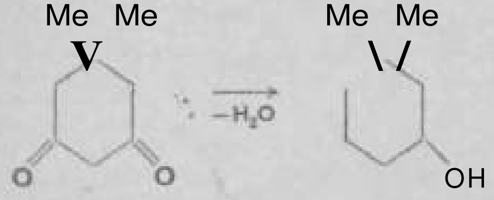
Carbonyl Compounds.—Hydrogenation of a carbonyl compound may yield either an alcohol or a hydrocarbon:



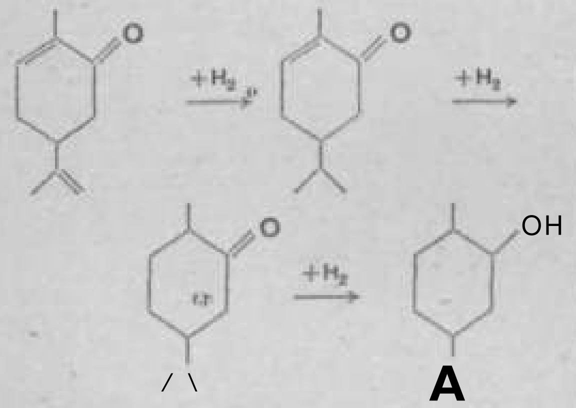
With platinum black, alcohol formation occurs readily with aromatic aldehydes and with cyclic ketones; in other cases the reaction is generally slower. In those cases in which much hydrocarbon tends to be formed (*e.g.* citral, acetone, acetoacetic ester, acetophenone) the use of aqueous alcohol as solvent diminishes the yield of hydrocarbon (Vavon, Compt. rend. 1911, 153, 68; Ann. Chim. 1914, [ix], 1, 148 ; Shriner and Adams, J. Amer. Chem. Soc. 1924, 46, 1683). Faillebin (Ann. Chim. 1925, [x], 4, 156) observed that the presence of traces of iron or aluminium in the platinum catalyst favoured alcohol formation; a promoter action with these metals was observed by Shriner and Adams (J. Amer. Chem. Soc 1923, 45, 2171) and by Carothers and Adams (*ibid.* 1925, 47, 1047). Sabatier and Senderens (Compt. rend. 1903, **137,** 301; *cf.* Amouroux, Bull. Soc. chim, 1910, [iv], 7, 154) found that aliphatic aldehydes and ketones were satisfactorily hydrogenated to alcohols in the vapour-phase over nickel; *cyclopentanones* generally gave considerable amounts of by-product (*cf.* Zelinsky, Ber. 1911, 44, 2779, 2781, 2782; Godchot and Taboury, Compt. rend, 1911, 152, 881; 1913, 156, 470; Bull. Soc. chim. 1913, [iv], 13, 591) but cyclohexanones were reduced normally (Sabatier and Senderens, Ann. Chim. Phys. 1905, [viii], 4, 402; Haller and Martine, Compt. rend. 1905, **140.** 1298). Using nickel under pressure, Ipatiev (Ber. 1907, 40, 1270) found that an equilibrium :

$$RR'CO \underset{-H_2}{\overset{+H_2}{\rightleftharpoons}} RR'CHOH$$

was set up, the same mixture of alcohol and ketone being obtained from either pure component. J. von Braun and Kochendörfer (*ibid,* 1923, 56 [B], 2172), however, applied the Schroeter procedure to a number of carbonyl compounds and achieved smooth formation of alcohols, except with aliphatic aldehydes, which yielded varying amounts of bimolecular *sec*-alcohol (*cf.* Von Braun and Manz, *ibid.* 1934, 67 [B], 1696). Both Raney nickel and copper chromite are good catalysts for the hydrogenation of ketones to alcohols by the Adkins method (Adkins and Cramer, J. Amer. Chem. Soc. 1930, 52, 4349; Adkins and Connor, *ibid.* 1931, 53, 1091; Covert and Adkins, *ibid.* 1932, 54, 4110; Zartman and Adkins, ***ibid.*** 1932, 54, 1668). Delépine and Horeau (Compt. rend. 1935, 201, 1301; 1936, 202, 995; Bull. Soc. chim. 1937, [v], 4, 31) find that the hydrogenation of carbonyl compounds with Raney nickel is facilitated by the addition of alkali; the effect is not due to enotiaation since it is observed **with** benzophenonc. Zelinsky, Packendorff and Chochlowa (Ber, 1935, 68 [B], 98) observed the following curious facile hydrogenntion with platinised charcoal:



In the case of ethylenic ketones hydrogenation frequently takes place in stages. Wallach (Annalon, 1911,381, 51), using colloidal platinum or palladium under mild conditions, found that it was usually possible to hydrogenate the double bond in an unsaturated aldehyde or ketone without affecting the carbonyl group. The hydrogenation of earvone is a particularly interesting example of stepwise hydrogenatibn; it is possible to obtain any one of three products by stopping the hydrogenation at the appropriate point: .,



(Vavon, Compt. rend. 1911, 153, 68; 1912, **154'** 179f>;" Ann. Chim. 1914, [ixj, 1, 148). Similar ^tepwise hydrogenations were carried out by Skita (Ber. 1915, *8,1488,1685), who found it was desirable to modify the conditions in order to obtain the best yield of any desired product.

As a general rule carbonyl groups adjacent to aromatic nuclei are hydrogenated very **readily** to methylene. This reaction has been observed in the vapour-phase over nickel at atmospheric pressure (Darzens, Compt. rend. 1904, **139,** 868; Darzena and Rost, *ifrid.* 1908,148, 933; Sabatier and Murat, *ibid.* 1912, 156, 3S5) and at Jiigh pressures (fpatiev, Ber. 1908, 41, 993) and in solution with, *inter alia,* colloidal platinum (Skita, Ber. 1915, 48, I486), palladiaed charcoal (Harhing **Utd** Crossley, fT. Amor. Chena. Soc. 1934, 56, loS) and palladtsed barium sulphate (Rosenmund and Jorda.., Ber. 1925, 58 [B], 160). Many cases are, however, known in which such earbonyl groups are smoothly hydrogenated to alcohols *(e.g.* benzaldehyde with Adams' catalyst, FaiUebin, Anr. Chirn. 1925, [x], 4, 467). Many attempts have been made to obviate the tendency to hydrocarbon formation; thus the use of certain solvents tends to minimise hydrocarbon formation ; aromatic aldeh3'des yield only the alcoliols in ether, ethyl acetate or alcohol (Vavon, Compt. rend. 1912, 154, 359} and a similar result is obtained with aromatic ketones in aqueous alcohol (Vavon, *ibid.* 1912, **155,** 286). Skita and Brunner (Ber. 1915, 48, 1(585} sought to avoid hydrocarbon formation by using the enol acetate but with little success; Rnsenmund and Jordan (Ber. 1925, 58 [B], 160) were able to obtain 75% yields of alcohols from aromatic aldehydes 1 >y adding quinoline, which acted as a selective poison for the reaction leading to hydrocarbon formation.

Alcohols, Ethers and Oxides.—Smirnov (J. Rura. Phys. Chem. Soc. 1909, 41, 1374) observed that benzyl alcohol and ltd "there yielded toluene on hydrogenation by the Sabatier-Senderens method : •

$$\mathrm{PhCH_2OR} \xrightarrow{H_2} \mathrm{PhMe{+}ROH}$$

whereas other aromatic ethers *(e.g.* aaisole) are smoothly hydrogenated to the corresponding r.i/r/ohexyl ethers (Brunei, Ann. Chim. Phys. 1905, [viii], 6, 205; Sabatier and Senderens, Bull. Soc. .chirn. 1D05. [iiij, 33, 616). This reaction is analogous to the facile dc-oxygenation of carbonyl groups which are a- to an aromatic nucleus. Benzyl ethers readily undergo this " hydrogenolysis " with Raney nickel at 100-I50°/150-250 atm, whereas phenyl **alky]** ethers and dialkyl ethers are resistant under these conditions (Van Duzee and Adkina, J, Amer. Chem. Soc. 1935, 57, 147). Cyclic oxides are hydrogenated to alcohols :

$$\begin{array}{l}\text{—CH}\\ \text{—CH}\end{array}\!\!\big\rangle\text{O} \xrightarrow{+H_2} \begin{array}{l}\text{—CH-OH}\\ \text{—CH}_2\end{array}$$

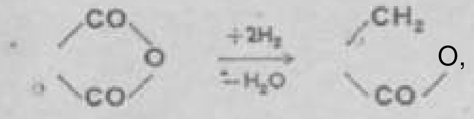
with nickel at room temperature (Weill and Kayser, Bull. Soc. chim. 1936, [v], 3, *HI)* or by the Sabatier-Senderens method (Brunei, Aim. Chim. Phys. 1905, [viii], 6, 237).

Carboxylic Acids and Esters.—Cftrboxyl and carbetboxyl groups are generally little affected by ordinary methods of hydrogenation. In 1931, however, three groups of workers successfully converted esters into primary alcohols:

$$\mathrm{RCO_2R'} \xrightarrow{+2H_2} \mathrm{R{-}CH_2OH{+}R'OH}$$

by hydrogenation at high temperature and pressure (Adkin& and Folkers, J. Amer. Chem. Soc. 1931, 53> Ifi95; Schrauth, Sehenck and Stiokdotn, Ber. 1931. 64 [B], 2051 ; Normann. Z. angew. Chem. 1931,44, 714). Adkins and his co-workers have since made an extensive study of thiflhydrogenolysis; copper ehromite appears to be, the most useful catalyst and a carbethpxyl group adjacent to an aromatic ring is usually reduced to a hydrocarbon since the intermediate product is a benzyl alcohol (Adkins ind Folkers, J. Amer. Chem. Soc. 1932, 54, 1145; Wojcik and Adkins, *ibid.* 1933, 65. 1293, 4939; Adkina, Wojcik and Covert, ***ibid.*** 1933, 55, 1669). Recently, Palfray and Sabetay (Bull. Soc. chim. 1936, [v], 3, 682} have carried **out** the same reaction using nickel at comparatively low pressures.

The anhydrides of monobasic acids yield mixtures of acid, alcohol, aldehyde and ester on hydrogenation by the Sabatier-Senderens niethod (Sabatier and Mailhe, Compt. read. 1907, 145, 18} or with palladium black (Mannich and Nadelmann, Ber. 1930, 63 [B], 796); the latter authors state that acetic anhydride is fairly readily hydrogenated to aeetaldehyde especially in the presence of hydrochloric acid, and it is therefore necessary to exercise caution when using acetic anhydride as a hydrogenation solvent. Dibasic anhydrides, on the'Other hand are smoothly hydrogenated to lactones.



in the vapour-phase over nickel (Eijkmann, Chem. Weekblad, 1907, 4, 191; Godchot, **BuD** Soc, chim. 1907, [iv], 1, 829) or in solution over copper chromite or Ranoy nickel (Austin, Bosquet and Lazier, J. Amer. Chem. Soc 1937, 59, 864); B.P. 290319, however, claims the hydrogenation of succinic anhydride to propionaldehyde and of phthalic anhydride to benxaldehyde.

Nitrites are hydrogenated by most of the known lnethoda to the corresponding primary armne3 i

$$RCN \xrightarrow{+2H_2} RCH_2{\cdot}NH_2$$

but the process is not very satisfactory since, on further reaction secondary and tertiary amines are formed with the elimination of ammonia *(cf.* amines, p. 304e). By the Sabatier-Sendereus method the see-amine is the main product with aliphatic nitriles (Compt. rend. 1905, 140, 482 j Bull. Soc. chim. 1905, [iii], 33, 371) while aromatic nitriles undergo almost complete load of nitrogen, yielding ammonia and tho hydrocarbon; a special 'procedure is neeessary for the hydrogenation of aromatic nitrites to amines (Fn-bault, Compt. rend. 1905, 140, 1036). By working with a nickel catalyst under reduced pressure, Grignard and Eseiturrou *{ibid.* 1925, 180, 1883) were able to arrest the reaction at the aldimine stage:

$$PhCN \xrightarrow{+H_2} PhCH{:}NH$$

At high pressures-^n the liquid phase a mixture of primary and secondary .->mine is formed, production of **primary** amine being favoured by high concentration (Von Braun, Blessing and Zobel, Ber. 1923, 58 *[li],* **1988).** Colloidal platinum (Paal and Gerum, ***ibid.*** **1909,** 42, 1553) and Adams' catalyst alao give rise to mixtures of amines; the reaction has boon studied in some detail from the mechanistic point of view by Rupe anil his co-workers (Helv. Chim. Acta, 1922,5,037; 1923,6,865). Tho use as solvent of acetic acid containing a little hydrochloric acid is said to increase the proportion of primary amine (Rosenmund ami l'fankuch, licr. 1923, 56 [B], 2258) while, by using acetic anhydride as solvent, Carothera and Jones (J. Amer. Chem. Soc. 1925, 47, 3051) obtained the acetyl derivative of the primary amine as the sole product. Succinonitrile ts readily reduced to oS-diaininobutane with a palladium catalyst in alcoholic solution (Strack and Schwanoburfe Ber. 1934, 67[B],39).

Hydrogenation of a mixture of a nitrile and an aldehyde or ketone yields the expected *sec*-amine,

$$RCN + R'R''CO \xrightarrow[-H_2O]{+3H_2} RCH_2NHCHR'R'',$$

(Winann and Adkins, J. Amer. Chem, Soc. 1932, 54 [JJ], 30(>). Tertiary amines may be prepared similarly by hydrogenating. .,' mixture of nitrile and sec-a mine,

$$RCN + R'R''NH \xrightarrow[-NH_3]{+2H} RCH_2.NR'R'',$$

(Kindler and Hesse, Arch. Pharm. 1933, 271, 439). Certain quaternary ammonium salts undergo fission on hydrogenation, *e.g.*

$$\{PhCH{:}CH\text{-}CH_a.NMe_a\}Cl$$

$$\xrightarrow{+H} PhCH{:}CH\text{-}CH_3 + \{NHMe_3\}Cl$$

(Emde, Helv. Chim. Acta, *1932,*15, 1330), *but* the reaction is by no means general (Einde and KulU Arch. Pharm. 19.16, 274, 173).

Oxlmes,.—Like nitriles, oximes yield mixtures of primary and secondary amines on hydrogenation by the Sabatier-Senderens procedure (Maiihe, Compt. rend. 1905, **140,** 1691; 141, 113; Maiihe anil ***Mxupb,*** Bull. Soc. chim. 1911, [iv], 9, 464), with colloidal palladium (Paal and Gerum, Ber. 190!), 42. 1553; Gulevich, *ibid.* 1924, 57 [B], 1645), and with Raney nickel (Winans end Adkins, J. Amer. Chem. Soo. 1933,65, 2051; Paul, Bull. Soc. chim. 1937, [v], 4, 1121). Many methods for avoiding the formation of other tian primary ^mine have been devised; Paul *(Lc.)* found th*t, using Raney nickel at 70-85750-60atm,, ketoximes gave onjy primary amines. Rosenmund and PfankufJi (Ber. 1923, 56 [B], 2258) hydrogenated oxhno acetates and obtained only the aeetyl derivative of the primary amine. Hartung (J, Amer. Chen;, Soc. 1931,53, 2248}, reducing o-oximinoketones in the presence of a palladium catalyct, avoided *sec-* and (erf-base formation by adding hydrochloric acid to the solution, while Schales (Ber. 1935, 68 [B], 1943} avoids the production of #ec-amine by slowly adding the oxime in acetic acid solution to the catalyst (Adams*) in a mixture of acetic and sulphuric acids.

Mignonac (Compt. rend. 1920,170, 936), working with a nickel catalyst at ordinary temperature and pressure, succeeded in arresting the hydrogen a ti on of ketoximes at the ketjmine **itage:**

$$RR'C{:}NOH \xrightarrow[-H_2O]{+H_2} RR'C{:}NH$$

Vavon and *Ma* co-worfeers (Bull. Soc. chim. 1925, [iv], **37,** 296 r **1927,** *[iv],* 41, 357, 677; 1928. [iv], 43, 231) found that, when hydrogenated with platinum black in aqueous alcohol, nwn oxiines yielded the hydroxylaminea:

$$RR'C{:}NOH \xrightarrow{+H_2} RR'CHNHOH$$

Nitro- Compounds.—Aromatic nitro-com-lounds ui solution with platinum and palladium catalysts av. very readily hydrogenated to amines.

$$\mathrm{RNO_2} \xrightarrow[-2H_2O]{+3H_2} \mathrm{RNH_2}$$

(Paal and Aaiberger, Ber. 1905, 38, 1406; Paal and Gerum, ***ibid.*** 1907, 40, 2209; Skita and Meyer, ***ibid.*** 1912, 45, 3579; Vavon and Callier, Bull. Soc. chim. 1927, [iv], 41, 357, 673; Adams, Cohen and Reos,.'. Amer. Chem. Soe. 1927, 49, 1093). Evidence Lie been advanced pointing to the following mechanism for the reaction,

$$\mathrm{RNO_2} \xrightarrow[-H_2O]{+H_2} \mathrm{RNO} \xrightarrow{+H_2}$$

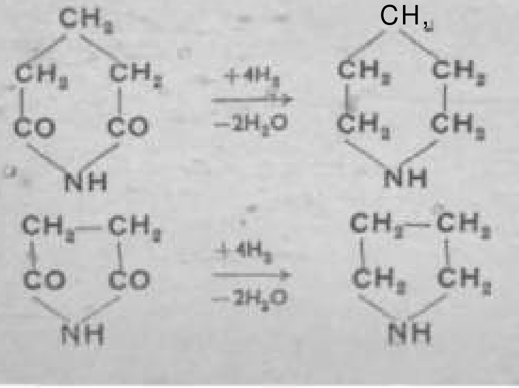
$$\mathrm{RNH{\cdot}OH} \xrightarrow[-H_2O]{+H_2} \mathrm{RNH_2},$$

usmano, Atti R. Accad. Lincei, 1917, 26, ii, 87; Nord, Ber. 1919, 52 [B], 1705). Paal and Hartmann (*ibid.* 1910, 43, 243) recommend a solution of sodium picrate containing colloidal palladium as an absorbent for hydrogen in gas analysis; a recent development of the same idea is the use for this purpose of a suspension of dinitroreeorcinol and a nickel catalyst on kiesclguhr as carrier (Banerjea, Bhatt and Forster, Analyst, 1939, 64, 77). The Sabatier-Senderens process ia unsatisfactory, being usually complicated, by the formation of by-products (Compt. rend. 1901, 133, 321; 1902, 135, 225). The earlier results on the hydrogenation of non-nuclear nitro-compounds are complicated and variable (Sonn and Schellenberg, Ber. 1917, 50, 1513; Kohler and Drake, J. Amer. Chem. Soc. 1923, 45, 1281, 2144), but Johnson and D«gering (*ibid.* 1939,61,3194) have recently reporter', the hydrogenation of aliphatic ritro-compounds to amines in good yield with Raney nickel at 40-5076-110 atm.

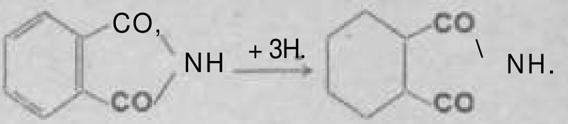
Amides resemble nitrilesin yielding mixtures of primary and secondary amines on hydrogenation by the Sabatier-Sonderena method (MailKe, Bull. Soc. chim. 1906, [iii], 35, 614). Adkins and Wojcik (J. Amer. Chem. Soc. 1934, 56, 247, 2419) found that copper chromite in dioxan. at 175-2007100-300 atm. was the most satisfactory catalyst for the hydrogenation of amides to the corresponding primary amines:

$$\mathrm{RCO{-}NH_2} \xrightarrow[-H_2O]{+2H_2} \mathrm{RCH_2{\cdot}NH_2}.$$

Paden and Adkins (J. Amor, Chem. Soc. 1936, 58, 2487) brought about the hydrogenation of glutariniides to piperidines and of auccinimides to pyrrolidines:



It is remarkable that WifhstiLtter and Jaqt (Ber. 1918, 51, 767) found that, with platinum black in acetic acid, only the aromatic ring in phthiilimidc was attacked:



Other Nitrogen Compounds.—The Sabatier-Senderens hydrogenation of azobenzene and of phcnylhydrazine yields aniline (Bull. Soc, chim. 1»06, [iii], 35,' 259). Whitmore and Revukas (J. Amer. Chem. Soc. 1940. 62, 1(187) have successfulJy used hydrogenation with Raney nickel in dioxan or alcohol for the quantitative fission of azo-dyes. Aldehyde phenylhydrazones are hydrogenated by the Sabatier-Senderens method to aniline and a nitrile (which undergoes further hydrogenation}:

$$\mathrm{RCH{:}NNHPh} \rightarrow \mathrm{RCN{+}NH_2Ph}$$

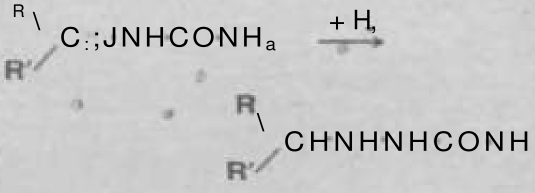
while ketone phenylhydrazones yield aniline and a primary amine:

$$\mathrm{RR'C{:}NNHPh} \xrightarrow{+2H} \mathrm{RR'CH{-}NH_2{+}NH_2Ph}.$$

Unsubstituted hydrazones behave similarly (Mailhe, Compt. rend. 1921, 172, 1107; 1922, 174, 465; Bull. Soc. chim. 1921, [iv], 29, 417; 1922, [iv], 31, 340; 1923, [iv], 33, 83). Azines undergo lisaion to amines on hydrogenation. by the Sabatier-Senderens method {Mailhe, Compt. rend. 1920, **170,** 1120, 1265; 1921, **172,** 692; Bull. Soc. chim. 1920, [iv], **27,** 541; 1921, [iv], 29, 219), but they may readily be hydrogenated to hydrazines with SkJta's colloidal platinum in diMte hydrochloric acid,

$$\mathrm{R_2C{:}N{-}N{:}CR_2} \xrightarrow{+2H_2} \mathrm{R_2CH{-}NH{-}NH{-}CHR_2},$$

(Loehte, Bailey and Noyes, J. Amer. Chem. Soc. 1921, 43, 2597) or with platinum black in acetic acid (Taipale, Bt'r. 1923, 56 [B], 954). With platinum black in acetic acid or alcohol, semicarbazones are hydrogenated to semicarbazides,



$$\mathrm{RR'C{:}NNHCONH_2} \xrightarrow{+H_2} \mathrm{RR'CHNHNHCONH_2},$$

(Taipale and Smirnoff, *ibid, 1923,* 56 *[B], 1194).*

Sctiff's bases are readily hydrogenatcd to,aec-aminea,

$$\mathrm{RCH{:}NR'} \xrightarrow{+H_2} \mathrm{RCH_2NHR'},$$

with nickel in the liquid phase at 170° {Mailhe, BuU. Soc. chim. 1919, [iv], 25, 331; 1921, [iv], 29, 106). Based on this reaction, Mignonac (Compt. rend. 1920, **171,** 1148 ; 1021, **172,** 223 ; Skita and Keil, Ber. 1928, 61 [B], 1452, 1682; Kmerson and Walters, J. Amer. Chem. Soc. 1938, 60, 2023) have developed a method for preparing amines from aldehydes and kotones *hy* hydrogenation in the presence of ammonia or a primary amine:

$$\mathrm{RR'COt\text{-}NH,R''} \xrightarrow[-H_2O]{+H_2} \mathrm{RR'CH{\cdot}NHR''}.$$

In this reaction the amine may be replaced by a nitro-compound (Emeraon and Uraneck, *ibid.* 1941. 63, 749) or an azo-com pound (Emerson, Reed and Merner, ***ibid.* 1841,** 63, 751).

Dehalogenation occurs somewhat readily under hydrogenating conditions, especially with aromatic halogen compounds:

$$\mathrm{R.Hal} \xrightarrow[-H\text{-}Hal]{+H,} \mathrm{RH}.$$

As catalysts for this reaction-there have been used, *inter alia,* palladised calcium carbonate (Busch and Stove, Ber. 1916, 49, 1063), nickel (Kelber, *ibid.* 1917, 50, 305) and platinum black (Swarts, *Ball. Acad.* roy. *Belg.* 1920, 399; J93U, 22, 122; Vavon and Mathieu, Compt. rend. 1938, 206. 1387); it is generally desirable to work in the presence of alkali, to absorb the hydrogen halide formed in the reaction (Ro3en-mimd and Zetzache, Ber. 1918, 51, 578; Paal and Miiller-Lobeck, *ibid.* 1931, 64 [K], 2142).

Kosemund and his co-workera *{Hid.* 1918, 51, 585, 594; 1921, 54 [BJ, 425, 038, 1092, 2888; 1922, 55 [B], 609, 2357; 1923, 56 £B], 1481) have worked out an excellent hydrogenation process for the preparation of aldehydes from acid chlorides:

$$\mathrm{RCOCl} \xrightarrow[-HCl]{+HL} \mathrm{R\text{-}CHO}$$

The catalyst used is palladised barium sulphate and it is advantageous to add a partial poison such as quinoline or " sulphurised " quinoline, in order to prevent further hydrogenation of the aldehyde. Zetzsche and his oo-workers (Helv. Chim. Acta, 1926, 9, 173, 177) have made a very thorough study of the experimental conditions for this reaction.

Bibliography.—Ellis, "'Hydrogenation of Organic Substances," 3rd ed., Routledge, London, 1931 ; Green, " Industrial Catalysis," Benn, London, 1928: Hilditch and Hall, "Catalytic Processes in Applied Chemistry," Chapman and Hull, London, 1937; Maxted} "Catalysis and its Industrial Applications," Churchill, L«ndon, 1933; Sabatier (transl. Reid), "Catalysis in Organic Chemistry," Library Press, London, 1923.

H. N. B.

HYDROGENATION ANALYSIS (Destructive Hydrogenation). This method was introduced by H. ter Meulen *• in 1922, and since that date there have been numerous publications by ita author and also from Belgian, French, German and American laboratories. In outline the method consists in heating the substance in a current of hydrogen and passing the mixed gases over a catalyst. Oxygen, nitrogen, halogens or sulphur respectively are estimated by absorbing H_2O,NH_a,HCI,HBr,HI or H_2S from tho gaseous products, in reagents which are afterwards weighed or titrated,^{3,} 5 **The** method is in general inconvenient for the^imultaneous determination of two or more elements. Mercury,*' " arsenic,*$^{1\ 67}$ cadmium $^{s\&}$ and zinc ^{M} have been determined in organic compounds of these elements by weighing the metallic deposits obtained by destructive distillation in hydrogen. This process has not been studied so closely as the foregoing methods.

Special interest attaches to the direct estimation of oxygen in organic^{1} analysis (Vol. II, **6226}.** The lack of a met'.od as part of tho routine has even Jed to some erroneous formulations" and has been discussed by J. Lindner.^{4344} -The method has been adapted to the semi-micro and the micro scale, the latter especially by A. Lacourt.*^{11} A mierotitrat.ion method for oxygen has been developed independently by Lacourt and by Lindner and Wirth.^{37}

Estimation of Oxygen, *gravimelrkalty {v.* Vol. II, 622*) N,CI,S absent. Since the oxygen in an organic compound can bo completely converted to water by heating in an exceU of itydrogen, and the water absorbed in a iIrving agent and weighed, the method outwardly resembles an ordinary C,H combustion and many precautions of the latter operation may be imitated when oxygen is determined both on the macro and especially on the micro scale.$^{1'}$- ". ». w. «. B3 A]] authors take great care to purify and dry the hydrogen ; opinions differ as to whether the soWce is preferably a cylinder,^{38}- " a Kipp ^{l} or a gas-holder.^{34} A precision adjusting valve is recommended for cylinder hydrogen,^{47} The following three wash bottles contain respectively acid permanganate, alkaline permanganate and silver sulphate. There is some latitude of choice in the selection of tho next apparatus; regjj/ator and flow meter,$^{7,\ 10}$- a7< 37j Xt w preliminary drying tube,^{3}* hard glass or quartz tube for eopjGr gauze or platinised asbestos, cooling spiral immersed in water,^{34} bubble counter*' *$^{B|\ n}$ containing 50% KOH or cone. $HjSO_4$, dfying tubes, of calcium chloride,^{32,4S} magnesium **per**chlorate** (" *Anhydrom* ")$_f$'^{T} magnesium jn'r. chlorate and **P$_s$6j**; soda-aebestos^{S4} {" *Ascarilt*") and soda-lime in a largo U-tubc, one arm of which contains anhydrous $CaSO_d$ (" *Drieriie* "); NaOH pellets followed by $CaSO_4$.^{3S} The final drying^{3}"is with P_2O_0. A Mariotte flask is frequently connected last of all, aa a regulating aspirator when the **weighed** absorption, tubes put on too much back-pressure.. This attachment may render unnecessary the Friedrich'e pressure regulator. The apparatus of Vol. II, 622, Fig. 7, has been improved- The hydrogen is admitted through a side tube. Asbestos is not used as a support for the catalyst or for plugs, ^ilver wool makes satisfactory plugs,^{38}

The connections for dry hydrogen are preferably ground gkss, and covered with Kro'nig's cement,^{37}- * but Hennig^{4}* is content with Pregl rubber connections.^{48} Such precautions are advisable in the micro method but were not adopted in the earlier macro apparatus of ter Meulen,^{4,} ° Gauthier" and Lacourt.^{7} When not in uae the tube is kept filled with hydrogen under a slight pressure. Precautions against hydrogen-air explosions are taken by filling the tube with carbon dioxide before admitting hydrogen. The dry gas should enter the combustion tube through a side tube.[60] The boat containing the substance can then be inserted into the tube without disturbing the hydrogen inlet, while the direction of the gas is reversed by closing the outlet with a ground cap,[49]* [37]» [M] meanwhile increasing the flow of gas to exclude air from the tube.[8] Altering the manipulations affects the blank vrlue of the tube.[34]

The substance to*?)e analysed is weighed into a nickel or platinum' boat and mixed with an excess of reduced nickel, or of activated nickel if halogens are absent. Even in the original form of the apparatus designed by ter Meulen [2] the tube contains two catalysts of different function. That nearest the boat is a decomposition or cracking catalyst maintained at a high temperature, 750-1,100°, in different forms of the apparatus. The second or methanation catalyst, which consists of a preparation of finely divided reduced nickel, is heated to about 350°, here CO and CO_2 react with H_2 to yield CH_4 and H_2O. With pure nickel the conversion is not quite complete, some CO_2 escapes reduction and must be estimated in the usual way in a soda-lime tube, and th'e amount of oxygen it contains added to that calculated from the gain in weight of the $CaCI_2$ tube. The factor $O_2/2H_2O$ is unfavourable compared with those of combustions' for C and H. The rate of liberation of traces of water from the tube or catalysts must be ascertained in blank experiments. In the following summary of the catalysts used in the determination of oxygen, the methanation catalyst is in brackets; reduced nickel is termed nickel: rsbestos (nickel)[3]; nickel wire (njckel-asbestos)[2]; nickel wire (nickel) [M]; pumice (nickel-pumice) [8]» [45]; nickel wire (nickel+10% thoria) ••[7]' •• [37]; nickel gauze (nickel+2% thoria) [32], [34]; nickel chromite (nickel chromite) [36]» [41]; platinised pumice (nicfol+10% thoria) [8]»[9]; platinised quartz {nickeH-10% thoria)[38]; extracted or " desoxide*" nickel chromite (desoxide nickel chromite).[27] Several authors •• [7]» [32]« [a9] state that asbestos should not be used since it is very slowly dehydrated.

Halogens interfere, the hydracids formed reacting with activated nickel [6] and with nickel chromite forming the equivalent weight of water which is absorbed in the drying agent and increases the oxygen figure. Oxygen in compounds containing halogen Js .correctly determined if the ordinary reduced nickel catalyst is used in larger quantity than usual and in two portions, and the small amount of halogen hydride which still escapes is trapped in silver sulphate solution. This is contained in one arm of a U-tube, the other arm being filled with calcium chloride; a second $CaCI_2$ tube and a soda-lime tube are also weighed. The halogen as silver salt is estimated and the oxygen figure obtained from total H_2O and CO_2 is corrected for the oxygen equivalent to the halogen titrated.[3]

Nitrogen would interfere since the ammonia formed would be absorbed in the $CaCI_2$ tube and weighed as water. The error is avoided by absorbing the ammonia in standard acid contained in the lower part of a U-tube, of which the further arm is charged with $CaCI_2$.[3] The ammonia is titrated, and the total oxygen figure corrected by subtracting the oxygen equivalent to the NH_8. If pellets of NaOH are used to absorb water,[33] the ammonia escapes unweighed. Alternatively nickel chromite if used as catalyst[35] does not form NH_3.

Gauthier [8]»[9] who employed pure pumice for a cracking catalyst and nickel-pumice for hydrogenation obtained satisfactory O figures for *i.a.* tartaric acid which latter was an unsolved difficulty to Gopdloe and Frazer.[36] They state that an analysis required about 90 minutes with a weigh-out of 45-135 mg. For picric acid 90 c.c. H_2 per minute were passed, for less difficult substances 30 *c.c.* Their catalyst was prepared from precipitated ammonium nickel chromate.[36]

H. ter Meulen[9] successfully determined oxygen in triphenylmethyl peroxide and cholesterol. The substances were mixed with activated nickel in the boat and the vapours crarked by passage over two 5 g. nickel wire spirals[6] before entering the *activated nickel catalyst* [4] at 350°. This catalyst is prepared by mixing thorium nitrate solution with black nickel oxide in proportions to give $10Ni{:}lThO_2$. The mixture is dried, powdered and reduced in a current of dry H_2 at 350° until ammonia or more than traces of .water are no longer evolved.[6]* [64] Russell and Fulton [32] reduced their nickel catalyst containing 2% thoria for 2-3 days, the blank value of the tube was then 1 mg. H_2O per hour. The cracking catalyst was platinised quartz. The weigh-out was about 0*2 g. and the time 1 hour. Russell and Mark's,[33] and Mark's [36] methods and results were similar.

In court[7] used an activated Ni catalyst heated by an aluminium block [6] bored to hold the tube. A constant temperature between 350° and 400° is necessary, since more H_2O is evolved from the catalyst if the temperature is raised. In Kirner's [34] *micro method* a quartz tube 65 cm. long contained as cracking catalyst a 17 cm. Ni gauze roll, and 14 cm. of $IMi\text{-}ThO_2$ catalyst[38] reduced foi 7 days at 400°. The small errors due to inserting the boat, etc., were determined, but an empirical factor obtained by analysing a pure substance was preferred. Substances with low percentages of oxygen, cholesterol 4-25 (1-14), gave excellent results, but the O found in sucrose was too low. Hennig[46] worked with 3-5 mg. substance. For details, *see also* Hennig and Weygand [46] gas regulator [47] and absorption tubes.[49]

Unterzaucher and Bürger [M] (fig. 1) weigh out 3-6 mg. substance which is vaporised in a current of dry hydrogen, during the decomposition 100 c.c. passing through the tube in 10 minutes. The cracking catalyst is platinised quartz at 1,000°, this is followed by nickel gauze and activated nickel on quartz, at 300°. The absorption tube contains freshly ignited CaO, which does not absorb NH_8. Seven hours are allowed for reduction of the catalyst, the tube is then ready for the blank experiment. The quartz tube is 66 cm. long and 0-7 cm. internal diameter, it contains a silver wool plug, the boat, 16 cm. cracking catalyst, 3 cm. granular CaO, 3 cm.

nickel spiral, 18 cm. hydrogenation catalyst, the layers are separated by Ag piugn. Flaschcntr&ger absorption tubes [4'"] ara used. After a few analyses the deposits of carbon on the catalyst must be burnt off in a current of dry " respiration air." Among the results were: nitroguanidtne 30-49, 30-75,3089 (30-70) and sucrose 51-18(51-44).

Mif.roiitrivwtric Estimation of Oxygen.—In 1937 there were two independent publications of microvolumetric methods for this purpose, by Mile, A. Lacourt *°-[il] and by Lindner and Wirth.[37] Both depend on the reaction of water {ljberated as in the earlier processes) with an Rcyl" chloride, and titration of the HCI formed. In Laeourt's process the gases emerging from the tube pass through 1 c.c. of cinnamoyl chloride'[1] (b.p. 130°/12 mm.) contained in a spiral bubbler [ls] kept at 65-70° by immersion in a bath of half-melted sfcearie acid. The HCI formed is absorbed in slightly alkaline water and titrated in stages in a U-tube fitted with *ci* uiieroburette containing OO.S.V-NaOH. The blank value should not e?ceed 0001 c.c. per minute during an hour's run, when the flow of H_a ia 20 c.c. The time required is about C-7 minutes per mg. of substance. 20 analyses of eueeinie acid gave 0% between 54-20 and 5440 {54-24).. The catalyst is nickel chromite [36] which gives straightforward results with C,H,O,N,S compounds. In presence of halogen, the gases arc passed over a boat containing'Ted-hot lime which retains the halogen while liberating the equivalent of H_2O, which is estimated together with the H_aO from the oxygen present.

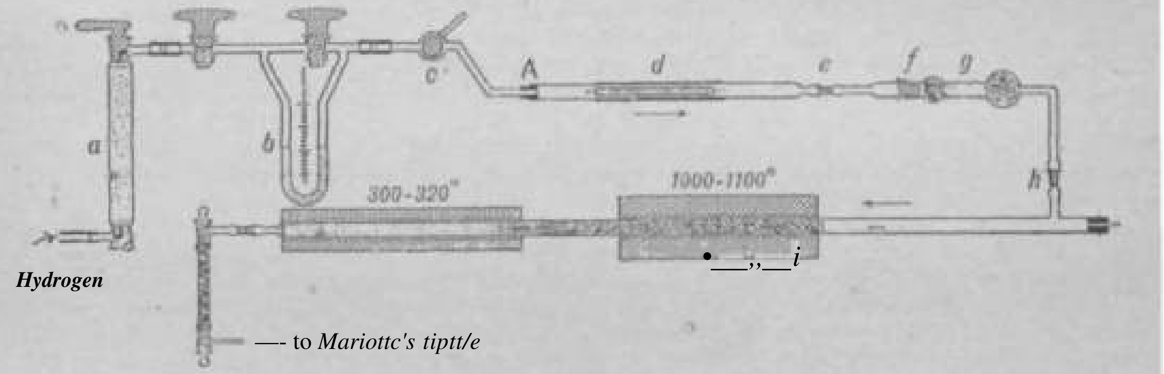


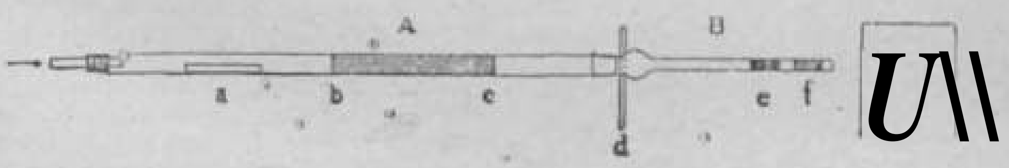
FIG. I.—UNTEBZATJCHER AVD Bt-KQEs's AFPAEATUS.[38]

a. {?. PiOj-pumlce,
e. Tan.
t,J, ft, **Ground glass Joints.**
b, **Fricdrich pressure re«iiliitor.**
d, **Copper spiral (G00°C,).**

Lindner and Wirth[37] describe a two-stage process in which the water is-first absorbed in a layer of lime at 150° while ammonia (if N is present) passes on ; secondly, the linae is ignited to drive off the water which reaches a specially designed reaction vessel** containing a-naphthyloxychlorophosphine kept at 110S The HCI liberated is'absorbed pjid titrated as described in Lacourt's proc*s. For missing details references are given to Lindner's book.[44] Specimen analyses : sucrose 4-381 rag., O 5110% (-0-33), j>-nitraniline, O 23-15% (-003).

For a different method, *see* references 54 and 56.

Estimation of Arsenic, Mercury, Cadmium and Zinc.—Arsenic in organic compounds is liberated when the sample is heated in a current of hydrogen, and is collected and weighed by means of tho apparatus shown in Fig. *I.*



Fio. 2.

A is a transparent quartz tube (45 cm. long) ground into tho smaller quartz tube B, *a* is the porcelain boat containing the substance, *be* is a filling of pure asbestos, *e* is a short roll of platinum foil and / a plug of ignited long-fibre asbestos. A email screen of asbestos card *d* (figured on the right of tho tube) prevents the bulb from being too strongly heated. The red-hot platinum absorbs any traces of arsenic that may escape condensation in the bulb, but gives it up again when heated in air. An estimation is carried out as follows: a well-glazed porcelain boat containing 0-05 to 0-1 g, of substance is placed in the tube through which a current of pure dry hydrogen is*passed at the rate of two bubbles per second. After nil the air is displaced, the asbestos *he* is heated to redness in a small furnace, while the platinum roll *t* is heated by a small Ennsen to dull reduces. The boat *a* is heated with the precautions usual in a combustion analysis for C and H. After about half an hour the deposit of arsenic may be carefully driven over into the weighed tube B. Any organic sublimate in B is washed out with light petroleum before weighing. Among the arsenicals which gave good results by this method were "*Stovarsol*" and cacodylic acid.[57]

Mercury.[51]—The apparatus is very similar to that used for arsenic, except that a weighed U-tube cooled in a water bath acts as the receiver. If the substance contains any halogen element it is mixed with sodium sulphide, and the boat is enclosed in a cylinder of filter paper to protect the quartz tube.

*Cadmium.***—The*, substance is mixed with calcium carbonate h sulphur or halogens are present, and the cadmium is distilled over into a weighed tube.

Zinc[68] compounds when treated in the same way yield a deposit of metal mixed with oxide, which is dissolved in nitric acid, the solution evaporated and the residue ignited and weighed.

Note.—The asbestos layer, which acts as a decomposition catalyst, is heated by a Fletcher gas furnace, or electrically. Ter Meulen and Lacourt however recommend for this purpose Van den Berg's furnace simply constructed by boring a diatomite brick with holes for the tube and for three Bunsen burners.[6* 26* 27]

Estimation Of Sulphur.[1* 4* fl]—A quartz tube 40 cm. long contains a bdkt holding 20-50 mg. of the sample followed by a 20 cm. layer, of platinised asbestos.[1* 3* 4* 6] The air in the tube is displaced by $CO_?$ before admitting a current* of hydrogen which has passed through acid permanganate, alkaline permanganate and silver sulphate solutions but need not be dried. Substances which char, considerably must be mixed in the boat with 0-5 g. platinum black.[60] The absorbent for the H_2S evolved is a 10% solution of zinc sulphate to which aij equal volume of 10% sodium acetate and a drop of acetic acid have been added. This is contained in a U-tube with one wide arm. The analysis is finished by adding an excess of standard iodine and a few c.c. of dilute" HCI to the cool absorbent and titrating with N*,^{S}2°3 (Vol. II, 666). Gauthier[8] used platinised pumice in a hard glass tube for his accurate analyses of sulphonal, thiourea, etc. Alkali sulphonates were heated as usual, allowed to cool, a little HCI added to the residue in the boat and the process repeated. Similarly a second heating with addition of 10 mg. borax was necessary for metallic organic compounds (20 mg. taken) and for coal (50 mg»). Sulphates are mixed with H_3BO_3 before reduction.[61] For' difficult substances, *e.g.*• thianthrene, ter Meulen [6* °] replaced the usual catalyst by two separate spirals of platinum foil; *see also* Lacourt.[7] In Gel'man's *micro method for sulphur* [ll] the vapours from 3-5 mg. of the substance pass with the hydrogen over Pt gauze; *cf.* Lacourt.[10]

Nickel catalysts absorb-S and can not be used here. Pure asbestos at a high temperature, instead of Pt-asbestos or Pt-pumice, has Jbeen^tried.[52] The substance may be heated by an Al block, bored to hold the tube, while the catalyst is conveniently heated in Van den Berg's furnace. Small quantities of sulphur are estimated colorimetrically.[3]

Estimation of Halogens.[29]—A current of hydrogen saturated with ammonia is passed over 50 mg. of the sample which is cautiously heated in an otherwise empty quartz tube heated to redness beyond the boat. A sublimate of ammonium halide forms in the 40 cm. cold part of the tube.[30] When decomposition of the substance is complete *(ca.* 50 min.) the tube is washed out with water, the solution acidified with acetic acid, boiled for a few minutes (to expel any H_2S or HCN present) and the halogen finally estimated gravimetrically (Br, I) or volumetrically (Cl).[4*7] In an improved method [13> 66] the gases pass through a spiral of nickel foil or wire and finally over a boat containing $BaCO_3$, both spiral and boat are heated to redness. The intermediate length of the tube is not heated. Halogen as barium and ammonium salt is estimated as usual. Results differed from those calculated by the following amounts: hexachloroethane, —0-4% Cl; dibromoanthracene, +0*1% Br; iodoform, —0-2% I. Gauthier[8] and Lacourt[7] were equally successful.

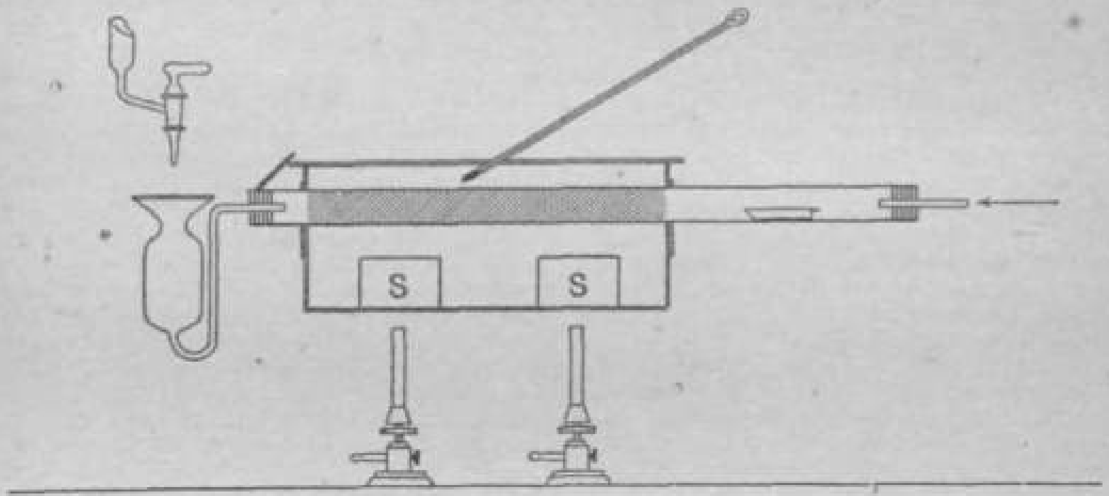
The *micro method for halogens* worked out by Lacourt[10* 27] depends on the properties of a nickel chromite catalyst[32* 33* 35] after prolonged treatment with aqueous and gaseous HCI until free from oxide. The substance, 2-5 mg., is heated in a. current of pure H_2, the vapoura pass over 2 boats of the catalyst, for cracking and for hydrogenation at 450° respectively. The hydrogen •halide formed is titrated after being absorbed in water in a U-tube *{v.* Sulphur) kept just alkaline to Methyl Red by additions of 0-02^-alkali from a microburette.[23] Among the results were: carbon tetrachloride, 2-163 mg., found 92-25% Cl (92-22), time 5 minutes. Pentabromotoluene, 2-751 mg., fo'und 84-62% Br (84-55), 16 minutes. Iodocamphor, 4-952 mg., foii* 45-67% I (45-65), 12 minutes. A new tube is in condition when the escaping hydrogen has no effect on the indicator.[27]

Estimation of Nitrogen.[8* 4* 12]—The svbstance, 10 mg.,[7*10] is mixed with 0-1 g. activated nickel " and heated by an Al block,[6] 9x4x4 cm., bored to hold,J>he hard glass tube; another block, 12x4x4 cm., serves to heat the catalyst (Ni+10% ThO_2 on asbestos) to 350°, or to 250° for hydrazides. A current of purified hydrogen (i>. " Estimation of Sulphur," *supra)* carries the NH_3 forced through a little water contained in the U-tube already described. This water is kept faintly acid uo Methyl Orange by adding OliV-HCI from, a microburette [23] (fig. 3).

Wcygand [1B] recommends asbestos cardboard ovens[3] for heating the tube, nickel reduced from the formate in the tube and *0-05N*-HCI for titrating. A cork connection is avoided by drawing out and bending the outlet end, of the tube. If the sample contains S, Cl, Br or I, 2 cm. of soda-lime is placed before the catalyst.[14* 20] The preparation of the activated catalyst has been described already (p. 360c). Several workers have compared Kjeldahl*s method with ter Meulen's, the latter being preferable except when a large number of analyses must be made daily.[14*16* 21* 25» 31]

Heertjcs [22] analysed 10 mg. samples of trinitro aromatic bodies by mixing 10 mg. with 1 g. of activated Ni in the boat, improving contact by adding a few drops of acetone, Similarly dilute KOH is added to a mixture of protein and catalyst.[a]-[1J] The accuracy of the method is about ±0-2%. Gauthier[8] rouud 14-66% N in antipyrine (calc. 14*89). Activated nickel is essential for difficult substances such as fleroicftrbazides.

The progress of the analysis is followed and regulated by means of ter Meulen'a method of continued titration. When ammonia ceases to be evolved, the bout is heated by the full tlaine of, the burner until decomposition has ceased. Owing to the small volume of absorbent water in the U-tube, U-015 c.c. of O'OliV-aeid causes a change in the indicator, corresponding to about 0-002 mg. N. An analysis requires about 10 minutes. Nickel formate, "• [3B] oxalate *[5] and oxide usually contain nitrogen ; they are reduced in the tube while a titration is carried out as for an analysis until all the nitrogen has been expelled.



S, S = A-shoperf *asbtitos* screens *above holes for the flames, thus* 

Fio. 3.—ESTIMATION OF NITBOQEN.

The references may be classified mainly according to the elements determined :

Oxygen, gravimetric, 2, 3, 4, 10, 27, 32, 33, 34, 35, 36, 38, 39, 45, 46. *Oxygen, volumetric,* 27, 37, 40, 41.

Nitrogen, volumetric, 3, 10, 12, 14, 15, 19, 20, 21, 22.24, 25,31.

Sulphur, volumetric, 1, 3, 4/6, 7, 8, 10, 11, 52.

Halogens, volumetric and *gravimetric,* 3, 13, 14, 29, 30, 55. *Halogens, by direct tUration,* 27.

Arsenic, 3, 4, 7, 67. *Mercury,* 3, 4, 7, 57. *Cadmium,* 7, 58. *Zinc,* 58, „

Jtevkws of the methods, 3, 4, 6, 7, 8, 9, 10, 65. *Monographs,* 3, 5, *Textbook hrtick on nitrogen,* 19. *Nickel catalyst,* 2, 3, 4, 14, *lQ.'Nickel-thoHa catalyst,* 6, 7, 32, 33, 34, 37, 38. *Nickel chromite catalyst,* 27, 28, 35, 40. 41. *Absorption tubes* and *Flow meters,* 16, 17, 18, 19, 23, 48, 49, 62,63. *Furnaces,* 3, 4, 6, 19, 20,32, 62. *Cinnamoyl chloride,* 27, 40, 41, 61. *a-Naphtf\yloxy-chlorophosphine,* 37, 47. *Errors,* 34, 42, 43, 44. *Comparison with Kjddahl's method,* 14, 21, 25. *MicrotilTalions,* 64.

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J. N. G.

HYDROGENATION OF COAL. Coal. compared with oil, is deficient in disposable hydrogen, that is, hydrogen surplus to that required for combination with oxygen, nitrogen and sulphur. It follows that one essential of a complete transformation of bituminous coal to petrol, if such were possible, is to increase the hydrogen content by about 170%, or in the case of lignite, *by* 140%. These figures must, of course, be modified considerably in cither direction with the different varieties of bituminous coals and lignites.

Historical Survey.—The original conception of the hydrogenation of coal to give oil was due to Dr. Friedrich Bergius. His experiments started before the war (1914-18) and ended with a small semi-technical plant at Rheinau, near Mannheim, which was in operation until 1927. After the war, the I.G. Farbeninduetrie started work independently and brought to bear on the problem their knowledge of high pressure technique and of catalysts. *They mode* two important advances—the discovery of catalysts immune to sulphur poisoning and the division of the hydrogenation process into liquid and vapour phase stages.

Developments in Germany then passed wholly into their hands and they built the first commercial hydrogenation plant at Leuna in 1927. This was designed to produce 100,000 tons per year oi' petrol from brown coal, but at first it was operated mostly on low-temperature tar" made from brown coal and on German crude petroleum. Experimental work was alsq done with bituminous coal. The applicability of the process til the petroleum industry was soon rCcognised anda joint company For its exploitation was formed by the I.G. and the Standard Oil Co. (New Jersey).

Meanwhile the original Bergius process had been considered for British conditions, and tests on British coals were made at Rheinau. Research work was inaugurated at the Fuel Research Station of the Department of Scientific and Industrial Research in 1922, and in 1926 an intermediate-scale continuous plant, on the lines of the latest Bergius development, was set up. An agreement was entered into between the British Government and Dr. Bergiue 'or the pooling and mutual discussion of the results obtained in both laboratories, and an option on tho patent rights for the British Empire was secured by the British Bergius Syndicate from the International Bergin Company.

In 1927 Imperial Chemical Industries acquired the British Bergius Syndicate and started independent research on the process. It was decided that the original Bergius method in operation to give a variety of products—petrol, tar acids, heavy oil and pitch, was not profitable, but that it would be attractive if it could be modified to produce petrol as the only liquid product.

In 1929 I.C.I. built at Billingham a pilot plant to treat 10 tons of coal per day, and this plant was run until the end of 1931. None of the practical difficulties which arose were found to be **insuperable,** and in 1930 I.C.I. announced that they could produce a 60% weight yield of petrol from coal, and gave estimated costs which showed that commercial development was possible only with Government assistance.

As the process developed it was realised that many important patents in the hydrogenation field were held by the Standard-I.G. group. Discussions were opened, as a result of which the four major operators in the field—the *I.G.* of Germany, the Standard Oil Co. (New Jersey), the Royal-Dutch-Shell Group and I.C.I.—associated themselves through a pooling company, The International Hydrogenation Patents Company (I.H.P.), in order to pool their patent rights and to effect a general exchange of technical information.

In 1931 the I.G. resumed the hydrogenation of brown coal on a large scale and this now provides a large part of the output of the hydrogenation plants in Germany. Meanwhile, I.C.I. concentrated their research on the treatment of bituminous coal, and by the end of 1932 had prepared schemes for building a large hydrogenation plant at Billingham, which was put in hand in July, 1933, when the Government announced their intention to guarantee the continuance of the preference on light oils made from indigenous materials for a period of years.

The plant, **with** a production capacity of 150,000 tons per year of petrol, was started up early in 1935, and has been in continuous operation hydrogenating coal and creosote oil up to the present time.

Pursuing her policy of home production of essential materials, Germany has, subsequent to the erection of the Billingham plant, constructed a number of bituminous coal hydrogenation units of similar size.

General Theoretical Considerations.—**All** hydrogenation processes consist essentially in subjecting coal to the action of hydrogen at a high temperature and a high pressure.

Three types of reaction are involved. The **first** is the transformation of impure, carbonaceous material to a product of substantially hydrocarbon composition, elements other than carbon and hydrogen being removed by combination with hydrogen. Oxygen thus forms water, nitrogen forms ammonia and sulphur forms hydrogen sulphide.

The second type is the splitting of the " hydrocarbon " molecules to saturated and unsaturated hydrocarbons of lower molecular weight.

The third reaction consists of the saturation of the unsaturated hydrocarbons immediately they are formed.

For satisfactory control of the hydrogenation process it is essential that the second **reaction** should not be allowed to outpace reactions one and three. Otherwise, splitting to hydrocarbon gas and polymerisation of intermediate unsaturated products to coke takes place, with consequent loss in yield of liquid hydrocarbons.

Because the required severity of splitting conditions increases as the size of molecule to be split is decreased, this balancing of the reactions is assisted by dividing the process into stages. In the first stage the conditions may be such that the reduction reaction takes place with maximum efficiency, accompanied by relatively little splitting. This gives rise mainly to a heavy oil product, the approximate composition of which is shown in fig. 1. In the second stage rather more severe splitting conditions are employed, and heavy oil is broken down to give as the main product a middle oil of final boiling-point of the order of **SWC.** This middle oil is sufficiently volatile for **it** to be fairly easily vaporised under the temperature conditions required for the final stage of splitting to petrol. This enables the reaction to be carried out entirely in the vapour phase and in the presence of a high concentration of active solid catalyst.

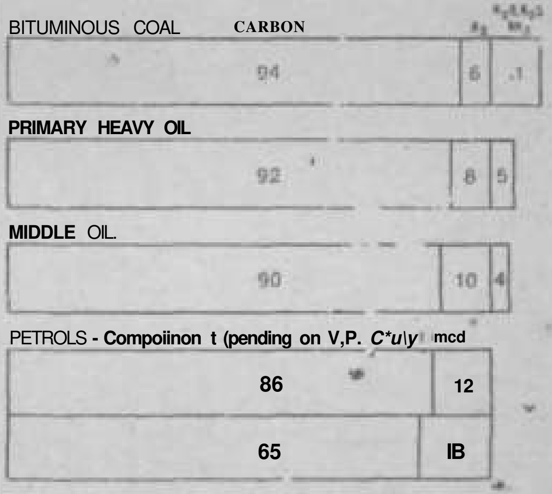


Fig. 1.

In practice, subdivision of the process into two stages—*liquid phase* hydrogenation of coal to middle oil and *vapour phase* treatment of middle oil over solid catalyst—has been found to be essential for production of good quality petrol in economic yield. The use of two liquid phase stages, although advantageous, is probably not worth the additional complications, except in very large plant.

LIQUID PHASE COAL HYDROGENATION.

(a) Plant.—The preliminary Bergius experiments were carried out in two-litre steel autoclaves arranged to rotate over a row of gas burners. The autoclaves were fitted with a pressure gauge and a thermo-couple pocket,

This type of apparatus utilises the batch principle. Coal or coal paste is placed in the autoclave, which is closed and hydrogen admitted to a pressure of about 100 atm. The converter ia then heated to a temperature of approximately 450°C, the pressure rising to about 250-atm., and is maintained at this temperature for about two hours. The apparatus is then cooled, and the gas let down to a holder for analysis. The liquid product remaining in the autoclave ia subjected to analysis to determine the extent of conversion of the coal and the character of the oil product.

The apparatus *I* as been studiously copied by later investigator^ in order to study the chemistry of the i. action and the effect of ciifltiysts.

Tii'/ larger continuous type of apparatus used by Bergius and later by the Fuel Research StatIon is shown in fig. 2. Coal made into a paste with recycle oil from the hydrogenation reaction is forced into the converter system by pump (A). From the pump the paste, which is kept agitated by mechanical stirrers, passes successively through three converters, C, D and E, which are surrounded by baths of molten lead, hydrogen of about 90% purity at the same time being pumped in at 200 atm. pressure by means of a four-stage compressor B. - In this Arrangement the first converter is used mainly as a heating chamber, being brought to a temperature, just short of that necessary for the hydrogenation reaction at 200 atm. The second and third converters are maintained at the temperature which previous experiments have shown to give the best results for the particular type of coal under treatment. On completing its course through the converters, which takes about two hours, the hydrogenated product and surplus hydrogen are cooled in the condensers F and are then passed throi'gh a reducing valve G which lowers their pressure to 60 atm. They are then allowed to separate in the separator H. From H the gas is taken to a scrubber I, where, still at a pressure of 60 atm., it is scrubbed with oil for recovery of the light spirit. At intervals of approximately an hour the liquids remaining in the separator H are blown down to the atmospheric separator K, when further gas is given off which is passed to the gasholder. The liquid product, which consults of a mobile oil, is periodically run off to storage tanks, either directly or after centrifuging.

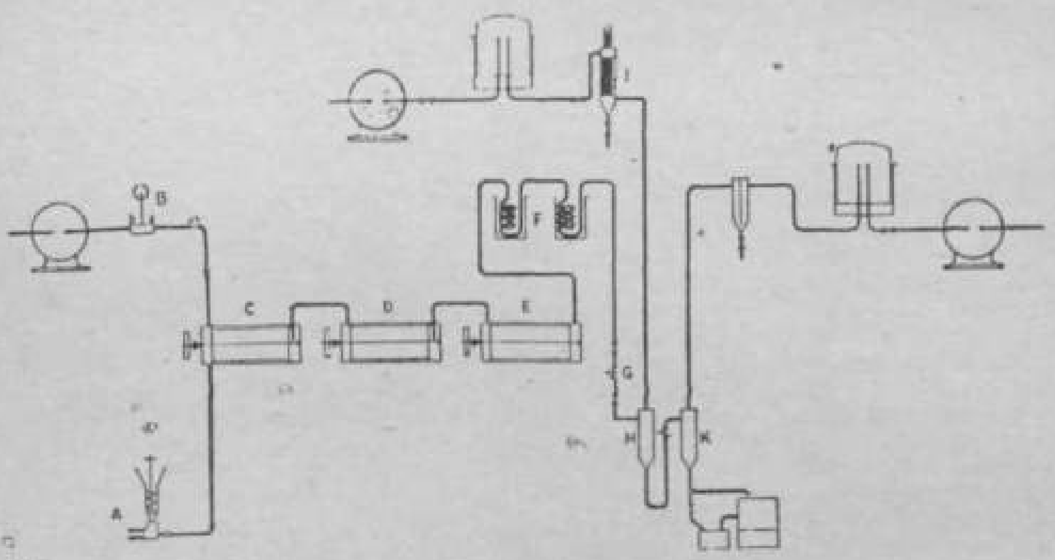


FIG. 2.—EERQIDS HYDBOQENATION PLANT. MEDIUM SCALE, CONTINUOUS PROCESS. ONE TON COAL FEJI DAY,

By 1938 both the I.G. and I.C.I, had independently shown that the process could be mo-e conveniently carried out using a relatively thin coal paste (50% coal) hydrogenated in a simple vertical reaction vessel. Because of the exothermic nature of the reaction, it is unnecessary to heat the conveners externally except in the case of very small experimental plant, and the passage of the hydrogen^ bubble* through the reacting liquid provides sufficient stirring action to expense with the use of mechanical stirrers.

The arrangement of a small semi-technical **plant** based on thw principle is shown Li fig. 3. Coal paste is injected by means of one of two hand-operated accumulators. Thia consists of a steam jacketed steel cylinder in which ia fitted a piston. Coal paste is introduced on the upper side of the piston by means of medium gaa pressure. The filling line is then closed and the paste forced from the accumulator by application of 300 atm. wa^r or gas to the under side of the piston. From the accumulator the paste passes to a preheater coil immersed in a lead batu and, just before entering the preheater, is joined by a stream of high-pressure hydrogen. From the preheater the mixed reactants pass, at a temperature of approximately 420°C, to a converter consisting of a vertical chrome steel tube 26' high and^{c}4" internal diameter. Excessive heat loss from the converter is guarded against by a scries of electric windings. The products from the top of the converter pass to a high-pressure vessel maintained at about 450°C, where products •which are liquid under reaction conditions are separated from those which are vaporised. The liquid contents of the hot separator are let down periodically to atmospheric pressure and the gas and vapours pass through a cooler to a cold high-pressure separator, which ia again let down

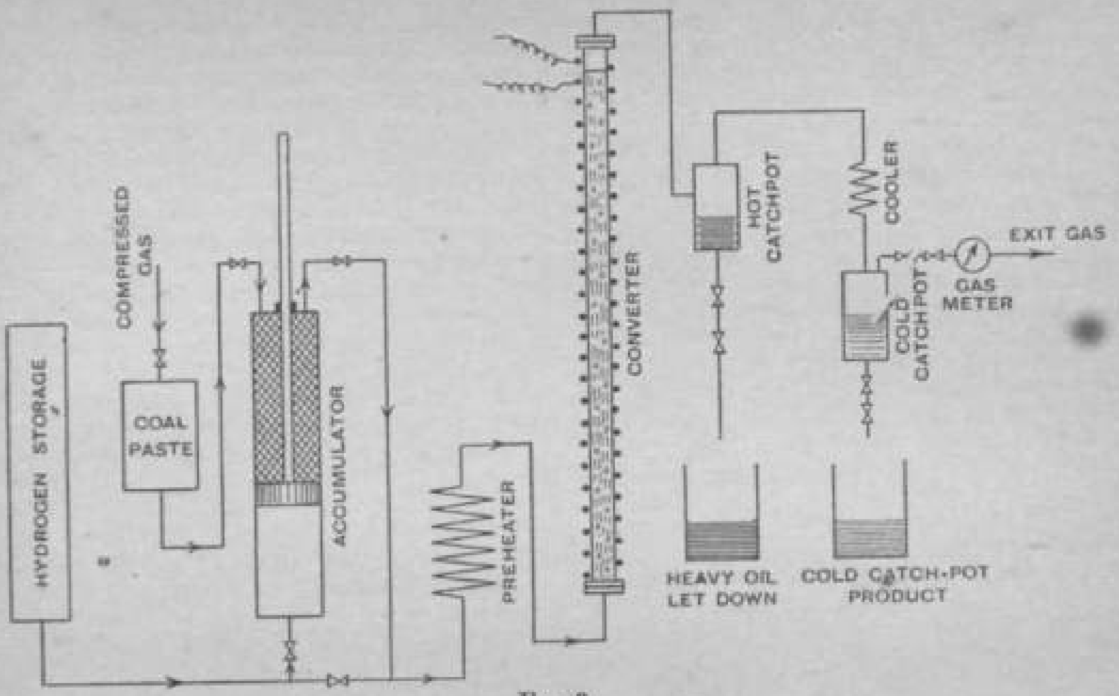


Fig. 3.

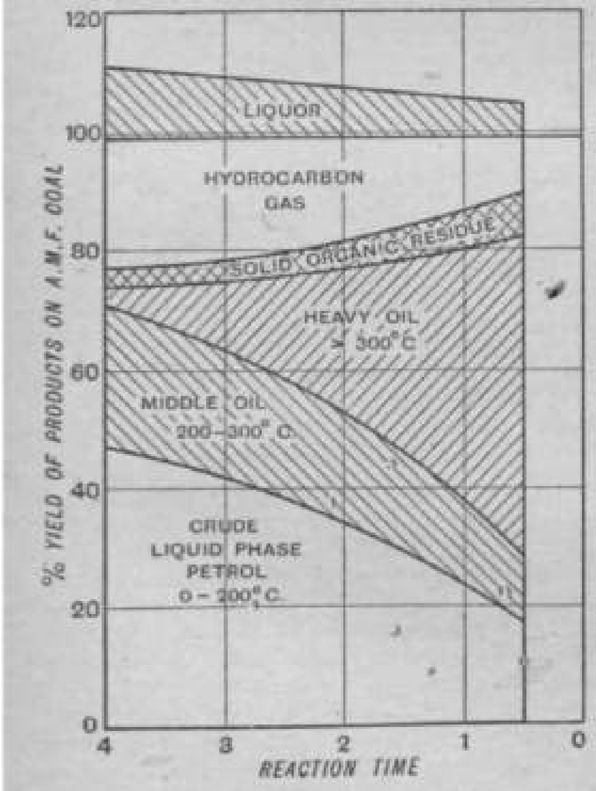


Fig. 4.

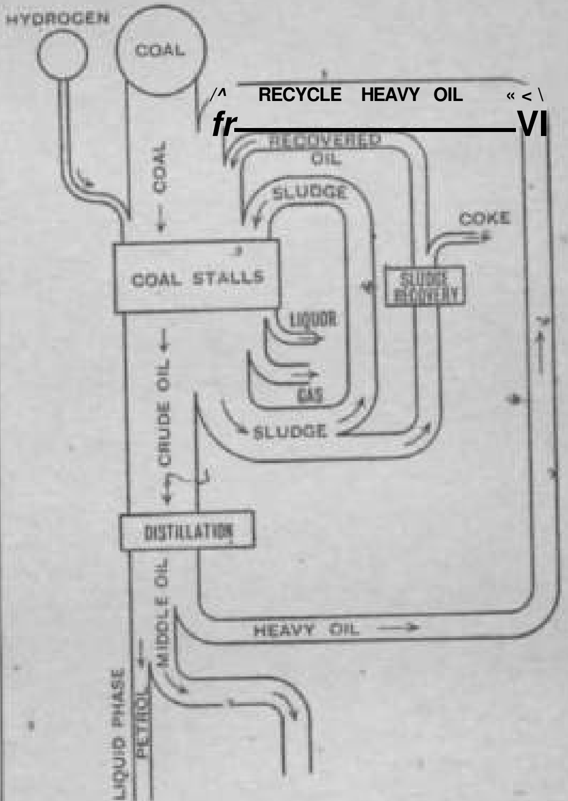


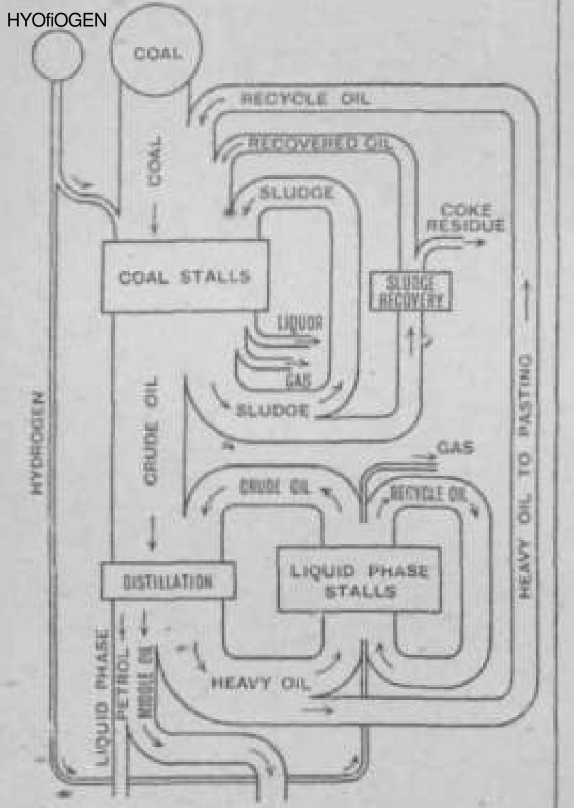
Fig. 5.

periodically. Exit gas is let down to atmospheric pressure, and measured with an ordinary rotary meter.

The heavy oil let down from the hot separator is centrifuged in order to remove ash and unconverted coal, and the filtrate is recycled as pasting oil. The cold catch-pot product is allowed to stand and liquor separated off. It is then fractionated into petrol, middle oil and heavy oil. Part or the whole of the heavy oil is recycled, depending on whether a single or two-stage liquid phase process is being employed. The proportion of heavy oil in the newly formed products can be varied by control of temperature or reaction time in the converters. This control is illustrated by fig. 4, which shows the effect of reaction time on the products of coal hydrogenation. The method of operation with single stage and with 2-stage liquid-phase hydrogenation is shown in figs. 5 and 6.

The large scale adaptation of the vertical converter principle ia shown in Fig. 7. Operation is the same as in the case of the aemi-tcchnical unit, except that the converters have to be cooled by the injection of cold hydrogen, and that heat exchangera are fitted before the prehenter by means of which the ingoing feed is heated by the exit product from the converter.

,*{b)* Catalysts .-^-No catalyst was employed in the original Bergiui experiments. Later it was found advantageous* to use a small quantity of *I masse.*



Fia. 6.

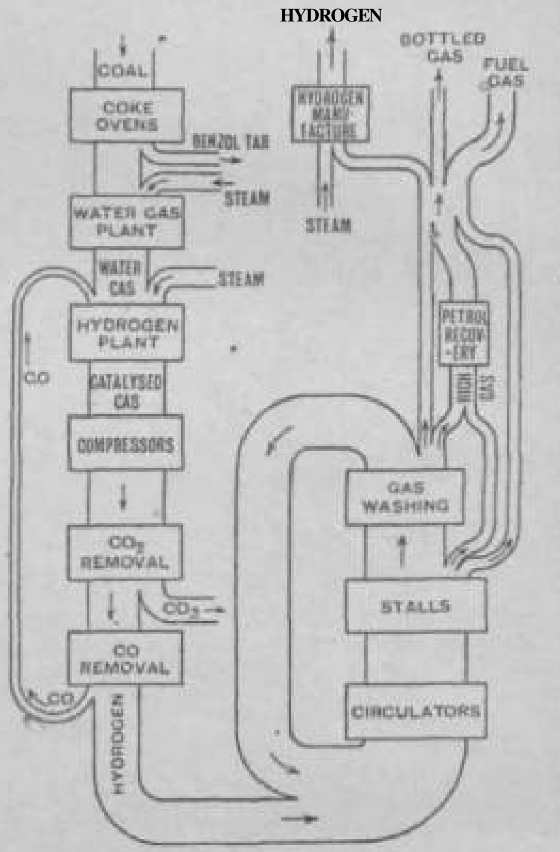
In 1929 I.C.I. found that tin was the most promising catalyst for bituminous-coal liquefaction. It was first used in the form of grids of tinned iron fixed inside the converters. Later, continuous injection with the coal paste of a, very small amount of certain organic compounds of tin was found to be preferable.

This superiority of tin compounds as catalyst for coal liquefaction was also demonstrated Uy experiments carried out by the Fuel .Research, Board and published in the Annual Report for 1932 *{see* Table I).

Alkalis have a deleterious effect on the coal liquefaction reaction. A large proportion of the alkaline constituent* of c«l can be removed by efficient coal cleaning, which, in any case, ia obviously beneficial in that it decreases the amount of material which has to be purged from the pro«?»n by oentrifuging.

Hydrogen chloride can advantageously be added to the reaction in order to neutralise any remaining alkali. This introduces corrosion problems on the exit side of the converter flystem, but in J933 a process wa» discovered and patented by I.C.I, for the scrubbing of the exit vapours from the converter with a suspension of alkali in oil at a temperature of about "450°C. This reduces corrosion to a negligible amount.

(c) Quality of Product (from Bituminous Coal).—The petrol fraction obtained by distillation of the crude cold catch-pot product of liquid phase hydrogenation of coal or heavy *oil* can easily be refined by normal petroleum refinery methods. Refined petrol cut to a volatility of 40% at JOO°C. has the following properties:



Ficr. 7.

Specific gravity at 15° . . .	0-740-0745
Initial b.p. . . . . . ^ .	35°C.
90% vol. recover*! at . . .	158°C.
Final kp.	170°C.
Residue . ".	1-0%
Loss.	1-0%
% distillation+loss at 70°C. .	20%
, ... 100°C. .	40%
„ „ „ 140°C. .	75%
Reid^Vapour pressure at 100°F. ,	9 lba./sq*.- in.
Octane No. C.F.R. motor method	71-73
„ C.F.R. aviation method	—
Colour.	+25 Say bolt
Odour.	Marketable
Sulphur, % by weight . . .	005
Doctor lest.	Negative
A.-S.T.M. copper strip corrosion test.	Negative
Gum, Pyrex dish without air jet (mg./lUOmls.).	2-0

TABLE I.—EFFECT OF CATALYSTS ON THE HYDBOGENATION OF COAL.

1 **Catalyst.**	**Percentage catalyst on coal charged.**	**Product per cent, of** ash-free **dry coal.**			
		Insoluble in chloroform.	**Soluble in chloroform.**	**Water.**	**Gas.**
—	2-5	49-2	27-6	7-1	10-7
Luxmasse	2-5	10-0	66-1	5-!t	8-2
ZnO	2-5	10-2	70-4	5-6^	**7-«**
SnOj.	2-5	7-7	71-2	7-7	6-2
MoO$_a$	2-5	14-1	59-2	7-6	9-3
FfuO,	2-5	27-3	52-4	2-0	8-8
TiO,	2-5	36-9	58-2	7-2	**10-8**
F O T?O	229\ 0-21/	12-0	03-7	6-9	**6-a**
FeC^O	2-5	18-0	50-8	6-2	9-4
V$_2$O$_s$	2-5	49-8	24-7	6B	10-2
Ni<kel%leate	2-5	10-2	07-0	6-3	8-7
Pb(OH)$_2$	**0-1**	*Y1--1*	65-4	7-0	**8-8**
CeO$_2$	0-1	10-5	B2-3	7-9	11-3
SnS	0-1	10-5	03-1	6-3	—
SnS,	0-1	11-6	61-8-	7-8	—
SnfOH),	2-5	til	Hi	7-0	5-8
"	0-5	U-0	70-6	7-9	6-4
"	0-1	10-fi	l>3-4	6-9	8-5
"	0-01	10-ti	IJ4-1'	7-1	6-2
"	**0-0O27**	15-1	58-8	7-2	8-5
"	0-0O067	38-3	**86-5**	7<0	16-fi

The middle oil fraction, which usually has a distillation range of 170-320°C, contains about *8% of* tar acids, the remainder consisting of about 95% of aromatic hydrocarbons. "Without further treatment the ignition properties of this oil are not suitable for its use as a Diesel fuel. It may, however, be saturated to a naphthenic product by vapour phase treatment at low temperature over active catalyst. The product is a reasonably good Diesel oil.

The heavy oil obtained directly from coal is suitable for use as fuel oil without any further treatment,

The products of liquid phase bituminous coal hydrogenation being mainly aromatic, it is unlikely that satisfactory lubricating oil fractiona could be'obtained by direct extraction or fractional um.

LIQUID PHASE HYDBOOENATION OF HEAVY OIL.

When the coal hydrogenation stage is operated under conditions which give heavy oil in excess of that required for recycle as pasting oil, the surplus heavy oil is hydrogenated in a separate plant which is practically identical with that used for coal hydrogenation,

Liquid product from the hot separator, instead of being cooled and let down to atmospheric pressure, is recycled hot and under pressure to the inlet of the prcheater. A comparatively smuJI continuous purge is rimrle from the hot catch-pot to prevent undue .accumulation of solids and heavy asphaltic material. In this way a high concentration of suspended catalyet can, if desired, be built up in the reaction vessel.

The above method for liquid phase heavy oil hydrogenation has been developed to *a considerable extent by the I.G., ..particularly in connection with the hydrogwation of brown coal tar. Supported molybdenum compounds are frequently used as catalyst.

For the hydrogenation of heavy oiia fren from asphaltic constituents the method *m$y* be modified by the use of fixed catalyst such as is used for vapour phase hydrogenation.

Temperature and throughout conditions Vi the heavy oil hydrogenation are controlled so that middle oil rafher than petrol is the main product. The middle oil is further processed in the vapour phase hydrogenation section.

VAPOUB PHASE HYDBOCENATION Of MIDDLE OIL.

(a) Plant,—In general, the plant used for vipour phase hydrogenation is very similar to that used in the liquid phase stage. Middle oil is injected into the plant by means of a pump usually working at a pressure of about 250 atm. It is joined by compressed hydrogen and passes to a preheater where it is completely vaporised at a temf«raturo of the order of 35O-4O0°C The mixed vapour and hydrogen passes to a converter, which ia packed with solid catalyst pellets, and operates at a. reaction temperature varying between 350° and 550"C, depending on the nature of the catalyst employed.

On the large scale the catalyst is arranged in bed*), between which cold hydrogen can be admitted in order to give control of the highly exothermic reaction. The vapour phase nature of the reaction allows the hot catch-pot to be dispensed with, and the outgoing products pass to a cooler after exchanging part of their heat with the ingoing reactants. After the cooler, condensed liquid product is collected in a. high-pressure separator, which is let down periodically. The product, which usually contains about 60-70% of petrol, is distilled to give petrol and a residual middle oil fraction, which is recycled to the reaction.

Apart from a simple washing of product to remove hydrogen sulphide and ammonia, petrol from vapour phase operation requires no refining treatment.

(b) Catalysts.—A range of catalysts satisfactory for the vapour phase hydrogenation of middle oils is known. At one end of the range these catalysts have a relatively high splitting and poor saturation activity, and these give rise to petrols of high aromatic content. Such catalysts require a comparatively high reaction temperature (about fiOO^C.) and, as a result, gas-make tends to be fairly high. At the other end of the range are catalysts of very marked saturation activity, which operate at lower temperatures (about 400°C.) and give high yields of petrol of low aromatic content.

TABLB II.

Constituent.	Vajiour phase petrol. (Fercenttige vol. total petrol.)		
	Group I.	Group II.	Group III.
Butane . . v .	0	5	5
isoParaffins (mainly single branch) .	5	28	30
Aromatics . . .	43	3	7
Unsaturated hydrocarbons . . .	3	—	—
Naphthenes boiling above110°C. . .	18	25	28
Straight chain paraffins -. . .	11	14	4
Octane No. unleaded (C.F.R. motor method) .	80	68-88	75-86
Octane No. with 4 c.c. T.EX./gallon {C.F.R. motor method) . . .	86	66-87	89-9C

An important class of catalyst has recently been developed with splitting-saturation activity intermediate between the extremes cited above. These catalysts, in addition to aiding the usual splitting and saturation reactions, also encourage isomerisation of eyefohexanes to substituted cyc&pentane derivatives and give rise to a high ratio of branched to straight chain paraffin lumen.

The yield of petrol obtainable from a substantially hydrocarbon middle oil varies between 80 and 02% by weight, depending on the catalyst employed.

For a more complete description of the control of the vapour phase hydrogenation of middle oils by suitable choice of catalyst, the reader *is* referred to papers by M. Pier of I.G. Farben-Industrie, *see* particularly Trans. Faraday Soe., 1939, 36, 967.

(c) Quality of Products.—Table II gives the composition and properties of petrols cut to 40% volatility at 100°C. obtainable from coal middle oil by vapour phase hydrogenation over the three types of catalyst mentioned above.

It will be observed that petrol from catalysts of Groups II and III, particularly that from Group III catalyst, has a very good lead susceptibility and that its octane number when leaded with 4 c.c. per gallon of lead tetraethyl is well up to the 87 requited by the Air Ministry specification for aviation fuel. Recycle oil, particularly from catalysts of Group II, is a highly saturated naphthenic product free from phenols and bases, and is a reasonably good Diesel fuel, having the following properties:

Sp. er. 15/15	0-8360
Flash point	178°]?. (81-2°C.)
Inst. Pet. Tech.:	
Initial b,p.°C	217-5
10% at	222-5
30% at	227-0
60% at . . . -. . .	2360
00% at	257-0
Final b.p.°C	2830
Total distillate	98-5%
Residue	1-5%
Ash	0-002%
Asphalt	nil
Setting point	below —50°F.

ToC 1 acidity equivalent to 13-5 nig. KOH/100 g. oil.

Inorganic alkalinity equivalent to 1-2 mg. H_BSO_4/100 g. oil.

Viscosity:

32°F. Admiralty viscometer	5-0 sees.
70°F. Redwoou No. 1 . .	33-5 „
I40°F. „ „ * . .	283 „

Carbon	85-94%
Hydrogen	13-46%
Sulphur..	0-08%
Calorific value	10,897 g.-cal.
Ho ore spontaneous ignition temperature	265°C.

The hydrocarbon gases produced in vapour phase hydrogenation of the middle oils are composed largely of butane and propane, which can be transported as liquids and used for lighting, heating or petrol substitutes (u. (JA8. BOTTLE, Vol. V, 480).

HYDROGEN CERCULMIOH AND POEGE OP MTROGEN AND HVDBOCABBON GASES.

On the large scale, the exit gas from the cold i^u-pressure separators of the liquid and vapour phase hydrogenation stalk is recycled to the reaction by means of circulators. Circulating AyclcMgon becomes impure, partly through accumulation of nitrogen from the makeup gas and partly through accumulation of methane, ethane, propane and butane formed in the process. Part of these gases is removed by solution in the products themselves and VJ recovered when the cold catch-pot products are let down to atmospheric pressure. Final control of the purity of the circulating gas is obtained by scrubbing it with oil at full process pressure in a separate plant specially designed for the purpose.

The cold separator product and the oil used for washing circulating gas is usually let down to atmospheric pressure in a number of stages. In this way the least soluble of the gases, such as nitrogen, ethane and methane, are concentrated in the purge obtained on letting down from 250 to say 50 atm. pressure, and can conveniently be used as gaseous fuel. As the pressure is further released, richer gas containing increasingly high concentrations of butane and propane is evolved.

These rich gases are scrubbed with oil for recovery of pentane and low boiling petrol constituents and are the source of pure butane and propane.

HYDROGEN MANUFACTURE.

Hydrogen for hydrogenation is made from coke by first converting it to water gas, which is then treated with steam over a catalyst for conversion of the CO to CO_2. Alternatively H_2 can be made by catalytic reaction of steam with the by-product hydrocarbon gas from the hydrogenation process. This latter process was worked out originally by the I.G. and the Standard Oil Co., which latter firm produce thereby all the hydrogen required for their hydrogenation plant.

The make-up hydrogen for the Billingham hydrogenation plant is made by combination of the two processes, and the flow diagram of the hydrogen production, and treatment of hydrogenation-plant gases at Billingham is shown in fig. 7.

Efficiency of Process.—The yield of petrol from bituminous coal calculated on an ash- and moisture-free basis is of the order of 60% by weight.

A more important figure is the overall coal consumption. In the case of a plant in which all the H_2 requirement is obtained from the by-product hydrocarbon gases using, the methane-steam process, it is estimated that the overall consumption of raw coal would vary from 3-5-4 tons of coal per ton of petrol, the exact figure depending on the ash and moisture content of the coal and its suitability for the process. This corresponds to a thermal efficiency of 40%, which compares favourably with 25% for generation of electric power and 65% for gasification.

In a plant in which the hydrogen is made via coke and water gas, the overall raw coal consumption is approximately 5 tons per ton of petrol, the higher figure being due to the lower efficiency of coke ovens followed by water-gas generators compared with catalytic manufacture of hydrogen from hydrocarbon gases. This is partly compensated for from the financial point of view by the tar, benzol and gas made as carbonisation by-products.

THE HYDROGENATION OF COAL TARS.

Considerable research into the possibility of single stage hydrogenation of crude tars to petrol and light oils has been carried out by the Fuel Research Station of the Department of Scientific and Industrial Research at Greenwich, where a large semi-technical plant has been operated.

Both liquid and vapour phase reactions occur in the same converter, which contains fixed solid catalyst particles. The chief catalysts investigated have been molybdenum supported on charcoal or alumina and pelleted molybdenum sulphide. The disadvantage of the process lies in the slow deterioration of catalyst caused by the presence in the feed of asphaltic and high boiling constituents. Certain of the catalysts can, however, be revivified by periodic treatment with air, and the rate of deterioration can be reduced by employment of high pressures of the order of 400 atm. The deterioration is greatest with tars produced under high temperature carbonisation conditions, and is negligible when distilled tar oils of reasonably low end-point are used as feed.

It was concluded that, although the single stage process may be suitable for certain selected tars of low asphalt content, division of the process into separate liquid phase and vapour phase stages is necessary for treatment of tars in general. Since 1936, work at Greenwich has been concentrated on the liquid phase stage using fairly high concentrations of dispersed catalyst. Low temperature, vertical retort and cannel tars and also shale oil have been studied.

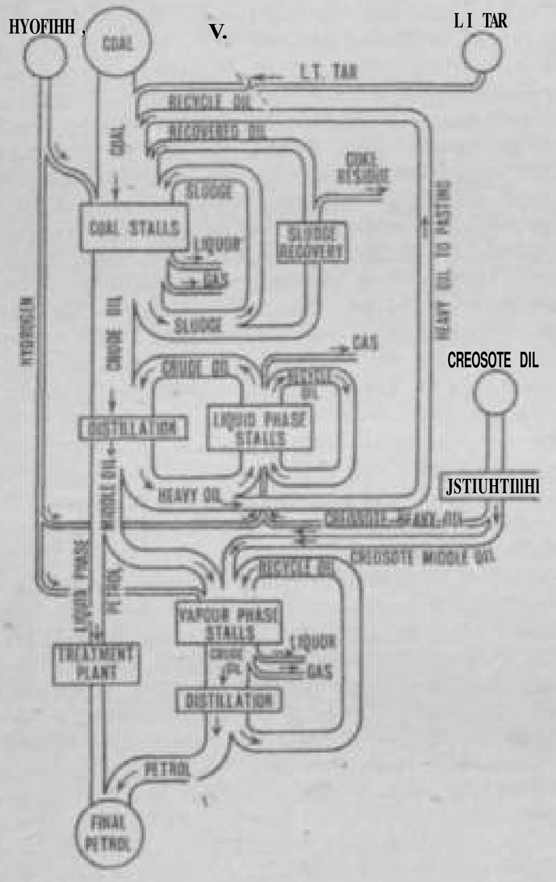
This work is fully described in the Annual Reports of the Fuel Research Board and in a number of publications by the Board's investigators.

Tar, and tar oils are being hydrogenated on a large scale in both Germany and England, using processes controlled by the I.H.P. Group. The exact method of operation varies in different plants, but the process consists essentially of separation of the tar or tar oils into a middle oil fraction suitable for true vapour phase hydrogenation and a heavy residue which is treated under the liquid phase conditions described for the hydrogenation of heavy oil from coal.

Fig. 8 illustrates a satisfactory method for the simultaneous hydrogenation of coal, creosote oil and low temperature tar which has been employed by the I.C.I, at Billingham. In order that solid and heavy asphaltic constituents can be purged from the system along with similar material present in the products of coal hydrogenation, crude low temperature tar is fed to the process as coal-pasting oil. Creosote is distilled to give a middle oil, which is treated in the vapour phase section, and a heavy residue which joins the feed of coal heavy oil to the second liquid phase hydrogenation stage.

Petrol yields from tar and tar oils are stated to be 80-90% by weight, depending on the raw material used.

The quality of hydrogenation products from coal-tar and tar oils depends on the character of the oil and on the type of cat a ly at employed in the vapour phase hydrogenation atep. Using highly aromatic oils, such an creosote and low temperature tar from bituminous coal, petrol obtained with a given vapour phase catalyst has substantially the Bamo properties as that produced by coal hydrogenation.



FIQ. 8.

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R. H.

HYDROGENATION MECHANISM.—The addition of hydrogen to inorganic and especially organic substances is a process of considerable technical importance; leading examples are the transformation of liquid into solid fats, the production of ammonia and the Fischor-Tropsch synthesis of hydiocarbons. Although the addition of hydrogen may be effected in certain cases at high temperatures in the absence of a catalyst, or by means of hydrogen atoms proiuced photo chemically, in general it is carried out through the agency of a catalyst. It is these catalytic reactions which will be discussed here.

THEORIES OF CATALYSIS.

The first observation on the effect of metals in inducing the reaction of hydrogen appears to be that of H. Davy (Phil. Trans. 1817, **107,** 77) who found that a heated platinum spiral placed in a mixture of coal gas and air continued to glow. Somewhat later, Erman (Abb. K. Preuss. Akad. Wiss., 1818-19, 368) showed th(u the combination of oxygen and hydrogen could be induced by platinum at as low a temperature as 50°C. Faraday discussed the mode of action of the catalyst and concluded that it was intimately connected with the forces exerted by the metal on the gases—a view which is still held. Manv theories have been proposed to account for catalytic phenomena. One explanation is that an* increase in the rate of reaction is brought about simply by the increase in concentration caused by condensation on the surface.. This explanation is inadequate, not only on account of the extremely high concentrations which* would be required, but also because it fails to account for the highly specific nature of catalysts and their sensitivity to traces of poisons. Catalysis cannot be interpreted simply as the modification of an already existing reaction inechaniam, but involves the provision by the catalyst of an entirety new path of reaction in which the energies required to effect the steps are less than those required for the uncatalyscd reaction.

Another explanation which has bc*en put forwurd is the intermediate-com pound theory. According to this, reaction takes place through the formation of a compound between one reactant and the catalyst; the other reactant then attacks this compound to form the finul products. The failure in muny cases to isolate these intermediates, together with the somewhat improbable nature of the compounds that in certain instances had to be postulated, caused this theory to fall into disrepute. More recently, however, it has been revived with a more liberal interpretation of the nature of the intermediate compounds. These are now regarded as special surface compounds, not necessarily having an existence independent of the surface. For example, in the adsorption of hydrogen on nickel a surface nickel-hydride is postulated, in which each hydrogen atom is bound to a nickel atom, and the remaining valency forces of the nickel atom are satisfied by its neighbours in and below the surface.

The most important advance in the theory of heterogeneous catalysis is due to Langmuir (J. Amer. Chem. Soc. 1910, 38, 2268) who suggested that reaction occurs in a unimolecular layer of gas adsorbed on the catalyst. The concentration or fraction *6* cf the surface covered by the gas was deduced aa follows. The rate of evaporation of gas from the surface is proportional to the fraction of the surface covered, while the rate of condensation Is proportional to the product of the free surface and the pressure *p* of the gas. At equilibrium these conditions give;

$$\theta = \frac{k_1 p}{k_2 + k_1 p}$$

At low surface concentrations, *8* is proportional to the pressure, while, when the surface is nearly saturated, *8* ie independent of the pressure. The same general considerations, with modiiications, hold if there are two gases. Thus, on this theory, if the rate of the reaction under examination is proportional to the surface concentration of a reactant, then the apparent, order of reaction, as deduced from the dependence of the rate of reaction on the pressure in **tip** gas phase, will vary between unity, when the gas is only slightly adsorbed, and zero, when the gas is strongly adsorbed. In-this way observations of the order of reactioo provide information as to the adsorption of the reactants on the catalyst, and this has been,ₜthe main method used in the elucidation of reaction mechanisms {C. N. Hinslielwood, " Kinetics of Chemical Change in Gaseous Systems," **dareadoa** P., Oxford, 1940. *V.* thia vol., pp. 208-217).

The relationship between adsorp^on and catalytic activity'Ti&s been explored at considerable length (G. M. Schwab, *ti.* by H. S. Taylor and R. Spence, " Catalysis fronijthe Standpoint of Chemical Kinetics," Macmillan, 1937, Chap. 11). The observations of A. F. Benton and T. A. White {J. Amer. Chem. Soc. 1930, 52, 2325) on the adsorption of hydrogen on nickel led to the concept of" activated adsorption ",j(H. S. Taylor, *ibid.* 1931, 53, 578). At low temperatures, adsorption is rapid and does not involve high energies; the adsorbed molecules are not dissociated and are held to the surface by Van der Waals forces. At high temperatures, a slow adsorption occurs, involving a large energy of activation; this type of adsorption is known aa activated adsorption. Taylor regards activated adsorption as being the formation of chemical bonds between ₜthe **catalyst** and the adsorbed molecule (chemisorption) and in general involving the dissociation of the molecule {*e.g.* K. Morikawa, W. S. Benedict and H. S. Taylor, *ibid.* 1636, 58, 1445). He considers that activated adsorption is intimately related to catalysis, and in many cases controls the rate of the catalytic reaction. There is, however, evidence that the phenomena of activated adsorption are more complex than is implied by this view, and may involve, for instance, solution in the bulk of the eatpiyst. *On* charcoal it appears that chemisorption may be a slow activated process, but, on, the other hand, with metals it seems to be instantaneous and to require no energy of activation (J, K. Roberts, Proc. Roy. Soc. 1935, A, 152, 445). The strength with which the chemisorbed layer is held suggests that the picture of catalysis as a two-dimensional gas reaction is incorrect. E. K. Rideal {Proc. Camb, Phil. Soc. 1839, 35, 130) is of opinion that the essential feature of catalysis *in* the interaction between an absorbed molecule held by Van der Waals forces with the chemisorbed layer. This does not imply that the Langniuir-Hinshelwood relationships between gas pressure and order of reaction no longer apply, for these will still apply to ,the Van der Waals layer and even to the chemisorbed layer at high temperatures.

Observations of the kinetics of reactions alone have not proved adequate to unravel the detailed mechanism, an4 more recently new techniques have been developed to deal witJi catalytic reactions. The reconversion of parato ortho-hydrogen has been used as an indicator of the presence on the catalyst of atomic hydrogen (S. R. Craxford, Trans. Faraday Soc. 1939, 35, 940). Reactions involving hydrogen-containing molecules can be^ further investigated by means of deuterium (exchange reactions) (A. Farkas, L. Farkas and E. K. Rideal, Proc. Roy. Soc. 1934, A, **146.** 630; K. Morikawa, W. S. Benedict and H. S. Taylor, *I.e.* and *ibid.* 1790). Several new lines of investigation, into the nature of the catalysing surface and the adsorption of gases on it have been opened up. Among these may be mentioned the use *of electron-diffraction to examine the lattice pattern of the surface (O. Beeck, A. E. Smith and A. Wheeler, Proc. Roy. Soc. 1940, A, **177,** 62), the accommodation coefficient of neon on the surface as a means of studying the adsorbed film of gas (J. K. Roberts, *ibid.* 1932, *A,* **135,** 19:!; 1935, A, 152, 445), the measurement of contact potentials (D. 0. Eley and E. K. Rideal, *ibid.* l»4rj A, **178,** 429), and the study of catalyst poisons i» investigating the question of the uniformity of the surface (E. B. Maxted and H. C. Evans, J.C.S. 1938, 2071).

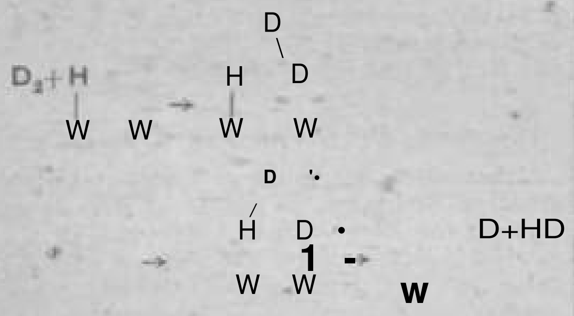
THE OHTHO-PABA "HYDHOIJEN CONVERSION.

Before discussing Actual examples of hydrogenation mechanism, it will be of interest to consider the interaction of hydrogen with the catalyst in the absence of a second type of molecule. Of all catalytic reactions the ortho-para conversion of hydrogen is the simplest (A. Farkas, " Orthohydrogen, Parabydrogen and Heavy Hydrogen," Cambridge University Press, 1335). These two forms of hydrogen differ only in that the atomic nuclei composing

the molecules have parallel spins in the one case and antiparallcl spins in the other case. The **catalytic** intereon version of these two modifications c in tnKp-place by two mechanisms. One of these, the low temperature mechanism, does not. **involve** the separation of the atoms in the molecule. The catalyst used in this type of conversion is generally charcoal, and operates at temperatures **below** about 150°K. The conversion is ascribed to the existence of magnetic **dipoks** on the charcoal surface. The second type of ortho-para cOi'.yersion, **which** in of greater interest in its bearing-on catalytic hydrogenation, takes place **generally** on metallic catalysts and at higher temperatures—room temperature and above—though on specially active catalysts it has been detected at temperatures as low as 77°K. This type of conversion operates through the dissociation of the molecule into atoms. Exactly analogous to this latter reaction is the equilibration of light and heavy hydrogen, $H_2+D_2 \rightleftharpoons 2HD$. The differences between the two reactions are small and are those expected from the greater mass of the heavy hydrogen. In. the original mechanism proposed for these reactions (K. 1*. Bonliooffor and A,. FnrkiiB, Z. physikal. Chem. 1931, B, 12, 231) the hydrogen molecules in their adsorption on the catalyst are dissociated into atoms. These atoms then recombine and evaporate as molecules, the recombination providing a chance for each atom to acquire a now partner. In this way, an equilibrium corresponding to the temperature of the catalyst is produced.

The, validity of this explanation was brought into question by the work of J. K. Roberts (*Proc. Roy. Soc.* 1935, A, **152,** 445) who showed that a clean tungsten surface on exposure to hydrogen is immediately covered with a complete film of the gas, which is present on the surface as atoms, and furthermore that this film shows no detectable sign of evaporation at room temperature. The extreme stability of the adsorbed hydrogen and the high energy required to bring about evaporation militate against the explanation of Bonhoeffer and FarkaH.

According to an alternative explanation suggested by E. K. Rideal (Proc. Camb. Phil. Soc. 1939, 35, 130), conversion (or equilibration) takes place through an interchange between an adsorbed hydrogen atom and a molecule adsorbed above the atomic layer. In the case of the reaction $H_2+D_2 \rightleftharpoons 2HD$ the scheme is as follows:



This **explanation** demands a certain fraction of gaps in the atomic layer; this has been shown to exist, as the surface is bare to the extent of 8% (J. K. llobcrts, *l.c.* p. 404). It will be seen that this mechanism leaves the total amount of hydrogen on the surface unaltered and enables the reaction to proceed with much less **Energy** than would be required for the evaporation of molecules. An experimental proof of this **mechanism** has now been devised (D. D, Eley and E. K. Hideal, Proc. **Roy.** Soc. 1941, A, **178,** -129). Clean tungsten films, prepared by evaporation, were found to bring about the equilibrium $H_2+D_2 \rightleftharpoons 2HD$ in a few minutes at 77°K. A clean film was brought in contact. with deuterium and then thoroughly pumped out at room temperature. After being cooled to 77°K. it was exposed to a low pressure of light hydrogen, when an interchange of light and heavy hydrogen was observed in a time similar to that required for attainment of the equilibration $H_2+D_2 \rightleftharpoons 2HD$. This can only have taken place through such a mechanism as that outlined above. It follows from the mechanism of these reactions that the ortho-para conversion and the equilibration reaction can be used to indicate the presence or absence of atomic hydrogen on a catalyst.

THE HYDROGENATION OF ETHYLENE.

The catalytic addition of hydrogen to substances containing an ethylenic double bond is probably the most important type of hydrogenation. The simplest of these reactions was discovered by ?. Sabatier anil Senderens (Compt. rend. 1897, 124, 1359) who showed that in the presence of nickel, ethylene could be quantitively **hydroganated** to ethane. Later it was found that a number of other metals, notably copper, platinum, cobalt and iron, were effective as catalysts; nickel, however, remains the chief catalyst in practice. Although the hydrogenation of ethylene has been intensively studied since 1897, the mechanism of the process is **still** not completely explained, and it is only of recent years, through the discovery of deuterium, that the necessary means for its elucidation have become available. Earlier attempts were made to find the mechanism by **a** study of kinetics and, the application of Langmuir's theory. Pease (J. Amer. Chem. Soc. 1923, 45, 1196) found that on copper the rate of reaction was proportional to the hydrogen pressure, but decreased as the ethylene pressure increased. From this it was deduced that the hydrogen was weakly adsorbed, whereas the ethylene was so strongly adsorbed that it tended to displace the hydrogen from the surface. Hideal (J.C.S. 1922, **121,** 309), using nickel, found that at high ethylene concentrations the hydrogen displaced the ethylene. Many other investigations have given similar results, and all show that the ethylene is very strongly adsorbed and the hydrogen only weakly adsorbed. Further progress along this line was not possible.

The Exchange Reaction between Ethylene and Deuterium.—A new approach to the problem was opened up by the discovery of A. Farkas, L. Farkas und E. K. liideal (Proc. Roy. Soc. 1934, A, **146, 630)** that when ethylene interacted with deuterium on a nickel catalyst, in addition to the normal hydrogenation,

$$C_2H_4+D_2 \rightarrow C_2H_4D_2,$$

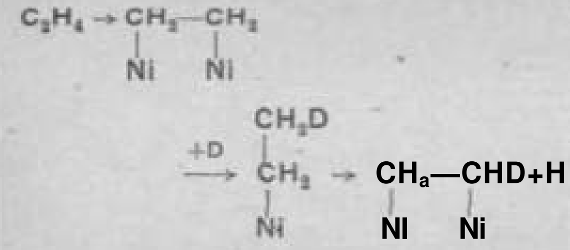
there also occurred an exchange reaction between the deuterium and the light hydrogen of the ethylene; this may be formulated:

$$C_2H_4 + D_2 \rightleftharpoons C_2H_3D + HD.$$

This exchange reaction offered a means of investigating the state of the ethylene adsorbed on the catalyst. Two mechanisms for this reaction are possible:

(1) *Dissociative Mechanism.—In* this, it is supposed *that* on adsorption the ethylene molecule is split up into a hydrogen atom and a C_2H_3 fragment, and the deuterium is dissociated into atoms. Exchange takes place through the addition of one of these deuterium atoms to a C_2H_3 fragment, and the consequent desorption of a substituted ethylene molecule.

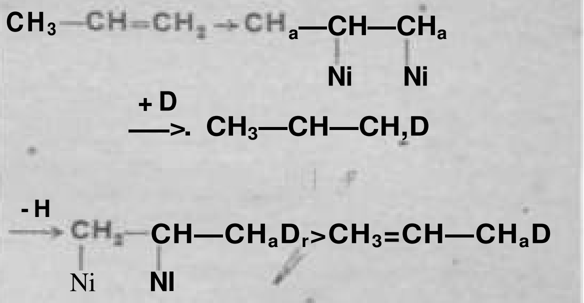
2. *Associative. Mechanism.*—Assuming this mechanism (I. Horiuti and M. Polanyi, Trans. Faraday Soc. 1934, 30, 1164) to operate then ethylene is adsorbed on the catalyst by the opening of the double bond and attachment of the molecule to two nickel atoms. A deuterium atom then adds on to give, a nickel-ethyl radical which breaks up to reform an adsorbed ethylene molecule and liberates a light hydrogen atom. This mechanism can be represented as follows:



$$C_2H_4 \rightarrow \underset{Ni}{CH_2}{-}\underset{Ni}{CH_2} \xrightarrow{+D} \underset{Ni}{\overset{CH_2D}{CH_2}} \rightarrow \underset{Ni}{CH_2}{-}\underset{Ni}{CHD} + H$$

The balance of the evidence suggests that this second mechanism is the correct one. The low temperatures at which exchange between ethylene and deuterium occurs are in contrast to the high temperatures required for exchange with ethane, which can only proceed through a dissociative mechanism. A direct test was made (G. K. T. Conn and G. H. Twigg, Proc. Roy. Soc. 1939, A, **171,** 70) by examining the possibility of exchange between light ethylene (C_2H_4) and heavy ethylene (C_2D_4) in the absence of hydrogen. On the dissociative mechanism, the ethylenes should on adsorption be broken down into C_2H_3 and C_2D_3 fragments, and hydrogen and deuterium atoms; on recombination and evaporation, exchange should occur with the formation of compounds of the type C_2H_3D, $C_2H_2D_2$, etc. Analysis, effected by means of the infra-red absorption spectra of the ethylenes, showed no exchange.

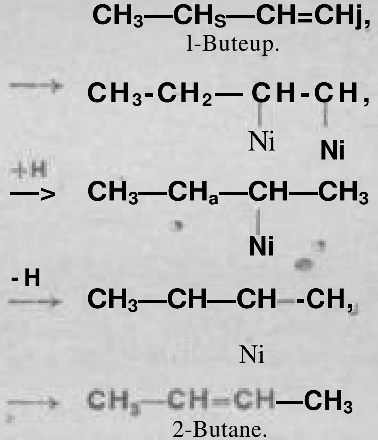
Further evidence in favour of the associative mechanism was obtained by examination of the exchange reactions of the higher olefins (G. H. Twigg, Trans. Faraday Soc. 1939, 36, 934). On the dissociative mechanism, one might expect that the hydrogen atoms not immediately attached to the double bond would be no more reactive for exchange than those of ethane. On the associative mechanism, however, all the hydrogen atoms ought to be equally reactive. For example, in the case of propene the associative mechanism gives the following picture:



$$CH_3{-}CH{=}CH_2 \rightarrow CH_3{-}\underset{Ni}{CH}{-}\underset{Ni}{CH_2} \xrightarrow{+D} CH_3{-}CH{-}CH_2D \xrightarrow{-H} \underset{Ni}{CH_2}{-}\underset{Ni}{CH}{-}CH_2D \rightarrow CH_2{=}CH{-}CH_2D$$

In this way a deuterium atom can be introduced into the methyl group. The equivalence of the hydrogen atoms in a number of substituted ethylenes has been demonstrated.

In a similar manner the migration of the double bond, which occurs in higher olefins when they are brought into contact with a catalyst in the presence of hydrogen (G. H. Twigg, Proc. Roy. Soc. 1941, A, **178,** 106), is more readily explicable if one assumes the associative mechanism for exchange. For example, in the case of the isomerisation of 1-butene to 2-butene, the scheme of reaction is:



$$CH_3{-}CH_2{-}CH{=}CH_2$$

1-Butene.

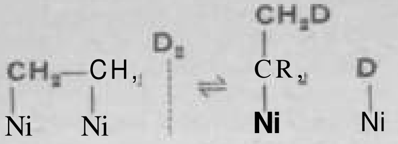
$$\rightarrow CH_3{-}CH_2{-}\underset{Ni}{CH}{-}\underset{Ni}{CH_2} \xrightarrow{+H} CH_3{-}CH_2{-}\underset{Ni}{CH}{-}CH_3 \xrightarrow{-H} CH_3{-}\underset{Ni}{CH}{-}\underset{Ni}{CH}{-}CH_3 \rightarrow CH_3{-}CH{=}CH{-}CH_3$$

2-Butene.

No double bond migration was found in the absence of hydrogen. Other evidence in favour of the associative mechanism for exchange was obtained from a consideration of the energies of activation of the various reactions.

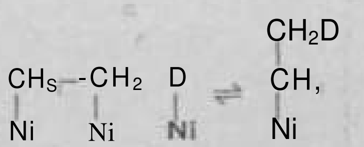
This proof of the mechanism of exchange gave the first clue to the process of adsorption of ethylene on the catalyst surface. Before this is discussed more fully, however, there is the question of the adsorption of the hydrogen to be considered. On an active hydrogenating catalyst, the ortho-para-hydrogen conversion is very fast at room temperature. By using para-hydrogen in the hydrogenation of ethylene, it was shown that the ethylene completely prevented the ortho-para conversion, although a rapid hydrogenation occurred. Similarly, when deuterium was used, the equilibration reaction $H_2 + D_2 \rightleftharpoons 2HD$ was found to be inhibited up to about 140°C. These observations confirm that the ethylene is strongly adsorbed, covering most of the catalyst surface, and also show that there is practically no atomic hydrogen on the surface. The kinetics of the exchange and hydrogenation reactions were studied simultaneously and found to be identical, the rate of reaction in both cases being independent of the ethylene pressure and projwrtional to the first power of the hydrogen or **deuterium** pressure (G. H. Twigg and E, K. llideal, ***ibid.*** 1939, A. 171, 56). It had been expected that since hydrogenation requires two atoms of hydrogen and exchange only one atom, tiic rate of exchange would be proportional to the square root of the hydrogen pressure. Since it was not so, the stow atep in exchange must involve the undissocia:_ed molecule.

To explain ah* these results, it was assumed that the first step in exchange was a reaction involving a deuterium molecule adsorbed in the Van der Waals layer above the chemisorbed ethylcne layer. This can be depicted as:



I.

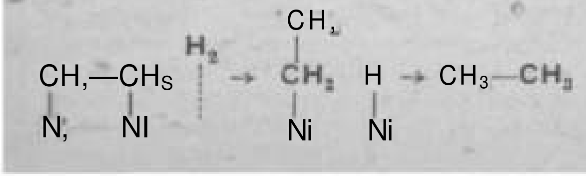
To explain the state of equilibrium of the hydrogen-deuterium mixture during reaction, it is necessary to assume another step, faster than (I):



II.

]\[n this way a Itiirly complete picture of the exchange reaction has been obtained. From the close resemblance in the kinetics of the hydrogenation and exchange reactions, including the fact * thai tho energy of activation for both reactions decreases at high temperatures, it appears that the state of adsorption of the gases *id* the stunu in both reactions. Thnl is. hydrogenation involves the interaction of an undissociated hydrogen molecule adsorbed by Van der Waals forces with an ethylene molecule chemieorbed at two points by opening the double bond.

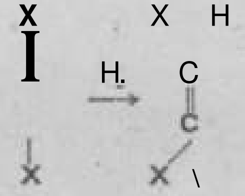
Addition of Hydrogen to the Double Bond and the Acetylenic Triple Bond.—Since exchange proceeds thi :>ugh the associative mechanism, there are two ways in vhicn bydrogenation of ethylene to ethane can be effected. The lirat involves the separate addition of two atoms (I. Horiuti and M. Polanyi, *I.e.).* The first atom adds on to form the intermediate nickel-ethyl complex *as* in the exchange reaction, but instead of tlr's breaking* down to re-form an adsorbed ethylene molecule, a second hydrogen atom may add ?n to it and form ethane, according to the following scheme :



The alternative mechanism for hydrogenatior* does not require tho formation of the nickel-ethyl complex. The hydrogen molecule is-nresumed to add directly to the adsorbed etbykuo without preliminary dissociation.

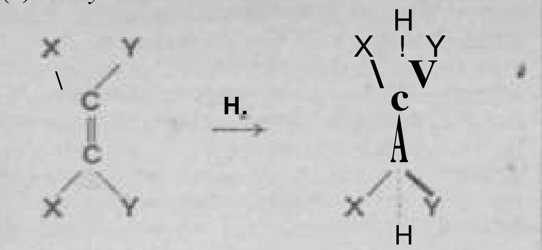
A considerable body of evidence, mostly indirect however, points to the second hypothesis as the true one. The first piece of evidence in favour of molecular addition was put. forward by *G.* Vavon (Bull. Soe. chim. 1927„ \[jv], 41,, 1253) who pointed out that in the-catalytic hydrogenation of conjugated double-bonds no 1:4 addition occurred, -whereas if hydrogenation was effected by nascent hydrogen, addition of two atoms of hydrogen in the 1:4-positions was usually found. The main evidence-for molecular addition, however, rests on the formation of stereochemical isomers by hydrogenation. A comprehensive survey of the literature has been made by A. and L. Farkas (Trans.FaradaySoc 1937,33,837). Theioauthors show that the hypothesis of molecular addition holds not only for ethylenic bonds, but also for aeetylenie triple bonds. It is assumed that if the hydrogen molecu'e add* as a whole without previous dissociation, then addition takes place in the eia-position. The schemes of reaction are as follows:

(1) *Acetylenic Bonds:*

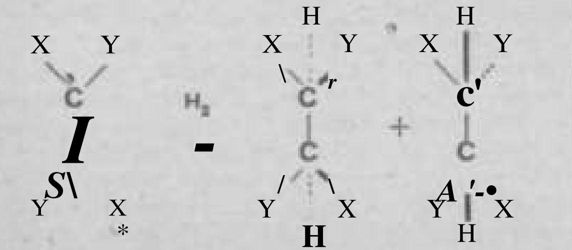


By,*h'⁸ mechanism the addition of a molecule of hydrogen to an acetylenic compound will produce a m-ethylenic derivative. If on *the.* other hand the addition of hydrogen proceeds atom by atom, then both CM- and *trans*-derivatives can be formed, and the product will be the thermodynamically most stable mixture of the two; in general, since *trans*-compounds are usually the more stable, the result of atomic addition will be the *trans*-derivatire. One point has to be noticed, however. There is the possibility of a *cis-trans*-isonierisation taking place on the catalyst in the presence of hydrtgen, by the mechanism discussed* above ^for double-bond migration and exchange. This would tend to cause the attainment of the thermodynamic equilibrium. Since exchange is known to be faster than hydrogenation at high temperatures, this *tis-travs*-isomerisation would be expected to be marked at high temperatures. Thus, if hydrogenation is molecular, the products of reaction ought, in general, to be the ets-ethylenic derivative at low temperatures, and the (rows-derivative at high temperatures or when nascent hydrogen has been used. The observations of A. and L, Farkas support this. For example, tolane on catalytic hydrogenation forms the cis-coinpound i«ostilbcne, whereas with nascent hydrogen it yields stilbene; phenyjpropiolic acid is hydrogenated on a catalyst to tjocinnamic acid, but with nascent hydrogen yields cinnamic acid.

(2) *Elhyhnic Ponds*:



"*-Conjpouiid. **ffifflO-Conipound.**



trani-Com pound. Racemic compound.

In these diagrams the dotted lines indicate bonds below the plane of the paper, and the heavy lines bonds above. From this scheme it is seen that low temperature catalytic hydrogenfttion should yield a racemic mixture from a *irana*-compound, and *n* me«o-eompound from a *cis*-compound, whereas at high temperatures or with nascent hydrogen the most stable form will be produced, which is, in general, the meao-compound. These predictions were confirmed. For example, the catalytic hydrogenation of *cis*- and fmnit-dimethylstilbene yielded the meao- and racemic products respectively. Again, when *ortho*- and yaro-xylene are hydrogenated at room temperature, they yield mainly *cis*-1:2-dimethylcyeiohexane *&nd^cis*-I:4-dimethyleycfohexane respectively; but if the hydrogenation is carried out at 180°c., the *trans*-compounds are produced in both cases (A. Farkas, *ibid.* 1939, 85, 90C).

From these observations, therefore, our present picture of the mechanism of hydrogenation is obtained. The olefin is adsorbed on the catalyst by the open ing Df the double bond and the formation of two nickel-carbon bonds; the hydrogen is adsorbed on top of this film in the molecular state. When the hydrogen piolecule reacts with the Jickel-carbon bond, exchange results (see I, p. 376«), and wien it reacts with the carbon-carbon bond, addition takej place and the saturated compound ia formed.

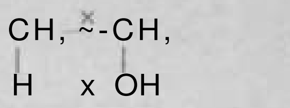
One feature of hydrogenation which is attll obscure is the reduction in the energy of activation which takes place at high temperatures and which may produce a diminution in the rate of reaction with increasing temperature. The most reasonable explanation of this phenomenon is that it is due to desorption or displacement of the olefin from the catalyst by hydrogen (H. zur Strassen, *Z.* physikal. Chem. 1934, A, **16S,** 81), though this does not agree with the observation (Twigg and Rideal, Proc. Boy. Soc. 1939, A, **171,** 65) that the reaction

$$H_2+D_2 \rightleftharpoons 2HD$$

is inhibited at temperatures above those at which the decrease ia energy of activation sets in. A, and L. Farkos (J. Amer. Chem. Soc. 1938 60, 22) have suggested that this decrease is due to an increase with temperature ,in the concentration of the dissociated fragments (C,H_S in the case of ethylene), these fragments not being available for hydroge nation to ethane. If this is so, the energy of activation for exchange should show no decrease with increasing temperature. Twigg and RideaI-(/.c.) have, however, found a decrease for exchange parallel to that for hydrogenation..

CATALYST STRUJSTURE AND TUB CIIEMISOHPTIOJf OF OLEFINS.

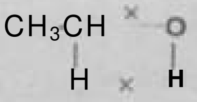
The lattice spacing of the catalyst and the fitting of the adsorbed reactants to the catalyst are of considerable importance in view of the specificity of catalysts and the marked effect of traces of promoters in increasing the rate of reaction. The effect of small alterations of the interatomic distances on the surface has been pointed out by A, Sherman and H. Eyring (J. Amer. Chem. Soc. 1932,64,2661), who calculated tho energy of activation for the adsorption oi hydrogen on charcoal at varying carbon-carbon distances.i They found that with a carbon-carbon distance of 3-GA. the energy was a minimum, but that on either side of this distance the energy required rose rapidly, Tho importance of the way in vhich the reactant is adsorbed was stressed by A, A, Balandin (Z. physikal. Chem. 1929, B, 2, 289) who considered that one catalyst atom could adsorb two atoms or radicals of the renctant, thereby causing these atoms or radicals to combine (the multiplet hypothesis). For example, "certain oxide catalysts cause the simultaneous dehydration and dehydrogenation of Jfleohol. Balandin suggested that when the alcohol wns'adsorbecVas shown :



$$\begin{array}{ccc} CH, & \sim & CH, \\ | & & | \\ H & x & OH \end{array}$$

a

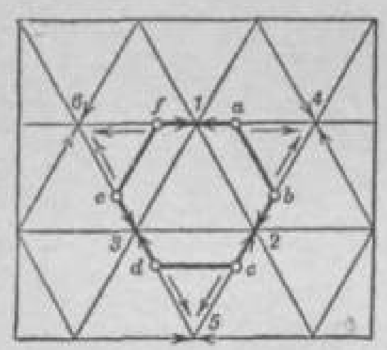
it was dehydrated to ethylene (the crosses represent catalyst atoms). But if it was adsorbed as



$$\begin{array}{ccc} CH_3CH & \times & O \\ | & & | \\ H & \times & H \end{array}$$

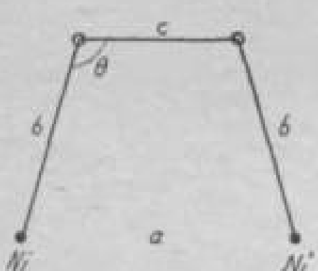
the products were^ aeetaldehyde and hydrogen. This concept was extended further to the dehydrogenation of cyr/cmexane. The **reacting** molecules are presumed to be adsorbed on the hexagonal lattice of. the catalyst (fig. 1). The catalyst atoms 1, 2 and 3 each hold two carbon atoms of the cyc/t^exane, while the atoms 4, 5 and 6 each attract a pair of hydrogen atoms and cause thern'to combine. Siniilarlv in hydrogenation the benzene molecule might be adsorbed in the same manner and the hydrqgen molecules adsorbed on the atoms 4, 5 and 6 would ihen add across the bonds *a—b,* etc.

An important contribution to the question of the effect of the lattice structure of the catalyst on its activity has been made by 0. Beeck, A. E. Smi^h and A. W'heeler (I'roc. Roy, Soc. 1940, A, **177,** 62). Those authors prepared evaporated metal films which had different crystal planes exposed to the gas phase. The crystal structure of these films was investigated by electron diffraction. Two types of nickel ii'hn could bo prepared, one completely oriented with the (110) crystal plane parallel to the surface on which the film was deposited, and the other with a random orientation. The activity of thea^ films was measured by the hydrogonation of ethylene. It was found that the oriented film was 5 times as active as the unoricnted film. Th'^s the {110} plane, the least densely packed piano appears to be morB favourable for hydrogenation than either the (100,) or the (111) plane.



Fio. 1.

Another approach to this problem has been made by *G.* H. Twigg and E, K. Ride&L (Trans. Faraday Soc'. 1940, 36, 533) who made the mechanism for exchange the basis of calculations on the fitting of olefins to the catalyst. When the olefin is chemisorbed on the catalyst, the double bond is. opened and attachment takes place between the two carbon atoms of the double bond and two nickel atoms. The first calculation concerned the fitting of the olefin molecule between the two nickel atoms (fig. 2).



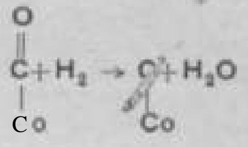
Fro. 2.

There are two nickel-nickel distances in the nickel crystal, the distance of closest packing, 2-47A., and the unj't cell side, 3-50A, The latter waa found to bo' too great to accommodate the olefin molecule as postulated. In fig. 2 an adsorbed ethylene molecule is drawn to scale. The Ni-Ni distance (a) h 247A., the C-C distance (c) is 1-52A., equal to the normal single bond distance, and the Ni-C bond distance *(b)* is assumed to be equal to that in nickel carbonyt, Tho molecule fits very well, the angle *6* being • listorted slightly from the tetrahedral angle 109° 28' to 105^{11}4'. This distortion can be made leas if the C-C axis is made to lie at a small angle to the Nl-NI axil. The effect of promotors on catalytic acth ity may be due to small distortions of the crj stal lattice causing *n* more favourable interatoiiue distance. The interatomic distance appears to be an important factor in determining the activity of the catalyst. In the chemisorption of olefins, as described here, the maximum possible interatomic distance in tho catalyst appears to be about 2-8A., which may explain why those catalysts active in hydrogenation have inteiatomic distances of closest approach between 2*47A. and 2-54A. (Fe, Nj. Co, Cu) and between 2-7*. and 2'8A. (Pt, Pd). In the latter group ihe form of the crystal lattice is important, 011I7 ithose metals having a face-centred cubic lattice being active in hydrogenation.

Another calculation was made on the interaction of neighbouring adsorbed molecules. A plan, drawn to scale, of the nickel surface with adsorbed olefin molecules is shown *in fig. 3. Two cases are shown: A, adsorption on the (UI) plane and B, on the (110) plane. For the ethylene molecule, tho hydrogen atoms have been drawn to scale (full circles). There is slight interaction between neighbouring molecules on the (111) plane, though this is probably insufficient to prevent them covering the whole surface. On the (110) plane there is no interaction, and thus ethylene can cover the whole surface. This ia in agreement with the fact that ethylene inhibits the reaction H_8+D,^=i2HD. The case of the methyl-substituted cthylenes is different, however. The methyl groups are drawn to scale (dotted circles, fig. 3). Here the interaction between neighbouring atoms is quite considerable even on the (110) plane, and these molecules should not be capable of covering the whole Burface. That this is actually so is shown by tho fact that the equilibration H_2 +D_a ^ 2HD still proceeds in the presence of 2-methylpropene or 2-roethyI.2-butene; again, in the hydrogenation of butene, the rate of reaction is not independent of the butene pressure. In this way confirmation of the general picture ot the adsorption of olefins has been obtained. The fitting of the molecule to the catalyst is probably the cause of selective hydrogenation in the case of complex molecules containing more than one double bond.

THE FISCHEH-TKOFSCH SYNTHESIS,

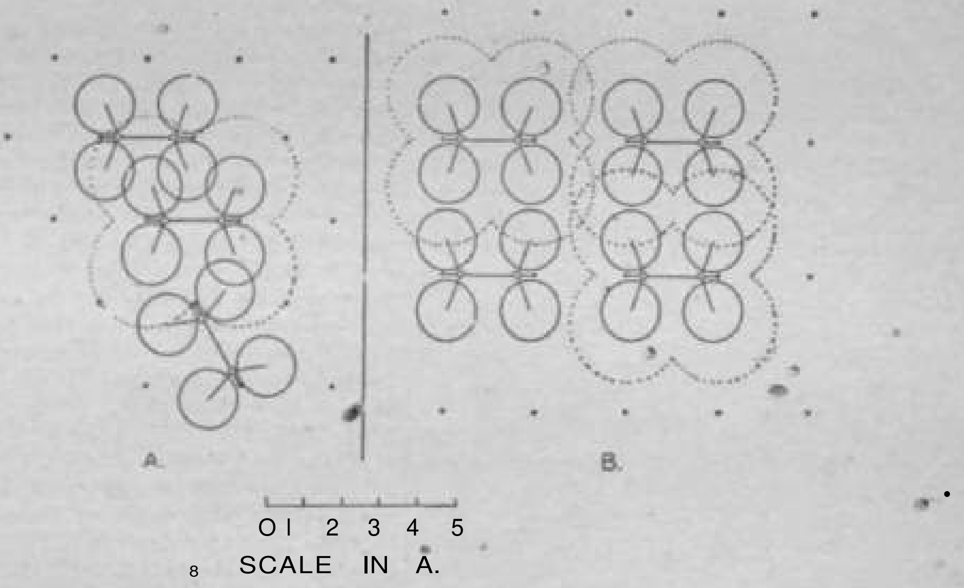
In the field of catalytic hydrogenation, one of the most important reactions is the Fischer-Tropsch synthesis of long chain paraffin and olefin hydrocarbons from carbon monoxide and hydrogen. The type of catalyst used consists of iron, nickel or cobalt with a suitable promoter and support. Investigations into the mechanism of the reaction have been made with a catalyst which consists of cobalt, thoria and kieselguhr in the proportions 100; 18:100; cobalt and thorium carbonate are precipitated on the kieselguhr and reduced in hydrogen at 375°c. (Report of the Fuel Research Board, 1938, 189), The genera] characteristics of the reaction are aa follows (F. Fischer, Ber. 1938, 71 [A], 56). When the synthesis gas, 1 part of carbon monoxide and 2 parts of hydrogen passed over the freshly reduced catalyst at 190°c. and atmospheric pressure, methane and carbon dioxide are formed. After some time the Fischer synthesis seta in and the product* are oil and water. The temperature range over which the oil synthesis occurs is email. Below 175℃. there is no reaction; between 175°c. and 225℃. oil is produced, and above 225°6. the main products are methane and carbon dioxide. At high pressures, oxygen-containing substances^re formed as well as the hydrocarbon oils. Investigations into the mechanism (S. R. Craxford, Trans. Faraday Soc. J939, 35, 94C) show that the reaction takes place through the formation on the catalyst of cobalt carbide. Evidence lor this ia that a used catalyst, when decomposed by hydrochloric acid, yielded a mixture of paraffins and olenns. Measurements of the electrical conductivity of the catalyst during synthesis showed that carbide was being formed in increasing amounts as the synthesis proceeded. Craxford showed that the formation of carbide does not occur through the reaction 2Co+2CO -> COJC+COJ. because this reaction is slower than either the reduction of carbide to methane or the Fischer-Tropsch synthesis; this reaction would thus not allow carbide to accumulate on the catalyst. The reaction postulated for carbide formation is the reduction of a surface carbonyl:



$$\overset{O}{\underset{Co}{C}} + H_2 \rightarrow \underset{Co}{C} + H_2O$$

Evidence for this ia that the oxygon product of the synthesis is water and not carbon dioxide. This water cannot have come from the reaction CO_a4-H_{fi}^$CO+H_aO$ as the equilibrium of this reaction is entirely on the carbon dioxide side at 200°o.

By using para-hydrogen in the synthesis gas instead of normal hydrogen, the ortho-para-hydrogen conversion could bo measured simultaneously with the synthesis.' At 200°c. when synthesis to give oil was taking pjace, no jortho-para conversion was detectable. Under other conditions, below 160°c. when no reaction occurred, or during the ru»ning-in of a catalyst when tho products were methane, carbon dioxide and carbide, or at 200°c. with hydrogen in great excess when only methane was formed, or at temperatures above 250°c. where the product is entirely methane, the ortho-para conversion occurred freely. As has been pointed out, the occurrence of the ortho-para conversion may be taken as an indication of the presence of hydrogen atoms on the catalyst. Hence, it is concluded that when the Fischer oils are Ijiing produced there ia little, if any, atomic hydrogen on the catalyst, whereas the production of methane ia associated with the presence OD the catalyst of atomic hydrogen.



Fio. 3.—PLAN OF £HEMISOBBED ETUYLENE AND METUYLETHYLENES ON THE NICKEL SURFACE.

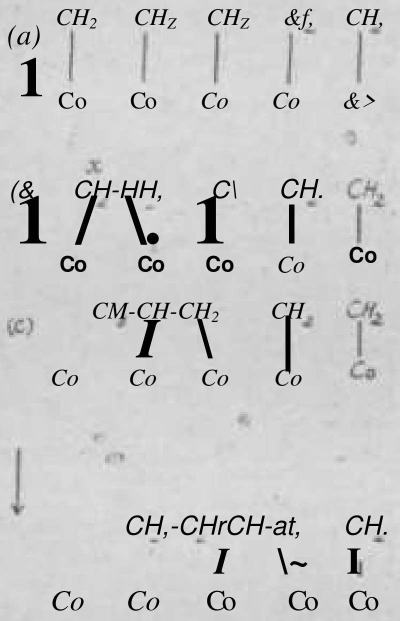
The water-gas reaction

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

exhibits a behaviour parallel to that of the ortho-para conve.wion. At 200°c. the equilibrium is almost entirely on the right-hand side, yet during, the Byntheaia of oil, the oxygen product is mainly water with only a trace of carbon dioxide. But under the conditions where the synthesis yields methane instead ol oil, the water-gas reaction occurs and carbon dioxide is formed instead of water. Thus this reaction is determined by the same conditions as determjre the ortho-para-hydrogen conversion.

From these observations, it is considered that the second step in tho synthesis is the reduction of the carbide by molecular hydrogen leading to the production of CH_a groups chemiaorbed on the cobalt. When atomic hydrogen is present on the catalyst, the CH_a groups are hydrogenated to methane. In the absence of atomic hydrogen, the groups link up with each other to form long'paraffin chains. That this linking-up process is more probable than a mechanism involving the addition of carbon monoxide to the end of a chain followed by reduction, is shown by the fact that cobalt carbide on treatment with dilute add gives rise to long-chain hydrocarbons.

The mechanism wlicreby the CH(groups link up is not completely understood. E. F. G. Herington (Trans. F-.raday Son. 1941, 87, 3U1) has calculated that i.i acetylene molecule "can be adsorbed on the nickel or cobalt lattice across the 3-50A. distance by the transformation of the triple into a double bond. This ia hi contrast to ethylene which can only be adsorbed across the shorter 2-47A. distance. It is found that if acetylene is added to the synthesis gas in the Fischer-Tropsch reaction, it polymerises in



Fie. 4.

dependency, and is not incorporated in the Fischer oil produced. On the contrary, if ethylene is present in the ingoing gas, it is inincorporated into the products. This gives grounds for thinking that the combination of the CH_2 groups during synthesis occurs across the short spaces of the cobalt lattice. From spatial considerations/ it can be seen that during the linking-up to form a large moleeu'.o, the individual CH_S groups cannot remain attached to their original catalyst atoms by Van der Waals forces. Consequently the scheme of reaction shown in fig, 4 has been proposed. Thin mechanism finds support in the fact that the products of the Fisrficr-Trojjsch synthesis contain a large quantity of olefins with the double bond in the terminal.position.

CATALYST UNIFOBMITI'.

The question of the uniformity of catalysts has not yet been decided satisfactorily, though it appears that there must be areas of different activity. The concept of active centres is largely duo to H. S. Taylor (J. Physical Chem. 1920, 30, 145) who considers these centres to be atoms or groups of atoms projecting above the plane of the catalyst and having a high activity 'by virtue of their instability. The evidence for and against this concept is mostly indirect. In its favour the fact is quoted that the heat of adsorption of a gas on the catalyst decreases with the amount adsorbed (H, S. Taylor, Z. **Elektroohem. 1929,** 35, 545), and the fact that poisons reduce the activity of catalysts many-fold while the adsorption is only slightly affected. Arguments from adsorption, however, **may** not be entirely conclusive since adsorption can be composed of several factors, chemisorption, Van der Waals adsorption and solution in the mass of the catalyst, of which the first only is concerned in catalysis; varying heats of adsorption have been explained as due to interaction between neighbouring adsorbed atoms or molecules (K. F. Herafeld, J. Amer. Chem. Soc. 1929, 51, 2608). More valid'evidence, however, is derived from eases in which two simultaneous reactions are possible with the same catalyst and reactants. When allyl alcohol vapour is passed over heated copper, it may either iaomerise to propionaldehyde or be denydrogenated to acrolein. F. H, Constable (Proc. Roy. Soc. 1926, A, **113,** 254) showed that the ratio in which the two reactions occurred was dependent upon the method of preparation of the catalyst. Many other examples of this kind have been found. Against the theory of active centres is the observation of E. W. R. Stearie and E. M. Elkin *(ibid.* 1933, A, **142,** 457) that there was no discontinuity in activit}' at the melting-point of zinc when this metal was used as a catalyst in the decomposition of methyl alcohol between 360° and 440°c. E. B. Maxted anc:-his co-workers (J.C.S. 1933, 502; 1934, 26, **672** ; 1935. 39:*, 1190) re-investigated the work of Vavon and Husson {Compt. rend. 1922, **175,** 277) on the effect of poisons on the hydrogenation of different organic substances, and found that the relative reduction in the rate of hydrogenation was the, same in all cases, even when the absolute rates differed considerably. Thus the same parts of the catalyst appear to be concerned in the different types of hydrogenation. Other evidence of catalytic homogeneity comes {•vim the fact that the energy of activation for the hydrogenation of crbtonic acid is the same on a fresh catalyst and on one of which the activity has l*een reduced by sintering or by poisoning. Other experiments using catalyst poisons point to the uniformity of the surface (**Maxted** and Evans, J.C.S. 1937, 1004; 1938, 2071), The comparative toxicities of hydrogen sulpbjde and various ulkyl thiola and sulptydes to *a.* platinum catalyst were measured. It was found that the **toxicrty** of the sulphides mi more than twice that of the thiols, and in both scries,of compounds the toxicity increased with the length of the alkyl chain. The ratio of the toxicitiea of methyl sulphide and hydrogen sulphide was 9*0:1. If these molecules are **presumed** to be anchored to the surface by the sulphur atom, then by drawing a scale model of these molecules on the surface, it can be seen that while the hydrogen sulphide occupies one phitinuni atom, the methyl sulphide molecule can cover nine atoms. Thus, over small areas, the catalyst is uniform. These experiments also show two types of .catalyst surface, each in itself homogeneous. The work of Beeck^ Smith and Wheeler (Proc. Roy. Soc. 1940, A, 177, 62) shows in another way that different types of surface can be present in the catalyst. The present position thus appears to be that while the catalyst may contain different types of surface, there is no evidence for isolated centres of high activity such as those postulated by Taylor/and the surface must be regarded as made up of areas of relatively uniform activity.

G. H. T.

HYPROLITH. A technical name for calcium hydride, CaH_2 *(v.* Vol. II, *205d,* and this Vol., p. 3306). Hydrolith has commercial importance as a reducing agent in metallurgy, and for generation of hydrogen by interaction with water, 1 kg. producing about 1 cu. m. of the gas at ordinary temperatures and pressures. For technical applications, *see* Alexander, Met. & Alloys, 1937, 8, 263; 1938, 9, 45.

HYDROLYSIS. The term hydrolysis (or hydrolytic dissociation) is given to a number of different chemical reactions, all of which consist in the addition of water to a complex, and the subsequent resolution of the product into simpler substances.

Some of the best-known types of hydrolysis are those of metallic salts, esters, acid chlorides, amides, etc., or generally acyl derivatives, complex carbohydrates and glycosides, and finally, polypeptides and proteins.

I. HYDROLYSIS OF SALTS.

The hydrolysis of a salt by water may be represented by means of an equation of the type:

$$KCN+H\text{-}OH \wedge HCN+KOH$$

The reaction is a balanced one, and may be regarded as due to the incomplete neutralisation of the acid and base from which the salt is derived; in terms of the ionic theory the acid in question (HCN) does not* yield sufficient hydrions to combine with the hydroxyl ions of an equivalent quantity' of the strong base (KOH). When equivalent quantities of a strong acid and a strong base are brought together in aqueous, solution complete neutralisation takes place, and a normal salt with a neutral reaction towards common indicators is formed. (Basis of methods of addimetry and alkalimetry.) In the cases of such salts appreciable hydrolysis would not be expected even in dilute solution. The following are the common types of salts which are hydrolysed by water: (l)^salts derived from feeble acids and rtrong bases;' (2) salts from strong acids and feeble bases; (3) salts from feeble acids and feeble bases. Examples of the first type are potassium cyanide *(v.8.)* and sodium phosphate,

$$Na_8PO_4+H\text{-}OH \rightleftharpoons Na_2HPO_4+NaOH$$

and even

$$Na_2HPO_4+H\text{-}OH \wedge NaH_2PO_4+NaOH$$

Solutions of such salts invariably have an alkaline reaction towards common indicators, *e.g.* litmus, phenolphthalein. The water may be regarded as a feeble acid, which, like any other feeble acid, liberates a certain amount of acid from the salt with which it is bibught into contact. In many cases acid salts are first formed, *e.g.* sodium phosphate, sodium carbonate, but free acid and free base may be liberated. The alkaline reaction of the solution can be accounted for by the fact that the feeble acid, or the acid salt formed, is iorised to a slight extent only, whereas with moderately dilute solutions the strong base is almost completely ionised, and thus there jo a great excess of hydroxyl ions over hydr&ms. Examples of the second type are ferric chloride and cupric sulphate, which are derived respectively from the feeble bases, ferric hydroxide and cupric hydroxide. The aqueous solutions of such salts invariably give an acid reaction. The hydrolysis may be represented by means of the equations:

$$FeCl_3+H\text{-}OH \wedge FeCl_2OH+HCl$$

$$\text{or even } FeCl_3+3H\text{-}OH \wedge Fe(OH)_3+3HCl$$

$$\text{and } CuSO_4+2H\text{-}OH \wedge Cu(OH)_2+H_8SO_4.$$

With moderately concentrated solutions basic salts, *e.g.*\ $FeCl_2$*OH are almost certainly formed, and it is only in very dilute solution that the hydrolysis will proceed to the formation of the metallic hydroxide, and even when this is formed it is not precipitated, but remains in solution in the form of a colloid. A group of salts which belongs to this type is that of the salts derived from the strong mineral acids, and feeble organic bases such as aniline, *e.g.*

$$\underset{\text{Aniline hydrochloride.}}{C_{fl}H_5NH_3Cl}+H\text{-}OH \rightleftharpoons \underset{\text{Aniline hydroxide.}}{C_{fl}H_6NH_3OH}.+HC1$$

$$\rightleftharpoons C_6H_5NH_2+H_2O+HCl$$

Examples of the third type are ferric phosphate, aluminium carbonate and sulphide and aniline acetate. The hydrolysis in the first case is readily shown by washing finely divided ferric, phosphate with distilled water, when it is found that the filtrate is always distinctly acid, owing to the free phosphoric acid which has been washed away by the water, and if the operation is continued nearly pure ferric hydroxide remains on the filter. In the case of the two aluminium salts, they are so readily hydrolysed that when brought into contact with water they yield the corresponding metallic hydroxide, and the free acids, carbonic acid and hydrogen sulphide?, which escape and thus destroy the equilibrium.

In the case of salt formation we may regard the water as capable of acting as either a feeble base or a feeble acid. When in contact with equivalents of a strong acid and a feeble base the water competes with the base for the acid, and hence neutralisation is not complete, or, in other words, hydrolysis of the salt occurs and the feebler the basO the greater the degree of hydrolysis. The mechanism of salt hydrolysis according to the ionic theory is as follows: In aqueous solution the given Bait, *e.g.* potassium cyanide, is ionised in the ordinary manner into K^4 and CN- ions, but water itself is ionised to a slight extent, $H_2O \wedge H^+ + OH^-$, and as hydrogen cyanide is a very feeble acid, and therefore ionised to only a very slight extent in aqueous solution, there is a tendency for the H+ ions of the water to combine with the CN~ ions from the cyanide, yielding undissociated **HCN**; the result is that the equilibrium $H_2O \rightleftharpoons H^+ + OH^-$ is destroyed and more molecules of water are ionised, but this results in further combination between H^+ and CN~ ions, and by this means an excess of OH^- over H^+ ions is produced, and thus the alkaline reaction. The changes continue until ultimately equilibrium is established between the *KCN,* C.N-, K+, H+, OH-, HCN and H_2O present. The degree of hydrolysis, i.e. the fraction of the salt hydrolysed, cannot be determined by direct titration of the free acid or free base present in solution; the addition of standard acid to the solution of potassium cyanide would immediately destroy the equilibrium which previously **existed,** and more salt would be hydrolysed in order to restore the equilibrium, and the point of neutrality would not be reached until acid sufficient to decompose the salt completely had been added. The methods commonly adopted for determining the degree of hydrolysis are (see Farmer, B. A. Report, 1904, 240): (1) Determination of the concentration of the free acid or free alkali present in the solution of the salt by its catalytic effect on the hydrolysis of an aqueous solution of ethyl acetate or on the inversion of a solution of cane sugar, and then determining the amount of pure acid or alkali required to produce the same effect (for acid, *see* Walker, Z. physikal. Chem. 1889, 4, 319; for alkali, see Shields, *ibid.* 1893, 12, 107; also Bruner, *ibid.* 1900, 32, 133; Ley, *ibid.* 1899, 30, 216; Walker and Aston, J.C.S. 1895, 67, 576). (2) Determination of the electrical conductivity of the solution (Walker, Z. physikal. Chem. 1889, 4, 333; Bredig, ***ibid.*** 1894, 13, 313; Lundy, J. Chim. Phys. 1907, 5, 574; Denham, J.C.S. 1908, 93, *41).* The molecular conductivity of a hydrolysed salt of the type aniline hydrochloride is made up of two quantities (a) conductivity due to the non-hydrolysed **salt;** (b) conductivity due to the free acid formed on hydrolysis—since the free base (aniline) is not an electrolyte. $M=(1-x)\mu_1+x\mu_{HCl}$ where M =molecular conductivity, x=degree of hydrolysis, μ_1=molecular conductivity of non-hydrolysed salt and μ_{HCl} that of the free acid formed. The various quantities in the equation with the exception of *x* can be determined and then *x* calculated. (3) Determination of the partition coefficient (Farmer, *ibid, 1901,* 79, 863). In the case of the hydrolysis of **aniline** hydrochloride the concentration of the free base is determined by shaking the aqueous solution at a given temperature with a known volume of benzene, and finding the concentration of the aniline in the benzene layer. Since C_B/C_{Aq} is always constant (C_B=concentration of aniline in benzene and C_{Aq} =concentration of aniline in water) for a given temperature the concentration of free aniline in the aqueous layer can be calculated directly, and thus the degree of hydrolysis determined. The assumption is made that the salt present does not affect the partition coefficient to an appreciable extent. (4) Observing the change in colour produced by a solution of the hydrochloride of an organic base in a solution of Methyl Orange of known concentration, and a comparison of this change with that produced by the addition of known quantities of hydrochloric acid (Veley, *ibid.* 1908, 93, 652, 2114, 2122; 1909, 95, 758; Trans. Faraday Soc. 1908, 4, 19).

The degree of hydrolysis of a salt may also be measured with the aid of the hydrogen or quinhydrone electrode and plotting the p_H-log. (concentration) curve (V. Čupr, Z. anorg. Chem. 1931; **198,** 310; Dupont. Compt. rend. 1931, **192,** 1643; Kolthoff and Kameda, J. Amer. Chem. Soc. 1931, 53, 832), or with the glass electrode (Cranston and Brown, J. Roy. Tech. Coll. 1937, 4, 46; Trans. Faraday Soc. 1937, 33, 1455; J.C.S. 1940, 578).

The following percentage values have been **obtained** with 1-0-CHM solutions *(v,* Cupr and Viktorin, A. 1931, 910).

Zinc sulphate . . .	0-0023-0-0048
Cadmium sulphate . .	0-0006-0-0016

Beryllium halides and sulphate are also hydrolysed (H. *Prytz, Z.* anorg. Chem. 1929, **180,** 355; 1931, **197,** 103). The hydrolysis is regarded as of the type

$$2Be^{++}+H_2O \rightarrow Be_2O^{++}+2H^+$$

as the values of K_0 in the equation:

$$K_0=A_H{}^2 \cdot C_{Be_2O}{}^{++}/C^2_{Be}{}^{++}$$

(where A_H represents the hydrogen ion activity) are practically constant and have the values $K_0 \times 10^7$: sulphate 1-4, chloride 1-7, bromide 5-9 and iodide 4-4. In many cases rapid hydrolytic reactions are accompanied by secondary slow reactions in which the products of the primary hydrolysis coalesce to form products of high molecular weight and the application of the law of mass action is difficult if not impossible. The hydrolysis of salts of weak polybasic acids leads to *isopoly* acids which can exist in a narrow region of hydrion concentration, whilst the hydrolysis of salts of weak poly-acid bases is characterised by isopoly bases which can exist in wide regions of hydrion concentration (K. F Jahr, A. 1938, 1, 202).

Most of the methods give only rough approximations *(cf,* Beveridge, Proc. Roy. Soc. Edin. 1909, 29, 648). A few of the results obtained are as follows:

Salt.	Temp.	4	Method.
	T.		
Glycine hydrochloride	25	19-00	Hydrolysis of ester
Acetamide ,,	25	3«'00	,, ,,
Urea ,,	25	90'00	,, ,,
,, ,,	60	81-00	Inversion of sugar
Sodium cyanide .	25	1-10	Saponification of ester
,, acetate .	25	0'008	,, ,,
,, carbonate .	25	3'17	,, ,,
,, phenate .	25	305	,, ,,
Aniline hydrochloride	60	2-60	Inversion of sugar
,, ,,	25	1-50	Conductivity
Zinc chloride . .	100	010	Inversion of sugar
Aluminium chloride .	100	6-10	,, ,,
,, ,, .	25	OM	Conductivity
Ferric chloride ,, .	40	iirdo	Inversion of sugar
Lead ,, . .	25	0-50	Conductivity

The whole question becomes more complicated when the acid or base formed by hydrolysis 'is unstable and is transformed into isomeric pseudo-acid or pseudo-base.

The influence of concentration on hydrolysis is given by Guldberg and Waage's law of mass action. According to this $\frac{C_S}{C_A \times C_B}$ = constant, where C» represents the concentration (molar) of the non-hydrolysed salt, C_A that of the acid formed by hydrolysis, and CB that of the base. If originally 1 g,-mol. of salt was dissolved in v litres of solution and *x* g.-molfl. were hydrolysed, then

$$\frac{1-x}{v} \div \frac{x^2}{v^2} = \text{constant, or } \frac{v(1-x)}{x^2} = \text{constant.}$$

It is'obvious that as *v* increases, *i.e.* as the concentration is diminished, x, i.e. the degree of hydrolysis, must increase in order to keep the whole expression constant.

The relationships are not quite the same in the case of a Bait derived from a feebif **base** and a feeble acid, *e.g. aniline* acetate,

$$C_6H_5\text{-}NH_3\text{-}O\text{-}CO\text{-}CH_3+H_2O \rightleftharpoons C_6H_5{\cdot}NH_3{\cdot}OH+CH_3{\cdot}CO{\cdot}OH$$

If the reaction is represented as taking place betweea the ions of the salt and the water, and the salt is practically completely ionised, and the base and acid not appreciably, then CCH'CAD/CU'CB^ constant, where $C_{c,t}$=eoncentraction of the cation and CAII=concentration of the anion. But Cc.t= CAH=C_{Salt}.

$$\therefore C^2_{Salt}/C_A C_B = \text{constant, or } \left(\frac{s}{v}\right)^2 \Big/ \frac{a}{v}\frac{b}{v} = \text{constant}$$

where *s, a, b* are the gram-mols. respectively of salt, acid and base in *v* litres of solution. *But this expression is independent of *v,* and hence dilution docs not affect the degree of hydrolysis

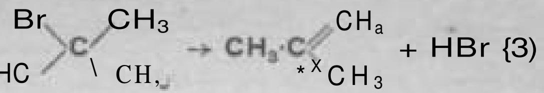
Another factor which affects the degree of hydrolysis is the addition to the solution of one of the products of hydrolysis, *e.g.* free acid or free base. Thus the hydrolysis of aniline hydrochlorideinaqueoui* solution can be stopped completely by the addition of hydrochloric acid or of aniline. This follows again directly from the equation CS/CA'CJ)=constant. If C_A, i.e. the concentration of the acid, is increased it\s necessary, in order that the whob expression may remain constant, that either CB should diminish or Cg increase or both, and the only way in which this can be effected is by a diminution in the degree of hydrolysis.

The velocity of salt hydrolysis has been determined in a few cases, *e.g.* ferric chloride (Go-todwin, 2. physikal. Chem. 1896, 2i; 1); potassium ruthenium chloride, K_2RuCl_s (Lind and Bliss, J. Amer. Chem. Soc. 1900,31, 868).

A type of hydrolysis analogous to salt hydrolysis is that of the chlorides of certain non-metals, e.y.$PCl_3+3H_2O = 3HCl+P(OH)_3$. This reaction proceeds to completion in the presence of an excess of water, and, as a rule, the chlorides of non-metals are hydrolysed more readily than those of metals. Nitrogen trichloride and carbon tetrachloride arc, however, stable in the presence of water and many metallic chlorides derived from feebly electropositive metals are appreciably hydrolysed, *e.g.* TeClj. $BiCl_3$, etc.

II. HYDROLYSIS OI? OSGANIC HALIDES.

A. Alkyl Halides.—A common method for the formation of alcohols is by the action of alkalis on alkyl halides, more particularly the bromides or iodides. With watir alone an equilibrium is established $RX + H_2O \rightleftharpoons ROH+HX$. With many aikyl halides secondary reactions can occur, more particularly when the alkali is dissolved in aqueous alcoStol, With ethyl halides and higher homologues there is always the possibility of the elimination of hydrogen halide and the formation of an olefin. This elimination Ea favoured when solvents rich in alcohol are used and moderately high temperature. It is essential that there should be a hydrogen atom in the position a- to the halogen. In certain cases hydrogen halide can be eliminated and a *cyclo*-paraffin formed (•». CYCLENES), An accumulation of alkyl groups at the carbon atom to which the halogen is attached favours the formation of olefin, and elimination of hydrogen halide **can** occur in a solvent like anhydrous formic acid in the absence of alkali:



{3)

With concentrated ethyl alcoholic solutions of alkali the halogen is often replaced by the cthoxyl, —**OEt,** group, and the reaction is termed alcoholysis (c/. p. 397A). Equivalent quantities of different alkalis give different rates for the hydrolysis of ethyl chloride and follow the order $NaOH>Na_2CO_3>CaO>MgO$ (Izmailski and Papov, J. Gen. Chem. U.S.S.R. 1938, 8, 695).

Considerable attention has been given to the mechanism of this type of hydrolysis by Hughes, Ingold, Shapiro and their co-workers {J.C.8. 1935,255; 1936,225; *1937,* 1177, 1183, 1.187, 1192; 1938, 881; *ef. also* Taylor, *ibid.* 1W5, 1514; 1937, 1902; 1938, 840, and reply to Taylor, *ibid,* 1940, 913, 920, 025, 935). The reaction between ethyl balides and water, acids or dilute alkali is one of the second order {Grant and Hinshelwood, ***ibid.*** 1933, 258).

$$C_2H_5X+HOH \rightleftharpoons C_2H_5OH + H^+ + Cl^- \quad (2)$$

whereas with *left-butyl* halides, CMe_3X, the reaction is one of the first order and can be represented as taking place in two stages (Hughes, *ibid.* 1935, 255):

$$\left.\begin{array}{ll}(a) & RX \rightarrow R^+ + X^- \text{ slow} \\ (6) & R^+ + H{\cdot}OH \rightarrow R{\cdot}OH + H^+ \text{ fast}\end{array}\right\} \quad (1)$$

The velocity actually, measured by estimating C! is that of the unimolecular reaction (a), i.e. the ionisation of thu alkyl halide, as the second stage, *{h},* is very rapid. .i

The bimolecular reaction (2) is characteristic of most'primary alcohols, but the accumulation of electron-releasing alkyl groups and still more of aryl groups at the seat of substitution of an alkyl halide causes the suppression of the reaction 2) and its replacement by reaction (I) involving the ionisation of the alkyl halide. The electron-repelling carboxylate ion -COjTacts in a similar manner. The suppression of reaction (2) is practically complete with tertiary h^h'des, *e.g. iert-* butyl compounds, but with secondary halides, *e.g.* wopropyl and /J-M-oetyl compounds, the two reactions (1) and (2) occur, and the coefficients of each reaction have been determined. In theipase of wopropyl bromide reaction {1) occurs in aqueous, acid or very faintly alkaline solutions, but with 0-1N. alkali reaction (2) runs concurrently, as shown by the fact that the values of *k* emulated for a first-order reaction fall during a iun and the fall becomes the more marked the greater the initial concentration of OH", and calculated for a second order reaction rise during a run and the rise becomes less with each increase in OH^- concentration. An increase in alkalinity also induces the elimination of hydrogen bromide and the formation of propylene.

For the second-order reaction for ethyl and isopropyl bromides the values of *k* are roughly 25:1 and in the first-order reaction there is a marked increase from fdopropyl to terd-butyl. The addition of water to the alcoholic **solvent** strongly accelerates the unimoleeul&r reaction (1), slightly retards bimolecular substitution (2) and more strongly retards elimination. A comparison of the velocity coefficients of fluorides, chlorides, bromides- and iodides of the Bame alkyl radical shows that there is a much greater difference between fluoride and chloride than between other pairs, *e.g.* for (erf-butyl the ratios are: F:CI = 10^6, CI:Br=40, Br;1=2*. and the flame holds good for activation energies. The velocity coefficients (first order) for /erf-butyl halides are sonitt 10* times those for the corresponding isopropyl compounds. The proof tfrit the hydrolysis of the feri-butyl compounds is of the uniroolecular type,

$$RX \rightleftharpoons R^+ + X^-,$$

is based on the following considerations: (a) The rate constant for a given coot pound is the sJme in water, dilute acid or *very dilute* alkali. *(b)* By using a solvent with an ionising power towards alkyl halides as great as or greater than that of water, *e.g.* anhydrous formic acid, and adding small amounts of water, the *initial* velocity is found to he independent of the concentration of the water and the curves (time —CI" concentration) are all the same in the early stages, but differ at later stages owing to the reversibility of the reaction, *(c)* By determining rates of both hydrolysis (replacement of CI by OH) and alcnliolysis (replacement of CI by **OEt)** in the case of *tert-hutyl* chloride it is found that the maximum rates of the two reactions have no connection with the composition of the product, nhereas if the reaction were bimolecular the composition of the product could be calculated frcrai the two rates (Oleon and Halford, J. Amer. Chem. Soc. 1937, 59, 2(544). For general discussion, *see* Bateman. Church, Hughes, Ingold and Taher (J.C.S. 1940, 979), ami for hydrolyses in liquid sulphur dioxide, *cf.* Bateman, Hughes and lngold *(ibid.,* I'll I and 1017).

Olefin is formed with anhydrous formic acid as solvent, but the formation *is* rapidly suppressed by the addition of small amounts of water. In both the unimolecular substitution reaction (1) and also in elimination reaction (3) tin.- first product is the cation $C(CH_3)_3{}^+$ which can then react either:

$$(1)\quad C(CH_3)_3{}^+ + OH^- \rightarrow C(CH_3)_3\text{-}OH \quad \text{or}$$
$$(2)\quad C(CH_3)_3{}^+ \rightarrow (CH_3)_2C{:}CH_2 + H^+$$

For the compounds wpropyl• bromide and /J-w-octyl bromide the following values for *k* have been obtained for the three reactions: (I) unimolecu'ar substitution, (2) bimolecular substitution, (3) elimination.

	(1)	(2)	(3)
isoPropyl	0-908	3-56	5-01
β-n-Octyl	0-519	3-58	4-40

Based on these views of kinetic substitution of OH for halide, •Cowbray, Hughes lngold, Mastcrman and Scott (J.C.S. 1937, 1252) have drawn a number of conclusions relating to the Waldcn inversion. They conclude that bimolecular substitution leads to inversion and unimolecular leads normally to racemi&ation aa the cation has a plane of symmetry, but that inversion can also occur if the life of the cation is very short. The reactions with silver oxide or silver salts are similar to unimolecular substitution. In. each of the series: j3-n-octyl, *a*-phenylethyl, a-substituted propionic acids, a-substituted - a • pheny 1 - and a-su bst itutcd-/3- phe ny 1 - propionic **adds,** mono-substituted auccinic acids the halogenated, hydroxy-, methoxy- and, in some cases, ami no-compounds which have the same sign of rotation, *e.g.* +, have the same relative configurations, with the single exception of (J-) a-hydroxypropionic acid which has a config uiation different from the (+) halogenatcd acids.

Based on these data conclusions are drawn with reference to the action of halides of phosphorus, thionyl chloride and hydrogen halides on hydroxy-compounds and the results confirm the views of Frankland *(ibid.* 1913, **103,** 725) rather than those of O.ugh *(ibid.* 1918,**113,**526).

Olivier (Rec. trav. ohim. 1934, 53, 869, 981), from a study of the reactions of the three chlorides CerVQr^CI, C_8H_6-CHC1? and C_8H_6-CCI_3 and various substituted deri /atives in aqueous acetone solution., of KOH and $\mathbf{H_2SO_4}$**,** shows tbat the reactions are pseudo-unimolecular and in no case catalysed by hydrions. The hydrolysis of the first is catalysed by hydroxyl ione but that of the second and third is not, hence in the preparation of benzaldehyde from benzal **chloride** the addition of alkali is unnecessary. The 'effect of substituents in the phenyl group is such that the more negative the chlorine is rendered the less pronounced is the effect of hydroxyl ions. The hydrolysis of C_aH_s-CH_2CI in water is slower than in aqueous acetone, probably owing to the higher dielectric constant of water and hence the more negative character of the chlorine, *see also* Hackel, Annulen, 1939, **540,** 274; and for effect of mercuric halides on hydrolysis of alkvl halides in aqueous acetone, *see* Read and Taylor, **J.C.8.** 1939, 1872 ; 1940, 679.

B. Halogenated Fatty Acids and their Salts.—Senter (J.CJS. 1907, 91, 460; 1909, 95, 1827; 1912, **101,** 2528) has shown that hydrochloric acifi or neutral salts **have** little or no effect on the hydrolysis of the free acids by **water** and that within wide limits the rate of hydrolysis is directly proportional to the concentration of the acid." At 102° the reaction is of the first order in dilute solutions, but deviations are met **with** in more concentrated solutions. With alkalis the reaction is of the second order in dilute solution. The hydrolysis with water is favoured by the introduction of alkyl groups into the molecule, whereas such groups retard the hydrolysis with alkalis.

Dawson and his co-workers *(ibid.* 1933, 49, 1133 ; 1934, 778; 1936, 1S3, 497) attribute the catalytic effect of acetate ions on the aqueous hydrolysis of sodium broruoacetato to the formation of an acetoxyacetate ion,

$$CH_3\cdot CO_2\cdot CH_2\cdot CO_2^-,$$

and in the absence of acetate ion the bromoacetate ion can catalyse by forming bromoacetoxyacetate ion, $CH_9BrCO_a\text{-}CH_a\text{-}CO_a^-$. The whole process comprises two distinct reactions:

(1) A reaction of the first order with excess water:

$$CH_2BrCO_2\sim\text{-f-H-OH}\wedge HOCH_2CO_{fi}H+Br\sim$$

(2) A bimolecular reaction occurring in two stages :

(a) $2CH_2BrCOj\sim$
$\text{-* } CH_2Br\text{-}CO_2CH_2CO_a^- + Br\sim$

(b) $CH_2Br\cdot CO_2\cdot CH_2\cdot CO_2^- + H_2O$
$\rightarrow CH_2Br\cdot CO_2^- + OH\cdot CH_2\cdot CO_2H$

and $v=v_1+t)_a=A_1c+fc_3c^a$ /

where v_l and v_z are the velocities and k_x and fc_a are the velocity coefficients of reactions *[a)* and (6) and c is the concentration of the $CH_2BrCO_s^-$ cation.

In the presence of an added catalyst, e.£. acetate ion, formate ion or fiydroxyl ion, the reaction can be represent ad as :

$$v=v_1+v_2+v_3=k_1c+k_2c^2+k_3cc'$$

where c' is the concentration of the, added catalyst and k_s the corresponding velocity coefficient. The most active catalyst is the hydroxyl ion and the fact thatr.the course of alkaline hydrolysis can usually be expressed with close approximation to a simple bimoleeular reactionjs entirely duo to the large value of $\&_3$ {for OH) as compared with $k_\pm$ and k_2.

Wjth a mixture of free acid and sodium salt the reaction is more complex:

$$v=v_1+v_2+v_3+v_4$$
$$=k_1[A]+k_2[A]^2+k_3[HA]+k_4[HA][A]$$

where [A] represents the concentration of the bromoacetate cation and [HA] the concentration of the un-ionised acid. The collisions between pairs of bromoacetic acid molecules have no measurable effect. By varying the conditions of the reaction any one of the four component reactions can be made the dominant factor in the observed rate of change, and under certain conditions the general velocity equation reduces to very simple terms. The reaction becomes more complex when appreciable hydrolysis has taken place as the gly collate, OHCHj-CO,~, ions exert an influence and the whole velocity then becomes

$$v=k_1[A]+k_2[A]^2+k_3[HA]+k_4[HA][A]$$
$$+k_5[A][G]+k_6[HA][G]$$

where [G] represents the concentration of the-glycpllate ions. The reactions between bromoacetic acid and hydrions^and collisions between pairs of bromoacetic acid molecules, glycollic acid molecules or bromoacetic acid and glycollic acid molecules have no measurable influence.

The relative values of *, x I0« to k_t x 10* are : 0059, 19-3, 0041, 72, 35, 136. To render the results comparable all experiments were made with the same total salt concentration by the addition of sufficient sodium nitrate or sodium perchlorate.

The course of alkaline hydrolysis can be represented by the equation:

$$v=v_A+v_B+v_C+v_D$$
$$=k_A[A][OH^-]+k_B[A][H_2O]+k_C[A]^2+k_D[A][G]$$

and as k_B, k_0 and kn are all less than 001 k_A it follows that the rate of alkaline hydrolysis is almost entirely dependent pn fc_A, so long as the concentration^ of OH~ >B not too small. With very low OH⁻ concentrations the whole process cannot be represented as a simple bimolecular reaction.

III. HYDROLYSIS OF ACVL DERIVATIVES.

Practically all acyl derivatives are hydrolysed more readily than the corresponding alkyl compounds; the esters and acid anhydrides mere readily than the ethers; the aeyl halidos more readily than the alkyl haltdes; the amides, imides and anilides more readily than the s&ble amines.

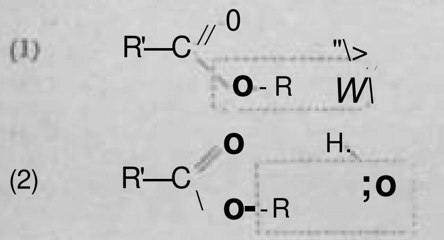
A. HYDROLYSIS OF ESTERS.—The hydrol^tia of an ester may be brought about by water alone, by solutions of neutral metallic salts, by aqueous solutions of strong alkalis or acids, by water in the presence of finely divided solids, such as charcoal, and also by means of enzymes.

(1) Hydrolysis with Water.—The reaction witfi water may be represented by an equation of the type :

$$CH_3\cdot CO\cdot OC_2H_5+H\cdot OH$$
$$\wedge\ CH_3COOH+C_aH_BOH$$

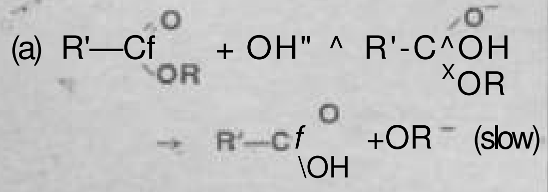
The reaction is the reverse of esterification, and is hence a balanced bimolecular reaction; in dilute solutions, however, the mass of the water may be regarded as remaining constant, and the reaction becomes practically n on-reversible. Like esterificatiou the reaction is slow and lends itself to study as a tfme reaction and also has a relatively high activation energy E. The corrae of the reaction can bo followed by estimating the amount of free acid in the solution after given intervals of time; this is accomplished by removing an aliquot part of the solution at the given time and titrating the free acid by means of standard alkali solution. In most cases it is necessary to use a feeble alkali for titration, e.y. ammonium hydroxide with litmus as indicator, as nearly all estera which are hydrolysed appreciably - by water are decomposed very readily by strong alkalis, and it becomes impossible to detect the end point of the titration when sodium or barium hydroxide solutions are used. Esters derived from comparatively strong acids, *e.g.* methyl sulphate, ethyl formate, ethyl trichloroacetate, 'ethyl pyruvate and ethyl tartrate are readily hydrolysed by water at room temperature. In these cases the velocity of the reaction does not eo^espond with that of a simple uni molecular ruction, the values for *k* calculated from the first order equation *k=ljl* log *[aja—x],* increase aa *t* increases, and the probable reason is that the acid formed during the hydrolyaia reacts catalytieally on the reaction *(see- under* hydrolysis by acids). Hydrolysie of natural glyceryl esters by means of superheated steam is used as a commercial method for the production of etearic acid for the manufacture of candles (u. this Vol., p. 4,'>6).

Mechanism of Hydrolysis.—Two different types of fission of the ester molecule under the influence of water are possible :



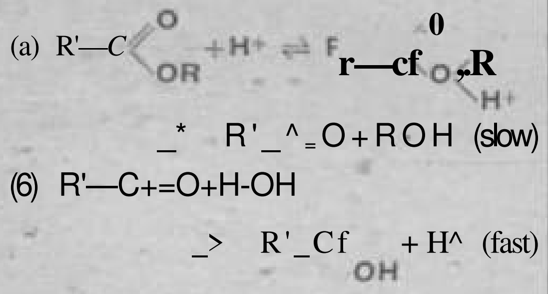
i.e. the fission occurs at the -f-O—R bond or at thn, O- -R, and all available evidence supports the former view, which was first suggested by Ferns and Lapworth (J.C.S. 1912,101, 273).

Alkaline hydrolysis is represented by the scheme:

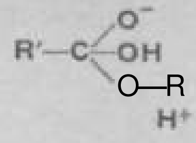


{b) OR" + H-OH -* HOR + OH "{fast)

and acid hydrolysis by the scnemc:



The two points of attack in the ester are the O of **the** OR group, **which** attracts protons,and the C of the CO group which attracts hydroxyl ions. If both function then an ion common to both acid and alkaline hydrolysis would be formed:



The main arguments in favour of Ferns and Lapwoith's view are: (a) An optically active ester containing a dissymmetric alkyl group gives, on **hydrolysis**—both acid and alkaline—the pure optimally active alcohol (Holmberg, lier. 1012, 45. 2997). If the hydrolysis followed scheme (2) the free alkyl radical would give a racemic alcohol, *(b)* When the ester contains an unstable ttnsaturated alkyl group, hydrolysis involving the elimination of R would bring about isomerisation and the alcohol formed would not correspond with tho ester, *e.g.* the este^

$$\mathbf{CH_3COOCHMeCH{:}CH_a}$$

yields the alcohol

$$\mathrm{HOCKMe\text{-}CH{:}CH_2}$$

and not the isomer:

$$\mathrm{CHMe{:}CHCH_2OH}$$

or a mixture- of the two (Ingold and Ingold, J.C.S. 1932, 758). (c) The strongest **axgomant** is the fact that when hydrolysis—either acid or alkulinc—is carried out in the presence of water rich in heavy oxygen ^{1B}O, the alcohol formed contains no heavy oxygen and hence the O of the OR of the alcohol is derived from the ester and not from the water (Polanyi and Szabo, Trans. Faraday Soo. 1934, 30, 508; Datta, Dayxuid Ingold, J.C.S. 1939, 838; Herbert and Blumcnthal, **Nature,** 1939, **144,** 248).

According to Kirrmann (Bull. Soc, chim. 1934, [v], 1, 247) the hydrolysis of the four esters: (1) allyl pyruvate, (2) ethyl pyruvate, (3) allylidene acetate, (4) propylidene acetate, in water proceeds in two different ways: (o) a uiiimolecnlar spontaneous reaction (velocity coefficient *k), (b)* a reaction with a velocity proportional to hydrion concentration (proportionality constant *b).* The values for **E** and *b* for the *bur esters at 25" and expressed in gram-molecules, litres and hours are: (1) 0-062, 8; (2) 0025, 10; (3; 0010, 8; (4) 0004, 7. It is claimed that the results support Ferns and Lapworth's view of ester fission. In pure water the rate of hydrolysis of ethyl formate is proportional to hydrion concentration anrt is retarded by addition of sodium formate. With ethyl, acetate hydrolysis starts only after several days and is due to unknown impurities.

Experiments made with water and mixtures of water and deuterium oxide (Kailan and Ebeneder, Z. physikal Cheni. 1937, **180,** 157; 1938, 182, 397), at 205° and in absence of a catalyst show that tho D_sO retards the hydrolysis of methyl, »-propyl and n-butyl acetates and benzoates, but does not alter the equilibrium,

Kcndal and Harrison (Trans. Faraday Soc. 1928, 24, 588) by an cx;i mi nation of freezing-point curves of mixtures of water with various esters show that compound formation is common in all the systems examined, and that the tendency increases with the strength of the acid radical of the ester, whereas the nature of the alcohol radical appears to be of little influence *ih* this respect.

For discussion on the evidence that hydrolysis is preceded by the addition of water to the O of the CO groups, *v.* Adickea, Chem.-Ztg. 1937, **61,** 167.

{2) Acid Hydrolysis.—The hydrolysis of esters by means of dilute mineral acids is slow and readily lends itself to study as u time reaction. The velocity is directly proportional to the concentration of the mineral acid, *i.e.* prob'Ably to that of the hydrions which act as a catalyst, and the reaction may be represented by the differential equation

$$dx/dt=k(c_{\text{Ester}}\times c_{H_2O}\times c_{H^+})$$

In dilute solution (and most esters are somewhat sparingly soluble in water) CH_2O can be regarded as not changing, and $c_H{}^+$ is also constant, since the catalyst *ie* not used up during the reaction. The process thus becomes a typical unimolecular reaction, and the velocity constant con be determined with the aid of the usual formula &=l/(log *[aj(a*~at)].

The catalytic activity of the acid is not entirely due to the hydrions, but also to the un-ionised acid {</. ESTKRIFICATION). E. Ramstedt (J.C.S. 1915,108, ii, 541) givs& the following formula:

D=fchxCxs+imxC{1—*a)*

where f=rate of hydrolysis, *k*\\ and k_m are coefficients characteristic of the hydrion and un-ionised acid respectively, C is the concentration of the acid, and a n a the degree of ionisa•tion. Experiments were made with **0fchy]** acetate using various organic acids as catalysts, the degree of ionisation of the acids being determined by measurements of electrical conductivities of the free acids and sodium salts over a considerable range of dilution.

The concentration of the organic acid at any given time is obtained by titrating a portion of the solution with standard barium hydroxide solution and phenol phthalein (unless the eater is derived from a strong acid when ammonia and litmus are used) and subtracting from the total alkali used the amount, required by the mineral acid. The following relative values have been obtained at 25°, wit'j O-ljV-hydrochloric acid as catalyst acting upon the methyl, ethyl and propyl esters of acetic, propionic, butyric and valeric acids :

it methyl ester: *k* ethyl ester=0-97
aiH?£ ethyl ester : *k* propyl ester^1-01
k acetate eater: *k* propionate ester=l-07
k propipnute ester: *k* butyrate ester=l*75
k butyrate ester; *k* valerate ester=2-93.

From these values it is clear that in the hydrolysis of an ester R'-COOR by means of a strong mineral acid the acyl group **R'-CO** has a much greater influence than the ulkyl group R on the velocity of hydrolysis (Heinptiune, Z, physikal.- Chem. lfcW, 13, 562). Loewenherz *[ibid.* I$y4, 15, 389) working at it temperature of 40° found that ethyl formate is hydrolysed much more readily than ethyl acetate {ratio 20:1); that methyl and ethyl monoehloroacetates are hydrolysed at much the same rates, ratio l-01:l_; that the ratio ethyl acetate: ethyl uionochloroaeetate=l-7; that ethyl dichloroacet&te : ethyl monochloroacetate=l-6; and that ethyl benzoate is hydrolyeed extremely slowly.

Palomaa (J.C.S. 1914,**106,** i, 130) shows that with eaters which contain an oxygen atom ia the chain (whether as OH, OR, CO or O) the velocity of hydrolysis by mineral acids is reduced to a minimum–'when the oxygen atom is in the ^-position with respect to the ester group. On the other hand, a cyano-group always has a retarding effect on the hydrolysis of *an* ester by dilute hydrochloric acid, and the effect is more pronounced in the a- than in the j3-position (Amer. J. Sci. 1914, [iv], 37, **514).** Drushel and Dean *{ibid.* 1912, [iv], 34, 293) show that in the case of acetic acid the rate of hydrolysis is increased by the introduction of the hydroxy-group, but retarded by an alkyloxy-group. The introduction of hydroxy -groups into the butyric acid, on the other hand, **had** ;i retarding jffect (Dean, *ibid.* 1914, [iv], 37, 331). For hydrolysis of halogenated esters, see Drushel, *ibid,* 1912, [ivj, 34, 69; for hydroxy- and alkyloxy- derivatives of propionic acid, *ibid. 1*913, [iv], 35, 486. As the result of experiments on the hydrolysis of the ethyl esters of propionic, acrylic, 7i-butyric, crotonic, /3-phenylpropionic and cinnamic acids with dilute hydrochloric acid at 20°, Williams and Sudborough (J.C.S. 1912, **101,** 412) show that the rate of hydrolysis of the ethyl ester of an ajS-unsaturated compared with the rate for tt\B corresponding saturated acid is about l;30. ^The difference is however, not nearly so marked when an alttili (barium hydroxide) is. used as hydratysing agent.

"Salmi (Ber. 193<J, 72 [B], 1707) claims that most of the structural effects noted ir> the catalytic esterification of saturated and unsaturated fatty acids are also observed in the acid hydrolysis of the esters of these acids ('/. **ESTEKIFICATION).**

The effect of oletin linkings in the alkyl group of an ester, as typified by the formates and acetates derived from ally], A -butenyl and a -pentenyl alcohols, is only slight in the case of acid, but is somewhat more marked in alkali hydrolysis (Palomaa and Juvala, Ber. 1^28, **61** [B], 1770J.

Dawsonand Lowson (J.C.S. 1928, 2146, 3218), by the elimination of autbcatalytic effects on the hydrolysis of ethyl acetate by dilute hydrochloric acid and by determining the initial velocities, proved that, for -concentrations of the hydrogen chloride between 00002 and 0-2 moh per litre the initial velocity ia proportional to the concentration of the acid. They claim that at ah* stages the velocity is determined by the hydrogen ion concentration of the solution. With concentrations of catalyst **below** 0'01 mol. the course of the hydrolysis is modified by the catalytic action due to the acetic acid produced. The relative importance of this autocataly tic effect increases as the concentration of the hydrogen chloride diminishes, and it is not possible in practice to determine the initial velocity of-the reaction when the concentration falls below 0-0002 mol. per Utre. By a careful study in silica vessels, as traces of alkali have a pronounced effect, it is shown that in moderately dilute solutions the reaction may be divided into two stages; in the first of these the velocity is determined by the joint catalytic activities of the H+ and OH- ions, and in the second by the H+ ions only. It would appear that the speed of the uncatalysed reaction and the catalytic activity o^the water molecules are too small to have any appreciable influence on the course of the reaction. Dilatometric study of the acid hydrolysis of ethyl orthoformate and acetal shows that hydrolysis other than by H+ ions is undetectable, and hence such a reaction is suitable for determination of hydrogen ion concentrations and for the investigation of the salt effect. In the case of all other ortho-esters, and of ketal, water molecules and substances like *m*- and ^-nitrophenol, cacodylic and acetic acids produce catalytic effects in addition to the H^+ ions.

For a résumé of evidence that catalytic effects are due to undissociated acid molecules as weU as to H^+ ions, *see* Brönsted and Wynne-Jones, Trans. Faraday Soc. 1929, 25, 59. Working with a mixture of alcohol (42-34%) and water, Berger (Rec. trav. c'uim. 1924, 43, 163) shows that the acceleration of the hydrolysis of esters with H^+ ions decreases with the strength of the acid from which the ester is derived, and with methyl and ethyl esters of the same acid the difference in velocity is not constant, but decreases with the acidity of the ester. Olivier and Berger (*ibidi* 1927, 46, 609, 861) show that hydrogen ion concentration is without effect on the hydrolysis of esters of strong acids or of compounds such as picryl acetate, and *s*-trinitrophenetole.

Fof- effect of emulsifiers on hydrolysis, we Smith, JT.C.S. 1925,127, 2602.

Strong organic acids such as trichloroacetic and picric, the HSO_4~ ion, and aqueous solutions of salts which give rise to hydrions act catalytkally. Concentrated sulphuric acid at 15° rapidly hydrolyses ethyl phenylacetate and alkyl salicylates but only slowly ethyl phthalate and alkyl benzoates. At 80° the benzoates and phthalates are immediately hydrolysed and at the same time slowly sulphonated (Senderens, Compt. rend. 1904,198, 1827**. An ester which is not hydrolysed by heating with strong hydr.-chloric acid or alkali, *e.g.* ethyl tetraethylsuccinate, can be hydrolysed by heating to 200° with hydrogen chloride and a little aluminium chloride, the products being ethyl chloride, water and the aciu anhydride (Ott, Ber. 1937, 70 [Bl, 2362).

PracticaUy all acid-catalysed reactions, including the inversion of sucrose and the hydrolysi:- of esters, proceed more quickly in heavy Vater, D_2O, than in water. This has been shown to be true of methyl acetate with sulphuric acid (Hornel, Nature, 1935, 135, 909) and of ethyl formate and methyl acetate with hydrogen chloride (Butler and Nelson, J.C.S. 1938, 957), and in all such cases the complex of the ester and hydrion is in equilibrium with the medium (Bonhoeffer and Keitz, Z. physikal. Chem. 1937, 179, 135; Wynne-Jones, Chem. Reviews, 1935,17, 115).

The mutarotation of ^-glucose proceeds more slowly in D_2O than in water.

(3) Alkaline Hydrolysis.—The hydrolysis of an ester by means of an alkali hydroxide can be represented by an equation of the type:

$$RCOOEt + KOH = RCOOK + EtOH$$

The reaction is non-reversible, as the alkali salt cannot react directly with the alcohol, and as both ester and alkali are used up as the hydrolysis proceeds the reaction should be bimolecular. Hydrolysis by alkalis proceeds more rapidly than that by mineral acids (*cf.* Van Dijken, Rec. trav. chim. 1895,14,106), and is the common method used in the laboratory. The ester is boiled for some time with an excess of sodium (or potassium) hydroxide solution in a reflux aj^paratus. If the ester is an oil only sparingly soluble in water, the completion of the reaction is denoted by the disappearance of the oily layer, unless the alcohol formed is also insoluble in water. If, however, the ester itself is soluble in water, the disappearance of its characteristic odour indicates complete hydrolysis. In order to separate the acid and alcohol formed, the mixture is (a) boiled, when the alcohol passes over together with water, provided the alcohol is a comparatively simple monohydric one; or *(b)* extracted with ether if the alcohol is complex and is not readily volatile. To obtain the acid the alkaline solute left after treatment (a) or *(b)* is acidified with hydrochloric acid, when the organic acid is directly precipitated if it is sparingly soluble in water, or can be extracted with ether if soluble in water,

Ail'alcoholic solution of potassium hydroxide is sometimes used for hydrolysing purposes, especially when the ester is practicaUy insoluble in water. In the case of esters other than ethyl, alcoholysis occurs resulting in the formation of ethyl esters which are then hydrolysed, *e.g.* glycol diacetate a .d alcoholic potash give ethyl acetate and glycol anji finaUy ethyl alcohol, potassium acetate and glycol. Bryant and Smith (J. Amer. Chem. Soc. 1936, 58, 1014) recommend heating the ester with excess of 2AT-sodium hydroxide in 90% methyl alcohol at 60-100° in closed vessels,

The decomposition of esters by alkali hydroxide solutions iB the basis for the usual methods for the manufacture of hard and soft soaps, and hence a common name for the process is *saponification.* The common fats are glyceryl esters of monobasic acids of high molecular weight, more especiaUy of palmitic, stepjic and oleic acids, and on saponification yield the trihydric alcohol glycerol and the sodium or potassium salts of the acids, *e.g.*

c H (nrn·r H \ 2 , QM*nu
^ " s l -1 -OH/o m ^r H *mnN**
$$-C,H_{I}(OH)_{i}+3C_{1T}H_{M}-COONa$$

Anderson and Brown (J. Physical Chem. 1916, 20, 195) have studied the velocity of saponification of various fats in different media; they find that the velocity is practically independent of the molecular weight of the fat but varies considerably "with the solvent and of the three uLohols used, namely, methyl, ethyl and amyl, is greatest in aniyl alcohol.

The sapouification of fat occurs in stages and if insufficient alkali is used, the product is" a mixture of unaltered ^fat with mono- and diglyeerides and free fatty add *(cf.* Fortini, Chem.. Zt«. 1&12, 36, 1117; MareussonJ Z. angew. Clu-in. **1913,** 26. 173).

Reicher (Annalen, 1885, 228, i>57) was one of the first to determine the velocity of saponificntion undSr varying conditions. The reaction is a typical bimolecular one and the velocity coefficient can be calculated by* means of **the** equation for a second order reaction :

$$k=\frac{1}{t(a-b)}\log_e\frac{}{a(b-x)}$$

where *a* and *b* are the original concentrations, and *a~x* and *b—x* the concentrations at the time *t.* The concentration of the alkali at any given time is determined by titration with standard acid and the concentration of the eater calculated from that of the alkali, as with an ester of the type of ethyl acetate, the disappearance of each gram-molecule of alkali entails the disappearance of a gram-molecule of ester *{cf.* Warder, Amer. Chem. J. 1882,8, 340 ; Ber. 1881, **14,** 13U1). The velocity constant *k* can be calculated by means of the equation

$$k=\frac{1}{C_{\infty}t}\log_e\frac{C_t(C-C_{\infty})}{C(C_t-C_{\infty})}$$

where C, C(and C^ denote respectively the concentration of the alkali just after mixing, the concentration' after time *t* and the concentration after complete hydrolysis {24-^18 hours).

Reiohera experiments were carried out at 9'4^D, and show that the velocity is pruiAically the same whether sodium, potassium or calcium hydroxide is used as saponifying agent. With strontium or barium hydroxide the velocity constants are somewhat smaller and .with a feeble alkali, such as ammonium hydroxide, the value for *k* is much less, *e.g.*

&NiOH: A'aiitOH—200:1.

The addition of methyl alcohol, glycol, glycerol, dulcitol or mannitol in the alkaline hydrolysis of ettyl acetate reduces the rate and for di-, tri- and tetra-hjdric alcohols the relationship $k=k_0G^{\wedge e}$ holds good, wlnre *k* is the velocity coefficient in a solution having a concentration of alcoholic hydroxyl groups equal to *c,* k_0 is the velocity coefficient in the aqueous solution and G is a constant (Selivanova and Syrkin, Compt. Tend. acad. sci. UJK.S.S. 1930, 23, 45).

The results observed with different esters ehow that the alkyl group R in the ester

R'COOR

influences the rate of hydroly&ia to a greater extent than it does when mineral acids are used for hydrolysing; thus the valuta for *k* using sodium hydroxide at i)-4° are : methyl acetate 3-49, ethyl acetate **8*31,** propyl acetate I-!).!, t'tfobutyl acetate 1-62, and *isoauiyi* acetate 1-64. The influence of the acyl group **R'CO** is also marked, as shown by the following values for *k* at 14-4*, using sodium hydroxide and ethyl esters: acetate 3-2, propionate 2-8, butyrate 1-7, (jobutyrate 1-73, wovaleratfc 0-62, and benzoate 0-83.

Numerous investigations Jiave shown that sulistituents **introduced** into the acyl group of an add, whether aliphatic or aromatic, have **a** marked effect on ihe alkalinf hydrolysis of its esters. In many cases this is a retarding **effect,** *e.g.* alkyl groups, especially in the **a-pomtion** in an aliphatic or in the o-position in a benzoie ester, generally retard hydroJvsis (Hjelt, Bvr. It96, 29, 1804; Gyr, *ibid.* **1408, 41,** 4308; **Kdk«,** *'A.* physikal. **Chem. 1897,** 24, 243). On the other hand certain substiiuents, *e.g.* **chlorine** in **atniiu** acid (Sudborough and Feihnan, **Froo.** (hem. Soc. 1897,13, 243), a-hydroxyl- **En aliphatic** acids (Findlay and Turner, J.C.S. 1905, 87, 747; Findlay and Hickmans, ***ibid.*** 1909, 95, 11)04), o-halogcn or nitro- in benzoie acid (Kdlas, *I.e.*; .Blakey, McCombie and **Scarborough,** ***ibid.*** I92f>, 2863) increase the rate of **alkaline** hydrolysis. A comparison of the alkaline hydrolysis in 85% nli/uhol c)l the series of **esters,** RCOjEt, where R increases from CH_3 to)t-C_7H_{1s}|' shows that the velocity coefficient decreases from CH, to H-C_3H, and then remains almost constant. When R consists of a branching chain the constant falls and when R=CMe_3 or CHEtg the hydrolysis is remarkably slow. The change in velocity corresponds with a change in E in the Arrhenius equation with the exception of eaters where the alkyl group branches at the a-carbon atom. As a rule E varies with the inductive effect of R. ,

For the *ortho* efffjpt in the hydrolysis of aromatic esters, *see* Kindler (Annalen, **IS28, 464,** 278).

The generalisation drawn-1>y V*: Meyer (Her. 1895, 28, 12(53; *cf.* Wegscheider, ***ibid,*** 1895^28, 2356), viz. that there is a simple relationship between the rate of hydrolysis of an ester by alkalis and its rate of formation by the ct-ialytic method of esterih'cation, does not hold. In a given aeries of esters the affinity constants tf.the acids from which the esters are derived tfnd the saponnicatjon constants of the esters follow the same order, but there is no direct proportionality between the two sets of numbers.

Olsson (Z. physikal. Chem. 1928, **133,** 233) concludes that the velocity coefficient is mainly influenced by the strength of the acid component of the ester, but in certain cases steric influences aflectnthe velocity in the opposite direction. It may be that the two influences are manifestations of one fundamental property, viz. the force of dissociation of the separate components (<•/. Williams, Gabriel and Andrews, J. Araer. Chem. Soc. 1928, 50, 1207). Smith and OlBson (Z. phyaikal. Chem. 1925, 118, *'M)* . point out that when the alkyl acetates are arranged in th« order of decreasing rates of hydrolysis by eof'ium hydroxide the series is identical with the corresponding series fcr the rates _of ester formation from the alcohols and acetic anhydride, and Olsson *{ibid.* 1927, 126, 243), from a study of the rates of hydrolysis of numerous acetates by the same alkali, iinds that branching in the alkyl radical, in contra* distinction to simple lengthening of the carbop chain, has a marked retarding effect on the rate. This conclusion is confirmed by Hol'tzschmidt, Vorob'ev ard Potanov (J. Gen. Chem. U.S.S.R. 1936, 6, 757), who find that for a given acyl group the ratio *kEtlkMe—0-51,* fcp_r/Jfc^=0-84 am *TtBulkPr* = 0-93, but for a given alkyloxy-group and different acyl groups the relationships are not so simple. The saponification of the ethyl esters of tbp saturated aliphatic acids has been studied by Evans, Gordon and Watson (J.C.S. 1938, 1439) to determine the effects of increasing R' from Me to n-butyl on P and £ in the Arrhenius equation.

The alkaline hydrolysi^of acetylated hydroxy-acids, *e.g.* acetylmandelic and acetylsalicylic acid, is bimolecular and free from side reactions, and a comparison of a- and 0-aeetoxyphenylpropionic acids shows that the ion of the j9-compounds is hydrolysed more than twice as rapidly as the a-ion (La Mer and Greenspan, J. Amer. Chem. Soc. 1934, 56, 1492). Also with unsaturated and phenyl substituted esters there is no parallelism between the rates of ester formation and the rates of saponification. The addition of an organic solvent to a mixture of methyl acetate, sodium hydroxide solution and alcohol tends to decrease the rate of hydrolysis (Caudri, Rec. trav. chim. 1929, 48, 422).

Kindler (Annalen, 1926, 450, 1; 1927, 452, 90) has examined the rate of hydrolysis of ethyl benzoate by a solution of sodium in 87-83% aqueous alcohol, and also.of the esters with Cl, Br, I, NO_2, CH_3 and NH_2 substituents, and finds that the rate increases in the order 2>-NO_2, m-NO_2, m-l, *p-\9* m-Br, p-Br, ro-CI, *p-C\\,* w-MeO, *p-Ph,* p-MeS, m-Me, p-Me, *p-Et,* p-MeO, wi-N H_2, *p-N* 4_2, or, generally, the reactivity decrecses with the negativity of the group X in the complex XC_eH_4-CO_2Et. When siirilar esters are examined, but with -CH_2-, •CH_2-CH_2- or -CH:CH-, interposed between the nucleus and the carbethoxy group the substitufiits have similar effects and follow the same order, but the effect is most marked in theotienzoic series, and least in the substituted ptfenylacetates.

The same author (Ber. 1936, 69 [B], 2792) attempts to correlate the rate of hydrolysis of an ester, RCO_2Et, with the firmness of the union between the R and carbethoxy-group.

Olivier and Weber (Rec. trav. chim. 1934, 53, 899), by a comparison of the ratio &OH/&H« •.«• the ratio of the velocity coefficients for the alkaline and acid hydrolysis-.of an ester, show that with different esters from the same alcoh *d* the ratio increases with the strength of the acid from which the ester is derived.

Ingold (J.C.S. 1930, 1032) claims that the ratio *konlkn.* is free from all steric factors and represents only porar effects, and in a series of communications (Ingold *ind co-workers, *ibid.* ·1930, 1039, 1375; 1931, 2035, 2043, 2170) the values for this ratio for different series of este.-s are given, calculated by a method based on Dawson's equation *(ibid.* 1926, 2872, 3166; 1927, 213, 1148, 1290)

$$2p_a{}^* \text{-log}\,K_w = \text{log}\,fc_O\text{ii}/{}^*H^{l}$$

and thus involving the determination of the hydrolytic stability maxima of carboxylic esters. The ratio varies from 2 for ethyl acetate to 32 for ethyl chloroacetate, 160 for ethyl acetoacetate and 12,000 for ethyl aminoacetate.

The results for the two groups of esters:

$$XCH_2\text{-}CO\text{-}OCH_2\text{-}CH_2Y$$

and

$$XCO\text{-}OCH_2Y,$$

where X and Y represent substituents, show that the ratio increases regularly with the electron-attracting nature of X, *e.g.* from H through Cl, CH_3-CO to NH_3+, but decreases with the electron-donating value of X, and similar generalisations hold good for the substitueilt Y.

Three general conclusions are drawn: (1) that two methyl groups in the same position relatively to -COO* in R- CO OR' displace p_s* by roughly equal amounts ; (2) that the displacement of p_H* by the introduction of a methyl or *gem* cjimethyl group decreases approximately geometrically as successive carbon atoms are included normally between the group and the -COO* nucleus; (3) that the displacement of the minimum caused by any group in R' bears a nearly constant ratio to the displacement produced by the same group in R. It is further concluded that the same quantitative measure of polarity may be derived from other chemical reactions.

Conclusions on the relationship between polar effect and energies of activation (E) in processes of hydrolysis have been drawn by several investigators. Ingold and Nathan *(ibid.* 1936, 222) have examined the alkaline hydrolysis of *p*-substituted benzoic esters from the point of view of the Arrhenius equation $\&=Be^{-B/RT}$ in 85% aqueous alcohol at 25° and 50°; B is the reaction constant which depends primarily uponr -the frequency of collision of the reacting molecules (Moelwyn-Hughes, " Physical Chemistry," 1940, p. 532); *k* varies with the substituent in the following order:

$$NH_2 < OMe < Me < H < Cl < I < Br < NO_2$$

°ver a 5,000 fold ra*ige and the activation energy decreases in the order:

$$NH_2 > OMe > Me > H > Hal > NO_2$$

and the linear relationship between £ and logfc corresponds with a constant value of B in the equation. Timms and Hinshëlwood *(ibid.* 1938, 862), from a study of both acid and alkaline hydrolysis in iaqueous acetone and aqueous alcohol, show that the reaction is facilitated by recession of electrons from the seat of the reaction. The value of £ is high in acid hydrolysis and the effects of substituents arc smaller; also /\ increases with E in contrast with the cpnstant value in alkaline hydrolysis. The effect of the solvent is apparently the opposite in the two cases. The effects of the transmission of substituent influences have been studied by Newling and Hinshelwood *(ibid.* 1936,1357) and Tommila and Hinshelwood *(ibid.* 1938, 1801). The esters examined belonged to the scries:

$$XC_{fl}H_4\text{-}CO_2Et, \quad XC_{fl}H_4\text{-}CO_2Me,$$

$$CH_3\text{-}CO_2CH_2\text{-}C_6H_4X$$

and

$$CH_3\text{-}CO_2C_6H_4X$$

---

[1] Where p_H* is the p_H at which the velocity is at a minimum and K_v is the ionic product of water.

where X is in the *m-* or p-position. In all cases of alkaline hydrolysis B remains constant and changes due to the substituent are measured in change in £. In acid hydrolysis the change is similar but less regular. In the former case the value JE[l] gives a qualitative measurement of the influence of the different substituents for a given series, and the values are fairly constant for all the series. The changes in E are a measure of the transmission of the electronic effect of a given substituent through the given structured.

The same set of substituents does not produce equal effects in different reactions, but if JE_X is the change caused by any given substituent in one reaction and JE_2 that caused by the same substituent in a second reaction then $JE_2=aJE_2$ where a is practically constant for all the substituents. The transmission coefficient for the influence of the substituent to the reaction centre is greatest in the case of the alkaline hydrolysis of benzoic esters and decreases in the order phenyl acetates (alkaline) (0-71), benzyl acetates (alkaline) (0-36), benzoic esters (acid) (0-2), phenyl acetates (acid) and benzyl acetates (acid). The numbers in brackets give the relative values.

Ingold and his co-workers *{ibid.* 1931, 2035) from the values of k_H at different temperatures have calculated the values of A and B in the equation

$$\log_{10}{*}H=A-B/T .$$

Although the values of *k* do not fall regularly but exhibit a maximum with the propionyl radical, neither A nor B exhibits this anomaly; both A and B fall as the length of the acyl group increases from acetyl to pentoyl. A is primarily a steric function and B a polar function.

The activation energies and velocities of acid and alkaline hydrolysis of trilaurin, tripe knitin, tristearin, aa-dipalmitin and a-monopalmitin in the expanded state in monolayers approximate to those in homogeneous solution and on compression to the condensed state the values of E rise although those of *k* change only slowly (Alexander and Rideal, Prc 3. Roy. Soc. 1937, A, 163, 70).

The activation energies for alkaline saponification of substituted aromatic esters can be correlated with the dipole moments (ft) of the substituent groups according to the equation $E=E_H+flft+6/*^2$, where *a* and *b* are constants (Nathan and Watson, J.C.S. 1933,1249).

(4) Finely Divided Metals, Metallic Oxides and Salts as Catalysts.—Esters can also be hydrolysed by water with finely divided metals as catalysts, *e.g.* Neilson (Amer. J. Physiol. 1903,10, 191) has shown that platinum Mack accelerates the hydrolysis of ethyA butyrate. The reaction is, however, very slow, and increases with the amount of platinum present. The maximum effect is obtained at 50°, and the activity of the catalyst is readily destroyed by various " poisons." The reaction is reversible as platinum black can also accelerate the esterification of butyric acid in ethyl alcoholic solution.

Sabatier and Maihle (Compt. rend. 1911,152, 494) have shown that titanium dioxide is a good catalyst for the conversion of acids and alcohols into esters. The method adopted is to allow a mixture of molecular quantities of the vapours of the two compounds to pass over a column of the dioxide kept at 280-300°. The yield of ester is much'the same as in Berthelot and Menschutkin's experiments, but the process is extremely rapid. The reactior is reversible, and using equivalent quantities of acid and alcohol an approximately 70% yield of ester was obtained in most cases examined. A similar method may also be used for hydrolysis of esters. It consists in ullowing a mixture of the vapour of the ester with an excess of steam to pass over the titanium dioxide at 280°-300°.

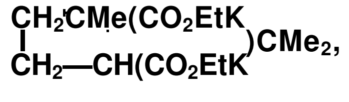
Similar results can be obtained with thorium oxide as catalyst provided aromatic acids of the type of benzoic are used *(ibid.* 1911,152, 358).

Certain neutral metallic salts also act catalytically on the hydrolysis of esters by water (Kellog, J. Amer. Chem. Soc. 1909,31, 403, 886). The salts which have been investigated are potassium chloride, bromide and iodide. The catalytic effects are comparatively small when compared with those of strong acids; the chloride has the greatest effect and the iodide the least, and when the concentration of the salt reaches a certain value the catalytic effect is negative.

Holmes and H. C. Jones (J. Amer. Chem. Soc. 1916, 38, 105), working with aqueous solution of methyl acetate and methyl formate, show that salts with water of crystallisation have a greater effect in increasing the velocity of hydrolysis than anhydrous crystalline salts. Certain salts sueh- as LUSO4, Nal,, $SrBr_2$, UBr and Kl produce retarding effects. On dilution the effect with salts > having water of crystallisation decreases mo*£ rapidly than with crystalline anhydrous salts, and this showe-^hat the decomposition of the esters cannot be due to the hydrolysis of the salts alone.

(5) Esters of Dibasic Acids.—J. Me;rer (Z. physrkal. Chem. 1909, 66, 81; 67, 257) by the study of the hydrolysis of esters of d*Hasic acids (tartaric, succinic and camphoric) with hydrochloric acid as catalyst, has proved that the reaction proceeds in two distinct stages: (a) normal ester+ water->• acid ester 4- alcohol; *(b)* acid ester-f water -> acid+ alcohol. With the ethyl esters of symmetrical dibasic acids, *e.g.* tartaric and succinic, the whole reaction appears to be unimolecular as the velocity constant* for the first stage is almost exactly double that for the second stage, and the whole is pseudo-unimolecular. This simple relationship docs not hold good for oxalic acid or unsaturated acids, *e.g.* maleic.

In the case of ethyl camphorate, the ester of an unsymmetrical acid, the two stages proceed at very different rat*s; the normal ester,



$$\begin{array}{l} CH_2CMe(CO_2EtK \\ | \qquad\qquad\qquad\quad)CMe_2, \\ CH_2—CH(CO_2EtK \end{array}$$

is rapidly hydrolysed to the j9-acid ester,

$CH_2CMe(CO_2EtK$

$CH_a-CH(CO_2H)/$

---

[1] $JE=E_U-E_x$, where E_H is the energy of activation of the unsubstituted acid and E_x that of the substituted acid.

but this latter is fairly stable, and the method is a convenient one for the preparation of the acid ester. For different esters of the same acid the influence of the alcoholic group on the rate of hydrolysis is scarcely noticeable, whereas the constitution of the acyl group has a marked effect.

Experiments carried out with the same esters using alkali hydroxide as hydrolysing agent show that here also the reaction proceeds in two distinct stages, but the relationship between the velocity constants of the two is not so simple as when hydrochloric acid is used.

The two stages are:

(1) $R(CO_2Et)_2+NaOH$
$\rightarrow R(CO_2Na)CO_2Et+EtOH$

and

(2) $R(CO_2Na)CO_2Et+NaOH$
$\rightarrow R(CO_2Na)_2+EtOH$

and their respective velocity coefficients are denoted by k_1 and k_2. Ritchie (J.C.S. 1931, 3112) has developed an accurate method for determining k_1; and k_2 can be readily determined by employing the sodium salt of the monoethyl ester, and using the usual bimolecular formula for calculation, whereas Nielsen (J. Amer. Chem. Soc. 1936, 58, 206) has used a conductivity method. Addition of ethyl alcohol diminishes very considerably the rate of the reaction in aqueous solution. The ratio decreases in all cases as the proportion of alcohol in the mixture is increased.

With ethyl oxalate the ratio k_1/k_2 is 10^4, with ethyl malonate 100, ethyl succinate 10 and ethyl sebacate 2-8 (Ingold, J.C.S. 1930, 1375; 1931, 2170), and the whole process cannot be represented as a simple bimolecular reaction. The values have been used for calculating *r*, the distance in cm. between the carboxylic groups and r x 10^8 varies from 2-9 for oxalic to 12-38 for azelaic. With the esters derived from symmetrical dihydric alcohols, *e.g.* glycol diacetate, $C_2H_4(OAc)_2$, although the hydrolysis proceeds in two distinct stages the velocity constants of the two stages bear a simple relationship to one another, *e.g.* 2:1, and hence the whole appears to be a bimolecular reaction. The same holds good for the hydrolysis of glyceryl triacetate, where the three distinct stages proceed at the relative rates 3:2:2.

Measurements of the velocity of hydrolysis by potassium hydroxide in mixtures of alcohol and water show that the velocity coefficient is not a continuous function of the composition of the solvent. At 15° the discontinuities in the plotted curves correspond closely with simple molar ratios of alcohol and water, and at higher temperatures the number of such discontinuities is small. Similar results are not met with in other reactions studied in alcohol-water mixtures (McCombie, Scarborough and Settle, *ibid.* 1921, **119**, 370; **1922**, **121**, 243, 2308). The values of k_1 and k_2 and also the ratio k_1/k_2 diminish as the percentage of alcohol increases (Ritchie, *ibid.* 1931, 3112).

(8) Esters of Sulphonic Acids.—Esters of sulphonic acids, are also hydrolysed by water, mineral acids or alkalis, and since most of the sulphonic acids are very strong acids, their esters are hydrolysed quite readily by water alone. The esters are also converted into the corresponding acids when heated with alcohol (Krafft and Roos. Ber. **1893**, 26, 2823; Kastle and Murrill, Amer. Chem. J. 1895, 17, 290), a reaction in which an alkyl ether is also formed

$$R{\cdot}SO_2{\cdot}OEt+EtOH=R{\cdot}SO_2{\cdot}OH+Et_2O.$$

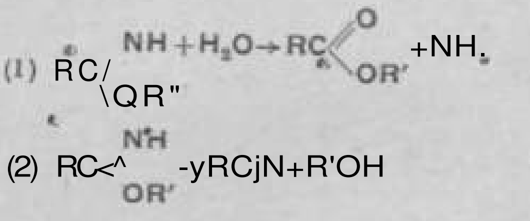
This decomposition proceeds slowly at the ordinary temperature, and is brought about more readily by methyl than by ethyl alcohol.

Kastle, Murrill and Frazer (*ibid.* 1897, **19**, *604*) have shown that 0·1N-solutions of sulphuric and acetic acids have no effect on the hydrolysis of esters of sulphonic acids by water. Hydrochloric and hydrobromic acids, on the other hand, have an apparent retarding effect, but this is due to the fact that the halogen hydracids can react with the ester according to the equation:

$$R{\cdot}SO_2{\cdot}OEt+HCl\rightleftharpoons R{\cdot}SO_2{\cdot}OH+EtCl$$

a reaction which does not affect the total acidity of the solution. A more detailed investigation has proved that this second reaction proceeds more rapidly and to a greater extent than the hydrolysis of the ester by water. The hydrolysis of a sulphonic ester by means of a large excess of water or alcohol in acetone solution gives concordant values for *k* when the equation for a unimolecular reaction is used. Alkalis are much more efficient hydrolysing agents than water for sulphonic esters; this may be due to the alkali acting independently of the water or to the alkali catalytically affecting the hydrolysis by water. The constants at 25° for methyl benzenesulphonate, using water and N-potassium hydroxide solution are in the ratio 1:90 (Wegscheider and Furcht, Monatsh. 1902, 23, 1093). When the neutral ester of a mixed carboxylic sulphonic acid is hydrolysed, *e.g.* $EtO{\cdot}SO_2{\cdot}C_6H_4{\cdot}CO_2Et$, the **$SO_2{\cdot}OEt$** group is hydrolysed much more readily than the CO_2Et group, and an acid ester of the type $HOSO_2{\cdot}C_6H_4{\cdot}CO_2Et$ is formed.

(7) Imino-ethers can be hydrolysed in two different ways:



$$(1)\ RC(:NH)OR'+H_2O\rightarrow RC(:O)OR'+NH_3$$

$$(2)\ RC(:NH)OR'\rightarrow RCN+R'OH$$

The former reaction is greatly accelerated by acids and the latter by alkalis. According to Stieglitz (Amer. Chem. J. 1908, 39, 29, 166) the former reaction consists in the hydrolysis of the complex cation $(RC(:NH_2)OR')^+$, and the latter in the decomposition of the anion

$$RC(:N^-)OR'$$

The effect of alkalis is much more pronounced than that of acids. When water alone is used it is the non-ionised ether which is decomposed.

B. HYDROLYSIS OF OTHER ACYL DERIVATIVES.—The chlorides, amides, anilides and anhydrides of organic acids can be hydrolysed in much the same manner aa estersj *e.g.*

$$RCO{\cdot}Cl\text{-}J\text{-}HOH = RCO{\cdot}OH + HCl$$
$$RCO{\cdot}NHPh + KOH = RCO\text{-}OK + NH_2Ph\text{-}$$

Amides.—As a rule the derivatives of aliphatic acids are hydrolysed more readily than those derived from aromatic acids, *e.g.* **ttoetam**ide more readily than bonzamide. The hydrolysis is usually effected by boiling with alkali **hydroxide,** but the prssence of ortAo-su bstituents in derivatives of beazoic acid retards hydrolysis to an appreciable extent (V. Meyer, Byr. 18E)4, 27, 2153; Sudborough. J.O.S. 1894, 65, 1030; 1895," 67, 587; 1897, 71, 229; Reed, Amcr. Chem. J. 1899, 21, 281). When two such substituents are present the amide cannot be hydrolysed by boiling with potassium hydroxide solution, but the hydrolysis may be accomplished by heati-ig with concentrated hydrochloric or hydrobromic acid under pressure in sealed tubes. One of the most convenient methods for converting a *diortho** substituted be nz on it rile into the corresponding acid is to liydrolyse to the amide $RCN+Hi,O = RC0NH_2$ by heating at 120-130° with 90% sulphuric acid^ nnd when cold to replace the amino group by hydroxyl by the addition of sodium nitrite solution (Bouveault, Bull. Soe. chim. 1892, [iii] 9, 368; Sudborough, J.C.S. 1895, 67, 602^.

AD a)3-olefin Unking in the acyl group haa a retarding effect on the hydrolysis of an acid amide with sulphuric acid or alkali (Yathiraja and Sudborough, J. Indian Inst. Spi. 1925, 55).

The hydrolysis of aeetamide by hydrochloric acid has been studied by Acree and Nirdlinger (Amer. Chem. J. 1907, 38, 489). The amount of hydrolysis after given intervals of time was determined by introducing known volucfe) of the reaction mixture into a Lunge nitrometer containing sodium hypobromite solution and measuring the nitrogen evolved. Their results show that at 05° the reaction ia practically unimolecular when dilute solutions are used, but that the values for *k* tend to increase with the time, probably owing to.,a slight catalytic effect of the ammonium chloride formed on hydrolysis.

The mechanism of the reaction is probably analogous to that of the acid hydrolysis of esters, the first sNige being the formation of a cation $RCONH_2H^+$ from the amide and hydrion and the second stage the reactior of tlus cation with water yielding the organic add and the ammonium ion.

Croker and Lowe (J.C.S. 1907, 91, 593, 952) have studied the hydrolysis of the amides of the simple aliphatic acids with hydrochloric acid, anS also with sodium hydroxide solution/"using the electrical conductivity method in order to determine the amount of amide hydrolysed. Tin; order of the amides when hydrochloric acid is used ia formamide, propionamide, ucetamide, frobutyramide, cupronamide, butyrainide and valcramide; but with sodium hydroxide *the* order ia formamide, acetamide, propionamide, capronamide, butyrainide, wobutyramide and valeramide; in both eases formamide ia the amide most readily hydrolysed, and in every case the hydrolysis with alkali proceeds more rapidly than that with hydrochloric acid under similar conditions.

Most compounds of the type of alkylated acid amides, *e.g.* compounds containing the grouping **R'CO** N H R, can be hydrolysed. Thus hippuric acid (ben zoyigJycine),

$$C_6H_5CONHCHgCO_2H,$$

is hydrolyeed to benzoic acid and glycine hydrociiluride when boiled with concentrated hydrochloric acid. For alkaline hydrolysis of compounds of the type $C_:CI_2\{CONHR\}_{2(}$ where $R\text{-}C_8H_5$, C_aH_4Me; C_aH,CI, C_TH_{Ifi}, CH_aPh, *sec* Naik, Trivedi and Melita, J, Indian Chem. Soc. 1938,15, 426.

Nitrites.—The hydrolysis of an aliphatic nitrile by either acids or alkalis occurs in two distinct stages, the intermediate product being the acid amide. The first reaction takes place much more slowly than the second, and is the ono actually measured when hydrochloric acid is used as catalyst (Kiipi, Z. physikal. Chem. 1914, 86, 041; for alkaline hydrolysis *cf. ibid.* p. 740).

E. Fischer (Ber. 1898, 31, 3206) has pointed out that uric aeid and similar cyclic nitrogen derivatives. are less readily hydrolysed by dilute alkalis'than their alkylated derivatives, *a.(j.* 1:3:9-trimethyluric acid. Similarly the amide and methyl ester of the methyl ether of salicylic acid are more readily hydrolysed than the corresponding derivatives of salicylic acid itself, and in all such cases the compounds most resistant to the hydrolysing agent are those which can form metallic salts with the alkalis.

The hydrolysis is analogous to the alkaline hydrolysis of esters, the comrjjex anion

$$R\text{-}C(O^-)(OH)(NH_3)$$

being the first product and the second stag^the decomposition of this into ammonia and Lie anion of the organic acid. When the **amide** contains a replaceable hydrogen atom, salt formation of a different type occurs, and the characteristic complex anion is not formed.

Lactones and Anhydrides of Dibasic Acids.—In the hydrolysis of both types of compounds water is added but no fission occurs; the first givoup gives the hydroxy-acids a-id the second the dibasic acids.

The relative rates of hydrolysis of lactones have been used by Haworth and Nicholson (J.O.S. 19*}, 1899) to determine whether a lactone derived from tho sugar acids is a *y* or a S-lactone, as the **formft** is hydrated much more slowly than thejatter.

For the ketouie and acid hydrolyaes of substituted ethyl acetoastates and their utilisation in the preparation of substituted acetoncs-»aud acetic acids, *see* ACETOACETIO ACID, and for hydrolysis of aromatic sulphonic acjtls by mineral auida, whero *o-* or p-methyl groups facilitate and o- or p-amino groups retard hydrolysis, *aee* Crafts, Bull. Soc. chim. 1907, [ivj, 1, **917.**

IV. HYDROLYSIS OF GLYCOSIDES, DI- AND POLY-SACCHAKIDES.

As a rule, compounds of the ether type, *i.e.* compounds containing two alkyl or substituted alkyl groups attached to oxygen, are not readily hydrolysed when boiled with alkali or acid solutions.

All the carbohydrates of the di- or polysaccharide type? take up water when warmed with dilute mineral acid and are resolved into monosaccharides. The best known examples **are:**

Sucrose (cane.sugar)-fv-ater
=glucose (dextrose)+fructose (laevulose)
Malt sugar+ water=glucose
Lactose (milk sugar)+water=glucose+galactose.

All these reactions can be represented by the equation:

$$Ci2H_{22}O_n+H_2O\text{-}C_6H_{12}O_{fl}+C_6H_{12}O_6$$

Starch is also hydrolysed by dilute mineral acids yielding as final product glucose:

$$(C_6H_{10}O_5)_M+nH_2O=wC_6H_{12}O_6$$

The hydrolysis of cane sugar (sucrose) by means of dilute mineral acid has been examined in detail; it is usually referred to as the inversion of sucrose, as the optical rotatory power changes from + to 77 during the reaction. The investigations ofWilhelmy (Pogg. Ann. 1850, 81, 413, 499) proved that in dilute solution the amount of sugar inverted is proportional to the amount present, or, in other words, the reaction is unimolecular. The method of determining the concentration of the sucrose at any given time is based on polarimetiic readings. If the original rotation ....of the sucrose solution be +x°, and after complete inversion be — *y*°, then the"total change is *x*°-\-*y*°. If after an interval of time / the rotatory power of the solution is +z°$_M$then the fraction of sucrose which has undergone inversion is $\frac{x-z}{x+y}$, and the velocity constant can be determined by substituting the values for t_t C$_o$, and C_t in the equation

$$K=1/t\log_e(C_o/C_t)$$

where C$_o$ represents the concentration of the sucrose at the beginning, and can be expressed by *x*+*y*$_9$ *Ct* represents the concentration at time *U* and is equal to *x-z*. The velocity of inversion is directly proportional to the concentration of the hydrochloric acid, and increases with rise in temperature (J. Meyer, Z. physikal. Chem. 1908, 62, 59 ; Hudson, J. Amcr. Chem. Soc. 1908, 30, 1165; Rosanoff, Clark and Sibley, *ibid.* 1911, **33,** J911).

The dilatometrfo method has been used for determining the rate of hydrolysis of sucrose with dilute hydrochloric acid and the results follow the unimolecular formula (Hitchcock an<*Dougan, J. Physical Chem. 1935, **39,** 1177) and the velocity coefficients agree wi|h those determined polariraetrically. The total contraction per gram-molecule at infinite dilution is 6-92 c.c. at 25° when the products are in inutarotation equilibrium.

The hydrolysis of other disaccharides, and of glycosides by dilute mineral acids also follows Wilhelmy's Law, but the relative rates are very different; the following values have been obtained for iV-sulphuric acid at 20°: iactose 1, maltose 1*27, sucrose 1240 ; also a-methylglucoside 100, and /J-methylglucoside 179. The hydrolysis of carbohydrates by means of dilute mineral acids is the basis of certain commercial methods for the manufacture of glucose. Large quantities of this carbohydrate are manufactured by boiling starch *(e.g.* potato or maize/ starch) with dilute sulph'aric acid, removing the acid by precipitating as calcium sulphate and" evaporating the clear solution under reduced pressure. Hydrochloric a,cid is used in U.S.A. and wood cellulose is hydrolysed by concentrated hydrochloric acid in Germany, and the resulting glucose fermented for the production of power alcohol.

All glycosides, including the simple synthetic alkylglucosides and all the more' complex natural glycosides *(v.* GLYCOSIDES), are readily hydrolysed by dilute acids or alkalis. In these compounds the alkyloxy- or more complex radical is attached to the first carbon atom of the aldose molecule, *i.e.* the carbon atom of the group with aldehydic functions in aqueous solution. The primary product is the corresponding *a*- or jS-form of the aldose, but as these rapidly undergo inutarotation in the presence of acid or alkali the final product is a solution of the a- and /J-forms in equilibrium. Other methyl derivatives, *e.g.* those with OMe in positions 2, 3, 4 or 6 of a pyranose, are not readily hydrolysed and behave as ordinary ethers.

Ultra-violet light can bring about the hydrolysis of glycosides, also of certain esters and amides, but not of polypeptides or proteins (Gui£aume and Tanret, Compt. rend. 1935, **201,**1057).

From determinations of the velocity coefficients for hydrolysis of certain fructo-furanosides and -pyranosides at 20-60° Heidt and Purves (J. Amer. Chem. Soc. 1938, 60, 1206) prove that the generalisation log ifc=log a-6/T holds good, and that log a, *b* and E (activation energy) increase when methyl replaces benzyl, when an a- replaces a 0-isomeride and when a pyranoside replaces a furanoside.

Neutral Salt Action.—The* investigations of Ostwald (J. pr. Ghem. 1883, pi], 28, 460), Spohr *(ibid.* <*.1886*$_9$ [ii], **33,** 265), and Arrhenius (Z. physikal. Chem. 1889, 4, 234; 1899, **31,** 207) prove that the addition of a substance which is largely ionised in aqueous solution accelerates the hydrolysis of esters or of carbohydrates by aqueous solutions of strong acids. This has beeifproved by the addition of metallic chlorides to mixtures in which hydrogen chloride is the catalyst, the addition of bromides to hydrogen bromide, and of nitrates to nitric acid. The majority of chlorides have much the same effect if readily ionised, whereas a salt such as mercuric chloride, which is only partly ionised, has a much feebler action.

Caldwell (Proc. Roy, Soc. 1906, A, 78, 272), working with weight-normal solutions, shows that the presence of metallic chlorides increases the catalytic activity of hydrogen chloride in the inversion of cane sugar, and that calcium chloride has the most pronounced effect. Similar effects on the activity of nitric acid are produced by nitrates {Why m per, ***ibid.*** 1907, A, 79, 576). Salts also tend to increase the activity of hydrogen chloride when used as a catalyst in the hydrolysis of methyl acetate (Armstrong and Watson, ***ibid.*** 1907, A, 79, 579), but their effect is not so marked as in the case of the inversion of sucrose (c/. Armstrong, *ibid.* 1908, A, 81, 90; Armstrong and Crothers, *ibid.* p. 102). Sentcr (**JICJS.** 1907, 91, 462) states that in equivalent solutions of different salts the effect is practically independent of the nature of the ealt (c/. Jones, Z. physikal. Chem. 190G, 65, 355, "429). Change of temperature has but little effect on neutral Bait action, and it is concluded that probably the earlier suggestion of Arrhenius is correct, namely, that the ions of the neutral salt have some action on the hydrions-or hydroxyl ions of the catalyst.

Heed (Amer. Chem. J. 1899, 21, 342) states that neutral salts retard the hydrolysis of acid amides by alkalis; and Arrhenius (Z. physikal. Chem. 1887, 1, 110) and Rpohr ((6M*. 1888, 2. 1194) claim that the same effect is produced by salts on the rate of hydrolysis of esters by alkalis. For the action of neutral salts on hydrolysis of chlorbacetic acid, c/. Section IIIB, p. 385a.

V. HYDBOLYSIS BY ENZYMES.

Many of the hydrolytic processes induced by aqueous solutions of acids or alkalis can also be brought about by the complex organic substances found in animal and plant tissues known as enzymes. For chemical nature of enzymes, purification, factors influencing enzyme action and kinetics of enzyme action, see ENZYMES.

The name given to a particular hydrolysing enzyme usually indicates the substance it is capable of hydrolysing and in these cases the termination *ase* is used. Thus maltase is the enzyme which hydrolyses maltose, amylase the enzyme which hydrolyses starch; but in some cases older names which were in use before this scheme was adopted, are still retained, *e.g.* suerase, the enzyme which inverts sucrose (cane sugar), is still called invcrt&se or even invertin, the common digestive enzymes are termed trypsin and pepsin. The substance which is decomposed by the enzyme A usually termed the substrate.

The more important types of hydrolysing enzymes are i

(I) Ester- and fat-splitting enzymes—lipases and estorases.

(II) Carbohydrate- and glycoside-spnVing enzymes. Invertase or suerase, maltase, amylases and the naturally occurring glycoside-splitting enzymes, *e.g.* amygdalin, myrosin, etc.

(III) Proteolytic enzymes which hydrolysc proteins and polypeptides (for list, *see* ENZYMKH).

All three groups are of great interest as they play an important part in the digestion and ussimilation of food. Many arc also of value in industry, *e.g.* in the malting of barley where the invertase or amylase breaks down the starch through dextrins and maltose to glucose.

As catalysts they differ in several respects from the general hydrolytic catalysts, mineral acids and alkalis:

(1) They are more sensitive to temperature differences. The activity of all is destroyed at a temperature below 100° and for each there is usually an optimum temperature.

(2) They are also sensitive to the acid or alkaline reaction of the substrate and for each enzyme very narrow limits of p_s give the best results.

(3) They are extremely readily poisoned, but can withstand antiseptics which kill most micro-organisms; strong antiseptics such as formaldehyde destroy their activity.

(4) It is not essential that the products obtained by the two processes should be identical. Thus in the case of the inversion of cane sugar by invertase the products are aglucose and a-fructose, whereas when mineral acids are used the products are equilibrium mixtures of a- and jS-glucose and a- and /J-fruetoae, as the a-glueose and the a-fructose undergo immediate mutarotation in the presence of the mineral acid. Another example of a similar type is met with in the trisaccharide, raffinose; when hydrolysed by acid this yields galactose, fructose and glucose, the same sugar with raffinase yields molibiose and fructose, and with emulsin it yields galactose and sucrose. Similarly natural products of protein character yield comparatively simple amino-acids when hydrolysed with acids or alkalis, whereas with enzymes, more complex intermediate products are formed.

(5) Although the processes of hydrolysis by acids and by enzymes are frequently compared it should be borne in mind that the rate at which a given substance is hydrolysed by the two different types of catalysts is frequently quite different, *e.g.* sucrose is hydrolysed by invertase much more readily than by a JV-solution of hydrochloric acid; in fact, with a **conceat&tad** solution of invertase at 0° the inversion is practically instantaneous.

(6) An important point of difference between hydrolysis by means of acids or alkalis and hydrolysis under the influence of enzymes is that any particular enzyme has a very restricted use as a catalyst or the action of enzymes is essentially selective. Thus lipase can hydrolyse esters and not carbohydrates; maltase can hydrolyse maltose but not sucrose. That a slight difference in the configuration of two isomeric compounds is sufficient to affect their reactivities with a particular enzyme is shown in the case of the two stercoisomeric methylglucosides and of corresponding a- and /J-glycosides (both natiral and synthetic). *(See* FE it MENTATION and GLYCOSIDES.)

The lipases, *e.g.* ftum castor oil or blood serum, hydrolyse glycerides in three distinct stages characterised by three velocity coefficients and corresponding with the elimination of the three acyl groups (Virtanen and Lindeberg, Suoraen Keni. 193G, 9 B, *2),* but do not readily hydrolytte ethyl estern (Rdihel and Reinmuth, Z. physio). Chem. 1D3G, **244,** 78). Whereas pancreatic lipase splits both ethyl esters and glycerides (Balls and Matlock, J. Biol. Chem. 1938, 123, 678) but,,the former less rapidly. A careful study (B&mann and Rendelen, Z. physiol. Chem. 1936, 238, 133; *cf. ibid.* 1933, 222, 121; Langenbeck and Baltes, Ber. 1934, 67 [B], 1204) of the splitting of acid esters, dimethyl esters and methyl ester amides,

$$\mathrm{Ctf_2Me\text{-}[CH_2]_w\text{-}CONH_2}$$

of the dibasic acids, malonic to adipic, by pigs' liver esterase and of the effects of altering H+ concentration and substrate concentration leads to the conclusion that die enzyme binding power of the ester group is controlled by the electrochemical nature of the adjoining groups. The carboxyl group inhibits the formation of the additive compound and can be counteracted or restricted by increasing the distance between the CO_2Me and CO_2H groups, by esterifying the CO_2H group or converting it into $CONH_2$ and also by reducing the dissociation of the CO_2H group.

Pigs* esterase hydrolyses maleic esters (methyl to hexyl) more readily than the isomeric fumarates, oleic somewhat more readily than elaidic ester but erucic and brassidlc esters at equal rates (Fabisch, Biochem. Z. 1931,234, 84).

Esterases, *e.g.* from human liver or pancreas, pig's kidney or liver, are further characterised by producing asymmetric hydrolysis with a racemic ester, *e.g.* eft-ethyl mandelate or homologues, as one enantiomorph is hydrolysed more readily than the other (Ammon and Geisler, Biochem. Z. 1932, 249, 470; *cf.* Dawson, Platt and Cohen, Biochem. J. 1926,20, 536). Similarly the rf-form of the butyrate of pjienylmethylcarbinol, CHMePh-OH, is hydrolysed more readily than the /-form *(ibid.-332,* 247, 113; 249, 446). By comparing the rates for *d-,* Z- and (tf-mandelates the ratio is 130:5-5 and with the ^/-compound the *d* inhibits the hydrolysis of the *I* (Schwab and others, Z. physiol. Chem. 1933, 215, 121). Many experiments have been made on the effect ofvt«dding compounds of different types; some Accentuate the difference, others lessen it.

(7) Enzymes can act not merely as hydrolysing but also as synthesising agents. The process of hydrolysis is thus, in most cases, a balanced reaction, but the equilibrium' is mainly in the direction of analysis and not synthesis. To obtain appreciable synthesis the amount of water must be restricted. The synthesising activity of an enzyme was fnst demonstrated by Croft Hill (J.C.S. 1898, 73, 634; 1903, 83, 5S8) in the case of maltose. The greater portion of the maltose is hydrolysed by the enzyme to glucose, but a certain proportion of disaccharide is always present.

A series of alkytyff-glucosides and galactosides has been synthesised /by Bourquelot using emulsin, and a-glucosides by an enzyme extracted from bottom yea*t by means of water (Arn. Chim. 1913, [viii], 29, 145; 1915, [ix], 3, 287; 1915, [ix], 4, 310; *cf, also* Bayliss, J. Physio]. 1913, 46, 236).

Bayliss has synthesised arbutin from quinol and dextrose by means of emulsin in the presence of glycerol (J.C.S. 1912, 102, i, 328). The synthetic action of enzymes in forming polypeptides and proteins has also been demonstrated (Abderhalden, *ibid.* 1915, 108, i, 725). Both glycogen and starch have been synthesised from glucose phosphoric acid (Hanes, Nature, 1940,145,335).

Lipases and esterases also have synthesising properties; natural fats have been synthesised by the action of lipases on mixtures of glycerol and the higher fatty acids in the absence of a large excess of water. Esterases can give rise to asymmetric synthesis. The lipolytic enzymes present in certain seeds are made use of on a commercial scale for the preparation of fatty acids from n'atural fats *(cf.* Welter, Z. angew. Chem. 1911, 24, 385; Pottevin, Bull. Soc, chim. 1906, [iii], 35, 693). For details of the synthetic functions of enzymes, *see* FERMENTATION, ALCOHOLIC.

In some of these balanced actions between carbohydrates or esters and enzymes it has been shown that the equilibrium mixture is the same, whether mineral acid or enzyme is used, *e.g.* Visser's experiments using invertase and emulsin; in other cases, however, the equilibrium mixture with the enzyme is quite different from that obtained when an acid is used, *e.g.* Dietz's experiments with lipase and isoamyl *n*-butyrate (Z. physiol. Chem. 1907,52, 279).

The effects of numerous compounds on the hydrolytic activity of enzymes have been studied and a dilatometric method for studying ester formation and hydrolysis by esterase from pigs' pancreas developed (Ammon and Bartscht, Biochem. Z. 1934, 268, 231).

Glycosidic Enzymes.—The rate of hydrolysis of phenyl-/M-glucoside by emulsin is not affected by cations, but anions increase the rate and the increase varies with the p_H value of the medium. The chlorate ion can increase it threefold. Increasing salt concentration increases the rate until a maximum is reached and the rate then remains constant (Helferich, Schmitz-Hellebrecht, Z. physiol. Chem. 1935, 234, 54). The enzymatic fission of glycosides is less in D_2O than in H_2O if the enyzme is almost saturated with substrate, but if'only a small amount of enzyme is combined with substrate the rate is more rapid in D_2O than in water (Salzer and Bonhoeffer, Z. physikal. Chem. 1936,175, 304).

Amylases.—Calcium chloride accelerates enzymatic amylolysis at certain-values of p_a, and sodium chloride ńs less active (Baumgarten, Biochem. J. 1932, 26, 539). Guanidine and creatine retard and creatinine accelerates such hydrolysis (Mystkovski, *ibid.,* p. 910). Carboxylic acids and amino-compounds retard and various proteins and amino-acids retard at values of p_H below but activate at values above p_H 4*5 (Filipowicz, *ibid.''1931,* 25, 1874). Dilute potassium cya?iidc or thionone can activate amylase (Borchardt and Pringsheim, Biochem. Z. 1933,259,134).

Esterases and Lipases.—Glick and King (J. Biol. Chem. 1931, 94, 497; 1932, 95, 477; Weber and King, *ibid.* 1935, 108, 131) find that w-alcohols have an inhibiting effect on esterase and that the effect increases as the series is ascended, but with the isomeric arayl alcohols there is a decrease in the effect as the steric hindrance around the OH increases; with secondary alcohols the effect of the steric factor is eclipsed by that of the length of the carbon chain. The effect of the salts of fatty acids is small in the case of Jip.ise but with esterase the effect increases tip to w-laurate and then decreases almost to zero for palmitate and stearate* The effect of the salt of an unsaturated acid is greater thnn that of the saturated compound ; hexyl and octyl alcohols have greater inhibiting powers than the corresponding .sodium soaps and there appears to be a relationship between their activity and their effects in lowering surfiice^tension. The butyl ether of glyeol, unlike the ethyl ethers of both glyeol and [•CHVCHOOHJE, is fairly active against esterasebutnotlipaae. CN, I, NO_3, SH, OH, Cl, CO, CONHj, NHj, attached to amyl or phenyl retard hydrolysis with esterase and benzylresorcinol has the greatest effect. The above scries is similar to the lyotropic series oi analogous ions in protein dispersion in aqueoue solution. **-Click** and King *(**ibid.*** 1932, 97, (575) find that the hydrolysis of tributyrin by pan creas lipase is accelerated in the decreasing order —hexylresorcmol, octyl alcohol, ainyl iodide, hexyl alcohol, amyi alcohol, phenol, hexoic acid, cyc/ohcxanol, reaorcinol—and claim to demonstrate that the activation is due to concentration of the activator on the substrate resulting in a decrease of interfacial tension between enzyme and substrate. *Cf. also* Clark and Archibald (Trans. Roy. Soc. Canada, 1932, [iii],26,III,87).

VI. THIOHYDROLYSIS, ALCOHOLYSIS, ACIDOLYSIS, AMMONOLYSIS.

Several types of reactions are analogous to hydrolysis and consist in the addition of a compound other than water, viz. hydrogen sulphide, alcohol or acid, to an ester or similar compound and the fission of the compound to simpler compounds. Some of the commoner of such reactions are:

(1) Thiohydrolysis.—Esters of thioacetic acid are thiohydrolysed in liquid hydrogen eulpliide into free acid and mercaptan just as carboxylie esters are hydrolysed by water to acid and alcohol. The degree.»of hydrolysis increases with the molecular weight of the ester, and even at —77° is several times the value for the hydrolysis of the corresponding carboxylic ester at room temperature (Ralston and Wilkinson, J. Ainer. Chem. Soc. 1928, 50, 2160).

(2) Alcoholysis.—Reactions in whi^h alcohols play much the samo part as water in hydrolysis are usually grouped together under the name alcoholysis. The reaction with methyl alcohol is termed *methaitoiy&is,* and that with ethyl *tthanolyaia.*

l i e ethanolysis of an acid amide in" the presence of a mineral acid is analogous to the hydrolysis of the amide by dilute mineral acids as shown, by the two equations:

$$\mathrm{RCONH_2+HOH = RCOOH+NH_3}$$

$$\mathrm{RCONH_{i!}\text{-(-}HOEt=RCOOEt+NH_3}$$

The latter reaction has been studied in detail by Reed {Ainer. Chem. J. 1909, **41,** 483; J.C.S. 1913, **104,** 075). The reaction is bimolecular as the catalyst is gradually neutralised by the ammonia formed in the reaction, and proceeds at an easily measurable rate at 50° in the case of benzamide. A determination of the ratio of *k* for *p-* and wt-nitrobenzamide shows that this ia 1-16, a value practically identical with the ratio for the hydrolysis of the two amides. The ratio of the constants for benzamide and m-nitro benzamide varies considerably with the concentration of the hydrogen chloride. The effect of small amounts of water on the rate of alcoholysis is alaq[marked, just as in the case of the eaterificatiort of an acid, and similarly oW/io-substituents appear to have inhibiting effects. The general conclusion drawn is that the mechanism of aleohoiysis is analogous to that of hydrolysis, and consists in the formation of salts between the amide and the mineral acid and the reaction of the complex cation with the alcohol. This alcoholysis occurs between thioamides and mercaptans (Reed, i.e.).

Another common type of alcoholysis met with is the conversion of an ester of a given acid into another ester of the same acid by means of an alcohol, *e.g.:*

$$\mathrm{R\text{-}COOEt+MeOH \ \hat{}\ R\text{-}COOMe+EtOH}$$

This ehangi does not take place readily except in the presence of a catalyst, the most efficient being sodium alkyl oxide (Purdie, J.C.S. 1885, 47, 862. 1887, 51, 027; 1888, 53, 391; Claisen, Ber. 1887,20, 646), hydrogen chloride (Patterson and Dickinson, J.C.S. 1901, 79, 280), sodium hydroxide (Henriques, Z. angew. Chem. 1898,**11,** 338; Pfannl, Monatsh. 1910, **31,** 301; Komnenos, *ibid.* 1910, **31,** 111. 687; 1911, 32, 77; Kxemann, *ibid.* 1905, 26, 783; 1908, 29, 23) or ammonia (Leuchs and Theodorescu, Ber.-1910, **43,** 1239). As a nil*) only a small amount of the catalyst need be used, but vyth the esters of aromatic acids saturation with hydrogen chloride is necessary. Bellet (Compt. rend. 1931, iaS, 1020; 1932, **194,** 1655) working with sirmll amounts of sodium hydroxide proved that the rate of the reaction is reduced as the solution becomes neutral (due to hydrolysis of esterl but is increased with rise of temperature; that high' r alcohols are readily displaced by lower and that tertiary are displaced more readily than primary. The reaction appears to be reversible, as it is possible to transform an ethyl into a methyl and conversely a methyl into an ethyl eater. The reaction is not limited to methyl and ethyl esters, but can be applied to more complex esters, such aa benzyl and phenyl, and also to glyeeryl esters (*cf.* Haller, *'ibid.* 1906, **143,** 667; 1908, **146,** 259; Fanto and Stritar, Monateh. 1908, 29, 299), and is a moat convenient laboratory method for the conversion of a given ester into another eater derived from the same acid. The esters of the great majority, of aliphatic and iromatic acids react in this manner, but Sudboroiigh and Edwards have shown that when the esters are derived from *diorlho-*substituted ijenzoio acids the transformation cannot be effected by using either sodium alkyl oxide or saturating with hydrogen chloride and boiling for some time. Even when several substituents are present transformation occurs, provided the *ortho-* positions are free. This indicates that the iransformation of esters under the influence vf hydrogen chloride is analogous to the esterification of an acid by the same catalyst.

This analogy has been further confirmed by deter mining the rates of alcoholysis of various esters. These changes cannot be measured by a simple chemical method as in the case of esterifi cation or hydrolysis, but use has been made of the volume changes which occur ami the results obtained by dilato metric readings at constant temperature indicate that with an excess of the alcohol and using hydrogen chloride as catalyst the reaction

$$MeOH+RCO_aEt->EtOH+RCO_aMe$$

is practically unimolecular. The steric effects are very similar to those met with in the case of catalytic esterifi cat ion (Kolhatkar. J.C.S. 1915,**107,** 921). For further analogies between esterincation and alcoholysia, *cf.* Sudborough and his co-workers (J. Indian Inst. **SaL** 1914, 1, 107; 1918-20, 2, 121; 1920-21, 3, 1; 1921, 4, 181; 1922,5,1; 1924, 7, 1) and for alcoholysis of j8-ketonic esters, *see* Connor and Adkins (J. Amer. Chem. Soc. 1932, 54, 3420), and for use of the Grignard reagent, *e.g.*

$$RCO_aR'+R''OMgBr \quad \hat{} \quad RCO_aR''+R'OMgB_r$$

Ivanov-and Roustchev (Compt. rend. 1932,**195,** 467) who show that the heavy R" can replace the lighter R' in theester and that if R' is sryl and R" alphyl, R" partially replaces R' but that the reverse process proceeds to a very slight extent only. The reaction

$$CH_3COOR+BuOH \; -+ \; CHjCOOBu+ROH$$

is catalysed morj actively by hydrogen chloride when R=bornyl, '^ut more actively by potasem'* .hydroxide when R=methyl.

Similar transformations can be brought about in the case of the alkyl ethers of carbouiurn bases, *e.g.*

,CH:CH

NTCH-OEt

(Decket, J. pr. Chem. 1890, [ii], 45, 182), and of the oxygen ethers of substituted thiocarbamides, *e.g.*

$$EtOCH.NHCSNHPh \; -» \; MeO\text{-}CH, NHCSNHPh$$

(Johnson and Guest, J. Amen? Chem. Soc. 1910, 32, 1279; *ef.* Kuntze, Arch. Pharm. 1908, 24o$_r$ 110). An interesting case of alcoholysis observed by Willst&tter and Stoll (Annalen, 1910, 378, 18) ia the conversion of amorphous chlorophyll into crystalline chlorophyll by ethyl alcohol in the pr&ence of an enzyme *chloro*phylUwe,* which aecoinp»nies chlorophyll in plant tissues. The reaction consists in the replacement of the complex phytyl group by the timpler ethyl group

$$CO_2H\cdot C_{31}H_{29}N_4Mg(CO_2Me)(CO_2C_{20}H_{39})+EtOH$$
$$=C_{20}H_{39}OH+CO_2H\cdot C_{31}H_{29}N_4Mg(CO_2Me)(CO_2Et)$$

(3) Acidolysis.—Just as an ester **reacting** with an excess of an alcohol in the presence of a catalyst can exchange its alkyl group, ao the same ester in presence of excess of an acid and a catalyst can exchange its acyl group :

$$RCOOR'+R''CO\cdot OH \; -+ R''COOR'+RCO\text{-}OH$$

This was first studied by Reid, (Amer. Chem. .1. 1011, 45, 479) and subsequently in detail by Sudborough and Karve (J. Indiaji Inst. Sei. 1922, 5, 1) for the ease of ethyl acetate and trk'hluroacetic acid where the valuesof *k* for the direct and reverse reactions are practically the same in the absence of a catalyst.

With ethyl acetoacetate and different, acids the rate ia not a simple function of the strength of the acid R"CO$_a$H. The reaction is catalysed by H_2O and cone. **H_aSO_4,** but not by gaseous HCI (Cherbuliez and Fold, Arch. Sci. phys. nat« 1938, fvj, 20, Suppl.52).

A series of experiments by Sowa (J. Amer. Chem. Soc. 1938, 60, 654) using as catalyst BF_3,2Ac0H at 100° shows that n-propyl, ?i-butyl and taopropyl eaters of propionic, beuzoic and salicyjic acids yield the corresponding acetates and that the yields are muck smaller with t'sopropyl, sec-butyl and *tert-butyl* esters. A comparison of the catalysts H_aSO_4, 2nCl$_a$, BF_3 and BHFj(OH)$_s$ gives the percentage yields of n-butyl acetate as 20, 31, 40 and 60 respectively.

(4) Ammonolysis.—This term is sometimes applied to the reactions in which halogen atoms, sulphonic groups or alkyloxy-groups are replaced by NH, by using liquid ammonia or ammonia under pressure. With esters ammonium chloride acts as a catalyst and the effect of R in CH_aRCO_2Et ia shown to be

$$C."{>}CO\text{-}NH_s{>}CO_2Et{>}OEt{>}Ph{>}H$$

(Audrioth and Kleinberg, J, Org. Chem. 1938,3, 312). Many compounds are electrolytes in liquid ammonia (Groggins and Stirton, J. Ind. Eng, Chem. 1933, 26, 42, 169, 274).

J. J. S.

HVDROMAGNESJTE. Hydratetl basic carbonate of magnesium,

$$3MgCO_3\cdot Mg(OH)_2,3H_2O,$$

occurring as small, acicular "or bladed (orthorhombic or monodinic) crystals, but more often as while, earthy or chalky masses. It is a mineral of secondary origin, and usually occurs aa veins in serpentine, from which it has been derived. It is softer and less heavy (sp.gr, 2-16) than magncsite. When calcined it can *hu* used for the same purposes as magncsite. A large'deposit is quarried at Atlin, in British Columbia (for analyses, see G. A. Young, Sum. Rep. Geol. Survey, Canada, 1915); and there is a considerable quantity available at a spot 93 miles north of Ashcroft, in the Lillooet district of British Columbia. Several occurrences are known in California. It is also found with the massive magnesitc of Eubcca in Greece.

L. J. S.

" *HYDRONAUUM* " (*v.* Vol. I, 253b).

HYDRON YELLOW G (*v.* Vol. I, *423b).*

" HYDROPYft/N." Trade name for lithium ace tylsal icy late, which is claimed to be more soluble than aspirin and to combine the advantages of lithium salts and a specific for rheumatism. ,

HYDROQUINENE (». Vol. III. 107c).

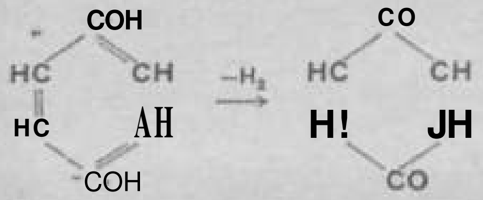
HYDROQUINICINE («. Vol. I1l, 166c).

HYDROQUINIDINE *(v.* Vol. I1l, 164rf).

HYDROQUININE•(». Vol. I1l, 166a).

HYDROQU1NINONE *(v.* Vol. I1l, 167o).

HYDROQUINONE, QUINOL, l:4-dihydroxybenzene. The p-dihydroxy-derivatives of benzene and its homologues are readily oxidised to quinones and termed hydroqtiinones :



The oxidation is effected by nitric acid, chlorine-persulphate and other oxidising agents. A peculiarity of the reaction ia the formation of a " half-way stage " in the oxidation. This highly coloured molecular compound of hydroquinune and quinone ia called *quinhydrone ;* it finds important applications *in* potentiometric and conductometric titrations. It has been suggested that it ia a " zwitterion " between the benzenoid and quinonoid forma {Sidgwiek, "Organic Chemistry of Nitrogen," 1937). Its autoxidation has been studied *hf* E. Dubrisay and A, Saint-Maxen (Compt. rend. 1929, 189, 694), A. Samt-JIaxen *(ibid.* 1930, **191,** 212) and T. W. Evans and W. M. Dclm (J. Amer. Chem. Soc. 1930,52,3204).

Hydroquinone occurs naturally, and by hydrolysis of natural products such as arb^tin.

It is prepared synthetically by oxidation of phenol with alkaline permanganate (G.P. 81068) or **with** hydrogen peroxide (G. G. Henderson and R. Boyd, J.O.S. 1910, 97, 1666), but in the laboratory it ia usually prepared from aniline as follows: 25 g. of sodium die^romate dissolved in 100 ml. of water are added dropwise to 25 g. of aniline dissolved in A)0 g. of concentrated sulphuric acid and 600 ml. of water, keeping the temperature below 100°C, The mixture at first becomes green, and towards the cn->. of the reaction blue-black in colour. After standing overnight a further 50 g. of sodium dichrnmate in 200 ml. of water are added to the cooled solution. Most of the precipitate then dissolves, giving a turbid mixture containing quinone is nd quinhydrone iu suspension. Sulphur **dioxide** is passed through, the suspended matter filtered offend the hydroquinone extracted from the filtrate with ether, which is subsequently distilled off. The product is purified by dissolving in the smallest quantity of hot water, a little sulphur dioxide passed through, boiled •with charcoal, filtered and allowed to crystallise (L. Gattermann, " Die Praxis des organischen Chemikcrs," 12 Auf. 1914, pp. 249, 253).

^

Hydroquinone may also be prepared by heating }>-chlorophenol to a high temperature, under **PWMure.** with the addition of copper (G.P. 269544), An improved preparation of hydroquinone from quinhydrone is given in G.P. 380503; for the electrolytic reduction of quinone to hydroquinone, *SP.Z* Seyewetz and Miodon, Bull, Soc. chim. 1923, [iv], 33, **448.**

Hydroquinone is dimorphous, the stable form crystallising from water, the labile form being obtained by sublimation, m.p. 170-3°, b.p. 285°; suhh'mation commences about 10° below-the melting-point. It is soluble in alcohol, ether and in hot water. - Ferric chloride oxidises it to quinone and quinhydrone. In aqueous solution it gives no precipitate with lead acetate. Its alkaline solution darkens on exposure to air. and it reduces Fehling'a solution in the cold **and** amraoniacal silver nitrate on warming. **When** heated with phthalic anhydride and zinc chloride it is converted into the colourless hydroquinonephthalein (F. Grimm, Ber. 1873, 6, 5%).

Hydroquinone condenses with amylene in the presence of sulphuric and aeetie acids to give di-isoamylhydroquinone (W. ICoenigs and **0.** ***Mai, ibid.*** 1892,25,2650).

The very valuable property of hydroquinone of inhibiting oxidation, **particularly** of aldehydeB, has been studied by C. Moureu and C. DuFrftisse rnd others (Compt. rend. 1924, **179,** 1229; Bull. Soe. chim. 1924, [iv], 85, **1664)** *(see Vol.* V, *306a).*

HYDROQUINONE ETHERS. The methyl and ethyl ethers of hydroquinonc **hare** recently found considerable use in **perfumery.** The ethyl ether is prepared by heating *p*-diazophenetole sulphate with dilute sulphuric acid, or by boiling hydroquinone with ethyl iodide and potassium hydroxide under a reihix condenser. It forms colourless needles melting at 66° and boiling *St* 247°. The dimethyl ether is a modern synthetic havinjr % powerful odour resembling coumarin, and is "employed in perfumes of the new-mown hay type. It forms colourless crystals melting at 55-56".

E. J. P.

HYDROQU1NOTOXINE *(v.* Vol. I1l, **166c).**

HYDROX POWDER *{v.* Vol. IV, S623j>

HYDROXYACETOPHENONES, o-*flydroxyacttophcnone,* HOC,HjCOCH,, Prepared from phenol and acetic acid by heating with zinc chloride (H. Pauly and K. Lockemann, Ber. 1915, 48, 30); together with p-hydroxy-Ketoplii-none **by the rearrangement of pheoyl** acetate with aluminium chloride (K. Fries and W. Pfaffendorff, *ibid.* 1910, 43, 215); and by heating diazotised' o-Jiminoacetophenone prepared from o-nitrophenylpropiolic acid (P. Friedlaender and J. Neudorfer, *ibid.* 1897, SO, 1080). It is an oil, b.p.] 06-107°/17 ram., 93-97°/10 mm. Acctyl derivative, m.p. 89°,

m-Hydroxyacetojihcnone.—Prepared from *m*-nitroaeetophenone tli rough the diuzo- com pound (Biginelli, Gazzctta, "1894, 24, i, 440; E. Besthorn, K. Bauzhaf and G. Jaeglc, Ber. 1884, 27, 3042), m.p. 9C°.

p-*Hydroxyaceto-pkenone,* m.p. 108°.—Prepared from *f*-acetylanisolc, by demethylation with hydrogen bromide (Charon and Zauiauos, Compt. rmd. 1901, 133, 742).

Hpxac&topkenone., 2:4-dihydroxyaeetopbenone.—Prepared from resorcin and acetic acid by heating with zinc chloride at 145-150° (Nencki and Sieber, J. pr; Chem. 1881, [ii], 23, 147), m.p. 142°C. Ferric chloride gives a wine-red colour with the aqueous solution.

3:5-Dihydroxyacetophenone.—Obtained by demethylation of the dimethyl ether with aluminium chloride in chlorobenzene solution (Mauthner, *ibid.* 1927, [ii], 115, 274).

2:5-*Dihydroxyacetophenone.*—May be prepared by heating 1 part hydroquinone with 1£ parts acetic acid and 1J parts zinc chloride at 140-145° (Nencki and Schmid, *ibid.* 1881, [ii], 23, 546). Also by the rearrangement of hydroquinone diacetate (K. W. Rosamund and H. Lohfert, Ber. 1928, 61 [B], 2605; R. W. Stoughton, R. Baltzly and A. Bass, J. Amer. Chem. Soc. 1934, 56, 2007). M.p. 202°. Crystallises from water in yellow-green crystals.

Oallacetophenone (2:3:4-trihydroxyacetophenone).—Prepared by condensation of pyrogallol with acetic acid using zinc chloride (Nencki and Sieber, J. pr. Chem. 1881, [ii], 23,151, 538). Also from acetyl chloride (6-23 parts) arid pyrogallol (10 parts) by heating on a water bath (A. Einhorn and F. Hollandt, Annalen, 1898, 301, 107; E. Fischer, Ber. 1909, 42, 1015). M.p. 173°. Crystallises from water.;

HYDROXY-ACIDS.—The hydroxy-acids are derived from the carboxylic acids by replacement of one or more hydrogen atoms in the hydrocarbon radical of the acid by one or more hydroxyl groups. The nomenclature is similar to that of the carboxylic acids *(q.v.)₉* for example, lactic acid, CH_3-CH(OH)COOH, may be called " o-hydroxypropionic acid " or " propan-2-ol-l-oic acid."

Methods of Synthesis.—-The syntheses fall into three divisions; s (I) introduction of the carboxyl group into the alcCliol or phenol; (IT) introduction-of the hydroxyl group into the carboxylic acid; and (III) the simultaneous introduction of both hydroxyl and carboxyl group into the hydr.tcarbon molecule.

INTRODUCTION OP THE CARBOXYL GROUP INTO THE ALCOHOL OR PHENOL.

(i) Glycols, diprimary, primary secondary and primary tertiary, may be oxidised by dilute nitric acid or platinum black and air to the hydroxy-acid, *e.g.* propylene glycol to glycollic acid (A. Wurtz, Annalen, 1868, 105, 206; 107, 192).

(ii) By fusing the homologous phenols with alkalis when the alkyl group attached to tfce nucleus is oxidised to a carboxyl group. Salicylic acid is obtained by heating o-cresol with caustic soda with the addition of copper oxide at 260-270°, manganese at 250° or iron oxide at 300° (G.P. 170230; Chem. Zentr. 1906, II, 471).

(iii) Oxidation of phenolic aldehydes with alkali, *e.g.* salicylic acid from salicylaldehyde. The phenolic aldehydes may be prepared by the method of Tiemann and Reimer {*see* Gattermann, " Die Praxis des organischen (Chemikers," 12 Aufl., 1914, p. 318, Leipzig).

(iv) Carbon tetrachloride condenses with phenols to give a mixture of o- and p-oarboxylic acids, the p-acid usually predominating, *e.g.* p-hydroxybenzoic acid from phenol, carbon tetrachloride and caustic potash (K. Reimer and F. Tiemann, Ber. 1876, 9, 1285; G. Hasse, *ibid.* 1877, 10, 2186; G.P. 258887, using 40% caustic potash and copper powder).

(v) By hydrolysis of the hydroxy-cyanide, *e.g.* hydracrylic acid, $HOCH_2{\cdot}CH_2{\cdot}COOH$, may be obtained by treating 0-chloroethyl-alcohol with potassium cyanide and hydrolysing the nitrile with caustic soda solution (J. Wislicenus, Annalen, 1863, 128, 4; 1873, 167, 346; *see,* however, Erlenmeyer, *ibid.* 1878, 191, 278).

II. INTRODUCTION OP HYDROXYL GROUP INTO THE CARBOXYLIO ACID.

(i) Aldo- acids and keto-acids can be reJuced with sodium amalgam or with zinc and hydrochloric or sulphuric acid, *e.g.* lactic acid from pyroracemic acid. Glycollic acid may be obtained by the reduction of oxalic acid with zinc (A. H. Church, J.C.S. 1863,16, 302).

(ii) The most important method is by the replacement of halogen by hydroxyl in halogeno-carboxylic acids by means of a metal oxide or hydroxide, *e.g.* silver oxide or alkali hydroxide. Water is often sufficient to replace a labile halogen atom without the use of metal hydroxide, *e-9-* glycollic acid from monochloroacetic acid (G. C. Thomson, Annalen, 1880, 200, 76); hydracrylic acid from jS-bromopropionic acid (W. Lessen and E. Kowski, *ibid.* 1905, 342, 128); y-butyrolactone from y-chlorobutyrio acid (Henry, Bull. Soc. chim. 1886, [ii], 45, 341).

(iii) Treatment of the amino-acids with nitrous acid ($NaNO_2$+ HCI), followed by warming in the case of aromatic amines, replaces the $NH_?$ group by OH, *e.g.* glycollic acid from glycine, and salicylic acid from anthranilic acid.

(iv) By treating unsaturated acids with hydqpbromic acid or with dilute sulphuric acid, *e.g.* y-valerolactone from allylacetic acid.

III. SIMULTANEOUS INTRODUCTION OF BOTH HYDROXYL AND CARBOXYL GROUPS.

(i) Hydrogen cyanide followed by hydrochloric acid on aluehydes and ketones as well as on ethylene oxides gr.es finally an acid with the hydroxyl group in the a-position to the carboxyl group in the case of aldehydes and ketones.

$$\begin{aligned} \mathrm{R{\cdot}COR'+HCN} &\rightarrow \mathrm{RR'C(OH)CN} \\ &\rightarrow \mathrm{RR'C(OH)CO_2H} \end{aligned}$$

The cyanohydrin first formed is hydrolysed to the acid by hydrochloric acid. In the preparation of mandelic acid, benzaldehyde bisulphite compound is treated with sodium cyanide and the raandelonitrile hydrolysed \»Ith concentrated sulphuric acid (" Organic Syntheses," Coll. Vol. I, New York, 1932, p. 329). Other preparations are those of lactic acid from acetaldehyde (Simpson and Gautier, Compt. rend. 1867, 65, 416), and hydracrylic acid from ethylene -oxide (Erlenmeyer, Annalen, 1878. 191,^78).

(ii) By fusion of the arylsulphonic acid with alkalis, *e.g.* salicylic acid from o-toluenesulphonic acid (Wolkow, Z. Chem. 1870, 326).

(iii) By passing air at 160° through paraffin wax (m.p. 52°), mixtures of hydroxy-acids are produced, *e.g.*

$C_{12-17}H_{26-34}(OH)COOH$ aild

$C_{3S}H_{M}(OH)COOH$

(I?. P. Scliorigin and A. P. Kreshkov, Amer. Chem. Abstr. 1934, 28, 6106; 1935, 29, 2147).

Properties.—The hydroxy-acids are divided into two classes, the alcoholic acids and the phenolic acids, having soruo properties in common, sucluas the replacement of the hydrogen of the hydroxyl group by metals or alkyl groups, la the case of alcohols, alkali metal is necessary, but caustic alkali will replace the more acidic hydr^en of the phenol. Acid chlorides replace the hydroxyl hydrogen of the phenol or alcohol giving the corresponding ester. The carboxyl group yields the normal ester, amide, nitrile and salts.

In the .aliphatic scries hydriodic acid reduces the hydroxy-aeids to the corresponding fatty acid, *e.g.* propionic acid from lactic acid. The aliphatic hydroxy-acids are in general more soluble in water but less so in ether than the corresponding fatty acids and are less volatile and cannot as n. rule bo distilled. On oxidation or by the application of heat the aliphatic hydroxy-acids show different properties accord' ing as they are a-, *fl-* or y- hydroxy -acids, *e.g.* hydracrylic acid, a primary hydroxy-acid, $HOCH_2*CH_a-COOH$, yields semi-nialonic aldehyde and malonic acid oe primary products. Secondary hydroxy-acids, *e.g.* lactic acid, $CH_3CH(OH)COOH$. yield ketonic acids. The a-ke tonic acids change to aldehyde and carbon dioxide, *e.g.*

$$H_3CH(OH)COOH \rightarrow CH_3COCOOH$$

Lactic acid. Pyruvlc ncld. *

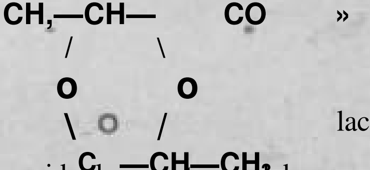
$$\rightarrow CH_3{\cdot}CHO+CO_2$$

Aeotaldehyde.

Tertiary a-hydroxy -acids yield ke tones, *e.g.* *a*-hydroxyi'sobutyric acid, ^

$$(CH_3)_aC(OH)COOH \rightarrow CH_3CO{-}CH_3$$

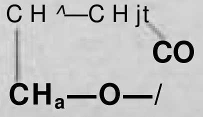
o-Hydroxy acids on heating lose water and beeomf cydic double esters—the lactidee, *e.tj.* lactio acid gives *



lactide.

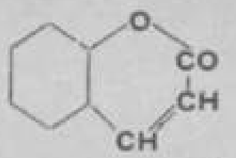
f, Hydroxy-acids lose water and become ungaturated acids, thus hydracrylic acid becomes acrylic acid.

y- and 8-Hydroxy-acids lose water at the ordinary temperature and change more or leas completely intoeimpleoyclicesters—thelactones.



y-Butyrolactone.

This property is shared by BO me phenolic acids auch as coumaric acid which gives



Coumarin.

The phenolic acids decompose into the phenol and carbon dioxide when distilled with soda-lime. The o-acids give a deep violet colour with ferric chloride, am>are volatile in steam, in contrast to the *m-* and y-acids which are not volatile and give no distinctive colour with ferric chloride. The m-aeids are the moat stable and are converted into hydroxyanthraquinonea when heated with concentrated sulphuric acid. Boiling hydrochloric acid decomposes the ji-acids into CO_2 and phenols. S. KrishnaandF. (i. Pope (J.C.S. 1922,121, 798) find that the action of potassium iodide and iodate on some aromatic hydroxy-acids is to give the tri-iodophenol, the carboxyl group being eliminated. Thus salicylic acid and p-hydroxybenzoic aiiid both give 2:4;6-tri-iodophenol; 3- or 5-nitrosalicylic acid gives tri-iodonitrophenol and 3:5-dinitrosaIicyIic acid gives tri-'tododinitrophenol. *{See* CABBOXYLIO ACIDS, 0-HYDEOXYBUTYiaO AdD *&Ad* HYDROXYSTEARIC ACIDS.)

a- ami jS-HYDROXYANTHRAGALLOL *(v.* **Vol. I, 212d).**

HYDROXYANTHRA PURPUR IN *(v.* **Vol. I, 213a).**

0-HYDROXYANTHRAQUINONE *(v.* **Vol. I,** *212d).*

HYDROXYANTHRAftUFIN *(v.* **Vol. I, 224c).**

0-HYDROXYBUTYR1C ACID,

$CH_3CH(OH)CH_2{-}COOH$.

Prepared by the reduction of aeetoaeetic ester with sodium amalgam (J. Wislicenus, Annalt'n, 18GD, 149, 205); or by the action of potassium cyanide on a-propylenechlorohydrin and hydrolysis of the resulting nitrile (VV. Markownikoff, *ibid,* 1870,153, 237). It is a thick ayrup volatile in steam'and decomposes on heating into water and crotonic acid. It has been resolved into its optical enantiomorphs by means of the quinine salts (A. M^Kenzio, J.C.S. 1902,81,1402). J-iS-Hydroxybutyric acid occurs in the urine in considerable quantities in cases of *diabetes mtilitus* and is the source of acetone in the urine. For its detection in urine, *see* Molhant (Bull. Soc. chira. Eelg. 1924, 88, 261); Bierry and Moquet (Compt. rend. 1924, i"78, 816); Engfeldt (Biochem. Z. 1924, 144, 556; *cf.* Lublin, *ibid.* 1924,147, 187, and Goldbtatt, Biochem. J. 1925, 19, 026),

HYDROXYCHRYSAZIN *{v.* *Vol.** **I,** 212rf).

HYDROXYCITRONELLAL. This valuable synthetic perfume is a somewhat variable commercial product, in which citronellal hydrate predominates. It is very liable to polymer (nation and should be stored in full containers in the dark. The main constituent has the following constitution:

$$Me_2C:CH_2CH_2CH_2CHMeCH_2CH(OH)_2$$

The best commercial samples have $d^{15\cdot5}$ about 0-930; optical rotation +8° to +10°; n_D 1-448-1-465.

It is a viscous liquid with a fine lily of the valley note, and is valuable in muguet, hyacinth, narcissus, sweet pea and lily of the valley perfumes.

E. J. P.

HYDROXYEREMOPHILONE (*v.* Vol. IV, 324c).

a-HYDROXYETHYLANILINE, PhNHCH$_2$CH$_2$OH.

Prepared by heating equimolecular quantities of aniline and ethylene chlorohydrin under pressure at 110° (Knorr, Ber. 1889, 22, 2092), or by boiling under a reflux aniline (2 mols.) and ethylene chlorohydrin (1 mol.) with water (G.P. 163043). It has b.p. 286°, 167°/17 mm.; *d*° 1-11, is slightly soluble in water, readily so in alcohol and ether; it yields indoxyl on fusion with alkali.

HYDROXYFLAVOPURPURIN (v. Vol. I, 212d).

jS-HYDROXYGLUTAMIC ACID(v.Vo). I, 318c).

HYDROXYLAMINE, NH_2OH. Discovered by W. Lossen (Annalen, Suppl. 1868, 6, 220) in 1865, but only known in the form of its salts or in aqueous solution until 1891.

It may conveniently be prepared in the laboratory by the following method: 2 mol. of commercial sodium nitrite in concentrated aqueous solution and 1 mol. of sodium carboL?w3 are kept at —2° to —3° with constant stirring, and sulphur dioxide passed in until just acid. The solution is warmed gently with a few diops of sulphuric acid and kept at 90-95° for 2 flays. It is then neutralised with sodium ca^AJKate, concentrated by evaporation to 10^-11 times the weight of nitrite taken and sodium sulphite allowed to crystallise out by "ooling. Hydroxylamine sulphate left in the mother liquor may be purified by crystallisation (E. Divers and T. Haga, J.C.S. 1887, 52, 661; 1896, 70, 1665). For a modification of this process giving a 70% yield of the pure hydrochloride, *see* Organic Syntheses, 1923, III, *65*.

Much work has been done MI the electrolysis of nitric acid, nitrous acid and other derivatives to produce hydroxylamine salts (G.P. 133457, 137697; J.S.C.I. 1902, 21, 1458; F.P. 322943; J.S.C.I. 1903, 22, 425; J. Tafel, Z. anorg. Chem. 1902,31, 289; E. P. Schoch and R. H. Pritchett, J. Ainer. Chem. "Soc. 1916, 38, 2042). J. Stscherbakow and D. Lihrna (Z. Elektrochem. 1929,35, 70, 826) and G. Ponzio and A. Pichetto (Annali Chim. Appl. 1924,14, 250) have studied the electrolytic reduction of nitric acid to hydroxylamine.

It may also be prepared by the reduction of nitric acid with metals under suitable conditions (E. Divers, J.C.S. 1883, 43. 443; 1885, 47, 597). Nitrates, nitrites, nitro-bodies, etc., in neutral solution are reduced by finely divided metals to give hydroxylamine (B. P. 11216/1894; J.S.C.I. 1895, 14, 595).

Catalytic methods include the reduction of nitric acid by hydrogen in the presence of spongy platinum at 115-120° (A. Jouve, Compt. rend. 1899,128, 435).

To isolate free hydroxylamine, the hydrochloride is dissolved in, methyl alcohol and sodium methoxide in methyl alcohol added. The sodium chloride is filtered off and the alcohol removed by distillation under reduced pressure. Hydroxylamine distils 'at about 70°/60 mm., and about 58°/32 mm. Vaseline may be addecTto inhibit frothing during distillation, and care should be taken to exclude air as at 60-70° explosive mixtures may be formed (C. A. Lobry de Bruyn, Rec. trav. chim. 1891, 10, 100; 1893,11, 18; J. W. Briihl, Ber. 1894, 27, 1347). L. Crismer obtained the anhydrous substance by passing ammonia through the complex salt, dihydroxylamine zinc chloride, $ZnCl_2,2NH_2OH$, distilling off first the solvent ether and then the hydroxylamine (Bull. Soc. chim. 1891, [iiij, 6, 793). R. Uhlenhuth (Annalen, 1900, 311, 117) obtained it by distillation of the phosphate under reduced pressure. O. Baudisch and F. Jenner (Ber. 1916, 49, 1182) added the dry, finely powdered sulphate to liquid ammonia in a quartz tube, removed the ammonia and extracted the hydroxylamine with alcohol. Owing to the danger from explosion attending the distillation of hydroxylamine, H. Lecher and J. Hofmann (*ibid.* 1922, 55 [B], 912) prepared the free base by suspending the hydrochloride in absolute alcohol, adding a solution of sodium ethoxide in absolute alcohol, filtering off the sodium chloride and cooling the filtrate to -18° when NH_2OH crystallised out.

Hydroxylamine forms white inodorous scales or hard needles, sp.gr. about 1-3, m.p. 33°, b.p. 56-57°/22 mm. When kept at ordinary pressures above 15° hydroxylamine darkens; at higher temperatures explosion is likely to occur. Readily soluble in water and to a less extent in ethyl and methyl alcohols, and in boiling ether. It is decomposed by ^alkali giving nitrogen, nitrous oxide, nitrous acid and water (S. S. Kolotoff, J. Russ. Phys. Chem. Soc. 1891, 28, 3). The aqueous solution is colourless and odourless and has a strongly alkaline reaction. In many of its properties hydroxylamine resemble:, ammonia but it is less basic. For example, Zn, Fe, Ni, A I, Cu, are precipitated from their soluble salts as hydroxides insoluble in excess, but the alkaline earths are not precipitated. It acts as a strong reducing agent, *e.g.* with $CuSO_4$ solution red Cu_2O is precipitated, $HgCl_2$ is reduced to Hg_2Cl_2 and Ag, Au, and Pt are precipitated from their salts. In alkaline solution it converts ferrous to ferric hydroxide, whilst in acid solution it reduces ferric to ferrous salts.

The salts of hydroxylamine are readily soluble in water and alcohol, crystallise well and are anhydrous. The three hydrogen atoms of hydroxylamine are replaceable by sulphonic acid groups, *e.g.* jB/Miydroxylamincdisulphonic acid $(SO_3H)_2N\cdot OH$ (Raschig, Chem.-Ztg. 1888, 12, 219), the alkali salts of which are stable.

For the ajB/J-trisulphonic acid derivative, $(SO_3H)_2NOSO_3H$, and the aj8-disulphonic acid (or âsodisulphonic acid)

SO3HNHOSO3H,

see F. Raschig, Ber. 1923,56 [B], 206.

Hydroxylamine hydrochloride or

$(SO_3N\&)_2NOH$

reacts with furfuraldehyde at 155-160° under pressure to give 2:5-dihydroxypyridine (K. Aso, A. 1939, II, 386). Complex salts analogous to the amines have been prepared (Goremikin and Gladishevskaja, A. 1939,1, 533).^{J}

Hydroxylamine and its salts have been used as photographic developers and for recovering silver from fixing baths (Lainer, J.S.C.I. 1890, 9, 890); as a substitute for chrysarobin and pyrogallic acid (Schwarz, Pharm. Ztg. 33, 659). Manganese brown has been discharged by application oҲ the hydrochloride (Schaeffer, Bull. Mulhouse, 1883; *see also* J.S.C.I. 1884, 3, 166).

Hydroxylamine has been reported in the cells of *Chlorella,* formed under ordinary conditions of growth (D. Michlin, A, A938, III, 1062). Its formation in culture media from the reduction of nitrates by micro-organisms has been reported (J. Blom, Biochem. Z. 1928,194, 385). *See also* papers by M. Lemoigne, P. Monguillon and R. Desveaux (Bull. Soc. Chim. biol. 1938, 20, 441) on hydroxylamine in biological processes.

It "is used for preparing oximes of aldehydes and ketones. Aldoximes are usually prepared by adding the aldehyde (1 mol.) to an aqueous solution of hydroxylamine hydrochloride (1 mol.) and sodium carbonate (1J mol.). Aqueous alcohol is used for water-insoluble aldehydes. Ketoximes are somewhat more difficult and are prepared by heating the calculated quantity of ketone, hydroxylamine hydrochloride** and sodium acetate in aqueous or alcoholic solution 1-2 hours on a water bath. Also by heating the ketone dissolved with alcohol, and NH_2OH-HCI,. in a sealed tube for 8-10 hours at 160-180° (I. Schmidt Houben, " Die Methoden der organischen Chemie," 3 Aufl:*1930, 584). Certain oximations may betcarricd out by the use of *sodium hydroxylamine monosulphonate,*

$HONHSO_3Na$.

For a laboratory* preparation of this reagent, *see* Organic Syntheses, 1930,»X, 23. For the determination of the aldehyde in oil of citronella with hydroxylamine hydrochloride, *see* Vol. Ill, 191c. For the use of hydroxylamine in the determination of camphor, *see* Vandoni and Desseigne, Bull. Soc. chim. 1935, fv]. 2, 1685.

detection and Estimation.—Hydroxylamine may be detected by its reducing properties on silver nitrate, and Fehling's solution. By adding sodium nitroprusside to a neutral solution and a little caustic soda, a magenta-red coloration is produced (A. Angeli, Gazzetta, 1893, 23, ii, 102). It yields benzhydroxamic acid on treatment with sodium acetate and benzoyl chloride and this gives a violet-red coloration with ferric chloride (E. Bamberger, Ber. 1899, 32, 1805). As little as 00001 g. can be detected colorimetrically by means of *p*-broniouitroaobenzene and a-naphthol (J. Blom, Biochem. Z. 1928, 194, 385). Another sensitive test depends on the formation of a fugitive purple coloration on treatment with yellow ammonium sulphide and excess *of* ammonia (W. M. Fischer, Chem.-Ztg. 1923, 47, 401). An ammoniacal solution of diacetylmonoxime with hydroxylamine forms dimethylglyoxime which can be identified by its reaction with nickel salts. Hydroxylamine gives with resor' cinol and potassium periodate in solution buffered to p_H 2, a stable cherry-red colour-reported sensitivity 1 part per million (G. G. Rao and W. V. B. S. Rao, Analyst, 1938, 63, 718).

It may be estimated* by titration in alkaline solution with mercury acetamide, which is reduced to metallic mercury (M. O. Forster, J.C.S. 1898, 74, 785); by oxidation with vanadic sulphate, measuring the nitrogen evolved and titrating the vanadous sulphate with potassium permanganate (K. A. Hofmann and F. Küspert, Ber. 1898, 31, 64); also by adding excess of standard titanium trichloride and back-titrating the excess with potassium permanganate (A. Stahler,*ibid.* 1904, 37, 4732; *ibid.* 1909, 42, 2695). Of three methods investigated by W. C. Brajr, M. E. Simpson and A. A. MacKenzie (J. Amer. Chem. Soc. 1919, 41, 1363) the two following methods were found to be accurate: (1) Reduction to ammonia by excess of titanous salt in acid solution, and (2) oxidation to nitrous oxide by excess ferric sulpilate in sulphuric acid solution with subsequent titration of the ferrous salt with permanganate. Also it may be estimated by adding an excess of 0-lA^T$KBrO_3$ solution and sulphuric acid, and after J-J hour adding potassium iodide solution and titrating the liberated ioding with sodium thiosulphate (A. Kurtenacker and J. Wagner, Z. anorg. Chem. 1922,120, 261). «**

For the colorimetric determination, *w-* W. Pucher and H. A. Day (J. Amer. Chem. Soc. 1926, 48, 672). The method depends on Bamberger's benzhydroxamic acid reaction • with ferriQ chloride *(v. supra).* For the determination of small quantities of the order of 1 mg. *n*< oc., the hydroxylamine is oxidised by iodine to nitrous acid which is determined photometrically by the diazo-method, using sulphanilic acid and j3-aminonaphthalene in acetic acid. Error ±2-3% for 01-0-2 X 10"« g. in 10 c.c. The method can be extended to solutions containing nitrite and nitrate (G. Endres and L. Kaufmann, Annalen, 1937,530,184). Hydroxylamine has also been determined coulometrically (L. Slebellédy and Z. Somogyi, Z. anal. Chem. 1938, 112, 400).

Ethylhydroxylamines *v.* **ETHYL.**

0-Phenylhydroxylamine, NHPh·OH.—This compound may be prepared by the reduction of nitrobenzene with zinc (Just in ammonium chloride solution (C. «. Marvel and O. Kamin; J. Amer. Chem. Soc. 1919, 41, 279 ; Organic Syntheses, 1932, •> Coll. Vol. 1, 435, yield 62-68%). Consistently good yields are obtained if the^zinc dust is previously treated with 2% mercurous nitrate solution slightly acidified with nitric acid (Kasanof, Ind. Eng. Chem. 1920, 12, 799). Many other methods have been recorded for its preparation : oxidation of aniline with Caro's acid in the presence of ether at 0° (E. Bamberger and F. Tschimer, Ber. 1899, 82, 1675) or electrolytieally in acetic acid solution (Haber, Z, Elektroehem. 1898, 5, 77); by the reduction of nitrobenzene with zinc amalgam in an aqueous-alcoholic solution of aluminium sulphate (E. Bamberger and M. Knecht, Ber. I89G, 29, 863) ; or with zinc dust in the presence of calcium chloride in ether or alcohol solution' {C. Goldschniidt, *ibid.* 2307 ; G.P. 84138; *see also* Wislicenus, J. pr. Chem. 1890, [ii], 64, 57). The substance is very poisonous and should not be allowed to come in contact with the skin {O. Baudisch, Chem.-Ztg. 1911,35,913).

j8-Phenylhydroxylamine forms colourless needles, m.p. 81-32°; soluble in 10 parts hot and 50 parts cold water, readily soluble in alcohol, ether, carbon disulphide and chloroform, sparingly soluble in light petroleum. Ammoniacal silver nitrate and Fehling's solution are reduced in the cold by /S-phenylhydroxylamine. Mineral acids yield p-aminophenol and azoxybenzene; alcoholic sulphuric acid gives azoxybenzene, *o-* and ^-phenetidine, *o-* and *p-*aminophenol, aniline and other compounds (E. Baniberger and J. Lagntt, *ibid.* 1898, 31, 1501). It dissolves in sulphuric acid with a deep blue colour. By heating at 100°, azobenzene togethor with aniline, azoxybenzene and other products are formed. Oxidation with permanganate gives first nitroso benzene then nitrogen and azoxybenzene (E. Bamberger and F. Tschirner, Ber. 1899, 32, 342). It dissolves in sodium hydroxide giving a sodium salt, which decomposes into nitrobenzene and azoxybenzene in the presence of air but into azoxybenzene and aniline if air is excluded,{E. Bamberger and F. Brady, *ibid.* IflOO, 33, 271). With aromatic aldehydes it yields" phcnylaldoximes of the type

(G. Plancher and G. Picetnini, Atti. R. Accad. Lin Mi; 1905, [v], 1*, ii, 36). The *i-A-dinitro-derivative,* (NOjUCarVNH-OH, is made by the action of an alcoholic solution of hydroxylamine on 2:4-dinitrodiphenyl ether. It has marked acidic properties and gives intensely coloured ammonium and aniline salts (W. Borsche, Ber. 1923, 56 [B], 1944).

Nftroso-/}-phenylhydroxylamine,

C_BH_S-N(NO)OH,

may be conveniently prepared by the action of sodium nitrite and dilute sulphuric acid on *fl*-phenylhydroxylamine (A. Wohl, *ibid.* 1894, SI7, 1435; E. Bamberger, *ibid.* 1553) or by the interaction of hydroxylamine and nitrobenzene in alcoholic solution in the'presence of sodium ethoxide (A. Angeli, *ibid.* 1896, 29,^884). It crystallises from light petroleum, m.p. 58-59°, and decomposes at 75°. Readily soluble in organic solvent-, sparingly so in water, Alcoholic or ethereal solutions give a brownish-red coloration with a few drops of ferric chloride.

The most important derivative is the ammonium salt, *cupferron,* C_gH_sN (NO)ON $H_{\#(}$ and is prepared as follows T An ice-cold solution of 25 g, nitrobenzene in 125 o.o., 96% alcohol and 25 c.c. water *is* saturated with ammonia and then treated with hydrogen sulphide for 2^-3 hours. To the resulting pale yellow, pasty mass, 500 o.c. ether are added, the solution shaken vigorously and filtered. The ether layer is separated and saturated with ammonia, withdrawn, cooled in ice and ethyl nitrite vapour passed in ($NaNO_a$ 25 g., H_aO 40 c.c, 96% C_SH,-OH 33 e.o. and 1:1 HC1 1)0 o.c.). The solution becomes dark at first, the colour slowly disappears and crystals of cupferron separate. It is washed with ether 'and dried over calcium chloride and ammonium carbonate. Yield 80% (K H. Slotta and K. R. Jacobi, Z. anal. Chem. 1930, 80, 97). *See also* Organic Syntheses, 1932, Coll. Vol. I, 171.

The mierocrystalline forms of several salts of nitroso-/9-phenylhydroxylamine have been fount! to be sufficiently characteristic to be employed in the identification of the particular metal (Martini, Mikrochem, 1928, 6. 152). Cupferron has been used to separate zirconium and uranium (Angeletti. Gazzetta, 1921, 51, 285).

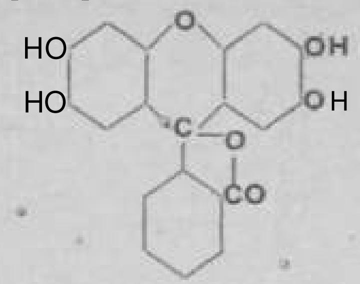
Cupferron is a brownish-white crystalline soluble substance and yields well-defined coordination compounds when its ammonium radical is replaced by many of the metals. It is most useful in the separation of iron, titanium and zirconium, since it precipitates these elements from strongly acid solutions containing aluminium, chromium, manganese, nickel, cobalt, zinc, magnesium and the alkaline earths. The ferric and copper salts may be separated by dissolving out the latter with ammonium hydroxide. The ferric salt ia soluble in chloroform, ether, acetone, etc., and may be dissolved and separated from other salts, such as those of lead, silver or tin, which may have been precipitated witti it {Baudisch, Chem.-Ztg. 1909, 38, 1298; 191 I,'u5, 913 ; H. Biltz and 0. Hodtke, Z. anor$_K$. Chem. 1910, 66, 426; J. HamtS and A. Soukup, *ibid.* 1910, 68, 52; R. Fresenius, Z. anal. Chem, 1911, 50, 35). *See also* CHEMICAL ANALYSIS and Lundoll and Knowles, Ind, Eng. Chem. 1920,12, 344, for further applications.

HYDROXYPROLINE {». Vol. I, 3I7c).

HYDROXYQUIN©L, 1:2:4-trihydroxybenzene. This substance is obtained by rapidly heating hydroquinono with 8-10 times its weight of caustic soda until evolution of hydrogen haB almost ceased (Barth and Suhreder, Monatsh. 1883, 4, 176); or ~*ay* dissolving 150 g. quinone in 400-450 g. acetic anhydride and 10 c.c. concentrated sulphuric acid, keeping the temperature at 40^50°, and finally pouring into much water. The precipitated hydroxyhydroquinonc triacetate is saponified with a methyl alcoholic solution of sulphuric acid, neutralised with anhyurous sodium carbonate, extracted with ether, filtered and the solvent removed. The residue is allowed to crystallise in a vacuum desiccator (Thiele, Ber. 1898, 81, 1248).

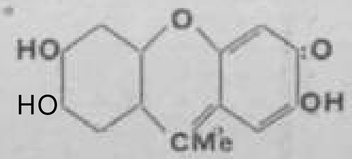
It crystallises from ether in microscopic scales, m.p. 140-5", and distils with partial decomposition to give quino). Its aqueous solution darkens rapidly on exposure to the air, and ferric chloride solution gives a transient bluiah-grecn coloration, which changes to dark blue, and then to wine-red on the careful addition of sodium carbonate solution.

Hydroxyquinol (2 mol.) when heated with plithalic anhydride (1 mol.) to 185-190° gives hydroxyquinol phthalein,



(W. SWerstein and M. Dutoit, *ibid.* 1901, 34, 2637).

Condensation takes place with aldehydes. Using concentrated sulphuric acid in alcoholic solution, paraldebyde gives the compound:



(C. Liebermann and S. Lindenbaum, *ibid.* 1904, 37. 1177, 2731).

For an account of the derivatives, *see* Bargellini (Gazzetta, 1910, 40, ii. 342; 1911, 41, ii, 612; 1912, 42, ii, 351; Atti. B. Accad. Lincei, 1911, [v], 20, i, 22; ii, 18, 118, 183). The trimethyl ether has been used by J. Reigrodski and J. Tambor (Ber. 1910, 43, 1964) for the aynthesiB of 2:3-dihydroxyflavone.

HYDROXYSTEARtCACIDS.a-tfjrtfrwy-*stearic AciU,*

$$CH_3[CH_a]_{1s}CH(OH)COOH.$$

Prepared by treating a-bromostoaric acid with aqueous potash. Separates from a mixture of benzene and light petroleum as a crystalline powder, m.p. 91-92° (C. Hell and J. Sadomsky, Ber. 1891, 24, 2391; H-. R. Le Sueur. J.C.S. 1904, 85, 827). By heating' to 270° it yielda margaric aldehyde, $C?_eH_{3!J}$'CHO, a lactide, CsgH^O^, formic acid and carbon dioxide. (Le Sueur, *I.e.)*

fl-Hydrozyatearic Acid,

$$CH_3\cdot[CH_2]_{14}\cdot CH(OH)CH_2\cdot COOH.$$

Prepared by treating jS-bromostearic actd with aqueous potash. Crystallises from chloroform in white plates, m.p. 89° (Ponzio, Gaszetta, 1905, 35, ii, 570).

y-Hydroxyatearic Acid.—-Exists most commvnly in the form of its lactone, «

$$CH_3\cdot[CH_2]_{13}\cdot CH\begin{matrix},CH_a—CH,\\O\end{matrix}$$

which ia prepared by heating oleic acid with concentrated sulphuric acid at 80-85° for 6 hours, diluting with water and warming on a water bath; it haa m.p. 52-53^e, and yields the acid, m.p. 89°, on heating with alkali and finally acidifying with hydrochloric acid (P. W. Olutterbuck, J.C.S. 1924, 125, 2330).

C. G. Totnecko and R. Adama (J. Amer. Chem. Soc. 1927, 49, 522) by condensing aldehyd esters of the general formula,

$$CHO[CH_2]_rCOOMe$$

(where ar=7, 8, 9, 10, II) with the Grignard reagent, CH_s-$[CH_a]$,,-MgBr (where *y* = 8, 7, 6, 5, 4) have obtained the esters of the following hydroxysfcearie acids, from which the pure acids are obtained by hydrolysis,

$$CH_3[CH_a]j,\text{-}MgBr+CHO[CH_2VCOOMe$$
$$\rightarrow CH_3\cdot[CH_2]_y\cdot CH(OH)\cdot[CH_2]_x\cdot COOMe$$

	M.p., acid,	M.p., methyl eater.
8 or 0-hydroxystcario acid ,	74-75°	45-46°
9 or i-hydroxyatearic acid .	81-82°	53-54°
lOorK-hydroxystearicacid .	76-77°	49-50°
11 orA-hydroxystearic acid .	78-79°	50-51°
12or^-hydroxystearicacid .	77-77-5°	52-52*5

i-Hydroxyflteario acid may also be prepared by the action of sulphuric acid on oleic acid (Tscherbakow and Saizew, J. pr. Chem. 1898, [ii], 57, 27). At 100° it yields the anhydride, and oxidation with chromic acid in acetic acid converts it into sebacic, azelaic and traces of suberic and a liquid monobasic acid, together with t-ketostearic acid,

$$CH_3\cdot[CH_2]_7\cdot CO\cdot[CH_2]_8\cdot COOH,$$

in.p. 76°. On distillation, i-hydroxyste&ric acid gives A*-elaidic and A^-elaidio acids and ordinary oleic acid (Vesel^ and Majtl, Chem. Listy, 1925, 19, 345; Bull. Soc. chim. 1926, [iv], 39, 230).

K-Hy&roxyaUari(Acid,*

$$CH_3\cdot[CH_2]_8\cdot CH(OH)\cdot[CH_2]_9\cdot COOH.$$

Prepared by the action of sulphuric acid on uooleio acid, Shukow and Schestakow (J. Russ. Phys. Chem, Soc. 1903, 35, 1) who give tb* m.p. as 84-85°. Oxidation with chromic acid gives sebacic acid, nonylene-at-dicarboxyhV' pcid (m.p. 124°) and *-ketostearic acid (m.p. 65°).*

\-Bydroxysttaric Acid,

$$CH_3[CHJ_5CH(OH)[CH,]_{10}COOH.$$

This acid was obtained (A. Griin and M. Woldenberg, J. Amer. Chem. Soc. 1009, 31, 490) by the reduction of the methyl ester of ricinoleic acid. •

Sativic Acid, obtained by oxidising linoleic acid is 8:9:ll:]2-tctrahydroxystearic acid,

$$CH_3[CH_2]_4CH(OH)CH(OH\}CH_2CH(OH)$$
$$\cdot CH(OH\}[CHJ_7COOH$$

and has been shown to ha^e this constitution (Reinger, Ber. deut. pharm. Ges. 1922, 32, 124) by progressive elimination of hydroxyl groups, confirming A. Ecfe«rt (Monatsh. 1917, 38, 1).

Four isomeric (a-)9-, *y*- and 8-) Bativic-ftcida have been prepared by B. H. Nicolet and H. L. Cox (J. Amer. Chem. Soc. 1922. 44, 144).

Mild treatment of oleic acid with alkaline permanganate gives fl-hydroxy-i-ketoatearic acid and 0-keto-(-hydroxysteario acid (Kiog, J.C.S. 1936, 1788).

flt-Dihydroxystearic acid has been prepared by the oxidation of oleic acid with alkali hypobromite at 10-20° in the presence of salts of Ni, Co. Fe and Mn (U.S.P. 2033538).

Hydroxvstearic acid from the hydrogen at ion of castor oil has been used in the form of its salts, Na, K, Ca, triethanolamine, etc., for the preparation of emulsions and creams (Fiero, J. Amer. Pharm. Assou. 1939, 28, 598}.

HYDROZINCITE. Hytlrated basic carbonate of zinc, $ZnCO_3$-2Zn(OH),j, containing Zn 60-5"%, of common occurrence as an alteration product of other ores of zinc. It is found in **the** upper levels of n-.ost zinc mines as soft, snow-white encrustations often in stalaetitic, botryoidat or other forms. Large masses with an earthy or chalky texture are not uncommon; sp.gr. 3-0-3-8. Much of the material often regarded as smithsonite ($ZnCO_3$) is really hyiirozinctte, as shown by its lower degree of li an! ness (hardness 2-2J, that of smithsonite being 5} and the presence of water. Large quantities have been obtained from the zinc mines of province Santander in Spain, Bleiberg in Carinthia, Sardinia, etc. It has been observed as a mineral of recent formation in the old galleries of lead-zinc mines in North Walts, Analysis of material occurring as minute blatled (monoclinic} crystals at Narlarla, Western Australia, leads to the formula SZnCOa^ZnfOHJst (R. T. Prider, Min. Mag. 1911, 26, 60).

L. J. S.

HYDURILIC ACID, CaHgOaN^H_2O or $2H_aO$;

$CO\langle{}^{NHCC}_{NH\cdot CO}\rangle CHCH\langle{}^{CONH}_{CO\cdot NH}\rangle CO$

was j)repared(l) by Schlieper (Annalen, 1846, 56, II), who obtained the acid ammonium salt together with alloxan by the action of nitric acid (sp.gr. 1-25) on uric acid. It is also prepare$,(2) in the form of its ammonium salt by pjolonged boiling of alloxan or alloxanlm **with** very dilute sulphuric acid (Finch, *ibid.* 1864, J32, 303); (3) by heating crystallised alloxantin under pressure at 170° when it is converted quantitatively into hydurilic acid, according to. the equation

$$2C_8H_4O_7N_4+6H_2O=$$

$$C_eH_BO_8N_1+4NH_8+[COOHj_{5!}+2CO+4CO_2$$

or by .similarly decomposing alloxan (**Murdoch** a$_f$;d Doebner, ***Bet.*** 1876, 9, 1102); (4) in the form of its acid ammonium salt by heating dialurio acid with glycerol at 150°, formic acid and caTbon dioxide being formed at the same time (Baeycr, Annalen, 18tS3, *W,* 14; *cf.* Biltz and Heyn, **Bar.** 1919, 52 [BJ, 1298*; (5) together with glyciue and carbon dioxide by heating uric acid with twice its weight of concentrated sulphuric acid.(Schultzen and Filehne, *ibid.* 1808, 1, 150), (W) by oxidutir>ii of barbituric acid in aqueous solution with potasrtiunt permanganate {Biltz ;nul Heyn, *I.e.]:* (7) by redueing dibromobarbituric acid with hydrogen iodide (Baeyer, .Annalen, 18o4. 130, 133); and it is also formed to a **small** extent *(S)* by mlueinguUoxantin with sulphuretted hydrogen (Murdoch and Doebner, *l.c.);* (9) by the condensation of ethyl ethanetetracarboxylate with urea in the presence of sodium ethoxide at '30-70°, or (10) by the hydrolysis of ethanetetracarbonylguanide

$NH:C\langle{}^{NH\cdot CO}_{NH\cdot CO}\rangle CH\cdot CH\langle{}^{CO\cdot NH}_{CO\cdot NH}\rangle C:NH,H_2O$

by means of dilute hydrochloric acid at 150° (Conrad, *ibid.* 1907, 366, 24; *cf.* Roeder, Ber. Z913, 46, 2560): whereas ethyl eiuanetetracar boxy late and urea yield only a trace of hydurilic acid", *dithiohyduriiic* acid is readily obtained from the ester and thiocarbajnide; this compound remains unaltered at 250°, and can be desulphurised to hydurilic acid by heating at 100° with concentrated sulphuric acid. Hydurib'c acid is most conveniently purified by precipitating the sparingly soluble copper salt from a solution of the neutral ammonium aalt, ami decomposing this with hot hydrochloric acid, in which the hydurilic acid is only slightly soluble (Baeyer, Annalen, 1863, **127,** 15).

llydurilic acid crystallises from hot water in **small** four-sided prisms containing **$2H_2O$,** or is precipitated as a fine crystalline powder containing $1H_SO$ by. the addition of hydrochloric acid to a hot aqueous solution. It is sparingly .soluble in alcohol or cold water, more readily so in hot water; its heat of combustion is OiiS-S kg.-cal. (Matignon, Ann. Chim. *Phyt.* 1893, [vi], 28, 328).

Hydurilic acid bears the same relation to dialurie and barbituric acids that alloxantin bears to alloxan and barbituric acid. Its constitution is established by its synthesis from ethyl ethanetetracarboxylate and urea *(v. supra),* anu also by the fact that on hydrolysis **with** concentrated hydrochloric acid at 200-230° it is converted almost quantitatively into carbon dioxide, ammonia and suceinic acid; barbituric acid when similarly treated yields carbon dioxide, ammonia and acetic acid.

Hydurilic acid is not attacked by reducing agents; it yields *%Λox* an and dibro mo barbituric acid when treated with bromine water (Biltz, Heyn and Hamburger, Ber. 1910, 49, 662).

Fuming nitric acid oxidises it into alloxan, whilst weaker acid converts it into nitrobarbituric acid (dilituric aeid), tdonitroaobarbituric acid (violuric acid) and violantin. Ferric chloride or silver oxide oxidises it to oxyhydurilic acid, which gives a blood-red coloration with ferric chloride. Hydurilic acid has marked acidic properties, and decomposes most metallic chlorides and acetates, yielding the corresponding hydurilate (for the basicity of the acid, *see* Biltz and Hamburger, *ibid.* "1916,"49, 655). The heat of neutralisation of bydurilie aeid with 2 mol. potassium hydroxide is 21*8 kg.-cjil.; but on adding a further quantity of alkali (up to 16 mol,) there is a further evolution of 4-2 kg.-eal.. thus pointing to the existence of a tliird very feeble **add function.** The following salts have been **described** : the *ammonium hydrogen salt* NH_4 $C_8H_SO_SN_V$ small netuhetliu. sparingly soluble, **precipitated by kcetio** acid from solutions of the *normal ammonium* salt $(NH_4)_3C_gH_1O_6N_4$, **which** crystallises in needles with 1 H_2O or in large monocliuic crystals with $4H_2O$.

a:b:c = 10821;1:07003.

Sodium salt $Na_2C_8H_4O_0N_4,4H_sO$ crystallises in prisms; *acid potassium* salt $KC_aH_5O_6N_4$ forms sparingly soluble microscopic needles; the *normal* salt $K2C_8H_4O_6N_4$,3H.jO ia soluble and crystallises in •'prisms {Matignon), The *calcium* salts CafCaH^OoNjJ^.SHjO and

$CaC_tH<_lO_{fl}N.i,3H_2O$

are crystalline and almost insoluble; the *barium* ealt $BaC_eH_4O_6N,,H;,O$; the *zinc* salts

$Zr\backslash(C_BH_6O_eN_4)_a$ and $ZnC_aH_4O_6N_4,2H_BO$

are crystalline; the *copper* salt

$Cu(C_8H_5O_6N_4),,8H_2O$

forma fine yellow needles or prisms, which become, red on heating with loss of water. The *silver* salt is unstable; the *ferric* salt is a dark green precipitate, and the formation of a dark green colour with ferric chloride js a characteristic **reaction of** the salts of hydurilic acid; the *ferrous* salt is white beco'ming green; the *lead* salt is insoluble in acetic acid.

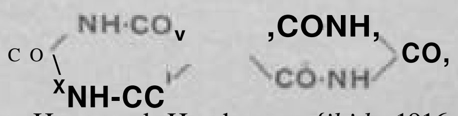
5:5'-*Dichlorohydurilic acid,*

ia obtained by the action of potassium chlorate on an intimate mixture of hydurilie and concentrated hydrochloric acids {Baeyer, Annalen, 1863, **127,** 26); a quantitative yield is obtained by chlorinating hydurilic acid in alcohol (Biltz and Hamburger, *l.c).* It is a sparingly soluble powder, soluble in concentrated sulphuric acid and precipitated therefrom by the addition of water, in small rhombic crystals containing $2H_SO$; it is readily decomposed by alkalis yielding the metallic ebloride. Hydrolysis to 5-chloro barbituric acid and alloxan occurs on boiling with water. The *potassium* Bait, $KjC_aH20_aN_4Clj,2HoO$, isia sparingly sol u Wo crystalline powder. 'Jjjie *ammonium* salt forma hydrated (2-5H,Oj, coltnirlojw or palo pink crystals. The anhydrous salt is dark red, in.p. about 235°, becoming discoloured at 140° (Bocki Ber. 1923, 56 **[BJ,** 1222). •

5:5"• *Dielhylhydurilic add* ja obtained from 5-cthy 1 barbituric acid by oxidation with potassium permanganate in sulphuric acid. It crystallised Mith $1H_2O$, in,p. above 310°. Concentrated potassium hydroxide gradually splits off ammonia; heating with concentrated hydrochloric acid at 210-240° results in hydrolysis to diethylsliceinic acid (Aspelund, J. pr. Chem. *IQB'A,* |»], **136,** 329).

B:5'-Dibenzylhydurilic acid is prepared similarly to the 5*:5'-diethyl derivative. It crystallises with $2H_2O$, ni,p. 315° (decomp.) (Aspefund, i.e.).

&-Bromo-5'-vwthoxyhi/diirilic acid is formed on brominating hydurilic acid in presence of methyl alcohol; it crystallises in Btout, hexagonal tablets which decompose above 360°; in presence of ethyl alcohol *H-bromo-5'-ethexyhydflritic* acid is formed which crystallises in stout, elongated prisms decomposing above 360°: these compounds yield *S-methoxykydurilic* acid and *5-etkoxtjhydurilic* acid on reduction, which lose methyj' and ethyl alcohol respectively when heated and yield *deAydrofii/durilic* acid



Biltz, Heyn and Hamburger {*ibid.* 1916, 49, 662; ***ibid.*** 1919, 52 [B], 1298); *cf.* Baeyer, (Annalen, 1863, **127,** 26), who fuund that hydurilic acid broke Jown under the action of bromine water into dibromobarbituric acid and alloxan.

Tetramethylhyduri Nc acid *(deoxyamalic* flnJ),$C_uH_{14}O_6N_{,i;}$

is obtained by the dry distillation of **nmalk** acid (Fischer and **Beese,** *ibid,* 1883, 221, 339), or more conveniently by heating it in a scaled tube for 3 hours at 180-185° {.Matignon, Compt. rend. 1893, **116,** 642); it has also been obtained by heating dimethylpseucfouric acid with fused oxalic acid at 170° {Fischer and Ach, Ber. 1895, 28, 2473). Deoxyamalicjtieid is crystalline, has in.p. 260°, with decomposition, and can be distilled, although with partial decomposition. It is almost insoluble in hot or cold water; readily soluble in chloroform or acetic acid; its heat of **combustion** is 1321-8 kg.-cal. {Matignon, Ann. Chim. Phys. 1893, [vi], 28, 327). Its- chemical properties are similar to those of hydurilic acid; it reduces ammoniacal *nilv^* nitrate solution on **warming,** and gives a beautiful green coloration with ferric chloride; on gentle osid&uYon it yields a product that gives JI blood-red coloration with ferric chloride ; but when oxidised by nitric acid it forms dimethylalloxan.

o:J5"- *Dt chloral el rarnethylhydurilic acid may* be obtained by chlorinating tetramethylhydi^ilk-acid in alcohol; it forms transparent crystals with rectangular section, m.p. 206°. It is devoid of acidic properties, Biltz and Haraburgcr (Z.c).

*5*BrQ?no-5'-meihoxtf>* (or *tthozy-) Utramethylhydurilic acid* is formed on brominating tetrametbylhydurilic acid in presence of methyl or ethyl alcohol. The bromomethoxy-derivative jf<Forms elongated*rhombic tablets and has m.p. 245-247" (decomp.) and the bromoethoxy-analogue forms elongated hexagonal tablets, m.p. 199-200° (decomp.).

5:5'-DibromotetTamethylhydurilic acid is formed by the action of brocupe on tetramethylliydurilic acid in carbon tetrachloride in complete, absence of water; A crystallises in snow-white lancet-shaped leaflets and yields alkyloxy-compounds on treatment with alcohols. It loses both atoms of bromine on heating at 14*M8G°, forming *tetraimlhyldekydrohyduTilic* acid, a highly reactive compound which melts at 284°. With boiling methyl alcohol it forms *5-methoxy-tetramelhylKydurilic* acid which crystallines in stout, four-sided prisms, m.p. 284° (decomp.).

5-AmitiotelmmethylkyduriUc acid,

C-,,$H_{1S}O,N_1.H_1O$.

m,p. 295-3uO° (decomp.) is prepared by acting upon *dehydTottiTamethyUiydwrilic,* acid **with** aqueous ammonia; it crystallises in silky rhombic leaflets, It is reduced by hydriodic acid and phosphonium iodide to *\&-dimelhyU uramil,* and on bromination in alcohol yields fi:5-dibromo-1:3-dimethy 1 barbituric acid.

5-Metktflaminotttramethyihydurilic acid crystallises in rhombic plates.

S-Anilinotetramelhylhydurilic acid has m.p. 160-161° (decomp.) and forms an aniline sa!t CigHi.OeNj.NHgPh which melts at 134°.

Deoxyamalic acid baa only two acidic functions; *the potassium,* $K,C_{11}H_{13}O_6N_4$, andthe sodium, $Na_3C_{12}H_{12}O_{(}rl_{it}$ salts are sparingly soluble (Mntignon, *I.e.*; Fischer and Ach, *I.e.),*

For the preparation of *B-dimethylkgdttrilic acid* and derivatives, *see* Biltz and Heyn (Ber, 1919, 52 [B], 1298).

M. A. W.

HYGRIC ACID *(v.* Vol. III, 226a).

HYGRINES *(v.* Vol. **III,** 225rf).

HYODEOXYCHOLIC ACID *(v.* **Vol. I,** 6896).

HYPACONITINE *(v.* Vol. I, I22c).

HY PAPHORIN E *(v.* Vol. I, *6SU).*

HYPERSTHENE. A rock-forming mineral belonging to the or*horhombic series of the pyroxene group, and consisting of metasilicate of magnesium and iron $(Mg,Fe)SiO_3$. With less iron it passes isomorphously into *brcmzt'te* and *enstatite (q.v.).* It id a common constituent of basic igneous rocks, especially norite. The very coarse-grained norite found as boulders on the coast of Labrador consist of labradorite (». FELSPAR) and hyp"™»thene, the former showing brilliant coloured reflections and the latter a brigin/ coppery sheen. This material is therefore sometimes used as an ornamental or precious stone-. The mineral is opaque, with a dingy, brownish-black body-colour, and the metallic reflection is due to the presence of minute crystalline enclosures arranged parallel to one plane. Sp.gr, 3-4,

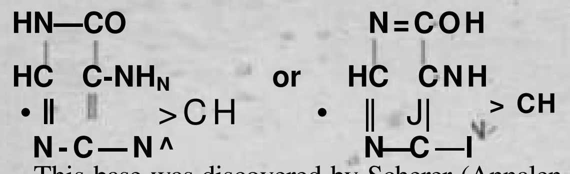
L. J. S.

" ***HYPNAL."*** Trade name for a compound of chloral and antipyrine which possesses the physiological properties of a mixture of the reactants.

" *HYPNOGEN."* A trade name for diethylbarbituric acid.

" *HYPNONE."* Trade name for acotophenone* a moderately active hypnotic.

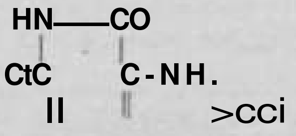
HYPOXANTHINE, *Harcine, G-Oxypurine*



This base was discovered by Scherer (Annalen / 1850, 73, 358) in heart muscle and spleen Strecker *(ibid.* 1858, **108,** 129) isolated & base from the' muscles of several animals which he railed *sarcine.* It was subsequently shown tha Baxcine was identical with Scherer's hypoxanthine *(tee* Salkoweki, Biochem. Z. 1913, 56 250; Yoahimura, *ibid.* 1911, 37, 481). Hypoxanthine has been isolated from a very large number of animal and plant tissues. It is, lowever, easily formed from adenine either *post n.ortem* or in processes used for its isolation, and there is some doubt as to how much of the base obtained from the tissues represents preformed jypoxanthine. For the ^isolation from various animal tissues, see *also* Heymann, Pfliiger's Archiv. 1872. 6, 184; Salomon, Z. physiol. hem. 1878, 2, 72; Ber. 1878, 11, 574; Kossel, ;. physiol. Chem. 1881, 5, 152; 188t>, 10, 268; Schindler, *ibid.* 1889, 13, 432; Buglia and Costantino, *ibid.* 1913, 83, 45; Smorodinzew, *ibid.* 1912, 80, 218 j Bass, Arch. exp. fath. Pharm. 19U, 76, 40; from urine, Strecker, *I.e.*; Salomon, Z. physiol. Chem. 1837, 11, 410; Kriiger and Salomon, *ibid.* 1898, 24, 385; 1899, 26, 356; and from faeces, Kriiger and Schittenhetm, *ibid.* 1902,36,158. Hypoxanthine has been found in beer yeast {Schiitzenberger, Chem. Zentr. 1877, 73), in fungi (Wmterstein, Reuter and Korolew, Landw. Versuchs-Stat. 1913,7&-80,541-562), in hops (Chapman, J.C.S. 1914, 105, 1895), ip potato juice (Schulze, Landw. Versuchs-Stat. 1882, 28, 111), in sugar beet (von Lippmann, Ber. 1896, 29, 2645), and in various plants (Schulze and Bosshard, Z. physiol. Cheat. 1885, fi, 420). Hypoxanthine has been isolated from steam-heated soils by Schreiner and Lathrop (J. Amer. Chem. Soc. 1912, 34, 1242) and Schreiner and Shorey (J. Biol. Chem. 1910, 8, 385).

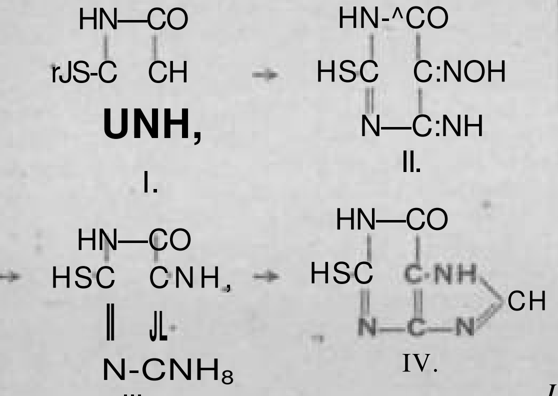
Hypoxanthine is formed in the animal body during the breakdown of nucleic acids. In man adenosine (adenine nucleoside) is first deaminised, forming inosine (hypoxanthine nucleoside) whinh is then hydrolysed giving hypoxanthine and a pen'ose (deoxyribose or ribose). In some other manuals enzymes are available which provide an alternative path for the formation of hypoxanthine. Adenoeine is first hydrolysed giving ndeniiie (3-attiinopurinc) and pentose, and the former is then dcaminiaed by the enzyme adenase giving hypoxanthine. The oxidation of hypoxanthine hi the body is probably confined to the live/, which contains the necessary enzyme, *xanthine oxidase,* for the conversion of hypoxanthine into xauthine (2:(J-dioxypurine) and uric acid (2:6:8-trioxypurine). The latter is cxcreU'd by man and the anthropoid ape but most other niamcals oxidise it still further to allantuin. For details and literature, *see* Jones, " Nucleic Acids," Longmans, Green & Co., 1920, or Levene and Bass, " Nucleic Acids " (American Chemical Society Slonograph 56), 1931.

The structure of hypoxanthine has been confirmed by syntheses. Fischer (Ber. 1897, 30, 2226; G.P. 17673/1898) by heating trichloropurine with normal aqueous potassium hydroxide obtained *%oxy2:^dichloTopi*



which he reduced to hypoxauthine by the action of hydrogen iodide. Hvpoxanthine was obtained by oxidation of adenine with nitrous acid

(Kossel, Z. physiol. Chem. 1886, 10, 258; Kriiger, *ibid.* 1894, 18, 445}. It can also be formed by reduction of uric acid with chloroform and alkali (Snndwik, *ibid.* 1897, 23, 476; 1898, 26, 131; 1912, 76, 480). Traube (Annaletij 1904, 331, 64) syiitflesised hypoxanthine by condensing ethyl cyanacetate and thiocarbamide in the presence of sodium ethoxide. *i-Amino-Q-ozy-2-thiopyrimidvte* (I) is formed and gives an wonitroao derivative (II) which yields 4: 5-*diaminoS-oxy-2-thiopyrimidine* (III) on reduction.



I. II. III. IV.

I

By heating the sodium salt of the *formy* derivative of this compound to 250°, *6-oxt/-2-thiopurine* (IV) is formed. The Bulphur is removed from this compound by heating at 100° with 25% nitric acid yielding hypoxanthine.

Hypoxanthine forms small colourless anhydrous crystals; an unstable hydrated modification has also been observed (Micko, Chem. Zentr. 1904, II, 914). Hypoxanthine decomposes without melting at 150° and dissolves in about 1,400 parts of cold (19°) or 70 partf^of boiling water {Fischer, Ber. 1897, 30, 3226). It has both acidic and basic properties, combining with one equivalent of acid or with two equivalents of baae. For dissociation constants, *see* Ogaton, J.C.S. 1936, 1713.

Hypoxanthine Hydrochloride,

$$C_5H_4ON_4{\cdot}HCl,H_2O,$$

crystallises in plates or "needles; the woll-crystallised *nitrate.* $C_iH_4ON_4HNO_3,H_IO$ 'is readily soluble in water but sparingly soluble in tbe presence c/ nitric acid. *Hypojanihine picrate,* $C_BH_4ON_4C_aH_30_7$^$_3$,$H_{i|}O$, forms rhombic plates which "dissolve in 450-500, parts of water at room temperature' {Kriiger and Salomon, Z. physiol. Chem. 1898, 26, 362). The *pkuspholungstaU* forma straw-coloured plates (Drummond, Biochem. J. 1918, 12, 5). There are two crystalline *auricldorides,*

$$C_BH_4ON_4HClAuCl_3,$$

m.p. 240-242° {decomp.), from dilute hydrochloric acid solution and

$$C_sH_4ON_4\text{-}2HCl\text{-}AuCl_3>$$

m.p. 259-262° (decomp,), from hot concentrated hydrochloric acid (Hoppe-Seyler and Schmidt, Z. physiol. Chem. **1928,** 175, 304). The *silver salt,* CsHjON^Ag^HjO, loses |H_aO at 100°; in the presence of excess of ammonia the compound crystallises in needles with $3H_aO$ and loses $2\text{-}5H_aO$ on drying at 120° for 2 hours (Bruhns, *ibid.* 1890, 14, 544. 566; Kriiger and Salomon, *ibid.* 1898, 24, 386).

Some sparingly soluble derivatives iormed with salts of metals have been used for the separation and estimation of the base. There ia a civstalline *mercurickloride,* $C_SH_4ON_4{\cdot}HgCl_2,H_2O,$ and a *compound* with *silver nitrate,*

$$C_5H_4ON_4AgNO_3,$$

which crystallises from nitric acid solution. One part of hypoxanthine silver nitrate dissolves in about 4,960 parts of cold nitric acid (sp.gr. 1*1), *Hypoxanthine silver picrate,*

$$C_sH_3ON_4Ag'C_8H_3O_7N_3,$$

is precipitated from a hypoxanthine solution by sodium picrate and silver nitrate and forms microscopic lemon-yellow neadles insoluble in cold water (Bruhns, *ibid,* 1890,14, 555).

Hypoxanthine-tf-glucoside crystallises in long needles, m.p. 245°, and has [a]g> —3i'5° in A'-sodium hydroxide and +12-92° in *N*-hydrochloric acid (Fischer and Helferich, Ber. 1914, 47, 210).

Bromo(iypoxanthine, $C_BH_3ON_4Br,2Hs,O$, is obtained by the action of 1 mol. bromine on 1 mol. hypoxanthine at 120° or by oxidaticn of bromoadenine with sodium nitrite at 70°; it is sparingly soluble in cold water. By heating hypoxanthine with excess of bromine for 6 hours at 100-150° *bromohypoxantkinetetrabrcmide hydrobromide,* $C_BH_3ON_4BrBryHBr$, is obtained (Kriiger, 2. physiol, Chem. 1894, 18, 449).

Hypoxanthine Urethane,

$$C_5H_3ON_4{\cdot}COOEt,$$

prepared from hypoxanthi^ and ethylchlorocarbonate, crystallises in sparingly soluble^' 11M, m.p. 185-190° (Bruhns and Kossel, *ibid.* 1892 16, 1).

Hypoxanthine forms a crystalline •»ro?n-*pwnd* with *adeniw,* $C_6HaON_4\text{-}C_BH_5N_{51}3H,O$ (Bruhns$_f$ Ber. 1890, 23, 225), and througu the imino group in position 7 forms coloured derivatives with diazobenzehe salts (Burian, *ibid.* 1904. 37, 690).

Separation and Estimation.—From mixtures of the purine bases adenine and hypoxanthine can be separated by means of the sparingly soluble compounds with silver nitrate. After removal of silver, adenine is precipitated as the very sparingly soluble jicrate, and hypoxanthine is precipitated from the filtrate by addition of ammoniacal silver nitrate *{set* Bruhns, *ibia* 1890, 23, 225; Kossel, Z. physiol. Chem. 1883,' 8.404; Schindler, *ibid.* 1889, 13, 432; Kruger, *ibid.* 1894, 20, 170). Hypoxantbine and xanthine can be estimated uAlood by oxidation to uric acid by means pf xanthine oxidaae (Cole-Ellet and Womack, J. Lab, Clin. Med. 1931, 16, "9^)' For microch'unical estimations, *see* Krebs and Orstrom, Biochem. J. 1939, 33, f184-Reifer, New Zealand J. Sci. Tech, 1940, 21, 171.

W. V, T.

" *HYRCOL"* Trade name for a preparation of colloidal mercury (Rosenthaler, Apoth.-Ztz. 1926,41, 578). . t- «

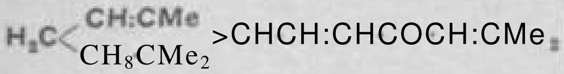
HYSTAZARIN (*v.* Vol, I, 222c).

I

tANTKINITE,—Hydrous uranous oxide $2UO_S$-$7H_2O$, occurring as velvety crusts of fine needles on pitchblende, of which it is a first alteration product, in the Kasolo mine, Katanga, Belgian. Congo, and also at Wolaendorf, Bavaria. The orthorhombic crystals are black with a violet or purple tinge and sub-metallic lustre. Pleochroism is intense—dark violet to colourless. On exposure to air the mineral is altered to greenish-yellow uranic oxide, UO_3'2HaO, as *becqtKreliie* or *8cko€j>i:<s,* (A. Schoep, Natunr wetensch. Tijds. 1926, 7 (for 1925), 97 ; 1927 9, 1 ; Ann. Soe. Geol. Belgique, 1927, 49 (fo 1926), Bull. B1S8, B310; Bull. Soc. beta Gool. 1931, «, 71; C. Palache, Amer. Min 1934, 19, 313).

L. J. S.

IANTHONE, $C_{ie}H_MO$, is a mixture of the two ketones,



$$H_2C\langle{}^{CH:CMe}_{CH_8CMe_2}\rangle CHCH:CHCOCH:CMe$$

b.p. 155-165" and

b.p. 160-172°

obtained by the condensation in presence of alkali of mesityl oxide with 0- and *a-cyclocitra,* respectively, *v.* Vol. Ill, 1846. It is obtained together with ionone when citral and mesityl oxide are condensed in the presence of alkali and the product treated-with an acid condensing agent* {Durand and Huguenin, G.P. 118288). It is a.-light yellow oil, b.p. 162-1^715 mm., d^M 0-9452, n_D ca. 1-5376 (Haarman and Reiiuer, G.P. 127231). When diluted it has a characteristic odour of violets and orris *root.*

13OG AIN E. *Tabernanthe Iboga* Baill., called Ibojpv or Aboua, grows in the French Congo; it has long been known that extracts from this plant are used as a tonic by the natives. Dybowaki and Landrin {Compt. rend. 1901,133, 748) succeeded in isolating a crystalline alkaloid, *ibogaine,* from Iboga (yield 0-6-1-0%), but it is not quite clear whether this base is responsible for the effect of the Iboga preparation. Almost simultaneously, Hnller and Heckel *{Hid.* 1901, 183, 850) found the base *ibogine* in this plant; ibogine is probably identical with ibogaine.

Ibogaine, $C_{S4}H_{a)(}O_2N_g$ (Dybownki and La!ldrin) or CJJHJJOJNJ (Hallcr and Heckel) has probably the formula C^H^ON;, (unpublished), colourless prisms, m.p. 149-152° (from abs. EtOH), $[a]_D$ -48-5° (in 95% alcohol). The base is soluble in ttOH, EtjO, $CHCi_3$, acetone * and C,H_{fl}, insoluble fn H,O. The hydrochloride and the picrate (red needles) are crystalline, other salts have not been obtained in crystalline form.

Ibogaine is an indole base, but not a earboline derivative *(tee* HABMALINE). (unpublished) ; it forms salts with one molecule of a monobasic acid. For physiological activity, *tee cited* articles and Lambert and Heckel, Compt. rend. 1901, 138, 1236; Rothlin and Raymond-Hamet, Compt. rend, Soo. Biol. 1934, 116,1340.

Schl.

!CACO or Cocoa Plum. The fruit of *Ckryaobala7iit& icaco* L., a native of Florida, the West Indies and the West Coast of Africa. It resembles a small plum (8 g.j and is used more commonly in the making of preserves than as a dessert fruit. Analytical data recorded by Chace, Tolman and Munson include:

Total solids, 69; protein, 0-46; acids (as malic), 0·13; reducing sugars, 41-5-1; sucrose, 0-36; uh,0-9(%).

The ash of the pulp contains: K_aO, 35-15; CaO, 5-84; MgO, 4-51; P_aO_6, 3·09; SO_3, 4-77; andCI, 18-82%.

A. G. Po.

ICE COLOURS {Vol. IV, 227ft),

ICELAND MOSS (Cetraria) is the dried lichen *Cetraria islandica* Linn.

ICELANDSPAR *{v.* Vol. II, 203c).

ICE-SPAR («. Vol. III, 4406).

ICHTHAMMOL (" *ICHTHYOL").* Ichthammol consists chiefly of the ammonium salts of the sulphonic acids prepared from an oily substance obtained by the destructive distillation of bituminous schists, together, with ammonium sulphate and water. These echista contain the remains of fish and marine animals, and are found in the Tyrol and on the coasts of the Adriatic, in Switzerland and parts of Italy. The Seefeld district between Southern Bavaria and Tyrol has long been noted for the crude iehthyol. Ichthyol oils from Kashpir shale have been reported (E. V. Rakovskii and S. I. SOEOIOV, J. Appl. Chem. U.S.S.R. 1930, 3, 81).

Ti'o oil usually contains about 10% of su)phur> As found in pharmacy, ichthyol contains 5-7% *ammonium* sulphate, about 50% water, and about 1% of an empyreumatic oil. The British Pharmacopoeia lays down standards for the pharmaceutical product.

H. Scheibler has purified the crude oil (Ber. 1919, 52 [B], 1903), and has isolated 2-n-butyl-liiojihcn from oil obtained from Achensce, and 3-n-propyl- and 2-iaopropyl-thiophen from Seefeld oil (H. Scheibler and F. Rettig, *ibid.* 1926, *69* [B], 1198; Arch. *Pharm. 1920, 258, 70). i

Ichthyol is soluble in water, partly so in alcohol (90%) and in ether. It ia used as a mild antiseptic in skin diseases and also internally. For ichthyolic medicinal preparations, *see* Stadnokov (Amer. Chem. Abstr. 1928, 22, 3261). *Siblioaraphy,* U.S. Bur. Mines, Inf. Circ. No. 7042, (*1918*).

ICOSANE (n-Eicosane), C_wH_{4a},

$$CH_3\text{-}[CH_a]_{ia}\text{-}CH_3$$

The hydrocarbon has been obtained in a high legree of purity from petroleum waxes (C. C. lut-hler and G. I). Graves, Ind. Eng. Chem. 1927, 19, 718). Synthetically, it may be prepared from n-decyl iodide and sodium (Krafl't, icr. 188li. 19, 2220), or by reducing eicosyl iodide with zinc and hydrochloric acid (Levene, West and Van der Scheer, J. Biol. Chem. 1915, 20, 526). Other methods include the reduction of ethyl-n-heptadecyl ketone with amalgamated zinc and hydrochloric acid in alcohol (A. Miiller and W. B. Savilte, J.C.S. 1925, 127, 599) and the reduction of the compound,

$$C_{13}H_{27}\cdot CCl_2\cdot C_6H_{13},$$

with phosphorus and hydriodic acid at 240*C. (Krafft, Ber. 1832, 15, 1717).

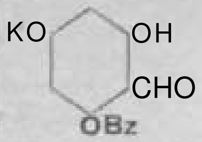
Evidence from X-ray diffraction experiments indicates two crystalline modifications of the hydrocarbon (Muller and Savilie, *l.c);* m.p. 36-4°^ heat of fusion 14,680 cals./mol. (G. 6. Parks and H. M. Huffman, Ind. Eng. Chem. 1931,2% 1138); b.p. 220730 mm. (H. Prophete, Compt. rend. 1S26, 183, 609), 205°/15 mm. (K. Ziegler, F. Derach and H. W oil than, Annalen, 1934, 511, 13), 148°/0-6 mm. {Levene, West and *V>n* der'Scheer, i.e.); «•* 14178; rf* 0-7417 (Buchlcr and Graves, *I.e.).* For thermal data, *see* G. S. Parks, H. M. Huffman and S.. B. Thomas, J. Amer. Chem. Soc. 1930, 52. 1032.

Eieosyl bromide and l:20(eicosy] dibromide as an unacparated mixture were probably obtained by J. von Braun and E. Kamp {Ber. 1937, 70 [B], 973) from the dicyefohexyl ether of I:2-eicosylgIycol and hydrogen bromide.

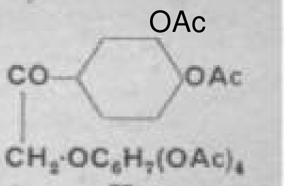
" *ICtL* " COLOURS (*v.* Vol. IV, 234a).

ID/EIN. The orange-red fruits of the cranberry {*Vatximum vitia~idcea-* L.) are coloured with an anthocyanin which is closely related to ehrysanthemin and cyanin *{<j.v,),* and to which the name idsein has been given (Wills tatter and Mallison, Annalen, 1915, 408, 15). The pigment was extracted from the skins of cranberries by means of acetic acid, and after precipitation as the *picrate* was converted into 'Ihe *chloride* {1-6 g. from 107 kg. of skinB). *. M. and R. Robinson have obtained the same colouring matter from the leaves of the common beech *(Fagu3 sylvalica).* An extract of the leaves (collected at the end of May in Oxford) in 1% HCI was saturated with NaCI and the anthocyanin taken up in *iso&myl* alcohol. Benzene was added, and the pigment re-extracted by means of aqueous HCI. The aqueous solution was thoroughly extracted with ethyl acetate, and then the pigment was transferred to w-butyl alcohol after agciil saturating with NaCI. The alcoholic solution was mixed w.lh light petroleum and the pigment taken up in (the miaimum volume of 1% HCI. A crude solid pigment was obtained by adding acetic acid and then ether, and repeating the precipitation in the same manner. The *pierate* was prepared, and then the *chloride, by* adding ether to a solution of the *picrate* in methyl-alcoholic HCI. The *chloride* crystallised at onee when 5% ethyl alcoholic HCt was added to its concentrated solution in *0-5%* aqueous HCI. *A hydrate o£* idiein chloride, $C_{z1}H_{2}iO_{u}CI,2\text{-}5H_2O$, crystallises from 5% HCI when alcohol is added to retard separation. The reddish-brown monoclintc prisms appear brownish-red to grey-violet under the microscope. The powdered salt is reddish-brown and melts with foaming at 210°. The salt becomes anhydrous when kept in a desiccator at the ordinary temperature. In solubility it differs markedly from cyanin. It dissolves fat 10 parts of water at 15° forming a brownish-red solution which becomes orange-red on dilution ; *paetidobose* formation is observed only at high dilutions. It is easily soluble in *Q-5%* HCI, sparingly in 3% HCI and almost insoluble in 8% HCI. It is rather more soluble in sulphuric acid; 0-03 g. dissolve in 100 c.c. of 7% sulphuric acid at 25°. From this solution characteristic rhombic plates of the *sulphate* crystallise *on* coo) ing . The *chloride* is easily soluble in alcohol with H bluish-red colour. The *picrate,* a brownish red powder which under the microscope is seen to consist of carmine-red *ieedles, dissolves in 30 parts of' boiling water but is very sparingly soluble in the cold. Idaein differs from cyanin in that with sodium carbonate or bicarbonaii- 'it gives a stable violet colour which iff changed to blue only on adding sodium hydroxide. The blue fades to green and finally to yellow. The violet colour is'restored when the blue solution is diluted (hydrolysis of the alkali salt of the *colour -base).* Ferric chloride added to the alcoholic solution gives a blue colour, and this becomes violet on diluting. Lead acetate precipitates a„ blue lead salt from the alcoholic solution. Alum gives a very stable violet colour with the aqueous solution, and bismuth nitrate a reddish-violet colour. The absorption spectrum in 7% sulphuric acid consists of a broad band (green-blue) which" resembles that of cyanin but does not extend so far into the blue. The absorption spectrum in the visible region and the alkali colour reactions of idiein resemble those of chrysanthemin very closely, but the behaviour of the two pigments on distribution between amyl altjolvol and aqueous acid is quite distinct. Idrein is lievorotat&nr. Hydrolysis by means of aqueous *HKtT* affords cyanidin chloride (I naol.) and galacfcose (1 molAi-Its behaviour on distribution between amyl alcohol and aqueous acid is that of a typical monoglucoside. <•

The structure of idfein has been established by Grove and Robinson (J.C.S. 1931, 2721, "who Hvrithesised the colouring matter by condensing 2-O-benzoylphloroglucinaldehyde (I) with *<u*-tetra-acetyl-j9-galactosidoxy-2:4-diacetoxyacetojjhenone (II) by means of hydrogen chloride, and obtained an acylated anthocyanin from which idtein chloride (III) was obtained by hydrolysis.



I.



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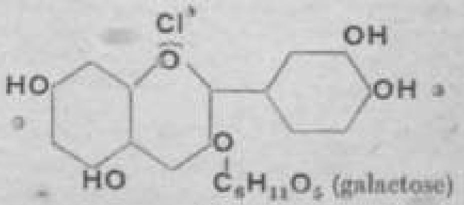

III.

W. B.

IDEAL OR PERFECT GAS.—I.

The behaviour of " permanent " gases can be represented by certain empirical laws.

{i) Boylt's Law.—At constant temperature the product of the pressure p and the volume V of a gas is constant, p Inconstant. Table I shows how closely this law is obeyed in a number of cases.

TABLE I.

Gns.	t°C.	P.	pv.
Helium[1] . .	0	1-00000	100000
		601487	1-00228
		8-95584	100397
		12-46478	100559
Hydrogen* . .	0	1-000	1-0000
		75-795	1-0478
		164-193	1-1078
		442-27	1-3070
		1089-67	1-7715
Nitrogen[3] . .	0	1-0000	1-0000
		190215	099274
		37-9527	0-98730
		522158	0-98459

(ii) Charles' Law or Gay Lussac'sLaw.—This law relates the volume of a gas at constant pressure to the temperature t of the gas;

$$V_t = V_0(1+at)$$

Combining this with (i) it follows that at constant volume

$$p_t = p_0(1+at)$$

where V_0 and p_a are the volume and the pressure oMhe gaa when the temperature / is zero. The value of a clearly depends upon the scale on which the temperature is measured. If t is measured on the Centigrade scale $\frac{1}{a}$=273-l°O: This value is not constant for real gases, and Table II shows values of a in a number of casea. A more useful scale of temperature can be obtained by setting $\frac{1}{a}(f-+t\backslash=T$. Making this substitution $V_t = V_0\frac{T}{T_0}$ and 2>(=i>osr« $\frac{T}{}$ where $T_n=\frac{1}{a}=273\text{-}r^jK$. When the temperature t is measured on the Centigrade scale, T is the *absolute temperature* (Kelvin scale).

(iii) Lawa (i) and (ii) abone can be combined to gjjve pV^CT, where C is a constant having the value $C=\frac{p_0V_0}{T_0}$. If we take as our standard of quantity 1 mol. then

$$pV = n\frac{p_0v_0}{T_0}T, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where n is the number of molecules in volume V and VQ the molal volume of the gas at pressure p_0 and temperature T_v.

TABLB II.

Gas.	p in. Hg.	$a_{0-100°} \cdot 10^7$.	$\beta_{0-100°} \times 10^7$.
Helium[4] .	0-608	—	36(308-6
	0-750	—	366079
	0-967	—	36C07-3
Krypton[5] .	0-862	36,916	—
	l'OOO	36,967	36899-0
Xenon[9] .	0-862	37,285	—
	100	37,395	372020

Heuse and Otto found:—

$$\left.\begin{array}{l} a_{0-100°} = 0\text{-}0036609 + 358 \times 10^{-7}\,p \\ \beta_{0-100°} = 0\text{-}0036609 + 290 \times 10^{-7}\,p \end{array}\right\} \text{f} \quad \text{krypton}$$

and

$$\begin{array}{l} a_{0-100°} = 0\text{-}0036609 + 785 \times 10^{-7}\,p \\ \beta_{0-100°} = 0\text{-}0086WKM\text{-}6MX\ 10^{-7} \end{array} \quad \text{xenon.}$$

(iv) Avogadro's Law states that under the same conditions of pressure and temperature the molal volume of all permanent ga^ea is the same. Thus the term ^-? in equation (1) is a constant applicable to all permanent gases and is called the *gas constant, R.*

$$pV = nRT.$$

The valve of R can be obtained from a know* ledge'-W the molal volume under some particular experimental conditions, *e.g.* J^t_0=273-l°2. p_o=1 atmosphere, $t>_0$=22-4 litreB, hence fl=$\frac{22{*}4 \times 1}{279}$ litre-atm./^C. mol,

Values of R fa *Different Units.*—R=1987 cals./°o. mol., 8-314xl,0^7 ergs/°c. mol,, 008205 litre-atm./°c. mol. Gases which obey exactly the law $pV=nRT$ are known as *ideal or perfect gastn.* Exact obedience to this law over a wide range of temperatures and preesmps is not found in practice even with gases which are most difficult to condense. The deviations from the perfect gas law are rcore marked in the case of gases which are more easily condensed.

Mixtures of Ideal Gases.—Dalton's Law of partial pressure states that in a mixture of ideal gases the total pressure P is the sum of the partial pressures pi of the constituent gtjes. P=$pi. The partial pressure $p$$ of any constituent i is the pressure which would be exerted by that gas i if it were present alone with a temperature and volume equal to the temperature and volume of the mixture.

II. "THEEMODYHAMICS OF A PBBFBCT GAS.

By definition a perfect gas is one for which the equation of state is

$$pV = nRT.$$

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[1] Kceaom and van Santen, Comm. Leiden, 1933, No-227b.

[1] MlclieJa, Nijhoff and Gerver, Ann. Phystlt. 1932, 12,, 562.

[3] Hlchels. Woutera and De Boer, Phyaica, 1934, 1, 687.

[4] Keesom, van der Horst and Taconis, Coinm. Leiden, 1034, So. *23Od.*

[8] Heuso and Otto, Fhysikal. *Z.* 1934, 36, 57.

* Heuso and Otto, *ibid.* p. 62S.

The Energy E of a Perfect Gas is a function of the temperature only.

In general we have $\left(\frac{\delta E}{\delta V}\right)_T = T\left(\frac{\delta P}{\delta T}\right)_V - P.$

But for a perfect gas $T\left(\frac{\delta P}{\delta T}\right)_V = \frac{nRT}{V} = P$

and hence $\left(\frac{\delta E}{\delta V}\right)_T = 0.$

The Heat Content H of a Perfect Gas is a function of the temperature only.

In general we have $\left(\frac{\delta H}{\delta P}\right)_T = -T\left(\frac{\delta V}{\delta T}\right)_P + V.$

But for a perfect gas $T\left(\frac{\delta V}{\delta T}\right)_P = \frac{n}{P}RT = V$

and hence $\left(\frac{\delta H}{\delta P}\right)_T = 0.$

The above two laws mean that for a perfect gas the *Joule effect and the Joule-Thomson effect are zero.*

In the Joule experiment a gas is expanded adiabatically and without doing any work. This process is in the case of real gases accompanied by a temperature change. Since it is an adiabatic process and no work is done, the process occurs at constant energy content and the effect is measured by $\left(\frac{\delta T}{\delta V}\right)_E$

$$\left(\frac{\delta T}{\delta V}\right)_E = \frac{P - T\left(\frac{\delta P}{\delta T}\right)_V}{C_v}$$

which is zero for a perfect gas since

$$P - T\left(\frac{\delta P}{\delta T}\right)_V = 0.$$

In the Joule-Thomson experiment the effect is measured by $\left(\frac{\delta T}{\delta P}\right)_H = \mu$ since no heat exchange occurs during the experiment.

$$\mu = \left(\frac{\delta T}{\delta P}\right)_H = \frac{-V + T\left(\frac{\delta V}{\delta T}\right)_P}{C_p}$$

which is zero for a perfect gas, since

$$-V + T\left(\frac{\delta V}{\delta T}\right)_P = 0.$$

See Table III for values of μ for nearly perfect gases.

TABLE III.—JOULE-THOMSON EFFECT FOR NEARLY PERFECT GASES.

$\mu = \left(\frac{dt}{dP}\right)_H$ in °C. per atm.

Helium[7] (pressure 1-200 atm.).

t°C.	-190	-140	-50	0	50	150	300
μ	-0·37	-0·52	-0·50	-0·60	-0·61	-0·62	-0·58

Argon[8] (pressure 1 atm.).

t°C.	-170	-150	-50	0	50	150	300
μ	3·01	1·75	0·68	0·42	0·21	0·18	0·002

The Heat Capacities C_v and C_p of a fixed quantity of a perfect gas are dependent only upon the temperature

$$\frac{\delta}{\delta T}\left(\frac{\delta E}{\delta V}\right)_T = \frac{\delta}{\delta V}\left(\frac{\delta E}{\delta T}\right)_V = \left(\frac{\delta C_v}{\delta V}\right)_T = 0$$

$$\frac{\delta}{\delta T}\left(\frac{\delta H}{\delta P}\right)_T = \frac{\delta}{\delta P}\left(\frac{\delta H}{\delta T}\right)_P = \left(\frac{\delta C_p}{\delta P}\right)_T = 0$$

The Relation between the Heat Capacities of a perfect gas

$$c_p - c_v = \left(\frac{\delta H}{\delta T}\right)_P - \left(\frac{\delta E}{\delta T}\right)_V$$

$$= \left(\frac{\delta E}{\delta V}\right)_T\left(\frac{\delta V}{\delta T}\right)_P + P\left(\frac{\delta V}{\delta T}\right)_P$$

But for a perfect gas

$$\left(\frac{\delta E}{\delta V}\right)_T = 0 \text{ and } P\left(\frac{\delta V}{\delta T}\right)_P = nR.$$

Hence $c_p - c_v = nR$ for n molecules of gas; or $C_p - C_v = R$ where C_p and C_v are the molal heat capacities.

Compressibilities of a Perfect Gas.—*The Isothermal Compressibility* κ of a perfect gas

$$\kappa = -\frac{1}{V}\left(\frac{\delta V}{\delta P}\right)_T = \frac{1}{P}.$$

The Adiabatic Compressibility κ_S of a perfect gas

$$\kappa_S = -\frac{1}{V}\left(\frac{\delta V}{\delta P}\right)_S = \frac{C_v}{C_p}\kappa$$

$$\kappa_S = \frac{C_v}{C_p}\frac{1}{P}$$

Equation for Adiabatic Change of a perfect gas

$\left(\frac{\delta P}{\delta V}\right.$ [illegible] (2)

where $\gamma = \frac{C_p}{C_v}$

If C_p and C_v are independent of temperature (not necessary in the case of a perfect gas, *see later*) the integration of (2) leads to

$$p \propto v^{-\gamma}$$

Value of γ for a perfect gas: $\gamma = \frac{C_p}{C_v} = \frac{C_v + R}{C_v}.$

Ideal Gas—Kinetic Theory Definition.—On the basis of the Kinetic Theory a perfect gas may be defined as an assembly of atoms or molecules between which there is no energy of interaction and in which the volume occupied by the atoms or molecules is negligible with respect to the total volume of the assembly.

The first of the above conditions means that the whole energy of the assembly is the sum of the kinetic energies of translation and of the rotational, vibrational and electronic energies of the individual molecules. The second condition means that the free volume available for the translational motion of the molecules is equal to the total volume of the whole system. For real gases these conditions are only held over a certain pressure range and as the pressure on the

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[7] Roebuck and Osterberg, Physical Rev. 1933, [II], 43, 60.

[8] *Idem., ibid.* 1934, [II], 46, 785.

gas is increased deviations from these ideal conditions will become more Berious

As defined above, the heat capacity of the ideal gas ia not necessarily independent of temperature. Some workers have defined a perfect gas not only as one obeying the law *pV^nRT* but

also obeying $(\tilde{}\ ) = 0$.

In terms of the above model this extra eon* dition limits a perfect gas to an assembly of systems for which quantised changes in the internal energy (rotational, vibrational and electronic) are not allowed. It is, however, sufficient to define an ideal gas as one obeying the law *p V=nRT* and this law can be derived statistically or kineticaliy on the basis of the above conditions of an ideal gas.

M. G. E.

IDENTIFICATION OF DYES ON TEXTILE FIBRES (*v.* Vol. IV, 147b-175c).

IDITOL(t\ Vol. II,29od).

IDOCRASE or VESUVIANITE. A mineral consisting of a complex silicate of calcium and aluminium, together with iron, magnesium, water, fluorine, boron, etc. F. W. Clarke's formula is $R'_4Al_2Ca_TSi_sO_M$, where $R'_4=Ca_a$, $(AIOH)_£$, H_4, etc. Crystals are tetragonal and usuul>y green or brown in colour; sp.gr. 3-35-3-45, hardness 6£. The mineral is of common occurrence in contact-metamorphic rocks, particularly crystalline limestones. Lustrous, brown crystals are common at Monte Sorama, Vesuvius (hence the name vesuvianite). Green crystals from Ala in piedmont are cut as gems at Turing A compact, massive variety, *californite* (Kunz, V_aer. J. Sci., 1903, [iv], 16, 31*7* has been found abundantly as blocks and boulders, measuring up to 6 by 3 feet, at several places in California (Siskiyou, Butte, Fresco and Tillage counties), and is used as a gem-stone and **for** larger ornamental objects. It is someu iiae viansluccnt, takes a high polish, and ranges from bright green to yeliowish-green and white in colour, thus closely resembling jade in appearance (D. B. Sterrett, Min. Res. U.S. Geol. Survey, Annual Reports for 1909 and 1910).

L. J. S.

IDRYLfu. Vol. V, 269c).

" *IGLOOiNE.'* Triiodoethylphenol. An antiseptic *(Iglodine, Neuxastle-on-Ti/ne)*.

IGMERALD(i>. Vol. 1^2796; V, 513a).

IGNOTINE (i>. Vol. 11, 3J2c). *

ILEX VOMITORIA, Aiton. **The leaves** of tin's tree, growing in the South **Eastern** States of America, have been found to contain m>tnble muounts of **caffeine;** the percentage obtained from ten samples i'rom different localities varied *fyom* I 05 to 0-40 (F. <*J. Pow^r and V. K. Chcauut, J. Amer. Chem. Soc. .1919, 41, 1307). The leaves are used by the Indians under the natc3 of " Yaupon " as a stimulant.

ILICYL ALCOHOL (*v.* Vol. I. *W><i)*.

ILLINIUM. 11. At. no. 01; at. wt. **147 (apptox.).**

J. A. Harris and K. S. Hopkins by fractionally crystallising the magnesium double nitrates of the ceria earths were able to secure a concentration of element no. Gl between neodymiuni and samarium. The amount present was insufficient to make its detection certain by X-ray spectra and attempts to identify it by its absorption bands were complicated by the fact that neodymium and samarium both exhibit broad bands capable of masking those due to no. 61. In separations; of these earths made through the bromates, terbium and gadolinium come between no. 61 and neodymium and samarium respectively. Terbium has but one absorption band while gadolinium has none. It thus became possible to observe strong bands at 5830, 5816 and 4520*,, and two fainter bonds all attributed to element 61; A'-r&y emission spectra of the samples showing these bands gave lines coi*responding with the calculated positions for La, and LJSf $_L$ of no. 01. To the element thus indicated, the name *' illinium" was given (J. Amer. Chem. Soc. 1«26, 48, 1585, 1594). Eolla and Femandes (Gazzetta, 192tJ; 66, 435) claimed priority for the discovery of clement 01 to which tbey gave the name " florentium." '

Cork, James and Fogg (Proc. Nat. Acad. Sci. 1926,12, 696), working on similar lines to Harris and Hopkins, examined the neodymium concentrates from large quantities of monazite sand since such concentrates might be expected to carry most of the illinium. JT-ray spectra of the fractions revealed in some of them the L series of element 61, the seven strongest lines being; $«_2$=2-289, ffl1=2-279, ft=2-078, £,=2-038, 0a= 1-952, y, = 1-799, y_z= 1-725. The amount of illinium oxalate estimated as being present in the fractions was from 1-1-5%.

Determinations of the basicity of the element by fractional precipitation with sodium nitrite places it after neodymium and before yttrium in lie series Pr, Nd, II, Y, Sm (Hughes and **Hopkins,** J. Amer. Chem. Soc. 1933, 55, 3121).

In spite of all the foregoing work illinium does not yet figure in international tables of atomic **weights** and it is doubtful if the suits **have** been obtained sufficiently pure to- establish definitely the individuality of the element. Indeed, Jensen (Naturwi&i. 1938, 26, 381) has suggested reasons for questioning whether element no. 61 can exist as a stable nucleus.

G. R. D.

ILLIPE BUTTER (v. Vol. 1,653c).

ILLfTPE NUTS(t>. Vol. >I, 3ltf, 32a).

ILLIPENE(f.Vol.I,fi53d).

ILUURIC ACID (0. Vol. III, 338ft).

ILLURIN BALSAM (». Vol. III,338ft).

tLMENITE, or Titaniferous Iron-Ore. A common **mineral** with approximately the formula $FeTiO_3$, but of variable composition. Analyses show TiO_4 22-59, FeO 20-46, **Fe,O_3 1-53%.** In its ihonibohcdral crystalline form it shows a close agreement with haematite, and it has consequently, until recently, been regarded as an isomorphous mixture of ferric oxide and titanium sesquioxide, the formula being written us an oxide $(Fe,Ti)_2O_3$. The discovery of the **rhombofaedial** tilanatea of magnesium and manganese, *geikielitz* ($MgTiO_3$) and *pyropftanile* ($MnTiO_a$), and the frequent presence of magnesium (and manganese) in ilnu-nite, suggest, **iowev«f,** that the mineral *in* really a titnnate of ferrous iron, $FeTiO_3$ (S. L. Pen field, Amer. J.

Sci. 1897, [iv], 4, 108). In the variety *picro-ilmenite* a considerable amount of iron is replaced by magnesium, the formula then beinj (Fe,Mf)TiO_3 (T. Crook and B. M. Jones, JMin. Mag. 1906,14, 165).

Ilmenite is black with a sub-metallic lustre, and often a smooth and lustrous conchoidal fracture, sp.gr. 4'5-5 ; hardness 5-6. The massive mineral somewhat resembles magnetite in appearance, from which it is readily distinguished by its feeble magnetic character. It is of constant occurrence as isolated grains in the more basic igneous rocks (gabbro, diabase, basalt, etc.); and in certain instances it forms rich **BCgrcgfttiuLiB ill «m!i roi[1] Its. Ennrmoun depot)** of ilmenite are found under these conditions at several places in Norway, Sweden, Canada and the United States. With the weathering and breaking down of these igneous rocks, grains of ilmenite {*manaccanitz,* from Manaccan in Comwall) collect in the beds of streams and on the sea-shore, sometimes forming considerable deposits of " black iron-sand."

Although large deposits of ilmenite are available for mining, the mineral has not yet found any important applications. It has been used for the preparation of tit&niuin paints and enamels; and in the future it may bo more utilised for the manufacture of titanium-steel, which possesses great ductility and a high limit of elasticity. (See J. T. Singewald.. The Titaniferous Iron Ores of the United States, their Composition and Economic Value, U.S. Bureau of Mines, 1913, Bull. 64.)

L. J. S.

ILVAITE, Llevrite or Yenite. Acid silicate of iron and calcium,

HCaFei'Fe'"SIıO,, -a

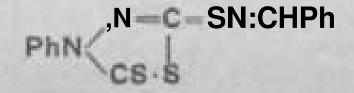
crystallised in the orthorhoiubic system. It contains theoretically FeO 35-2, Fe_2O_3 19-6% (Fe 41%), but the" ferrous oxide is partly replaced by an equivalent amount of manganous oxide (up to 8 6%). Sp.gr. 3-9-4-1, hardness 5J-6; gelatinises with hydroe'doric acid. The mineral is found somewhat abundantly as brilliant black crystals and as compact masses in the iron mines at Rio Marina and Cape Calamita in Elba. It is also known from Campiglia Jhmltima in Tuscany, .Jlebron in Nassau, British Columbia, Greenland and Japan,

UJ. 8.

IM IDES (v. Vol. II, 371a, 375c).

IMINES. The iminee are compounds in which the oxygen atom of a carbonyl group is replaced by NH, thus forming aldimines and ketimines from aldehydes and kc tones respectively. Ketimines are often termed kctin.*idc& in the literature.

The substituted aldimines arc known as Schiff'a bases, but the unsubstituled aldimines have been isolated in a few coses only. Busch (Ber. 1896, 29, 2136) isolated benzaJdimino hytlrochloride, C,H_6-CH:NH-HCI, by treating a benzene solution of the compound



witb hydrogen chloride; also {*idem. ibid.* 1896, 29,2144) by adding a saturated alcoholic solution of hydrogen chloride to hydrobenzamide in **diy** benzene at 5°C,

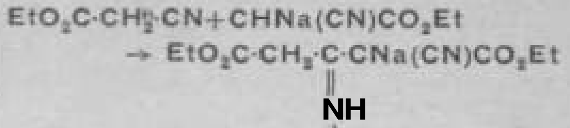
A. Hantzsdi and P. Kraft {*ibid.* 1891, 24, 3517) obtained the ketimine of benzophenone by converting the ketone to the dichloro-eompound, and treating this with urethane to obtain .

Ph^N-CO.Et,

which was decomposed by hydrogen chloride to give the ketimine hydro chloride. To obtain the base they passed dry ammonia into a chloroform Rolution *oftht* hydroehloride, filtered from the precipitated ammonium chloride and removed the chloroform *in vacua.*

Iminoacctoucetic tsUr may be prepared by the action of ammonia upon acetoacetic ester. The ketimine is tautomerie with 0-aminoaerylic acid ester. *See* K. von Auwers *tt al.,* on ketiminc-enamine tautomccism {*ibid.* 1930, 63 [B], 1072; 1931, 64 [B], 2768).

J. F. Thorpe and his colleagues investigated reactions of the type



$$EtO_2C{\cdot}CH_2{\cdot}CN + CHNa(CN)CO_2Et \rightarrow EtO_2C{\cdot}CH_2{\cdot}\underset{\underset{NH}{\|}}{C}{\cdot}CNa(CN)CO_2Et$$

(Thorpe, Baron and llemfry, J.C.S. 1904, 86, 1726).

For a summary of the Thorpe reactions, «e Linstead, *ibid,* 1941, 453.

Trichloroacetonitrile, in the presence of aluminium chloride, condenses with toluene, mesitylene, tetraline, phenol.)]:4:5-xylenol, 3:5-dimethylanisole, thymol 2nd carvacrol to give the corresponding ketimines {J. Hjjp'wn and W. Fischer, Ber. 1930, 63 [B], **2465).**

G. Jlignonac (Chem. Zentr. 1935, I, 1201) attempted to prepare the aldiminc by cataj^tic reduction of the nitrile or oxime and by dehydrogenation of the amiiie, but was unable to'L Jate the free base; he was more successful in tl.> preparation of kctiniKics, *e.g.* phony In aph thy 1-tetoxime gave phcnylnaphthylketimiue, in.p. 68–69°C.

'Substituted ketimines may be prepared from the ketone and the sodioamine (U.S.I'. 1938890; Chem. Zentr. 1934, I, 3S01).

" IMOGEN." " *Eik-onogen* " (p.) modified by the introduction of \ second ammo-group; used as-i photographic developer.

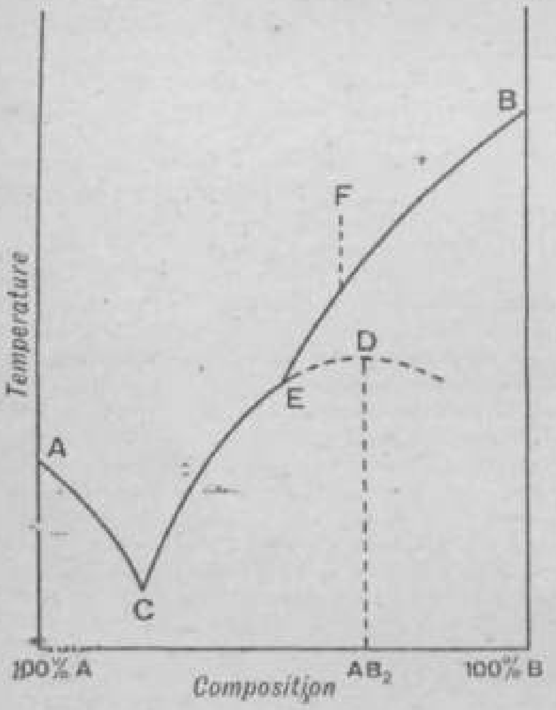
IMOGEN SULPHITE was an Agfa preparation said to consist of eikoiiogen mixed with sodium sulphite.

IMPERIALfNE (». Vol. V. 330a).

INCARNATRIN («. **Vol.III,** 207a).

INCONGRUENT, MELTING-POINT. —When two substances A and B form a comwund of the genera',type AjrB$_{tf}$ which, however, s so unstable that it decomposes completely it a temperature below its melting-point, the phase-equilibrium diagram for the system is that shown n the figure; the compound us illustrated in this case is a 1:2 compound AB_S. This diagram refers to the " condensed " system, i.e. only solid and liquid phases are considered. A and

B represent the melting points of the pure substances A and B respectively, and C represents the eutectic, the temperature below which no liquid phase can exiBt. At a temperature E below its hypothetical melting-point D, the compound AB_a dissociates completely into liquid and the pure component B, The point E ia called *the incongruent melting-point of ike compound.* It differs from a *true melting' point* in that the solid and liquid phases in equilibrium with one another at this temperature are of different composition. At the point E the condensed system is invariant, *i.e.* the temperature of E ia fixed, since there are two solid phases, AB_S and pure B, and one liquid phase in equilibrium. Hence if a liquid of composition F ia cooled, the solid which separates first is B, and when the temperature fiills to E, formation of the solid AB_2 begins. The



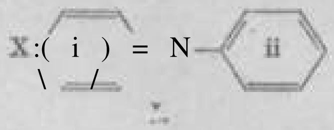
temperature then reroaina constant at E until one of the phases (either solid B or the liquiu phase, depending on whether F is to the left or the right of D) disappears, yielding either solid AB_3 + liquid or eolid B + solid AB_a. This arrest in the cooling curve it the incongruent melting-point is very similar to the phenomer.)n observed at the transition point when a substance exists in two enantiotropic forms *(i.e.* two modifications each of which is stable over a certain range of temperature and pressure and which undergo reVirsible transformation of one into the other under fixed^ conditions of temperature and pressure). For this reason the point E is frequently referred to a? a transition point. The, two caaes can, of course, easily be distinguished by an examination of the solid phases.

For m.p.—composition diagrams 01 other binary mixtures and compounds, *see* Vol V, *242d,* 250c.

G. C. H.

1NDACONITIN E *(v.* Vol. 1,122d).

INDAMINESand INDOPHENOLS are coloured compounds containing the ehromophore system (I) where X is either NH or O :



In the specific instance (1), the colour is assumecl to be due to resonance between the molecular structure *aa* depicted and alternative structures involving ring {ii) in a quinonoid system {Bury, J. Amer. Chem. Soe.'1935, 57, 2115). The dyestuffs of this group, usually blue-green to violet in colour, contain at leaat one basic auxochromie group in o- OE *p*-positions in ring (ii) so that " normal " indophenols {or more precisely " indoanilines ") (II) and " acid " indophenols (III) which are wholly phenolic in nature may be envisaged.

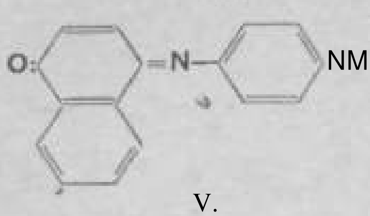
II.

III.

Historical.—Although an impure indamine had been obtained as an intermediate in the preparation of safranine and probably even easier by oxidation of aniline alone, the first puro"preparation was achieved by Witt (Ber. 1879, 12, 631; J.C.S. 1809, 75,'356) by the interaction of the hydrochloride of j>-nitro<io-dimethylaniline and wt-toluylcncdiamine. The first representatives of the " acid " indophenob were obtained by Hirsch (Bcr. 18S0, 13, 1909) by the condensation of quinone chlorimide with phenols in concentrated sulphuric acid (c/, *also* Mohlau, *ibid.* 1883, 16, 2845). Owing to their fugitiveneas towards acids indophenols are of little value *as* dyes tuffs, but commercial indoplienbl *{v. infra)* and othe.a of its etnss may be applied as v.t dyes as they readily yield leuco-derivatives (substituted diphenylaraines) and, moreover, yield with indigo a mixture which simulates in many respects indigo itself—owing, probably, to chemical association of the two dyestuffs. This vat blue has now, however, been largely replaced by synthetic indigo and sulpkur colours; many of the latter are directly obtained from indophenols which have thus assumed some renewed importance. Indophenola are also of value as intermediates in the dye industry. They also afford a ready source of diphenylaintne derivatives.

Preparation.—(a) By condensing nitrosoaminea or nitrosophcnols {quinone oximes) with aminea or phenols. Thus p-nitrosodimethylaniline affords with dimethylaniline *Bind' schedUfs* Green (IV) or with o-naphthol *Indophenol Blue (X).*

IV.

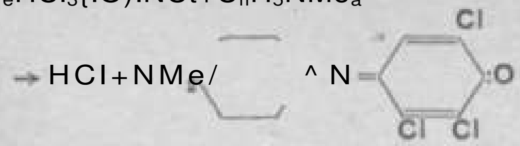


V.

(b) Indophenols and in da mines are obtained bv oxidising mixtures of p-diamines orp-aminophenola with bases containing a free position *para* to the basic group; suitable oxidising agents are manganese dioxide or lead peroxide (Nietzki, *ibid.* 1895, 28, 2969) or potassium chromate or dichromate in neutral or acid solution. Io this way aniline and p-phenyienediainirie yield the simplest indamine, *Phenyletm Blue (v.infra).*

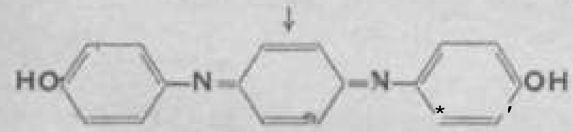
(e) Many in da mines and indophenols are obtainable by processes recalling *(b)* but in which the oxidation has been effected prior to condensation. Thus quinonechloroimides and aromatic bases yield indophenols :

$C_eHCl_3\{:O):NCt+C_{fl}H_5NMe_a$



whilst " acid " indophenols are formed when the second component is a phenol. Dichloroimides react with phenols to give more complex indophenols in which three nuclei may be regjrded as comprising the chromophore:

$p\text{-}C_8H_4(:NCl)_3+2C_6H_sOH$

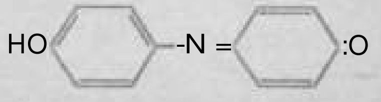


Indophenols of these simple types are often formed as intermediates in the production of phenazine, oxazinn and thiazine dyest)JFs (c/. Eichler, Alonatah. 1937, 70. 73)., and others such as carbazole indophenol (tf. *infra)* have found particular application in the minufacttfrs of sulphur colours.

Properties.—Most indophenols ara blue or green in colour, their simple salts being soluble in water. Such solutions have little direct affinity for vegetable fibres and their limited direct application is due to thoir ability to take up two atoms of hydrogen with formation of leuco-compounds which may be re-oxidised to the dyestuff. Indophenol itself has been used in this way in association with indigo. These dyeings are fugitive to acids as indophenols readily undergo fission into^-quinoncs and thus thrir more important application lies in their further conversion into sulphur colours. Occasionally it is advantageous to synthesise the leuco-compound and subsequently oxidiw it; thus the product of the reaction between *m*-Utluylenediantine and formaldehyde bisulphite compound is condensed with p-nitrosophenol and finally oxidised and the indophenol heated with sulphur and sodium sulphide to give Thionol Purple (B.P. 24008, 1906). The readiness with which indophenols are reduced makes them valuable indicators in the determination of oxidation.reduction potentials, particularly in bacteriological and other biological systems *(see* L. F. Hewitt, " Oxidation-Reduction Potentials in Bacteriology and Biochemistry," 2nd ed., London, 1933).

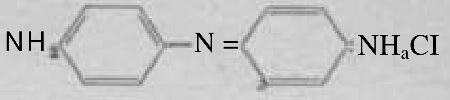
The following account includes the more important commercial"* dyestuffs and intermediates of this type:

Phenol indophenol

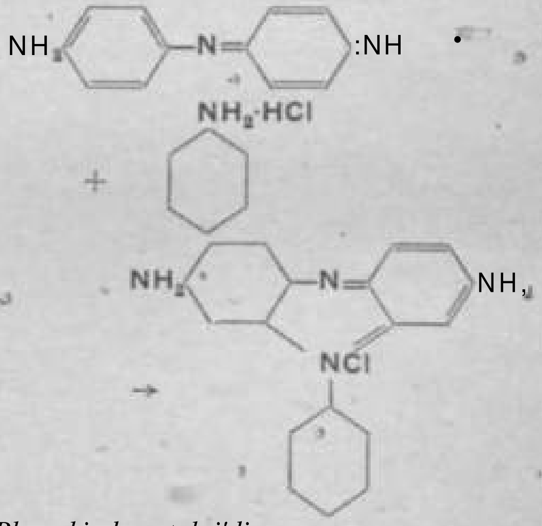


is of no direct importance but on treatment with sulphur and sodium sulphide yields a fast *flyo* resembling indigo (Fierz-David, " Kunstliche organische Farbstoffe," J. Springer, Berlin, 1933).

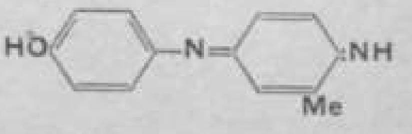
Aniline iildoaniline,



Ph&nylme Blue,, is prepared by oxidising an equimolecular mixture of ?)-phenylenedfamine and anihno hydrochloride with cold aq. potassium dichromate (Nietzki, " Chemie der organiscben farbstoffe,"5th ed., Berlin, 1906, p. 200). The hydrochloride crystallises in green oeedles which dissolve in water to a gnenish-blue solution. In acid solution Jr'^enylene Blue is moderately rapidly hydrolysed to benzoqu^".n. and possesses therefore little stability. It is converted by boiling with aniline hydrochloride solution into *Phenosafmnine :*

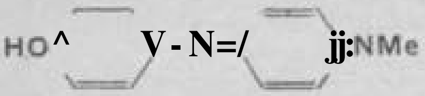


Phenol indo-o-tolui'dine,



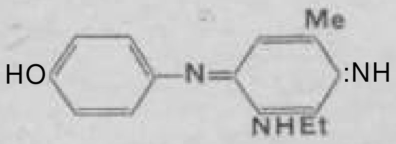
produced by direct condensation of o-toluidine with p-mtrosopbenol (U.S.P. 727387), is the source, after fusion with sodium sulphide and sulphur of the cotton dyestuff *Thionol Bh< >*.

Phenol indomethylaniline,



is, after sulphonation, converted into an indigo-like dye by fusion 'with sulphur and sodium sulphide (G.P. 129024, 129325).

Phenol intfo-4-*ethylamino-o-toluidine,*

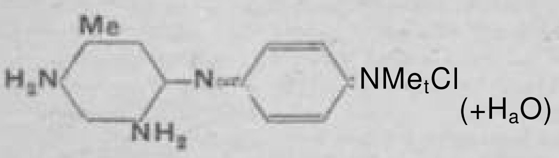


yields on fusion with sulphur a bright purple dyestuff of value in dyeing and printing cotton (U.S.P. 829740).

Tetrametkylphenyhne Blue,

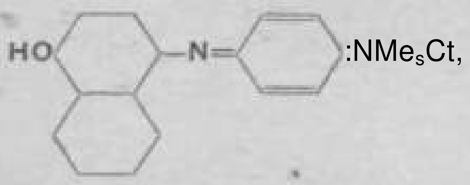
Bindtchedter's Green (Bindschedler, Ber. 1880, 13, 208; 1883, 16, 865), is obtained by condensing p-nitiosodimethylaniline with diraethylaniline *(cf. also* Wieland, ***Und,*** 1915, 48, 1087). The commercial dyestuff usually consists of its double salt with zinc chloride.

Toluyfone, Blue.,



is formed on oxidising p-dimethylaminoaniline and wt-toluylencdiamine **(Witt,** Ber. 1871), 12, 8»1^.-fi.P. 15272). The monohydro chloride crystallises in bronze-coloured crystals.

Naphthol Blue,

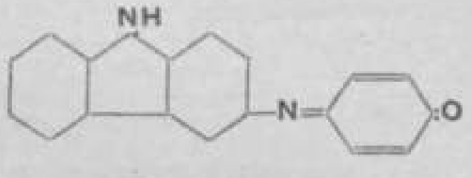


is prepared commercially by reducing y-nitroso-dimethylaniline and condensing the resulting amino-com pound with a-naphthol in warm caustic alkali, finally oxidising the leuco-compound at 0° to +2° with sodium hypochlorite (Witt, J.S.O.I. 18*82, 1, 255; G.P. 15915, 18903, 19231). The free'dye, which separates as a dark brown powder, is almost invariably applied as a vat dyestuff *(e.g.* in cotton printing) and hence is found on the market as the tin salt of its leuco-eonipound *(Indophwol While).* It is still more frequently used as a vat mixture with indigo, but its most important use lies in the production of the sulphur colour *Thto-^horindigo.*

An ill-defined indamine used for the preparation of coloured lakes and cheap coloured papers, etc., is obtained by oxidising l:2-naphthalene-diamine sulphonic acids (G.P. 224442) which contain halogen in the 8-position (G.P. 431943} with ferric salts. These yield particularly bright shades of green on incorporating yellow azo-dyesfcuffs.

The indophenol obtained from p-nitroso-phenol and a-naphtbylamine is the source of *Svldnm Green.*

Carbazole indophenol, a

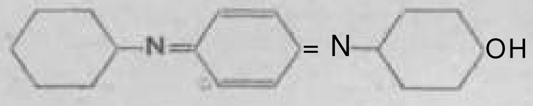


is the dye obtained by condensing ja-nitroso-phenol with carbazole in concentrated sulphuric acid at>30° (G.P. 230119; U.S.P. 919572, 931598, 1465853) or by oxidising carbazole and p-ammophenol in sulphuric acid with manganese dioxide.

Carbasole Indophenol forms a dark violet powder, insoluble in water, and is the source of sulphur colours (G.P. 218371) such as *Hydro Blue R* (U.S.P. 956348). The corresponding chloroindophenols derived from chlorocarbazoles or chioro-p-nitrosophenols are claimed to yield sulphur colours fastpr to bleaching {G.P. 235364).

The corresponding halogeno- N -ethylcarbazole indophenol is prepared similarly and converted Iiy boiling with sulphur and sodium sulphide in alcohol into *Sulpkantkrene Blue G* (G.P. 222640, 23536-t)- Similar products from benz- and na£)htho-carbazolea and nitroso-phenols or -eres(jjs have also been described (F.P. 818684).

The sulphur colours obtained from the complex indophenol,



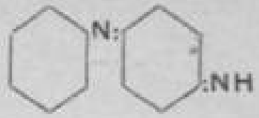
prepared from ^-nitr^ophenol and diphenyl-amine at —20°, is the subject of patent claims (U.S.P- 1777757). More complex compounds of the type.

where B'=H or alkyl and R=alkyl or *cych-*alkyl yield greenish-blue sulphur colours (B.P. 467920).

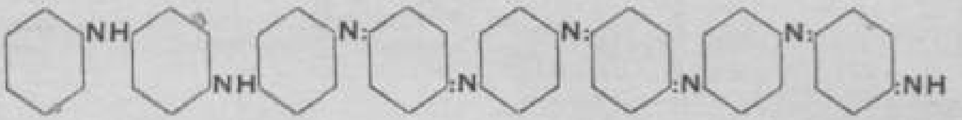
Another type of indophenol is obtained by replacing the hydroxyl group in a 6- or 8-arylamino-2-hydroxy-3-naphthoio acid by an indophenol residue, followed by loss of carbon dioxide and oxidation of the leuco-compound {B.P. 334700).

In addition to the above well characterised indophenols more drastic oxidation of aromatic bases containing a free position *p-* to the amino-residue gives rise to still more complex structures which may be regarded however as containing the indophenot chromophoric nucleus.

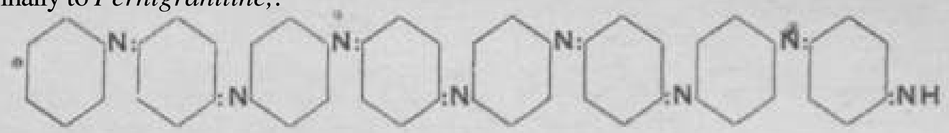
Thus oxidation of aniline with chloric acid in presence of vanadium salts affords the ocfca-nuclear *Emeraldine* (Green and Woodhead, J.C.S. 1910, 97, 2388 ; 1912, 101, 1117):



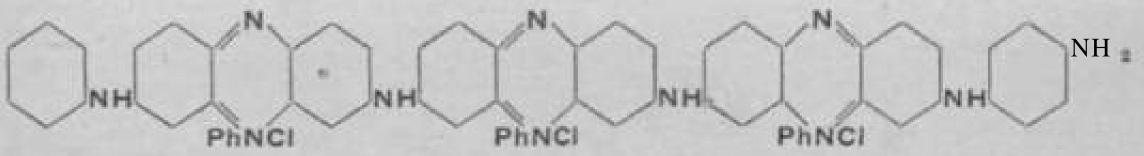
Emeraldine is further oxidised by hydrogen peroxide to *Nigraniline*;



and finally to *Pernigraniline,*:



In accordance with the proposed quinoneimine structure *{Literature: See* Schultz, Farbstoff-Tabellen, 7th ed,, I, 619) these are unstable towards acids, and for the stable Aniline Black a structure Is assumed in which alternate imine residues have become members of phenaztno systems;



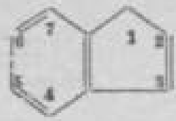
A. H. C.

INDANTHRENE COLOURS *(v.* Vol. I, 414^27).

INDANTHRONE (r. Vol. I, 411d, *414d).*

INDAZtNE *(v.* Vol. I, 577c).

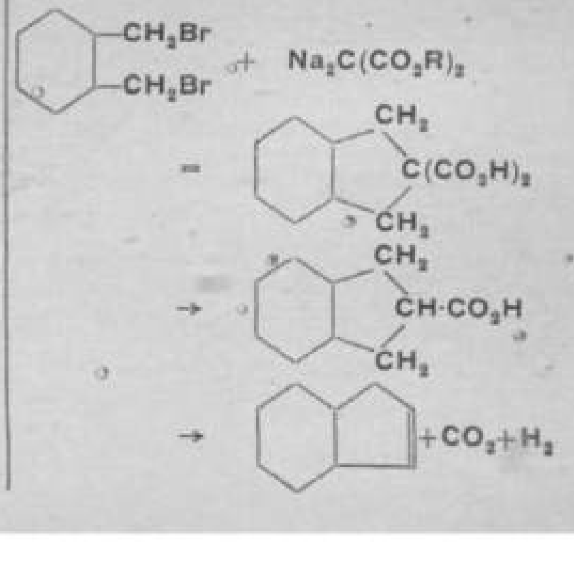
INDENE, $C_{fi}H_e$



is a liquid hydrocarbon of growing industrial importance. It occurs as a constituent o? coal-tar naphtha, being contained chiefly in the fraction of b.p. 175-185°, and in derived products such as coal gas and carburetted water-gas (Dennstedt and Ahrens, Bejr, 1894, R27, 602) which may contain as much as 100 g. of indene in 1,000 cu. ft. (Ward, Jordan and Fulweiler, Ind. Eng. Chem. 1932, 21. 969, 1236; 1934, 26, 947, 1028). Being produced by pyrolytic decomposition of carbonaceous material indene is found less abundantly in low-temperature carbonisation distillates (Weissgerber, Brennstoff-Chem. 1924,5,208; Ber. 1928,81 [Bj,2111),but on the other hand is formed in considerable amount by pyrolysing mixtures of acetylene and hydrogen (R. and W. Meyer, *ibid.* 1918, 51, 1571} or natural gas (Birch and Hague, Ind. Eng. Chem. 1934, 26, 1008).

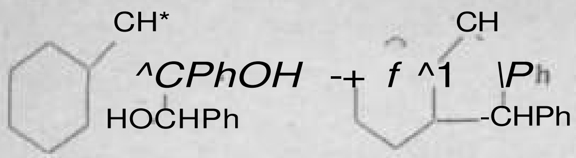
Tin; isolation of indene was first effected by fractionating higher-boiling portions of coal-tar light oil (Kramer and Spilker, Ber. 1890, 23, 327G) and converting the enriched mixture into picrates. On distilling the picrates in steam, those of naphthalene and coumarone are unaffected whilst indene picrate is broken down and indene is recovered from the distillate *(cf.* Orlow, Protjanowa and Flegontow, Chem. Zentr. 1937, I, 3435). Although 3 g. of crude indene were obtained from 10 g. of naphtha the method is unsatisfactory and even dangerous because of the explosive nature of the picrates. One hydrogen atom of indene i£ however replaceable by sodium by treating with the metal, preferably in presence of ammonia or other bases such as pyridine or aniline (G.P. 209694, 205465), and Weissgerber has utilised this reaction to isolate indene by distilling off unreacted material and then decomposing %ibe indene sodio- com pound with water (Ber. 1909, 42, 569 ,> *cf.* Courtot and Dondelinger, Ann. Chim#^925, [xj, 4, 231). More recently, processes consisting in frying indene out of naphtha fractions containing 80% indene at —25" have formed the subject of patent claims (U.S.P. 1943078; B.P. 4059*0).

The structure of indene is indicated by its unsaturated character, *e.g.* towards &Y$_u$mine, and by the formation of phthalic acid by **dJi-**dising with 30% nitric" acid (Kramer and Spilkcr, *i.c-},* and a number of syntheses such as the following (von BReyer and Perkin, Ber. 1884.17. 125; *cf.* Kipping and Hall, *ibid.* 1900, 77, 469) confirm this structure:

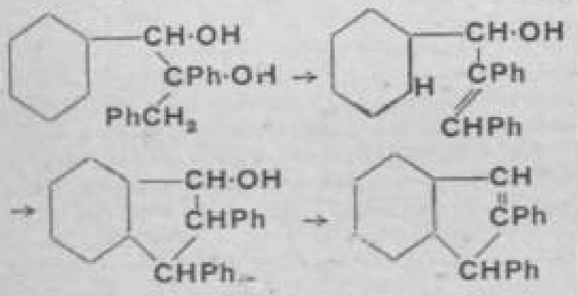


Indene is also available synthetically from its derivatives such as e-hydrindone. Raman spectra indicate (Matsuno and Han, Bull. Chem. Soc. Japan-, 1936, 11, 321) **that** indene is a resonance hybrid of the two structures:

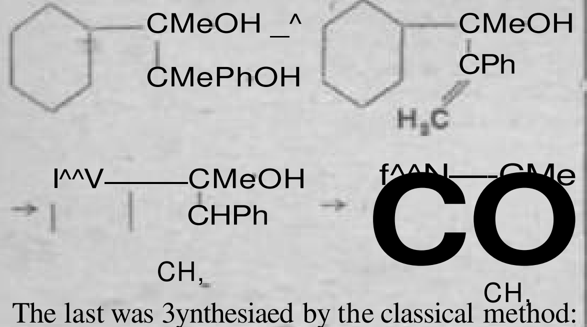
A recent synthesis of the indene nucleus which is of extended application consists in dehydrating suitable pinacones, *e,g.* o-benzyl hydrobenzoins, with acetyl chloride or phosphorus pentoxide to yield l:2-diarylindenea. Ordkhoff and Tiffeneau (Bull. Soc. chiin. 1922, [iv], 31, 253) formulated thereaction as a simple dehydration between one of the pinacone hydroxyl groups and a hydrogen atom attached to one of' the aromatic residues:



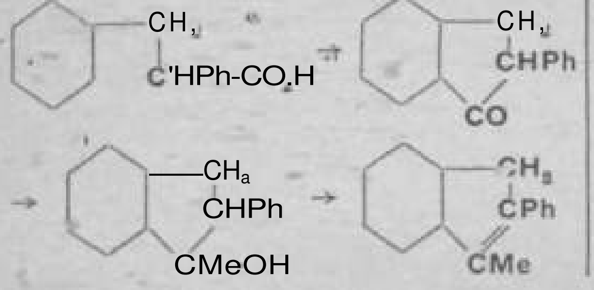
Blum-Eergmann on the other hand suggested (Ber. 1932, 65 [B], 109) the alternative scheme:



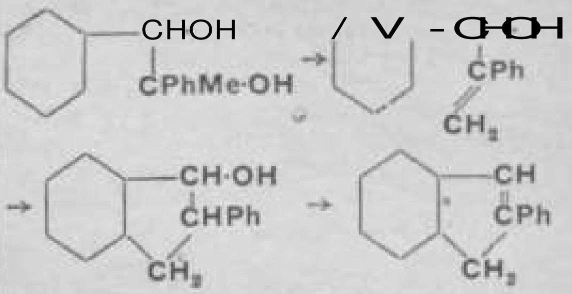
on tlit .vidence that the change is not exclusive to benzyl pinacones but can also take place with fatty-aromatic pinacones. Thus the product of dehydiating acetophenone pinacone, although previem^ly regarded as 9:10-dimethylanthraccne, wag. identified as 2-phenyl-3-met by Undone :



The last was 3ynthesiaed by the classical method:

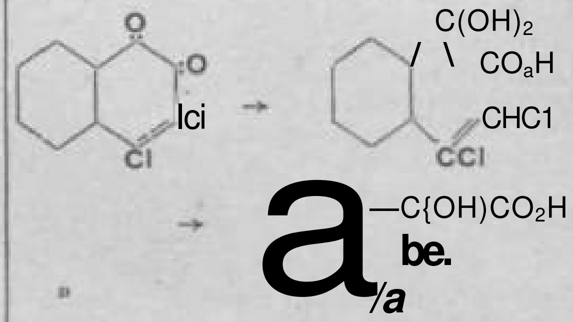


Again, the shnpler a-methylhydrobenssoin is now known to yield on dehydration not a hydrocarbon. $C_{30}H_{24}$, as formerly supposed, but 2-phenylindene, $C_{15}H_{12}$:



It should be mentioned that the reaction is not a general one and Blum-Bergmann states that ethylhydrobenzoin and benzylhydroanisoin and other aromatic pinacones do not yield indene derivatives.

The formation of indene derivatives (Zjncke and co-workers, *ibid.* 1886, 19, 2500; 1887, 20, 1265, 2894, 3216; 1888, 21, 491, 2381, 2379; 1894, 27, 744; Annalen, 1892, 267, 319; 1894, 283, 341; 1898, 300, 197) by the rearrangement of naphthalene compounds containing strongly negative substituents is of some interest, *e.g.*:



The purified hydrocarbon $C_{1a}H_{ia}$ from the coal-tar naphtha, b.p. 200-210°, yielded on oxidation a mixture of trimcllitic and hemimellitic acids **indicating** the probable presence of the four possible methylindenei* in the hydrocarbon mixture (Eoes, Ber. 1902,35, 1762).

Physical Properties.—Indene is a colourless mobile oil, b.p. 182°, m.p, -2°; this comparatively high molting-point, together with a high molecular depression (7-28°) make indene a convenient solvent in cryosco^ic determinations of molecular weight (Klatt, Z. physikal. Chem. 1934, **171,** 454). Indene readily polymerises not only by chemical reactions (w. *infra)* but also by the action of light, heat and high pressure (U.S.P. 1952116). Polymerisation by exposure to sunlight or ultra-violet light {Guntz and Minguin, Compt. rend. 1911, **1S2,** 373; Ciami'ian and Silbor, Ber. 1913,46, 420; Wegtsr and Billmann, *ibid.* 1903, 36, G42) can proceed in absence of other catalysts but *is* favoured by the presence of air. Thermal rearrangements with polymerisation giving rise to traxene, chrysene, etc., have also been described.

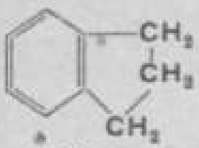
Chemical Properties.—The following reactions of indene are important:

(a) Those in which the double bond in the 5-membcred ring functions as an olefinic linking.

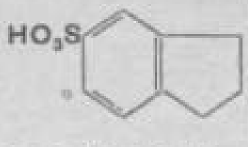
(b) Reactions in which the aromatic ring is substituted.

(c) Reactions of aliphatic character involving the methylene group.

(a) Indene exhibits many of the properties bf an olefin. Thus relatively mild reduction {Cook and Linatead, J.C.S. 1934. 946) affords the more stable compound *indent {hydrindene).* Indane possesses most of the aromatic properties of



Indane.



Indane-5-sulphonic acid.

indene but the 5-membered ring is practically devoid of the reactivity it exhibits in indene itself. Thus indane may be sulphonated to yield the readily erystaliisable 5-suIphonic acid (Cook and Linstead, *I.e.)* and nitrated to a mixture of 4- and 5-nitroindanes which are themselves reducible to aromatic bases (Braun, Arkuszewski and K6hIer,.Bcr. 1918, 51, 291). More drastic hydrogenation results in reduction of the aromatic ring to yield perKydro- (or hydr-) indane (Ipatiew, Chem. Zcntr* 1913, II, 1975) and finally in presence of ferric oxide on alumina (Ipatiew and Orlow, Ber. 1929, 62 [B], 593), benzenoid hydrocarbons, ^a resin and hydrindene are formed.

The difficulty of forming chrysene from steroid compounds by dehydrogenation over selenium or'palladium was solved by Ruzicka and his coworkers who showed that temperature was the controlling factor. The same effect was noted with o- and jS-methylhydrindene which are unchanged over selenium or palladium at 360$^{\mathrm{Cl}}$but form naphthalene, slowly at 400°, rea/iily at 450° (Helv. Chim. Acta, 1935, 18, 676; *cf.* G.P. 596191).

Hydrogen halides and halogens usually form simple addition products with indene. Whilst the action of hydrogen fluoride is polymerising rather than additive, chloroi'ndane is obtained by tho action of gaseous hydrogen chloride at 0° {Courtot and Dondelinger, Ann. Cbim. 1925, [x], 4, 345) and less stable bromo- and iodo-anologues are obtained similarly. A liquid indene dichloridj (Spilker, Ber. Io93, 26, 1541) and a crystalline dibronnide (Kramer and Spilker, *ibid.* 1890, 23, 3279) have btjen described; both are readily converted into characteristic hydroxyhalides by hydrolysis (Brown and Howard, Ind. Eng. Chem. 1923,15, 1147).

With nitrous acid indene affords two nitrosites (Dennstedt and Ahrens, Ber. 1895, 28, 1332). Addition of two hydroxyl groups to the olefinic bond may ,be effected with potassium permanganate (Hcusler and Sehieffer, *ibid.* 1899, 32. 29). A crystalline addition compound with nitrosyl chloride has been obtained (Perrot, Compt. rend. 1936, **203,** 329).

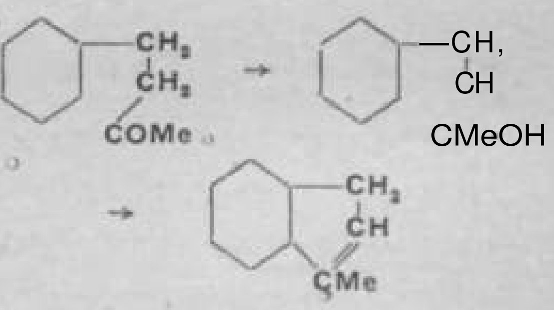
The double linkage in tho 5-membered ring of indene imparts to it many of the properties of cyc/opentadieno and" may also be responsible for its behaviour on oxidation, resinitication and subsequent polymerisation.

(b) Aromatic properties of indene and its derivatives call for little mention beyond that under (o). Derivatives are rarely if ever obtained by direct substitution in the aromatic ring owing to the readiness with which indene undergoes polymerisation. Derivatives of indene and especially of hydrindene of this type are purely aromatio in character.

(c) *Sodium indene* is readily formed by replacement of one hydrogen atom of the methyleno group by sodium using sodamide (Weissgerber, Ber. 1909, 42, 569). The sodium can be replaced by alkyl groups yielding 1-alUylindenea (Marckwald, *ibid.*]9fJ0, 33, 1504); these all exhibit the autoxidatton behaviour of indene itself, and higher indenes have for this reason been proposed with driers to replace linseed oil (G.P. 305515). Indene also condenses with aromatic aldehydes and kctones in presence of sodium" alkoxide (Thiele and Merek, Annalen, 1918, **415,** 262) to yield compounds of the typo:

Somewhat similar is the reaction "with ethyl oxalate in presence of alkali to yield *indene-1-oxalyl ester* (Weissgerber *el al,,* Ber, 1900, 83, 773; Thiele, ***ibid,*** 1900, 33, 851). With oxalyl chloride, however, a carboxyl group is introduced into the 2-posit ion whOst *i-ndene-l-carboxylic acid* is formed by the action of carbon dioxide on sodium indene (Wislicenus, Ber. 1911, 44, 1440; Annalen, 1924, **436,** 16). As with pyrrole the- roethj^ene group of indene confers on it the ability to react wityi 5rignard reagents with the formation *of indene-3-magnesium halides* (Courtot, Ann. Chim. 1915, **[ixp$,** 7C; Grignard and Courtot, Compt. rend. 1911, 152, 272).

Indene Derivatives.—A general metMbd for the ^production of indene derivatives consists essentially in the dehydration of benzenoid compounds containing the grouping ArCCCO. Thus benzylacetone and sulphuric acid yield *l-meihylindene:*



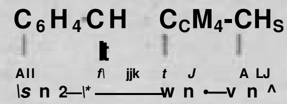
Pelyiiidents.—The, production of resinous products by the ready polymerisation of indei.e is of increasing industrial importance. Although the use of catalysts, *e.g.* sulphuric acid (Kramer and Soilker, Ber. 1900, 33, 2260; W^{r}eger, Z. angew, Chem. 1909,22,345) presents advantages, Whitby and Katz have shown that however prepared a regular series of polyindenes is obtained which may be separated by fractional precipitation (J, Amer. Chem. Soc. 1928, 50, 1160;

Canad. J. Res. 1930,4,344 ; mechanism of polymerisation, Tammann and Pape, Z, anorg. Chem. 1931, 200, 113). A number of workers have observed that under specified conditions, *e.g.* using dilute sulphuric acid, molecules of relatively well-defined complexity may predominate. Thus Weger *(I.e.)* prepared a tetramer by the action of concentrated sulphuric acid on a benzene solution of indene (e/. Stobbe and Farber, Ber. 1924, 57 [B], 1838) whilst Kramer and Spilker *[ibid.* 1890, 23, 3278 ; 1900, 33, 2260) and also Marcusson (Chem.-Etg. 1919, 43. 109, 122) obtained higher polymers [$(C_9H_8)_n$ where n= 11-12 *{paraindent),* and *metaindenes* where w=lG—22 are obtained by the action of sulphuric acid on indene in absence of solvent].

Somewhat similar control may be exercised in the use of other catalysts of which halogen hydrides *(v. supra)* and particularly Friedel-Crafts catalysts are important examples. Thus highly polymerised indenes and resins may result from the action of oxygen and peroxides (Staudinger and Lautenschlager, Annalen, 1931, 488, 1; Adkins and Houtz, J. Amer. Chem. Soc. 1931, 53, 1058) and of stannic, antimony and boron chlorides etc. {Staudinger *a al.,* Helv. Chim. Acta, 1929, 12, 934, 958, 962; Whitby and Katz, J. Amer. Chem. Soc. 1928, 50, 1166).

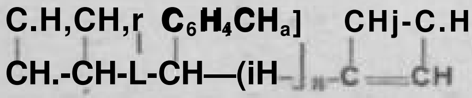
Crude polymers resulting from the action of sulphuric acid on indene are usually red, but purified products form colourless compounds the softening point of which varies quite regularly with the molecular weight. Each molecular variety contains one double bond in each molecule (for general accounts, *see* Risi and Gauvm, Canad. J. Res. 1935, B, 18, 228; Hugel, Bull. Assoc. franc. Te-ihn. Petrole, 1937, No. 39, 25).

Di-iwieve, m.p, I!"-58°, contains one olefinic linkB/Tfi. as it readily yields a dibromide, m.p. 120°, and is oxidised by chromic acid to a-hydrindone (Stobbe and Fttrber, Ber. 1924, 57 [B], .\838). It contains, however, only one reactive methylene group (Bergmann and Taubade!^,'Cicf. 1932, 65 [B], 463) and is formulated



$$\begin{array}{l} C_6H_4CH \quad C_CM_4\text{-}CH_S \\ \text{All} \quad f\backslash \quad jjk \quad t \quad J \quad A\ LJ \\ \backslash s\ n\ 2\text{—}\backslash^{*}\text{———}w\ n\ \bullet\text{—}v\ n\ \hat{} \end{array}$$

Whitby and Katz (J. Amer. Chem. Soc. 1928, 50, 1160) formulate higher polyindenes similarly as they behave as unsaturated compounds



$$\begin{array}{l} C.H,CH,r \quad C_6H_4CH_a] \quad CHj\text{-}C.H, \\ CH.\text{-}CH\text{-}L\text{-}CH\text{—}(iH\text{-}]_n\text{-}C{=}CH \end{array}$$

although Staudinger *et at.* represent them as large rings (Helv. Chim. Acta, 1929, 12', 934). These higher polymers undergo some depolymerisation on heating and may be hydrogenated with partial depolymerisation.

Indene polymers and coumarone resins *(v.* ¥o\. III, 413c) are finding application in industry, usually in association with tung oil, in paints, enamels, etc. (c/. U.S.P. 1U19666). They are also used in other combinations as softeners for rubber (U.S.P. 2095630), adhesives (G.P. 652007), binders for tiles {Canad. P. 372911), and it has also been proposed to utilise indene resins with formaldehyde (B.P. 319444), with pitch-resins from coal-tar {U.S.P. 1355103), and by condensation with maleic anhydride (B.P. 376479) and in other ways.

A. H. C.

INDERITE, Hydrated magnesium borate, $2Mg0\text{-}3B_aO_3\text{-}1\,5\,H_2O$. occurring as small, white to pinkish, reniform nodules in red clay in the borate deposits, which were discovered in 1934 near the Inder salt lake, 150 km. north of the Caspian Sea in western Kazakhstan, The acicular, orthorhombic crystals show relations to *inyoite* ($2CaO3B_aO_s\text{-}13H_2O$). (A. M. Boldyreva and E'. N. Egorova, Mat. Central Sci. Investig. Geol. Prospecting Inst. U.S.S.R. 1937. General ser. No. 2; A. M. Boldyreva, M6m. Soc. Russe Min. 1937, [ii], 66, 651 ; M. N. Godlevsky, *ibid.* 1937, [ii], 66, 315; G. B. Boky, Bull. Acad. Sci. U.R.S.S. eer. Chim. 1937, 871.)

L. J. S.

INDIAN BUFFALO GRASS *(v.* Vol. II, 482c).

INDIAN **FIRE,** *v.* BENGAL LIOHTS.

INDIAN GUM or GHATT1 GUM is a gummy exudation from the stem of *Anogeissus lalifolia* Wall., occurring in vermiform or rounded tears, coloured pale yellow and of o vitreous lustre. Soluble in water, forming a viscous adhesive mucilage.

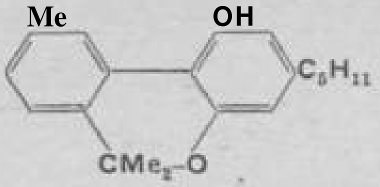
INDIAN HEMP RESIN *{v.* Vol. II, 269). Indian hemp *(Cannabia indica, O. saliva)* is official in the Spanish, French, Belgian, Swiss and U.S. Pharmacopoeias. The drug consists essentially of the resinous exudate of flowering and fruiting tops of *Canvalw sativa,* an annual indigenous to 'Central Asia and the Northern and Western Himalayas. Described according to origin and mode of preparation by a variety of names *{e.g. hashish, marihuana, ckaras, ganja,* 6Aanf, etc.) it is one of the commonest drugs of addiction in Asia, Africa and America. Eaten or smoked it produces an intoxication commencing with a pleasant lethargy in which there is distortion of space and time followed often by horror and depression. The resin separated from the leaves atid known in this form as *charas* is an important article of commerce between Turkestan and India. For reports on *C. indica* by the League of Nations Commission on Traffic in Noxious Drugs, see Amer. Chem, Abstr. 1938, Sa, 8073; 1939, 33, 2283. The cultivation of C. *sativa* "',nd its use in medicine is regulated 'n the U.S.A. by the Marihuana Tax Act, 1937. In the'fdrm of tincture or extract the drug has been prescribed as a narcotic and anodyne, but was removed from the British Pharmacopoeia in 1932.

In North America the name Indian hemp is applied not to *C. sativa* but to *Apocynum cannabinwn,* known also as Canadian hemp, which contains the cardiac glycoside cymarin (v. Vol. II, 836A; Vol. I1l, 638a), and accidents have been caused by the confusion of names. A comprehensive account of the hemp drugs is available in the monograph " Marihuana " by Walton (Lippincott, New York, 1938); short reviews are given by Adams (Science, 1940, 92, 115), Todd (Nature, 1940, **146,** 829) and Macdonald (Nature, 1941,**147,** 167).

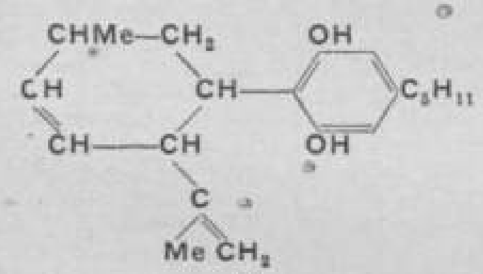
Cannabis resin yields on distillation an essential oil containing *p-cymene* with small amounts of other substances including 1-methyl-4-iuopropenylbenzene and a-caryophyllene (Simonsen and Todd, J.C.S. 1942, 188). and a high boiling viscous liquid known as " crude cannabinol " or " red oil " which contains the active principle of the drug. From this material the following inactive compounds have been obtained:

Cannabinol $0_tM^{\wedge}O_2$, m.p. 76-77°, b.p. 140-150°/10~^{a} mm. (bath temp.), occurs in large amounts in Indian and Egyptian resin and in smaller quantity in American resin. Its constitution as e"-hydroxy-2:2:S'-triniethyl-4"-n-amyl-dibenzopyran (I) has been established by complete synthesis (Ghosh, Todd and Wilkinson, J.C.S. 1940, 1121, 1393; Adama, Baker and Wearn, J. Amer. Chem. Soc. 1940, 62, 2204). For isolation from Indian resin as j>-nitrobenzoate, *see* Work, Bergel and Todd {Biochem. J. 1939, 83, 123).

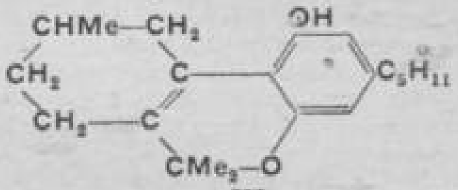
Cannabidiol, $C_{21}H_{3\{},O_2$, m.p. 66-67°, b.p. 160-180°/]0-^{s} mm. (bath temp.), has been isolated as 3:5-dinitrobenzoate from American {Adams, Hunt and Clerk, J. Amer. Chem. Soc. 1940, 62, J9G) and Egyptian (Jacob and Todd, J.C.S. Ifl4t), 649) resin. It is considered to have structure (II) and can be cyclised to a mixture of tetrahydroeannabinols yielding cannabinol on dehydrogenation (Adams *et al.,* J, Amer. Chem. Soc. 1940, 62, 2402, 2506).



I



II



III

Isolation of homogeneous active substances from American resin has been reported by Haagen-Smit *et al.* (Science, 1940, 91, 602) and by Powell *et al.* *(ibid.,* 1941, 93, 522), but these claims await confirmation. The tctra* hydrocannabinol (III) <0"-hydroxy-2:2:5'-trimethyl-4"-*n*-amyl-3':4':5':6'-tetrahydrodibenzopyran) obtained as an intermediate in the cannabinol synthesis of Ghosh. Todd and Wilkinson *{I.e.)* exhibits the characteristic physiological action of hashish in animals and in man, as also do the isomeric tetrahydrocannabinols obtained by cyclising cannabidiol. A large number of analogues of thes£ substances have been prepared and examined pharmacologically (Todd *et al.,* J.C.S. 1941, 169, 826: Adams *et al.,* J. Amer. Chem. Soc. 1941, 63, 1971, 1973, 1977). The purified cannabis resins freed from cannabinol and cannabidiol have the composition of tetra hydro cannabinol and may contain a mixture of isomers of varying activity. For fuller details of recent work the numerous publications of Adams *et al.* (in J. Amer. Chem. Soc.) and of Todd *et al.* (in J.C.S.) since 1940 should be consulted.

INDIAN OR CHINESE INK. This is an ink in solid form, made by pounding finely divided lampblack with a solution of glue into a paste which is then moulded into sticks. An ink was prepared in China about 2600 B.C, but according to Jametel (" L'Encre de Chine, d'apres des Documents Chinois," 1S82) this ink was a vegetable varnish and it was not until about the third century B.C. that the product as it is known to-day was introduced. Various substances have been used as the source of the lampblack, such as rice straw, pine wood and haricot beans, but these have been replaced to a large extent by vegetable oils, especially tung oil from *Aleuritee cordata*™ The oil is burned in small lamps of terra-cotta, chilled by water in a small depression at the top; these lamps are placed in a terra-cotta chamber, and the smoke is collected in inverted terra-cotta cones with polished interior, from which the deposited soot is removed from time to time by means of a feather. A row of bricks supports the cones, about twenty of which^rre used at a time. When the ink is made on a larger scale the terra-cotta condensing vessels are replaced by a hollow wooden tunnel with a hole bored in the wall.

According to Jametel the lampblack from sesame or tung oil yields a much bett*"- quality of ink than that derived from pine wood/-» In Japan also either Lmme or tung oil or pine wood are used for making the lampblack, and this is incorporated with strained ox-hide glue. Formerly a decoction of *Hibiscus mutabilis* Linn, was used as the medium in China, but has long been discarded in favour of glue.

At the present time the ink produced by different Chinese,manufacturers differs mainly in the fineness of the lampblack and the tone of the black.

Ink is imported into this country from China in the original boxes each holding 1 lb. According to the size of the sticks, 8, 20 or 40 may go to the pound, and are spoWn of in the trade as " eights," " forties," etc. The sticks are moulded in various forms, some being in squares, some in tablets and some octagonal. The best qualities of sticks are gilt and are stamped with fige impressions such as dragons, lions' heads, etc., which denote qualities well recognised in the trade, and they are also perfumed. The octagonal sticks, known as " Mandarin," are of fine quality, and are distinguished from ordinary sticks by the finer impression of the characters on the sides. The poorest quality is in the form of small sticks and stamped with white letters.

Examination.—The Chinese test the quality o ink by rubbing the tablet on a porcelain palette *If the* sound produced is faint the *ink k con*sidered to be of good quality *(Si-mo),* whereas * loud noise indicates an inferior quality *(Tsou-mo)*. This ia essentially a test for the fineness of the carbon particles* A Chinese ink of good quality should yield a uniform suspension when rubbed with water. The best inks are of a violet shade, whilst inks of the second quality are black, and inferior inka have a yellow tint.

A practical teat is to stir 0-1 g. of the powik-rvd ink in 10 ml. of water and to shake the mixture from time to time. Jnka of the best quality wil diffuse rapidly, whereas the cheaper grades wili hardly colour the water even after several hours' contact.

The tinctorial value may be ascertained by applying successive coatings of the suspensions to equal areas of Whatman paper. The best inks can be distributed much more smoothly than those of inferior quality, and an opaque coating is attained with fewer washes.

Specimens of the four grades of ink examined by Mitchell, " Inks : Composition jnd Manufacture," 4th ed., 1937, p. 37, gave the following results:

Ink.	Water, %	Carbon residue, %	Nitrogen in residue, %	Nitrogen in original Ink, %.	Ash, %
I. Octagonal stick .	8-16	53-9	00	7-74	4.80
II. Lion stick, fine letters	7-SO	52-53	—	4-87	3-69
III. L^nstick, coarse letters .	993	49-64	—	7-20	4-96
IV. Cmall Btick, jcoarse let-Wrfs . .	9-40	57-04	—	C-84	4-01

Liquid Indian Inks.—A preparation for the use of artists is made by grinding up broken fragments of the Chinese stick-ink with water. Other preparations are made directly from lampblack incorporated with a liquid medium containing a gum to keep the carbon in suspension. These are of the same typo is the carbon inks which are still used in the East.

Non-Coagulating Indian Ink.—An ink that is claimed not to coagulate even at —30° has been patented by Shinozaki {Japan. P. 110282,1935), The mixture consists of flue (30 parts) previously heated for'3 hours at 120°, potassium iiitrate {60 parts), urea ,[10 parts), urotropine (10 parts), carbon black (60 parts) and water (1,000 parts).

C. A. M.

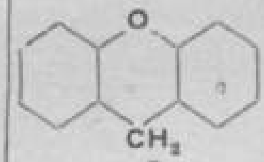
INDIAN MADDER («. Vol. I I, S2$s).

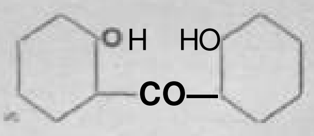
INDIAN YELLOW, PIURI, PURREE or PIOURY is a pigment used **mainly fan** India for colouring wails, doors and lattice-work, and by artists for water-colour work. It is, or was, made almost exclusively at Monghyr (Bengal) from the urine of cows which have been fed upon mango leaves. On heating the urine, the colouring matter separates out; this ia pressed into a ball and dried partly over a charcoal fire aud finfiliy hi the sun. Internally the balls are of a brilliant yellow colour, whereas the outer layers arc either brown or of a dirty-green colour. The undeeoinp* sed part consists only of euxanthic acid in the form of a magnesium or calcium salt; the outer and decomposed portion contains in addition euxanthone, both free arid combined. The composition of piuri appears to be variable ; » fine sample, according to Grixobo (Annalen, 1889, **254,** 272), contained euxanthic acid, 51-0; silicic acid and alumina. 1-5; magnesium, 4-2; calcium, 3-4; water and volatile matter, 390%.

Euxanthic acid ia iaolated by digesting piuri with dilute hydrochloric acid **and** treating the residue with a solution of ammonium carbonate. Addition of hydrochloric acid to the iiltered solution causes the separation of crystals of euxanthic acid. According to Spiegel (Ber. 1882, 15, 1965), euxanthic acid is decomposed by 2% sulphuric acid at 140° into euxanthone and the anhydride of glyeuronie acid.

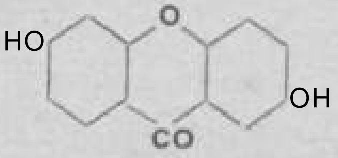
Euxanthone, Pvrrenone, Purrone, $C_{13}H_8O_4$, was first obtained by Stenhouse (Annalen, 1844, 51, 425) and shortly afterwards by Erdmann [*ibid.* 1844, **52,** 365) from euxanthic acid. It forms pale yellow needles or lamina?, m.p. 240° (corr.), which sublime with little decomposition on gentle heating.

By distillation with zinc duet (Salzmann and Wichelhaus, Ber. 1877, 10, 1397; Graebe and Ebrard, ***ibid,*** 1882, 15, 1675), euxanthone gives methylenediphenylene oxide (I) which is convened into xantbone by oxidation, indicating that ^uxanthone is a dihydroxy xanthone. When fused with alkali, euxanthone yields euxanthonio acid (II), hydroquinonc and reaorcinol.


I.

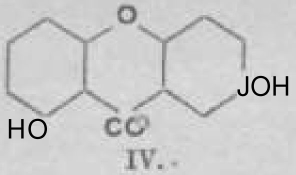

II.

Euxaiithono was first synthesised by Graebe (*I.e.)* by distilling.,a mixture of £-resorcylic acid and hyriroquinone carboxylic acid; it was shown later by von Kostanccki and Nessler {Ber. 1891, 14, 3983) that tho same product is obtained if in this reaction the /3-resorcylie acid is replaced jy resorcinol. Of the two constitutional formula (III and IV) indicated by these syn-


III.

theses, {IV, 1:7-dihydroxyjranthone) was shown to be correct by a study of the methylation of euxanthone by menus of methyl iodide (Von

Kostaneeki, *aid.* 1894, 27, 1992). Only a monomethyl ether was obtained, indicating that cuxnnt-hone contains a hydroxyl group

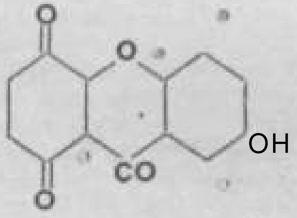


IV.

adjacent to the carbonyl group (IV). Final proof of the correctness of this formula was afforded by the following fly nth esis ofeuxanthono by UJImann and Panehaud (Annalen, 1906, 360, 108); condensation of 2-ehloro-6-methoxybenzoic acid with the potassium derivative of hydroquinone monomethyl ether, employing copper powder as catalyst, yielded 2-(4-methoxyphenoxy)-6-methoxybenzoic acid which was converted by the action of concentrated BUIpburic acid into euxanthone dimethyl ether, and this by treatment with aluminium chloride in the presence of benzene gave euxanthoge.

Euxanthono forms the following derivative!a : *l-niethyl ether,* pale straw-coloured rectangular plates, m.p. 235° (Robertson and Waters, J.C.S. 1920, 2239), m.p. 240° (Graebe and Aders, Annalen, 1901, **318,** 365}; 7*-methyl ether,* yellow plates, m.p. 130-5°; *dimethyl ether,* colourless needles, m.p. 149-5° (Graebe and Aders, *Lc.); **didhyl** ethtr,* prisms, m.p. 126° (Graebe and Ebrard, i.e.); *1-acelyl-,* elongated yellow prisms, m.p. 160* (Robertson and Waters", *I.e.); diacelyl-,* pule yellow prisms, m.p. 185° (Salzmann and VVichelhaua, *I.e.)\dibenzoyU,* colourless crystals, m.p. 221-222° (Zerner, Honatsh. 1910, 31, 797); *4:5-disazobenzene-,* red needles, m.p. 249-250° (decomp.); *acetyl*-derivative, ochre-yeJow needles, m.p. 107- 19<)ᵘ (Perkin, J.C.S. 1838, 73, 66G).

According to Nierenstein (Ber. 1913, 46, 649), oxidation ofeuxanthone with chromic acid gives the quinone:



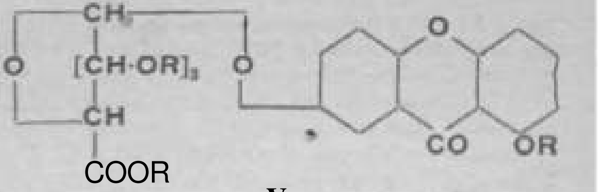
This consists of dark-red needles soluble in alkalis with a blue coloration and converted by reduction into l:4:7-trihydroxyxanthoiie.

£uxanthone possesses only feeble tinctorial properties; the respective shades obtained with woollen cloth mordanted with chromium, aluminium and tin being dull brown-yellow, pale bright*yellow and very pale bright yellow (Perkin and Hummel, J.C.S. 1890, 69, 1290).

Euxanlhic Acid exists as a stable hydrate, $C_{19}H_{,f1}O_{tm}H_aO$, melting at 156-158° with partial decomposition. The *methyl ester* and *ethyl ester* melt at 218° and 198°, respectively (Graebe *et al.,* Ber. 1900, 33, 3360 ; Annalen, 1901,318,345).

Nsnbeig and Neimann (Z. physiol. Chem. 1905, 44, 114) obtained euxanthic acid by the inter* action of a diacetylbromoglycuronolactone and the potassium derivative of euxanthone. The synthesis confirmed the suggestion. of Fischer and Piloty (Ber. 1891, 24, 521) that this plycuronate is structurally analogous to a glycoeide. Herzig and Stanger {Monatsh. 1U14, 35, 47) found that the two methyl derivatives obtained by the action of diazo methane on en x ant hie acid yielded, by acid hydrolysis, euxanthone 1-methyl ether, indicating that the glycuronic acid residue in euxanthio acid is attached at the 7-position.

By the action of methyl iodide and silver oxide on euxanthic acid, Robertson and Waters (J.C.S. 1931, I70S) obtained *methyl O-tetrametkyl-tuxantltale,* (V; $R=CH_3$), colourless needles, na.p. 168°. Hydrolysis of this eater with hydrochloric aeid gave 1-O-inethyleuxanthone and ;i trimethylglycuronic acid **wfaieh** by oxidation with nitric acid and estenfication of tho product yielded the methyl ester of 2:3:4-trimethylfiaccharolactone. The constitution of tho latter was confirmed by synthesis from 2-,3;4-triraethyl glucose. Euxanthic acid, **therefore,** has the following structure ($R = H$):



V.

The glycosidic linking present in euxantln'c acid appears to be of the 0-type.

The precursor *oi* Indian yellow is ***mangiferin*** *(euzanthogen)* which is present' in the bark and leaves of *Mangifera* trfEica Linn, (mango). Mangiferin is isomeric with enxanthic ^id, to which it gives rise in the organism (Gorter, Bull. Jard. bot. Buitenzorg, 1922, [iii], 4, 260; *see* Amcr. Chem. Abstr. 1923,17, J472).

A. G. P. and E. J. C.

INDICATORS. In ' volumetric anajvsis indicators are substances which are used to determine end-points in titration work. The three main types of reaction, namely neutralisation, oxidation and reduction, and precipitation, which predominate in this kind of analysis, all require suitable indicators in order to determine the points at which equivalent quantities of the reacting substances have been brought together. However, the use of the numerous organic compounds which are differently coloured in acid and in alkaline solution serves not only to determine end-points in acidimetry and alkalimetry, but also to mark the end-points as within certain limits of hydrogen, ion concentration. ThuB indicators for neutralisation are alnf> . employed colorimetr&ally to determine the five hydrogen ion concentration as distinct from the total acidity in liquids : a subject of great importance in biological work. Certain ty^es ot titratiins are carried out with the aid of *external* as distinct from internal indicators for determining the end-points. As Buch external indicators are really sensitive drop reagents which are specific teats for the presence or absence of particular substances their properties will not be considered in this article.

Since the year 1913 a series of indicators depending • upon a totally different principle from those adverted to above was studied by Paneth and his collaborators. The fundamental principle involved in the use of these radioactive indicators is that isotopes have identical chemical properties. If an element *A* has a radioactive isotope *A*\ the detection and determination of A^7 by electroscopic methods can be adapted to the detection and determination of *A*. A brief consideration of these indicators is given at the end of this article.

NEUTRALISATION INDICATORS. *(See also* CHEMICAL ANALYSIS, Vol. II, pp. 637 *et seq.)*

From the form and position of the titration curves (Vol. II, p. 639) it will be evident that for the titration of a strong acid by a strong base any indicator with a $j>_H$ range extending between the extreme limits of 3 and 11 units on this scale will give satisfactory results, if the acid and alkali are of the order of decinormal concentration. In consequence of acid hydrolysis, the titration of a weak base such as ammonia by a strong acid must be carried out with an indicator having a p_E range within the limits of about 3 and 6 units, such as Methyl Orange or Methyl Bed. · Similarly the occurrence of alkaline hydrolysis when a weak acid, such as *cetic acid, is neutralised by a strong base necessitates the employment of an indicator such as phenolphthalein with a pH range between 8 and 11. If the acid and alkali are of considerably lower concentration than decinormal, further restrictions within these ranges will become necessary.

The sensitiveness of indicators was first investigated by Tizarrt (B.A. Report, 1911, p. 268) who drew attention to a fundamental difference betwcJii two-colour indicators such as Methyl Orange and one-colour indicators such as phenolphthalein. When a two-colour indicator is used 'the end-point of a titration should be independent of the amount of indicator in the solution if the titration is carried to the half-way stage, because the titnation is being carried to a certain *fractional* change of the indicator. With the one-colour indicators the case is different, because the titration is carried or until there is a certain *amount* of coloured substance produced or removed. Similar views, with shades of difference, were expressed by N. Bjerrum (" Die Theorie der alkalimetrischen und azidimetrischen Titrierungen," Ahreps' Sammlung, XXI, Stuttgart, 1914) who pointed out that the difference in behaviour between two-colour and one-colour indicators will hold so long as there is no great difference in intensity between the acid„ and alkaline colours. If, however, this difference is considerable there will be a tendency for two-colour indicators to approach one-colour indicators in behaviour. In this connection it has been pointed out by Noyes (J. iimer. Chera. Soc. 1910, 32, 815) and by Bjerrum *(op. dt.)* that the change interval for Methyl Orange is not symmetrical on account of the considerably greater intensity of the red form. It is therefore better, for experimental verification of the characteristic behaviour of two-colour indicators, to select one of the sulphonephthalein indicators such as Bromcresol Green, which exhibits a striking contrast between the yellow (acid) and the blue (alkaline) colour. Bromcresol Green has a p_E range from 3-6 to 5-2, and it has been found that the quantity of *N/50* hydrochloric acid which is required to transform this indicator in concentrations extending over *t,* range of 1/20,000 to 1/100,000 to the half-way colour stage corresponding to a p_H v&lue of 4*4 is strictly constart. A suitable one-colour indicator for experiments of this kind is p-nitrophenol, having a p_K range of 50-7-0 and therefore insensitive to atmospheric carbon dioxide. It has been found that the quantity of *N/50* hydrochloric'acid required to extinguish theyellow colour of sodium 2>-nitrophenolate in solutions of concentration ranging from 1/5,000 to 1/50,000 is strictly proportional to the concentration of the indicator in the solution (Berry, unpublished work).

Reference may be made to Bjerrum's monograph for an elaborate discussion of the theory of the errors which are involved by the use of indicators in acidimetry and alkalimetry. If it is desired to titrate to a given hydrogen ion concentration it is necessary to consider two terms which have been known as the *indicator exponent* and the *titration exponent* respectively. Since the ionisation of a weak acid is regulated by the law of mass action, it follows that when an indicator is one-half ionised, the dissociation constant of the indicator is equal to the concentration of the hydrogen ions in the solution in which the indicator is one-half ionised. The indicator exponent, *pi,* is defined as — log K, K being the dissociation constant, while the titration exponent, *pT,* is the value of p_n corresponding to the optimum colour. At the half-way change it is clear that j)T=pI. From what has been stated above it will be evident that the titration exponent of a two-colour indicator is independent of its amount in the solution, because the titration is carried to only a certain fractional change. The titration exponent of a one-colour indicator can however be varied over a short p_E range^by suitable variation of the quantity of the indicator in the solution.

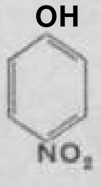
It has been estimated that with careful work it should be possible to titrate with a degree of accuracy corresponding to $\#>_H=pT\pm0{\cdot}3$, and by introducing cplorimetric methods the error may be reduced to ±0·1. For a discussion on the elimination of the titration error in acidimetric and alkalimetric titrations a monograph by Brennecke may be consulted ("Newer Methods of Volumetric Chemical Analysis," edited by W. Böttger, translated by Oesper, London, Chapman and Hall, Ltd., 1938, [U.k.A. Printed], p. 3).

The properties of indicators have been discussed in terms of two different theories, viz. the ionisation theory largely due to Ostwald and a theory which correlates change of colour with change of chemical constitution. The idea that the colour, in organic compounds, is due to the presence of certain groupings in the molecule appears to have originated with Witt (1876). Groups such as the azo group —N = N—and the nitro group — NO_a which are considered to be the source of colour are known as chromophores or chromagens, while groups which augment colour are known as auxochromes. Armstrong in 1888 put forward hia well-known quinonoid theory of colour, a theory which with minor modifications has survived to the present time. When a colourless compound becomes coloured, &.g. when alkali is added to a compound such as y>-iu'trophenol, tile benzenoid ring is considered to assume the constitution of a quinonoid nucleus. Addition of acid reverses the process. It would appear that the chief ground on which Armstrong formulated hia theory was that compounds known to have quinonoio reactions are all strongly coloured.

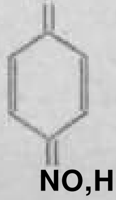
It is now recognised that neither theory alone can give as adequate explanation of the action of indicators, and that the correct way of studying the problem is by regarding indicators not as true acids or bases which ionise directly *(acid* indicators giving rise to hydrogen ions, or more correctly hydroxonium ions, and onions which arc differently coloured from the undissociated molecules, and *basic* indicators giving rise to cations of different colour from that of the undissociated molecules and hydroxyl ions} but as pseudo-acids or pseudo- bases, an important conception due to Hantzsch. Pseudo-acids and pseudo-bases are compounds, electrically neutral in themselves, which can undergo iHomeric changes into true acida and true bases and these latter compounds at once give rise to their appropriate ions. It must bo noted that the colonr9 of the neutral and acidic isomera of pseudo-acids must be different, and that the acidic anion must be similar in colour to that of its undissociated molecule. Similar considerations apply *mutatis mutandis* to the colours of the isomers of pseudo-bases,

Among the numerous compounds havirtj indicator properties the following may be selected as of particular importance, both on account of their theoretical interest and their practical value, namely the nitrophenols, the phthaleins {including the sulphonephthaleins) and the azo-compounds. The isomeric changes which are considered to follow the.,ionic changes of these classes of compounds will be briefly considered.

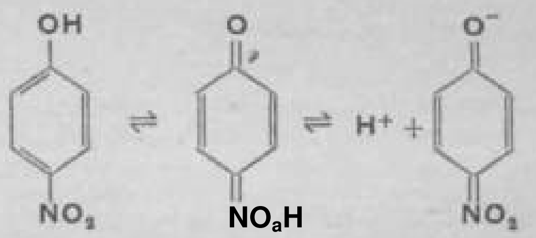
The nitrophenols, of which j)-nitrophenol will be considered as an example, are known to give rise to two series cf ethors, one derived iVom the true nitro-compound



which are colourless, the other derived from the isomeric nitronic acid form

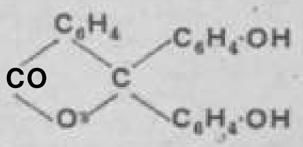


and are intensely red in colour. In the crystalline condition p-nitrophenol is colourless and therefore exists almost entirely as the true nitro-compound having a benzcnctd nucleus. In aqueous solution, there is an appreciable yellow colour, due to the formation of a perceptible quantity of the isomeric acid form which has a quinonoid ring. This nitronic acid at once ionises into hydrogen ions and the coloured anions, the equilibrium being represented by the equation:

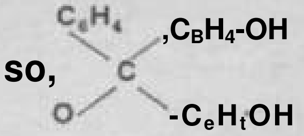


The yellow colour of p-nitrophenoj in alkaline solution is due to the formation of water by union of the hydrogen ions derived from the nitronic acid with the hydroxyl tons from the base, rcsul'ing in the liberation of the strongly coloured anion. In acid solution these changes aro reversed, and the colour is discharged in consequence of the formation of the true nitrophenol.

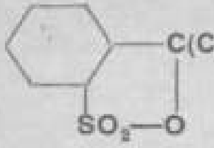
The phthaleins, such as phenolphthalein.



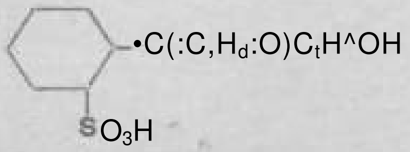
and Phenol Red, phenolsuTphonepbthalein,



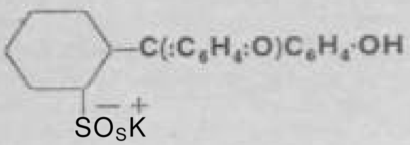
are acid indicators, the latter series having a p_{π} range of about 1 to 1-5 units numerically lower than the former. In a series of papers published between 1916 and 1919, Acree and his collaborators have brought forward convirtung evidence that the earlier theories relating to the colour changes which phenol* phthalein undergoes as being due to the opening of the lactone ring and one of the phenol groups becoming quinonoid aro incomplete. White and Acree {J. Amer. Cbem. Soc. 1919, 41, 1190) have concluded that the sulphonephthaleius and the phthaWns are to be considered as *dibasic* acids, the primary salt being produced from the carboxylic acid resulting from the opening of the lactone ring and the secondary salt from one of the phenol groups. Certain sulphonephthaleina such as Thymol Blue h»ve a double JJ_Krange, viz. from 1*2 to 2-8 and from 80 to 90, which affords additional evidence of the dibasic character of the indicator. Taking Phenol Red as a typical example *oi* the Bulphonephthalein indicators, White and Acres represent the changes of constitution due to neutralisation as follows:



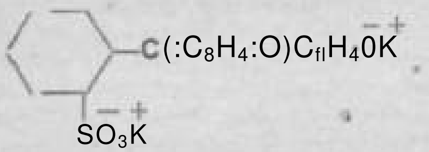
Colourless laclouc.



Yellow quirionoitl acid.



Yellow quinouoid salt.



Intense red quluoneplicuolate snlt.

The replacement of hydrogen atoms by bromine atoms in the molecule of a sulphonephthalein causes the colour of the alkali salts to change from red to blue. (See the Table, Vol. II, p. 640.)

Methyl Orange and Methyl Red are the most important indicators which belong to the class of azo-compounds. Tho parent substance, diinethylammoazobenzene, closely resembles Methyl Orange in indicator*[1] properties. Its p_a range is 2-9-4-0, that of Methyl Orange being 3-0-4-4. The sulphomc acid group in Methyl Orange[1] is inert, the indicator properties being determined, as in the parent **rabetauce,** by the dime^hylammo -group. Hutitzsi-li mid Voigt (Ber. 1929, 62 [B], 968) consider that tho yellow alkfrticr form of dinjethylaniinoazobcnzene has tr- formula $C_6H_8\sim N = N\text{-}C.H_4\text{-}N\{CH_3)j$. When it forms a salt wittan acid HX the product formed has a red cation haying a quinonoid formula, thus:

$$C_aH_s\text{-}N = N\text{-}C_6H_1NMe_2 + HX$$

$$\rightleftharpoons [C_6H_5{\cdot}NH-N=C_6H_4=NMe_2]^{+} X$$

A [though the colour of indicators in solution is determined primarily by the hydrogen on concentration, the presence of other substances, *e.g.* alcohol, proteins and neutral **aatta,** may have an appreciable influence on the colour. For a discussion of the effects of alcohol and proteins, *seel.* M. KolthonV" Indicators," translated by N. H. Furnian, New York, 1928, and W. Mansfield Clark, " The Determination of Hydrogen Ions," 3rd ed., London, B^illiere, Tindall and Cox. 1928. As regards neutral salts, their effect in titration work is as a rule wholly negligible (see Brennecke, *op. cii.).'* When, however, indicators are used for the colorimetric determination of hydrogen ion concentration the influence of neutral salt action may assume greater importance. The general effect of neutral salts is to cause displacement of the colour of acid indicators towards the alkaline side and of basic indicators to the acid side. It appears to be established that neutral salts cause alteration of the activity coefficients of the differently coloured forms of indicators. The influence of salts on chemical equilibria in solutions has been discussed by Brensted (J.C.S. 1921, 119, 574) in terms of the theory of complete ionisation of strong electrolytes and activity coefficients. Kolthoff (J, Physical Clieni. 1928, 32, 1820) has made a careful Study of the salt error of certain indicators in the colorimetric 'determination of p_a, and has emphasised that indicators differ very considerably in their sensitiveness to neutral salt action. Tims Methyl Orange and Methyl Red have very Binall salt errors, whereas indicators of tho triphenylnaethane series, such as Methyl Violet and Brilliant Green, have large salt errors.

In 1888 J. J. Thomson (" Applications of Dynamics to Physics and Chemistry," London, Macmillan & Co., 1888, p. 234) pointed out that capillury forces might have marked influence on chemical equilibria. Attempts to obtain experimental verification of J. J. Thomson's ideas were not very successful until Freiradlich. {Liversidge Lecture, J.C.S. 1930, 164) directed attention to some experiments due to Deutsch who found that indicators in solution near their turning point changed their colours if the solution was shaken with a non-miscible **liquid** Buch as benzene. Thus if Brointhymol Blue (p_H range 0-0-7-6) is placed in a mixture of tap water and distilled water so that the blue alkaline colour is well marked; on shaking with benzene the displacement is in the acid (yellow) direction, whereas when the layers are separated tlfc aqueous layer reverts to the blue (alkaline) colou-. If a triphenylmethane dyestuff such as Brilliant Green is shaken with JV/4 hydrochloric acid and benzene the displacement: *in* in tho opposite (alkaline) direction. In this acid concentration Brilliant Green is yellow, corresponding to a $j>_B$ value of 0-7. On shaking with benzene the coloi/r becomes green, corresponding to a p_H value of 2. ***fat* all** experiments of this kind the changes are strictly reversible.

The indicators in the list (Vol. II, p. 640) are amply sufficient for all ordinary purposes. For particular objects other indicators may have special advantages. Mention may be made of N»trazine* Yellow (2:4-dinitrobenzeneazo~l-naphthol.3:6-diaulphonic acid) which was described by Wenker (Ind. Eng. Chem. 1934, 26, **350)** as a very useful indicator for work close to the region of neutrality. The colour change is from yellow at p_a 00 to blue at 7-2, with'a violet grey tint between 6-4 and 6-8. Mixtures of indicators having different absorption bands or the addition to an indicator of a dye which transforms the regular colour change into a different one more easily perceptible by the eye as in Hickman and Linstcad's screened Methyl Orange (J.C.S. 1922,**121,** 2502) have been recommended from time to time. Universal indicators consist of a mixture of 3everal indicators having different colours and *Pa* ranges. Clark *(op. cit.* p. 97) quotes several mixtures of this kind. Other universal indicators are supplied by chemical manufacturers, and they should always be used under the conditions recommended by the makers. These mixtures are useful for making rapid colorimetric p_K measurements, usually to the nearest unit, over a wide range of acidity. When the approximate p_K value has been obtained with the aid of a universal indicator, a more accurate value may be obtained ty'using a single indicator having a short p_H range such as one of the sulphonephthalein series. In making determinations of,this kind either a solution of known p_K value may be used for reference (*see* BUFFER SOLUTIONS, Vol. II, p. 120) or the colonmetry may be effected with the aid of a Lovibond comparator having standard colour discs appropriate to the individual indicators, each colour differing from the next by 0-2 p_H unit. It is not difficult by estimation to obtain results accurate to 0*1 £>H unit. For the colorimetric determination of titration curves without buffer mixtures a paper by G)llespie (J. Amer. Chem. Soc. 1920, 42, 742) may be consulted. *See also* Kilpatrick (Chem. Reviews, 1935,16, 57).

Fluorescent Indicators. The determination of the acidity of dark coloured liquids, such as wines and fruit juices, may be effected by titration with the aid of indicators which show the end-point of the reaction by the appearance or disappearance of fluorescence in the liquid, the analyses being carried out in ultra-violet light. As more progress in the study of fluorescence has been made from the standpoint of physical optics than from the point of view of the constitution of substances which exhibit the phenomenon, a few notes on the subject may be added.

Fluorescent Indicators: An important paper on fluorescence was published by Stokes (Phjl. Trans. 1852, 463) who first used the ,term *fluorescence* from fluor spar, as the analogous term *opalescence* is derived from the name of a mineral. Stokes considered that the wavelength of the light emitted in fluorescence is always greater than the wave-length of the exciting light. Doubt has been thrown by later work on this general principle, and in particular it has been shown by Nichols and Merritt (Carnegie Institution of Washington, 1912, Publication 152) who used spectrophotometric methods, that fluorescence can be excited in a number of substances in solution by light of greater wave-length than that at the centre of the fluorescent band. The fluorescent efficiency of dyes in solution, i.e. the ratio of the secondary fluorescent radiation emitted by the solutions to the total energy absorbed has been determined by Wawilow (Z. Physik. 1924, 22, 266). The highest value for this efficiency, viz. 0-8, was obtained for aqueous solutions of fluorescein. In methyl alcohol the value was 0-74, and in ethyl alcohol it was 0-66. The influence of solvents on the intensity of fluorescence has been repeatedly emphasised by various investigators, *e.g.* Pringflheim (Trans. Faraday Soc. 1939, 85, 28). In defining fluorescent efficiency as the ratio of the amount of light emitted in fluorescence to the amount absorbed, R. W. Wood (" Physical Optics," 3rd ed., 1936, p. 653) has drawn attention to an important difference according as the measurements are made in terms of energy, or by the number of light quanta or photons absorbed or emitted.

Shortly after the discovery of fluorescein, Kriiger (Ber. 1876, 9, 1572) showed that this compound could be used as an indicator in acidimetrio titrations. He pointed out that it could be used in coloured solutions, and that the indicator was insensitive to carbon dioxide, which is in agreement with its p_H range as tabulated in a list compiled by Radley and Grant (" Fluorescence Analysis in Ultra-violet Light," 3rd ed., London, 1939, p. 312). Of the numerous other compounds having fluorescent indicator properties, mention may be made particularly of quinine, which has a double p_a range from 5*9 to 61 and from 9-5 to 100, of umbelliferone, first used by Robl (Ber. 1926, 59 [B], 1725), with a p_a range of 6-5-7-6, and of Acridine Orange with a p_H range of 8-4-10-4. Grant (Analyst, 1931, 56, 653) has adapted the indicator properties of quinine to the determination of the compound by titrating a known quantity in *N/100* sulphuric acid with AC/100 sodium hydroxide in ultra-violet light. A useful summary of some of the earlier work on fluorescence anafysis will be found in a paper by Haidinger (Mikrochemie, 1932, 11, 429).

OXIDATION AND REDUCTION INDIOATOBS.

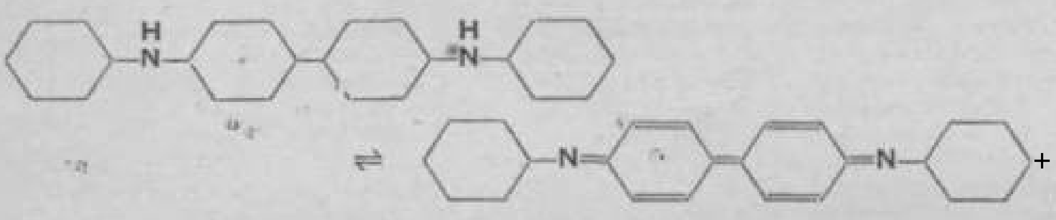
If an inert electrode, such as a platinum wire, is immersed in a solution oi a substance in two different states of oxidation, such as a mixture of ferrous and ferric ions, the electrode will acquire a charge the potential of which will depend upon the experimental conditions. For any particular reversible system, the value of the potential is governed by several factors, particularly the relative proportions[1] of the oxidised and reduced forms and tht^presence or absence of other ions which are capable of formingvu>mplex ions with either the oxidant or the reductant. In the absence of complications arising in consequence of the formation of complex fans, the value of the potential in any particular system is a function of the logarithm of the ra{ip of the concentrations, or more strictly of the activities, of the oxidised and reduced forms. Since the relation between the value of the potential and the concentrations of the oxidised and reduced ions is a logarithmic one, it will be evident that variations of these proportions will have a relatively small effect upon the potential. A considerable effect on the potential of a ferrous-ferric systeiti may be observed by the addition of sodium fluoride, because the net effect of adding this salt is to cause withdrawal of ferric ions on account of the formation of the very stable ferrifluoride ions.

Conant (Chem. Reviews, 1927, 3, 1) has stressed the importance of the distinction between reversible and irreversible oxidation-reduction processes, and has pointed out that the potential has a deAnite meaning only when applied to strictly reversible processes. In -discussing various equations for expressing potentials in terms of the logarithmic ratio of the concentrations of the ions, Conant (*op. cit.*) has pointed out \he advantages of doing this on the grounds of simplicity, but added that discussion in terms of activities ia more exact, particularly for inorganic ions. As regards organic compounds, dismission of the problem in terms of concentrations is considered to be sufficiently accurate, A valuable summary of experimental work on reversible oxidation and reduction in organic systems which is of particular relevance to indicators has been published by Clark *(ibid.* 1926, 2, 127). Many organic compounds, *e.g.* Methylene Blue, which function as oxidation-reduction systems are strongly coloured in the oxidised condition and colourless in the reduced or Ieuco-condition. In the presence of a solution •which has more powerful oxidising properties than the substance, the organic compound will be transformed almost completely into the coloured form, whilst with a solution having more powerful reducing properties the organic compound will change over into the colourless form. In short, Methylene Blue has the properties of an indicator. Clark (op. *eit.)* has pointed out that it should be possible to measure reduction intensities by applying colorimetric methods with oxidation-reduction indicators, just as various buffer mixtures are utib'sed in colorimetric investigations of pu with the aid of acid-base indicators. •

For the purposes of volumetric analysis it has been pointed out that the ideal oxidation-reduction indicator should be a substance having the properties^of an oxidising or reducing agent which undergoes a striking colour change at- some definite change of potential corresponding to the end-point in a reaction such as the oxidation of a ferrous salt in acid solution with potassium dichromate. The colour change should be completely reversible at the equivalence point of the reaction. It should be noted that reactions concerned with oxidation and reduction are frequently of a more complex character than those involving neutralisation. In the latter, the reactions are wholly ionic, and the corresponding colou changes of the indicator are brought about by ionic reactions accompanied by tautomeric changes. The oxidation of ferrous ions by eerie ions is similar.to neutralisation as the reactions consist wholly in the transfer of electrons. Other reactions concerned with oxidation and reduction may involve irreversible changes, such as the conversion of the oxalate anion into carbon dioxide when oxalates are oxidised by permanganate in acid solution.

Few compounds fulfil the requirements of the ideal oxidation-reduction indicator. Many subBtances undergo remarkable colour changes when they ara oxidised, but the changes are frequently of an irreversible character and on this account such compounds should be avoided for volumetric work'.'

Diphmylamine was introduced by Knop (J. Amer. Chem. Soc. 1924, 46, 263) as an indicator for the titration of ferrous salts by dichromate. The compound is first oxidised irreversibly to diphenylbenzidine, then reversibly to diphenoqui'none-4:4'-dianil, with a green menquinone as intermediate, possibly according to the equation:



$$+ 2\overset{+}{H}+2e$$

See Ilehrmann and Micewicz (Ber. 1912, 45, 2644- The colour change takes place at uhout 0-76 voii/on. the hydrogen scale independently of th« p_H of the solution. But the *rate* at which the violet colour developB when ferrouB ions are titrated by dichromate increases with the acidity. The sharpness of the end-point of this titration is increased by addition of phosphate or fluoride ions to the solution so as to produce the complex ferriphosphate or ferrifluoride ions and thereby reduce th^ potential of the ferrouB-ferric system below the valut'for simple ions.

ifoWwm *diphenylamine&idphonale* is in maiiy respects preferable to the parent substance. The colour change takes place at a potential of about 0-83 volt, and this indicator ia much less dbbject to interference by other substances than is diphenylamine. The compound is usually employed ih a solution OJ 0-3% concentration, two drops being sufficient for the titration of 25 ml. of a ferrous salt in *Nj'JS* concentration by pota-3ium dichromate or eerie sulphate. The colour change is from green to violeti-and is sharply reversible. The end-point is not strictly coincident with the equivalence point, *a* small correction being necessary in very exact work. The correction may however be eliminated if the oxidising agent is standardised with the indicator under conditions as nearly identical as possible with tlio^j in which it is to be employed. Cone and Cady *[ibid.* 1927, 49, 350) have used diphenylbenzidine as indicator in the titration of zinc by potassium ferrocyanide containing a trace of ferrieyanide. At the end-point the zinc is precipitated as a double ferrocyanide, so that the ratio of ferrieyanide to ierrocyanide in the solution is greatly increased with the result that the iniiicator is oxidised to the violet colour.

Another aeries of oxidation-reduction indicators belonging to the triphenylmethane series of compounds was suggested by Knop (Z. anal. Chem. 1929, 77, *Hi),* Furman and Wallace (J. Amer. Chem. Soc. 1930, 52, 2347) found t^vo, viz. tlrioglaucine and Eriogreen, of value in the titration of ferrous salts by eerie sulphate.

Tri-ortkopkenanthroline-ferrous sulphate, an oxidation-reduction indicator of a different type from those previously considered, was introduced for volumetric work by Walden, Hammett and Chapman *(ibid.* 1931, 53, 3908; 1933, 56. 2649). The compound has a very stable complex cation, $Fe(C_1jH_eN_s)_2{}^{+}+$, having a deep red colour. The change from the red ferrous complex to a pale blue ferric one takes place at a potential of 1-14 volte on the hydrogen Bcale according to the equation:

$$\mathrm{Fe(C_{ia}H_BN_a)_3^{++}}. \quad \wedge \quad \mathrm{Fe(C_{12}H_8N_2)_3^{+++}+e.}$$

The indicator solution is prepared by dissolving the calculated quantity of orthophenanthroline hydrate (mol. wt. 198) in a 0-025 molar solution of ferrous sulphate containing as little free acid as possible. One drop is sufficient for the titration of 25 ml. of a *NjlO* ferrous solution with either eerie sulphate or potassium dichromate. This sub&ance is apparently the best oxidation-reduction indicator which has so far been discovered, as the iron-phenanthroline complexes are not liable to further oxidation and foreign substances in solution are without effect upon them. Further, the addition of complex-forming ions (fluorides or phosphates) is not necessary nor is any correction required for this indicator.

For a useful monograph on oxidation-reduction indicators, see Brennecke *[o-p. cit.* p. 155.

ADSORPTION INDICATORS.

In 1923 Fajans and his collaborators introduced organic dyest riffs as indicators for the titration of silver and halidb ions. Most of the early experiments were carried out with fluorescein and certain halogenated fluoresceins such as Eosin and Hose Bengal (dichlorotetraiodofluorescein) (Fajans and Wolff, Z. anorg. Chem. 1924, 137, 221). Such compounds undergo striking colour changes at the erjd-point when solutions of halides are titrated with silver nitrate, fluorescein giving satisfactory results -with chlorides, Eosin with bromides, while Rose Bengal is particularly useful for iodides. Since the colour changes with these dyestuffs take place essentially upon the colloidally dispersed particles or upon the surface of the precipitate they are known generally aa adsorption indicators. Dichlor{R)-Fluorescein, having properties intermediate between those of fluorescein and Eostn, was recommended by Kolthoff, Lauer and Sunde (J. Amer. Chem. Soc. 1929, 51, 3273) for the. titration of chloride in very dilute solution. These indicators are generally used only in neutral solution, but Eosin may be used in very weakly acid solution;[1] Other dyestuffs, Buch as Phenosafranine, first used by Fajans and Weir, and tartrazine; Berry and Durrant (Analyst, 1930, 55, 013), can be used, in the presence of nitric acid up to about 0-S.Af.

It has been shown that when dilute solutions of halide and silver ions are brought together, the hydrosol of the silver halide acquires a positive charge if silver ions are present in excess, whereas if halide ions are in excess the hydrosol becomes negatively charged. If an ionisable dypetuff ia present in the- solution, compounds can be formed either with the adsorbed silver ions and the anions of the dye, or, alternatively, between the* adsorbed halide ions and the cations of the dydstuff. The colour changes which take place with adsorption indicators have been discussed by Fajans and Hassel (Z. Elektrochem. 1923, 29, 495) in terms of ionic deformation phenomena on the crystal lattice of the silver halides. Kolthoff {Chem. Reviews, 1935,16, 87) is of opinion that the explanations given by Fajans are not quite accurate and has suggested an alternative interpretation based upon exchange adsorption.

The capacity for adsorption of dyestuffs *by* analogous ions increases with diminishing solubility of the resulting silver halide.' The solubilities of the three salts in mols. per litre are 1-4x10-* for the chloride, 0-725x10"* for the bromide, and 1-0 x 10~^{8} for the iodide. Dyestuffs also vary considerably as regards capacity for adsorption by a given silver halide. Thus Erythrosin is much more strongly adsorbed than Eostn, and Eosin ia more strongly adsorbed than fluorescein. These differences are of great importance in the practical application of the compounds as indicators in volumetric work. Titration curves will 1M found in K. Fajans' monograph (" Newer Methods of Volumetric Chemical Analysis," edited by W. Bottger, 1938, p. 203). Dyestuffa of the fluorescein series and tartrazine may be used conveniently in 0-5% concentration, and one or two drops will be found suitable for the titration of halides by silver nitrate or *vice versa* in volumes of 20-^50 ml. of solutions of the order of *NIIQ* concentration. Fhenosafranine should however be used in more dilute solution, about 0-25%. Titra* tions are byst carried out in stoppered bottles with frequent shaking and it is desirable to add a few drops of some suitable electrolyte such as strontium nitrate solution to facilitate flocculalion of the colloidal silver, halide.

The properties of a few practically useful adsorption indicators for argentometric determinations are summarised in the following Table:

Indicator.	Titration with conditions.	Colour change.
Fluorescein.	$\bar{\mathrm{Cl}}$ by $\overset{+}{\mathrm{Ag}}$ in neutral solution.	Lemon -*• pink. AgCl becomes pink at t'Ae end-point..
Dichlor(R)-Fluoreseein.	$\bar{\mathrm{Cl}}$ by $\overset{+}{\mathrm{Ag}}$ in very dilute solution.	Yellowish-green -•pink
Eosin.	$\bar{\mathrm{Br}}$ by $\overset{+}{\mathrm{Ag}}$ in neutral or very feebly acid solution.	Yellowish - red -• red-violet.
Rose Bengal.	$\bar{\mathrm{I}}$ by $\overset{+}{\mathrm{Ag}}$ in neutral or very newly neutral solution.	Rose in the solution to violet on the **Agl** precipitate.
Phenosafranine.	$\bar{\mathrm{Br}}$ or $\bar{\mathrm{Cl}}$ by $\overset{+}{\mathrm{Ag}}$ or *vice versa.* Beat ,in very dilute $\mathrm{HNO_3}$ solution.	Red pi blue on the surface of the precipitate.
Tartrawne.	$\overset{+}{\mathrm{Ag}}$ in dilute HNO, solution by Cl or BrorSCN.	Dye renvoved from precipitate. Liquid becomes rich lemon colour.

1'lien osafranine is more susceptible to interforence by certain substances in solution than tuitrazine. In particular, sulphates must be absent as they prevent the formation of the blue silver derivative of the compound. Rose Bengal is useful for the titration of iodide in the presence of chloride by silver nitrate {Fajans and Wolff, *I.e.*; Berry, Analyst, 1936, 61, 310), as silver iodide absorbs this dyestuff strongly.

Diphenylcarbazide has been used by Wellings *(ibid.* 1933, 58, 331) for determining the endpoint in the titration of cyanides by silver nitrate, the colour change from red to violet being well marked. Adsorption indicators have been used in other p red/'Station reactions, such as Alizarin S (sodium alizarinsulphonate) in the titration of ferrocyanides by lead nitrate in neutral solution (Burstein, Z. anorg, Chcm. 1927, 164, 219), and Brouiphenol Blue in the titration of mercurous salts by potassium bromide and vice *versa* (Kolthoff and Larson, J. Amer. Chem. Soc. 1934, 56, 1881).

RADIOACTIVE INDICATOHS.

Electroscopic methods of detecting and measuring traces of radioactive substances far surpass spectroscopic methods-of analysis in sensitiveness. Thus a quantity of 1G~^{r7} g. of thorium-C, a radioactive isotope of bismuth, has been detected, as compared with 3 x 10~^{M} g. of sodium which has been stated to be the smallest quantity of that element detectable hi the flame spectrum. In selecting a radio-element for use as an indicator it is important to avoid one w,hich has too short a half-value period, i.e. the time required for the disintegration of half the initial quantity of the element. The intensity of radiation depends not upon the total number of atoms present, but upon the number of iitoii.j which disintegrate in unit time. The practical value of radioactive indicators may now be illustrated by one or two simple examples.

HevSsy and Rona (Z. physikal. Chem. 1915,89, 294>de^inined the solubility of lead chromate in «'*ter as follows. To a definite amount of a soluble lead salt a known quantity of the radioactive isotope thorium-B was added. The chromate was then prepared and placed in water to obtain a saturated solution. A definite; volume was then evaporated to dryness and the thorium-B on the dish determined electroscopically. The weight of lead was thus obtained" and hence the solubility of lead chromate. The value obtairTed was 2 x IO~* moles per litre at room temperature which is in good agreement with the value obtained by electrochemical methods. More recent applications of radioactive indicators to problems in analytical chetnistryjvill be found in a paper by Jlosenblum (Chem. Reviews, 1935, 16, 99).

The hydride of bismutlf was discovered by using thorium-C as indicator and causing hydrogen to be generated in" an apparatus in wlik-lriliiB radioactive indicator had been placed. The gas which escaped was found by l&meth to have radioactive properties (Ber. 1918, 51, 1704). Having found by radioactive methods that bismuth hydride was capable of existence, Paueth and Winternitz {ibid. 1918, 51, 1728) prepared a weighable quantity of the compound from non-radioactive nfatcrial.

Other examples of the use of these indicators will be found in Paneth's monograph " Radio-Elements as Indicators," McGraw-Hill Book Company Inc., New York, 1928, and in that of 0. Hahn (" Applied Radiochemistry," Cornell University Press, New York, 1936).

The discovery of artificial radioactivity by 1. Curie and F. Joliot (Compt, rend. 1934, 198, 254) has greatly extended the possibilities *of* using radioactive indicators in maixy different types of investigations. By attacking the atoms of ordinary elements with a-particles, protons, deuterons or neutrons, it is possible to prepare isotopes of these eleitnents with unstable nuclei and consequently radioactivo properties. The use of artificial radioactive elements as indicators in chemical investigations appears to have been first suggested by Groese and Agruss (J. Amer. Chem. Soc. 1935, 57, 591) who studied the exchange of bromine atoms between free bromine and sodium bromide dissolved in water. These experiments were carried out by subjecting the salt to bombardment with neutrons and thereby producing a radioactive isotope of bromine. Much progress has been made in the study of artificial radioactivity since that time, and a useful and interesting report on the subject, which includes a survey of a number of papers on radioactive indicators, has been published by Seaborg (Chem, Reviews,. 1940, 27, 199).

A. J. B.

INDIGO, NATURAL AND SYNTHETIC. Indigo is one of the most important, and at the same time the most ancient, of blue colouring matters. Extensively used for piguienting and for dyeing both cotton and woollen materials, it was until the end of the nineteenth century obtained exclusively from a variety of plants, most of them growing in tropical countries. The discovery of the chemical constitution of the chief colouring constituent of the natural indigo, called Indijotin, the invention of synthetic methods for producing indigotin from sub3tances obtainable from coal tar, and fine ultimate successful manufacture of synthetic indigo, first accomplished in Germany, constitute brilliant chapters in the hirtory of modern scientific and industrial chemistry. The triumph of the synthetic article, lowevcr, spelt disaster for the producers of natural'lndigo, -rhieh, as an article of commerce, is now practically dead.

The greatest advances in our knowledge of the chemistry of the process of manufacture of indigo from indigoierous plants, and of the actor? controlling the success of the operations, were gained during the last years of the nineteenth and the early years of the twentieth century by the labours of British and Dutch chemists. But these attempts to put the industry on a scientific footing came too late to save it. Far more scientific effort had been put into the search for a synthetic process, and the »attle was quickly won by German dyestuff manufacturers.

Indigo is insoluble in water, and *is,* therefore, useless its a dye without modification. The origin of the discovery that indigo could be dissolved in a vat of fermenting organic matter is unknown, but all early dyers must have used this process. In such a vat the indigo undergoes reduction and dissolves as "indigo-white" or leuco-indigo, which forms a yellow solution in alkaline liquors. When a piece of cloth is dipped in the liquor or "vat," it absorbs the almost colourless indigo-white, and when it is subsequently exposed to the air oxidation occurs and the blue dyestuff is formed in the cloth. This so-called fermentation vat is now only used for special purposes, mainly in the East. Chemical reducing agents are now used, the most important being sodium "hydrosulphite," ($Na_2S_2O_4$), although others such as zinc dust and lime (an older process) may be used. Dyeing with indigo is dealt with more fully elsewhere (*see* Vol. IV, 135).

NATURAL INDIGO.

Historical.—Methods for preparing indigo from the plant are given in ancient Sanskrit records, and, although it appears to have been known to the Romans only as a pigment, there is abundant evidence that it was used in ancient Egypt for dyeing mummy cloths. Knowledge of the dyestuff is said to have been re-introduced to Europe from the East by the great traveller Marco Polo about A.D. 1300, but its use in Europe was very limited until it began to be imported early in the sixteenth century via the Cape of Good Hope. The East India Company is stated to have been exporting large quantities of indigo by 1615. Its use met with much opposition from the growers of woad, and laws prohibiting its use were enacted on the Continent and in England. It use was legally permitted in France in 1737 and gradually its merits became universally recognised. Until near the close of the nineteenth century, when the manufacture of synthetic indigotin in Germany was successfully accomplished, the cultivation of indigo-yielding plants and the extraction of the colouring matter was an important industry in tropical countries.

The most important sources of indigo for the European market were India (Bengal), Java and Guatemala, the last being of minor importance. The quality of the product varied considerably from time to time and from place to place. According to Gorgievics, the best Indian indigo came from Lower Bengal and Bihar, and the quality deteriorated going from East to West. It was also grown in the Philippine Islands, China, Japan, Brazil and parts of Africa.

According to H. E. Armstrong (J. Soc. Arts, 1919, 67, 446), the acreage under indigo cultivation in India in 1897, the year in which synthetic indigo first appeared on the market, was 1,088,042; this had fallen to less than 150,000 by 1914. In 1897 India exported 169,543 cwt. of indigo worth £2,910,000, of which 62,669 cwt. came to the United Kingdom. Two-fifths of the production came from Northern Bihar, and, according to Rawson (J.S.C.I. 1899, 18, 467) the industry employed one and a half million people. The loss of this industry was a tragedy for India. A revival occurred during the war of 1914-18 when supplies of German indigo were cut off from most parts of the world and other countries had not yet started the manufacture. The acreage under indigo rose to 316,600 in 1921-2 but thereafter diminished rapidly. At the present time there is little demand for natural indigo; in 1933 India is said to have exported but 417 cwt. of which 20 cwt. came to the United Kingdom. It is said that natural indigo is still used to some extent in the Dutch Indies for batik dyeing (J. Soc. Dyers and Col. 1937, 53, 248).

In 1916-22 a serious attempt was made, largely inspired by Professor H. E. Armstrong, to rejuvenate the natural indigo industry in India by organised research. Many people considered that by improved methods of cultivation, manufacture, organisation and salesmanship it would be possible to make natural indigo once again competitive with synthetic indigotin. An account of the whole experiment and its abandonment owing to political disturbances and financial stringency is given by W. A. Davis (Chem. and Ind. 1924, 266-268, 303-307). Some of the results obtained by Davis and his collaborators are referred to later in this article.

The Plant and its Cultivation.—The most important plants yielding indigo belong to the genus *Indigofera* (Fam. Leguminosae); these have been cultivated in India, China, Egypt, the Philippines, Caracas and Brazil. The following species have been cultivated for indigo manufacture: *Indigofera tinctoria* Linn., *I. sumatrana* Gaertn. (the Indian plant), *I. disperma* Linn., *I. argentea* Linn., *I. arrecta* Hochst (the Natal plant), *I. paucifolia* Delile (the Madagascar plant) and *I. secundiflora* Poir. (Guatemala plant). Less important are *I. pseudotinctoria* R.Br., *I. angustifolia* Linn., *I. arcuata* Willd, *I. caroliniana* Walt., *I. cinerea* Willd, *I. Ingeracemosa* Boiv., *I. caerulea* Roxb., *I. endecaphylla* Jacq., *I. glabra* Linn., *I. hirsuta* Linn., *I. indica* Lam., *I. mexicana* Benth. and *I. leptostachya* D.C. In Japan, China and Russia the plant usually cultivated has been *Polygonum tinctorium* Ait. belonging to the genus *Persicaria*, and the native West African source of indigo has been almost entirely *Lonchocarpus cyanescens* Benth. The European woad plant, at one time largely grown in Europe, is *Isatis tinctoria*. Other plants which yield indigo are *Nerium tinctorium*, *Gymnema tingens* Spreng, *Eupatorium lave* D.C., *Tephrosia tinctoria* Pers., *Marsdenia tinctoria* R.Br. and certain species of orchids such as *Phaius grandiflorus* Reichb. and *Calanthe veratrifolia* R.Br.

The colour-yielding substance, indican, in *Indigofera* species is present almost entirely in the leaf, and to some extent in the mid-rib or rachis. According to Rawson (The Cultivation and Manufacture of Indigo in Bengal, J.S.C. 1899, 18, 467), the percentage of leaf in a well-grown plant is about 40, but other workers record values as high as 60-65%. The indigotin content of the leaf varies with the season of the year (thus Rawson found 0·2% on May 28 and 0·76% on August 25), the age of the leaf and its position on the plant. Although the maximum amount of colouring matter is present from the middle to the end of August, by this time much leaf has been lost from the plant; manufacture is, therefore, usually started in the middle of June. Gaunt, Thomas and Bloxam (J .S.C.I. 1907, 26, 1174) record a sample of air-dried leaves of /. *sumatrana* yielding 3-53% of indigotin, against 0*6% from other samples and 1*61% from /. *arrecta,* and they suggest that cultivation and selection should increase the indigotin content of the plant.

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According to W. A. Davis (Publications of the Agricultural Research Institute, Pusa, 1920, No. 7) Jiigh-quality plants rich in indigotin are obtained when the soil is poor in nitrogen so that the plant *is* forced to grow on nitrogen taken' up front, the air by the nodule bacteria. It seems probable that the activity C5f these organisms determines high indigotin content, and that the production of indican is due to the plant removing from the nodules nitrogen compounds which would be prejudicial to their continuous action. A good supply of soluble phosphates and of organic matter is necessary. Humus supplied must not contain nitrogen, and cover crops such as wheat or mustard which remove* nitrogen are advantageous.

The Manufacturing Process.-—The process of extracting indigo from the plant is a simple one, and the operations carried out in India and other plac«i in the twentieth century a*re said to differ but little, from those of the ancient Egyptians. There are two major operations, a steeping of the, plants in water, during^ which a fermentation takes place, followed by an aeration of the resulting sohition in a separate vessel, causing the precipitation of the indigo. The following description is given by Davis. The plant is cut in the field in the early morning, taken to the factory in bullock carts and loaded into cement-lined vats. [It has been shown by Watson (J.S.C.I. 1918, 37, 81) that when the plant is air-dried the amount of indican present diminishes. It has long been known that the indican rapidly disappears from the freshly-cut moist leaf.] The vats are then filled with water, warmed if necessary to 90°F., the plants being kept down and held in position by cross-beams fastened across the tops of the vats. The plants 3re left to steep in the water about 12 hours; after about 4 hours a bacterial fermentation sets in, the effect ρ^ which is that the parent substance of the djfe, the so-called *indican,* present in the leaves of the plant, passes into solution. The materials fermented consist of protein and carbohydrate exuded from the cut stems, and the gas liberated consists, in the early stages, of nitrogen and hydrogen, but in the later stages an increasing proportion of carbon dioxide is evolved and the vat liquor becomes slightly acid.

When the fermentation is complete the liquor has a slightly yellow colour and contains *indoxyl (see* p. 464c). From this liquor the dye is obtained by a process known as " beating." The liquor is run into large vats at a lower level, and is then thrown up into the air as a fine spray by means of a large paddle-wheel. The indoxyl becomes oxidised to *indigo;* after about 1£ hours the beating is stopped and the indigo is allowed to settle out as a fine blue mud. After a good fermentation the settling is nearly perfect, but with a bad fermentation it is very incomplete and 20-30% of the indigo may be lost. After settling, the supernatant liquor is carefully run off by special valves and the thick blue mud remaining is transferred to a boiling tank where water containing a small amount of dilute sulphuric acid is added and the mixture raised to the hftil by live steam. This treatment prevents further fermentation and dissolves out brown impurities *(indigo-gluten).* The indigo is again allowed to settle and after the clear liquor has been run off the residue is transferred to " filtering tables," large frames across which cotton cloth is stretched, and drained. The residue is then pressed between cloths in large wooden boxes, and slabs of indigo^ in. thick are obtained. The slabs are then cut up by wire cutters into 3 in. cubes which are dried slowly in air to a •moisture content of 6%, this taking 4-6 weeks. The cubA are finally brushed, polished and packed for market #n large wooden chests holding 300 lb.

Water.—In thfe manufacture of indigo, pure water in large quantities is needed. J. Bridges Lee, "Indigo Manufacture," Calcutta, 1892, recommends treating hard water with lime, and if much organic matter is present, with permanganate.* Alumino-ferric may also be used (Ber£theil). Davis (Indigo Publication, 1920, No. 8, Agricultural Research Institute, Pusa) says that in Assam at Panchnoi the water available for steeping gave a poor yield and quality of indigo because, coming by a small river from nearby hills, its bacterial character changed rapidly. The soft river water gave a slow growth of indican-splitting bacteria, making longer steeping necessary, and this is known to be disadvantageous.

Extraction.—As is to be expected, the manufacturing process varies in detail, in different places and at different times, and a considerable amount of experimental work on the influence of various factors is on record. The fermentation may be complete in 6 hours in very hot weather, but generally, at a temperature of 90-92°F., 12-15 hours appear to be necessary, both for /. *sumatrana* ancj /. *arrecta,* according to the indiean content of the plant. The addition of chemicals such as mercuric chloride, sodium ancT^wtassium carbonates, lime, carbolic acid, formaldehyde and sugar does not appear to be advantageous, but sodium nitrate^ is said to facilitate the deposition of the indigo in the oxidising vat. The work of Thomas, Bloxam and Perkin (J.C.S. 1909, **95,** 846) suggests that the addition of a small quantity of sulphuric or oxalic acid may be advantageous.

An account of a hot-water process of extraction is given by Dr. Roxburgh, dated 1797, in Bancroft's " Philosophy of Permanent Colours," London, 1813, who says that a more complete and certain extraction of the basis of indigo is effected by subjecting the plant to the action of water heated to about 15O-1CO°F. A hot-water method' of extraction was used by the Java planters using /. *arrecta,* and Rawson, who carried out experiments with the method on /. *sumatrana,* concluded that it gave a higher-quality indigo (75-77%) than did the ordinary method (50-55%), but that the method offered no practical advantage except in cold weather. For further details consult Bridges Lee *(op. cit.)*9 Georgievics, " Der Indigo," Leipzig, 1892, and C. Rawson (The Cultivation and Manufacture of Indigo in Bengal, J.S.C.I. 1899, 18, 467; J. Soc. Dyers and Col. 1899,15, 166)'.

Oxidation.—Much work was also done wit^ the object of improving the oxidation process. Rawson considered that the oxidation of^the fermented liquor was improved by air-blowing, a process patented by Geneste in 1*888, the yield being 20% better than by wheel beating. It had long been considered that certain " prccipitants " facilitated deposition of the indipp during oxidation, their action being probably to cause a more rapid oxidation. Coventry[1], in 1894, patented the addition of lime in a vat intermediate between the fermentation and oxidation vats. This caused the precipitation of calciunft and magnesium carbonates which carried down impurities. The supernatant Iiqu3r was run off and oxidised in the usual way, acid being added to prevent contamination of the indigo with lime. This process gave an increased yield of indigo of improved quality, not equal to the Java product, but resembling it in containing a quanNity of indirubin. Caustic soda, sodium peroxide and ammonia can also be used, but the best process of all appears to be to blow ammonia, steam and air simultaneously into the vat by means of aii injector. By this process Rawson claimed an increase of yield varying from 37 to 63-8% over that obtained by the ordinary oxidation process. It must be added, however, that Bergtheil (Report of the Indigo Research Station, Sirsiah, 1906) considered the ammonia process little, if any, improvement over the ordinary oxidising process when the latter is carried out under the **best** conditions.

Sometimes the indigo settles badly and the liquor which is run off (the " seeth " water) may contain as much as 20% of the product. , Rawson recommended the addition of alkali *td* promote sedimentation, and Bergtheil recommended alumino-ferric. Davis, however, as the result of later experiments (Agricultural Res. Inst., Pusa, Indigo Publication, 1918, No. 3) preferred Dhak gum which does not precipitate impurities as alumino-ferric does. When added 5 minutes before the heating is ended, Bhak gum in certain cases gave an increase of yield of 70% with /. *sumatrana* and 35% with the Java plant.

For the purification of the indigo paste, it appears at one time to have been the practice in the East Indies to boil it with water and soda (Bancroft), but writers such as Roxburgh and Cosigny recommended the action of dilute sulphuric acid. The practice of boiling with the diluted acid became general, and Rawson considered that the treatment improved the quality by 5-10%. After settling, the liquor wa& decanted arid the indigo again boiled with fresh water, filtered, pressed and dried. It is said to be advantage)us to dry the indigo slowly to get a strong product, because during this slow drying some impurities gradually decompose with evolution of ammonia.

As has been stated, indigo^was sold in cubes, but Briggs devised an apparatus, an illustration of which appears in Bergtheil's report of 1906, for drying the indigo to a powder. When synthetic indigo was marketed, the manufacturers secured an important selling advantage by offering it as a paste, of constant indigotin content, which was readily soluble in the dyeing vat. W. A. Davis, who started his work in India in 1916, quickly paift attention to this point, and he claimed to have succeeded in standardising the preparation of a similar marketable paste from natural indigo.

***Efficiency of Manufacture.*—As the atibve** description has indicated, there are several stages in the manufacturing process where lop? of indigo may occur. TJhe chief losses are that due to incomplete extraction of the plant, believed by Rawson to be about 5%; the loss in th$ " seeth " water through incomplete precipitation after oxidation, which may be 10-20%, or much more in unfavourable circumstances; and the conversion of the extracted indoxyl into products other than indigotin, for Perkin and Bloxam consider that from the moment of its production by hydrolysis of the indiean of the plant *(see later)* the indoxyl is undergoing destructive decomposition. Rawson in hit* paper on the Cultivation and Manufacture of Indigo *(ll.c),* considered that *jf* his suggestions were adopted there would be little room for remunerative alteration Mn the process, whilst Bergtheil, in 1906, considered that 87% of the extractable indigotin' was accounted for, and 62-72% of the theoretical yield was obtained as dry Colouring matter. Bloxam (J.S.C.I. 1906,25,735), however, from the results of careful analysis of the daily output from the Pembarandah factory in 1904, calculated that the highest efficiency obtained did not reach 50%, **the average was 25% (about 0·1495% from the**

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Extraction,—As is to be expected, the manufacturing process varies in detail, in different places and at different times, and a considerable amount of experimental work on the influence of various factors is on record. The fermentation may be complete in 6 hours in very hot weather, but generally, at a temperature of 90-92°F., 12-15 hours appear to be necessary, both for /. *mmatrana* aii^ /. *arrecta,* according to the indican content of the plant. The addition of chemicals such as mercuric chloride, sodium aniT\vjtassiuin carbonates, lime, carbolic acid, formaldehyde and sugar does not appear to be advantageous, but sodium nitratq, is said to facilitate the deposition of the indigo in the oxidising vat. The work of Thomas, Bloxam and Pcrkin (J.C.S. 1909, 95, 846) suggests that the addition of a small quantity of sulphuric or oxalic acid may be advantageous.

An account of a hot-water process of extraction is given by Dr. Roxburgh, dated 1797, in Bancroft's " Philosophy of Permanent Colours," London, 1813, who says that a more complete and certain extraction of the basis of indigo is effected by subjecting the plant to the action of water heated to about 150-1 C0°F. A hot-water method' of extraction was used by the Java planters using /. *arrecta,* and Rawson, who carried out experiments with the method on /. *sumatrana,* concluded that it gave a higher-quality indigo (75-77%) than did the ordinary method (50-55%), but that the method offered no practical advantage except in cold weather. For further details consult Bridges Lee *(op. cit.),* Georgievics, " Der Indigo," Leipzig, 1892, and C. Rawson (The Cultivation and Manufacture of Indigo in Bengal, J.S.C.I. 1899, 18, 467; J. Soc. Dyers and Col. 1899,15, 166)'.

Oxidation.—Much work was also done witj the object of improving the oxidation process. Rawson considered that the oxidation of'the fermented liquor was improved by air-blowing, a process patented by Geneste in 1888, the yield being 20% better than by wheel beating. It had long been considered that certain " prccipitants " facilitated deposition of the indipp during oxidation, their action being probably to cause a more rapid oxidation. Coven try, in 1894, patented the addition of lime in a vat intermediate between the fermentation and oxidation vats. This caused the precipitation of calciunfc and magnesium carbonates which carried down impurities. The supernatant liquor was run off and oxidised in the usual way, acid being au'ded to prevent contamination of the indigo with lime. This process gave an increased yield of indigo of improved quality, not equal to the Java product, but resembling it in containing a quantity of indirubin. Caustic soda, sodium peroxide and ammonia can also be used, but the best process of all appears to be to blow ammonia, steam and air simultaneously into the vat by means of ail injector. By this process Rawson claimed an increase of yield varying from 37 to 63-8% over that obtained by the ordinary oxidation process. It must be added, however, that Bergthcil (Report of the Indigo Research Station, Sirsiah, 1906) considered the ammonia process little, if any, improvement over the ordinary oxidising process when the latter is carried out under the best conditions.

Sometimes the indigo settles badly and the liquor which is run off (the " seeth " water) may contain as much as 20% of the product. , Rawson recommended the addition of alkali to' promote sedimentation, and Bergtheil recommended alumino-ferric. Davis, however, as the result of later experiments (Agricultural Res. Inst., Pusa, Indigo Publication, 1918, No. 3) preferred Dhak gum which does not precipitate impurities as alumino-ferric docs. When added 5 minutes before the heating is ended, Dhak gum in certain cases gave an increase of yield of 70% with /. *eumalrana* and 35% with tho Java plant.

For the purification of the indigo paste, it appears at one time to have been the practice in the East Indies to boil it with water and soda (Bancroft), but writers such as Roxburgh and Cosigny recommended the action of dilute sulphuric acid. The practice of boiling with the diluted acid became general, and Rawson considered that the treatment improved the quality by 5-10%. After settling, the liquor wa& decanted arid the indigo again boiled with fresh water, filtered, pressed and dried. It is said to be advantage JUS to dry the indigo slowly to get a strong product, because during this slow drying some impurities gradually decompose with evolution of ammonia.

As has been stated, indigo^was sold in cubes, but Briggs devised an apparatus, an illustration of which appears in Berg theirs report of 1906, for drying the indigo to a powder. When synthetic indigo was marketed, the manufacturers secured an important selling advantage by offering it as a paste, of constant indigotin content, which was readily soluble in tho dyeing vat. W. A. Davis, who started his work in India in 1916, quickly paiti attention to this point, and he claimed to have succeeds! in standardising tho preparation of a similar marketable paste from natural indigo.

Efficiency of Manufacture.—As the alftve description has indicated, there are several stages in the manufacturing process where lo£? of indigo may occur, ^he chief losses are that due to incomplete extraction of the plant, believed by Rawson to be about 5%; the loss in th? " seeth " water through incomplete precipitation after oxidation, which may be 10-20%, or much more in unfavourable circumstances; and the conversion of the extracted indoxyl into products other than indigotin, for Pcrkin and Bloxam consider' that from the moment of its production by hydrolysis of the indican of the plant *(see later)* the indoxyl is undergoing destructive decomposition. Rawson in his paper on the Cultivation and Manufacture of Indigo (M.c), considered that if his suggestions were adopted there would be little room for remunerative alteration'in the process, whilst Bergtheil, in 1906, considered that 87% of the extractable indigotin'was accounted for, and 62-72% of the theoretical yield was obtained as dry flouring matter. Bloxam (J.S.C.I. 1906,25,735), however, from the results of careful analysis of the daily output from the Pernbarandah factory in 1904, calculated that tho highest efficiency obtained did not reach 50%, the average was 25% (about 0-1495% from the plant, which should be capable of giving 0-6%] and the lowest figure reached was 12-6%.

When natural indigo was at its zenith, very many varieties were marketed, but in later years severe competition with the synthetic article brought about a large reduction in their number. From Asia came the indigos of Bengal, Oudh, Madras, Java, Manila; from Africa those of Egypt and Senegal; and from America those of Guatemala, Caracas, Mexico, Brazil: other* varieties from South Africa and the Antilles. The best varieties were -those of Bengal, Java and Guatemala, that of Bengal being most widely used in England. The Java variety was of high purity and was much used for the manufacture *of " Indigo Extract"* (Indigosulphonic acid; *see* p. 450a).

A good quality of indigo had a deep violet-blue colour and acquired a coppery lustre when rubbed with the finger nail; it was light, porous and adhered to the tongue. Inferior qualities, containing much mineral and extractable matter, were dull and greyish in appearance, heavy, tough and hard, and not bronzed by rubbing. The best qualities contained 70-90% of indigo tin, average qualities 40-50%, inferior qualities as low as 20%. A typical good Bengal indigo contained indigotin, 61-4%; indirubin, 7-2%; indigo brown, 4-6%; indigo-gluten, 1-5%; mineral matter 19\«%; water, 5-7%.

CHEMISTRY OF INDIGO EXTRACTION.

Indigo is not present as such in any indigo-yielding plant. The colour-yielding constituent of the plants cultivated for indigo is a substance which was named *indican* and was proved, after much research by many workers, to be a glucoside of indoxyi; a,.substance *(see* p. 464c) which by oxidation with air is converted into indigo. Early workers believed that the dye was present in the plant as indigo-white, the reduction product into which indigo must be converted for use as a dye (Chevreul, Ann. Chim. Phys. 1808, [i], 66_6; 68, 284; Gerardin and Preisscr, J. Pharm. Chim. 1840, [i], 26, 344), but Schunck (Phil. Mag. 1855, [iv], 10,;73; 1858, [iv], 15,117) isolated the glucoside from *Isatis tinctoria* (woad), *Polygonum tinctorium* and *Indigofera tinctoria* (Schunck and Roemer, Ber. 1879, 1ft, 2311). The indican was obtained only as a syrup which could be hydrolysed in the presence of air by acids or alkalis or by an enzyme present in the plant to a sugar, then termed *indiglucin,* and indigotin. In absence of air, however, hydrolysis gave a product which did not afford indigotin on oxidation. Cold acids converted the indican into a brown powder, a complex mixture from which Schunck isolated six substances called *indihumin, indifuscin* and *indireiin,* all soluble in warm sodium hydroxide solution, and a- and *fi-indifulvin* and *indirubin* insoluble in alkalis. Aqueous solutions of indican decomposed on boiling, not giving indigotin but indiglucin, indiretin and indihumin, brown amorphous substances. Cold alkalis converted indican into a new glucoside, *indicanin,* hydrolysed by acids to give indiglucin and indirubin.

Lt.-Col. G. S. A. Ranking (J. Asiatic Soc. of Bengal, 1896, 65, [ii], No. 1) first suggested that the fermented leaf extract contains a compound of indoxyi and that indoxylic acid might also be present; and Marchlewski and Radcliffe (J.S.C.I. 1898, 17, 430) independently suggested that indican was the glucoside of indoxyi. Hazewinkel, director of the Experimental Station for Indigo, Klaten, Java, then disclosed the results of work which had been kept secret, which proved the identity of indican and stated that the sugar was dextrose (Proc. K. Akad. Wetensch. Amsterdam, 1900, 2, 512). Eventually indican was isolated in a crystalline condition by Hoogewerff and ter Meulen *(ibid.* 1900, 2, 520) from *Indigofera leptostachya* and *Polygonum tinctorium.* Perkin and Thomas (J.C.S. 1909, 95, 795) isolated the pure, sugar from indican and proved that it is dextrose. Perkin and Bloxam (J.C.S. 1907, 91, 1715) also obtained the crystalline glucoside from */. sumatrana* and */. arrecta* as follows:—

Leaves and stems of */. sumatrana* (1,000 g.) were treated with 4 litres of cold acetone during 7 days, with occasional shaking, and the green extract evaporated to a small bulk. Light petroleum was adled, causing deposition of a brown viscous precipitate which was repeatedly agitated with small quantities of light petroleum. The product was then treated with water, giving a pale yellow liquid from which suspended matter was removed by shaking with ether. The clear aqueous solution was treated with 10 c.c. of AT/2 sodium carbonate and gradually evaporated *in vacuo,* giving eventually a semi-solid mass of crystals, of which 31-66 g. were obtained from 1,000 g. of leaf.

Pure crystalline indican, spear-shaped needles from water, has the formula $C_{14}H_{17}O_6N,3H_2O$ and melts at 57-58°. By adding boiling benzene to its alcoholic solution it is obtained anhydrous, m.p. 176-178°; this can be used as a method of purification.

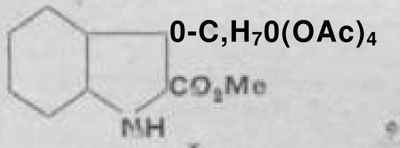
A modification of the above method is described by B. A. Amin (Agric. Res. Inst., Pusa, Indigo Publication, 1918, No. 5), by which the fresh leaves are extracted with hot water, tannins, gums, etc., are precipitated by slaked lime, the solution filtered and concentrated. The indican is then extracted from the concentrate with acetone, .the rest of the procedure being, as in Perkin and Bloxam's method. By this method pure indican was obtained for the first time from *I. arrecta* in large quantities. Perkin and Bloxam had trouble in extracting indican from this plant, owing to the presence of kaempferitrin and a colourless sugar-like compound, $C_eH_{12}O_6$, m.p. 186-187°. Amin's method is quicker and more economical in solvent than that of Perkin and Bloxam.

Beijerinck (Proc. K. Akad. Wetensch. Amsterdam, 1901, 3, 102) considers that the glucoside from woad, which he calls *isatan,* is not, as Schunck thought, identical with indican. Woad contains a specific enzyme, *isatase,* which does not attack indican, whilst the indigo enzyme does not hydrolyse isatan.

Indican can be detected in solution, and its amount determined, by reaction with isatin, when indirubin is formed, or by reaction with an aldehyde such as p-nitrobenzaldehyde, pipcronal or 2>-hydroxybenzaldehyde, when the corresponding indogcnide is formed (Pcrkin and Thomas, J.C.S. **1909,** 95, 795)- Analytical methods are described later; for indogcnides, *see under* INDOXYL COMPOUNDS (p. 405n).

No means appear yet to have been discovered for obtaining a quantitative conversion of indican into indigotin. There would, therefore, seem to be an inevitable lose at this stage in the manufacturing process. ">By hydrolysing the pure glucoside with hydrochloric acid in presence of ferric chloride as oxidising agent Hoogewerf and %T Meiilcn *{l.c.)* obtained 91% of the theoretical yield of indigotin; Gaunt, Thomas and Bloxam (J.S.C.I. 1907, 26, 1174) using ammoniuijj persulphate, which had been recommended by Ravaon (Report on the Manufacture and Cultivation of Indigo, Mozzufferpore, 1004) obtained only 82%. Perkin and Thomas ((.c.) obtained a maximum of 93-5% by passing air through a solution of 0'5g. of indican in 850 c.c. of water acidified with 15 c.c. of 33% hydrochloric acid at 60°C. Using air as oxidant, sulphuric add gave a lower yield than hydrochloric and the filtrate was more darkly coloured. Some indirubin was always formed in these experiments. Perkin and Bloxam also studied the action of hot dilute sulphuric acid on pure indican *(cf.* Schunck's experiments, *above)* and observed the formation of substances resembling indigo brown; they also noted the formation of indole.

The synthesis of indican, identical with the material" of the plant, haa been accomplished by A- Robertson (J.C.S. 1927, 1937), Methyl 3-hydroxyindole-2-carboxylate was condensed with tetra-acetyl-a-glucosidyl bromide to give methyl 3-O-tetra-acetyl-0-ghicosidoxyindole-2-carboxylate (I). This was hydrolysed to the free carboxylic acid which, on heating wJfch acetic anhydride and sodium acetate firet at 100° then at 160° was simultaneously decarboxylated and acetylated to give l-acetyI-3-O-tetra-acetyl-/9-gluco8idojcyindole (II); this by deacetyl&tion- gave indican, which is 3-j3-;lucosidoxyindole.



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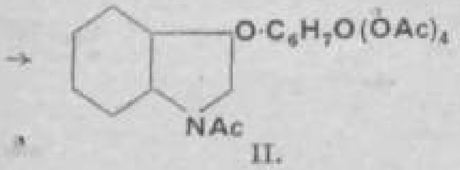


II.

A. K. Macbeth and J. Pryde studied the methylation of natural indican *{ibid.* 1922, **121,** 1660) and obtained a tetraraethyl derivative. The sugar residue was then separated by treating with methyl alcohol containing 1% of hydrochloric acid, when a mixture of the two tetramethyl-metliylglucosides was **obtained,** hydrolysed by acid to crystalline tetramethylglucose. Indican therefore appears to be a normal glucoside.

The Indigo Enzyme.—The indigo-yielding plants contain, as has already been mentioned, an enzyme capable of hydrolysing indican into indoxyl and dextrose, and this enzyme undoubtedly plays an important part in the manufacturing process. The enzyme, and its behaviour towards pure indican, have been studied by several workers. C. J. van Lookcren and P. J. van der Veen (Landw. Versuchs-Stat. 1894, 43, 401) described experiments pointing to the existence of an enzyme causing the hydrolysis of indican. Beijerinck (Proc. K. Akad. Wetensch. Amsterdam, 1900,2, 120,495; 1901, 3,101) prepared it in highly active forma. He extracted finely divided leaves tfcith cold 96% alcohol, removed the alcohol and extracted the residue with more dilute alcohol to remove chlorophyll, indican, wax, etc., and leave a highly active white powder. The enzyme is almost insoluble in water, sparingly in glycerol and more readily in 10% solutions of sodium and calcium chlorides. Ammonia destroys the enzyme. He observed that emulsin also hydrolyses indican, but only one-twentieth as fast as the indigo enzyme. Hazowinkel named the latter *indimulsin [ibid.* 1900, 2, 514; *see also* papers by Rom burgh, ***ibid.*** 1900, & 344; Bergtheil, J.C.S. 1904, 86. 877 ; ter Meulen, Rec. trav. chim. 1905, 24, 444).

The hydrolysis of pure *indican* by the enzyme and the oxidation of the indoxyl solution by air were studied by Thomas, JSloxam and Perkin (J.C.S. 1909, 95, 829). The fermentation was carried out in an atmosphere of pure hydrogen and the temperature and dilution, both for fermentation and subsequent oxidation, approximated to those of factory practice. Employing 2 g, of enzyme to 1 g. of indican, hydrolysis was complete in 2 hours at 50°. The solution contained only 93% of the theoretical quantity of indoxyl; 4% was adsorbe* by the enzyme and the loss of the other 3% was due to " decSy " of the indoxyl into products not convertible into indigotin. It was shown that by the addition of a trace of sulphuric acid to the fermentation both adsorption and decay of the indo^f I could be prevented and the yield raised to 99-6%. But although the hyd.olysis could be made practically quantitative, oxidation by air at 60°C. only gave 88% of theory of indigotin, owing .o secondary changes of the indoxyl. So mo indirubin is formed, and products of the indigo-brown type. It was proved that a trace of ammonia (e/. Rawson's recommendation for factory manufacture) or lime inhibits the ee/jondary changes of indoxyl and increases the yield of indigotin. Too much alkali, however, favours the formation of indirubin; this is probably due to production of isatin which condenses with indoxyl to form indinibin. Perkin (Proc. Chem. Soc. 1007, 23, 30) showed that Java, indigos, rich in indirubin, also contain isatin. The conclusion ia finally drawn that the best yields are obtained by fermenting under aeid conditions) and oxidising under feebly alkaline conditions. A quantitative yield of indigotih, or of this mixed with indirubin, cannot be obtained. For manufacturing purposes Thomas, Bloxam and Perkin (I.e.) recommended that the addition of a small quantity of sulphuric acid to the fermentation vut should be studied.

For the laboratory, however, the most satisfactory method for preparing indigotin from plant extract or from pure indican is by simultaneous hydrolysis with hydrochloric acid and oxidation.

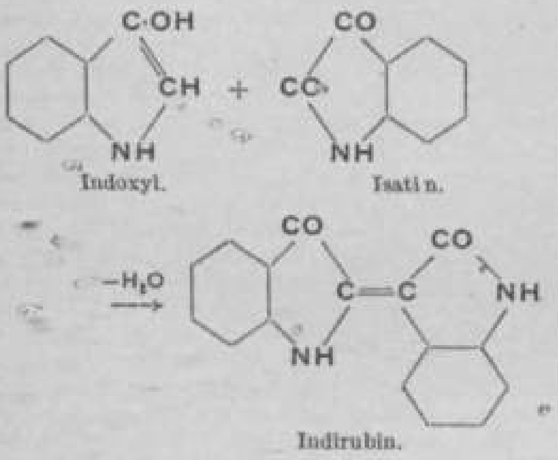
Bacterial Fermentation.—There is some evidence that bacteria play a minor part in the hydrolysis of indican, and in 1887 Alverez isolated from an extract of the indigo plant an organism, *Bacillus indigogenus,* capable of producing fermentation (Compt. rend- 1887, 105, 280).

Beyerinck *(I.e.* 1900, 2,503) studied the matter and found that infusions of garden soil had the same effect, common* gas -producing bacteria being the active agents. Bergtheil *(I.e.)* however, found that infusions of the indigo plant invariably contained large quantities of an organism capable of producing indigo fermentation.

CONSWTITEKTS OF NATURAL INDIGO.

Reference has already been made to the occurrence in varying amount of indirubirt in natural indigo. Some further account will now be given of this and other products which accompany indigotin in the commercial product.

Indirubin.—Indigo was long known to contain a redder constituent of higher solubility in organic solvents, termed indigo red or indirubin. This was eventually proved to be identical with the isomer of iudigotin which is obtained by condensing indoxyl with isatin thua:



At one time it was considered that two red substances might be present in indigo, but the examination of numerous samples by Pectin and Bloxam disproved this idea (J.C.S. 1907,91, 279; 1910, 97, 1460). Some varieties of indigo such *as* that from Java and that made by the Coventry process are especially rich in indirubin, and at least a tra^e *is* probably present in all samples of the natural dye. Analyses are given by Bloxam and Perkin iii the table in the next column.

H can be regarded as established that the indirubin arises during manufacture from the oxidation of some indoxyl to isatin, "and the condensation of the latter with more indoxyl. Thia side reaction is favoured when the air-oxidation of the leaf extract is carried out under add or alkaline conditions. Bloxam and Pcrkin have obtained from pure indican a sample of indigotin containing as much as 25-£3% of indirubin.

Indigo sample.	Total colouring matter.	Indtfcottit.	In.lt-nibin.
	%	%	%
Java Indigo. New process with hot water . . .	)75-20	67-67	7-43
do. • . .	73«0	63-86	9-51
do. . . .	62-91	57-35	*frfil*
Java Indigo. New process with cold water . . .	72-88	69-23	306
do. . . .	7102	66-35	4-04
do. . . .	58-30	55-61	• 215
Java Indigo. Old process without chemicals . .	74-96	72-89	1-74
do. . . .	69-54	68-26	0-99
Coventry Process Indigo . . .	61-76	56-63	5-23

The presence of indirubin in natural indigo probably is responsible in part for the difference in dyeing properties between natural and synthetic indigo; it has sometimes been claimed that natural indigo gives a more attractive " bloomy " shade. Indirubin can he reduced with sodium hydrosulphite solution to a pale yellow vat which dyes wool and silk but has little affinity for cotton. Indirubin is, however, much less readily reduced than indigotin and it is said that, in practice, the indirubin settles if.iattacked to the bottom of the indigo vat (MaHhewa, J.S.C.I. 1902, 21, 222). Perkin has shown, moreover, that the indirubin vat undergoes further reduction to an equimolecular mixture of indoxyl and its isomer, oxindole; the indoxyl becomes oxidised to indigotin, but the oxindole is a wasted product (Proc. Chem. Soc. 1909,25,127). '

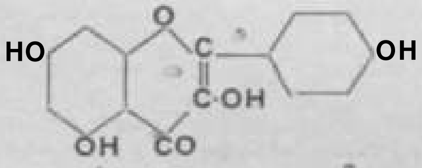
Indirubin crystallises in brown needles with a metallic Iu3tre, syblimee more readily and is less readily oxidisable tihan indigotin.

Indigo Brown.—All indigos contain an important impurity called ir.Vligo brown, which was isolated arl examined by both Chevreul and iBerzelius. Perkin and Bloxam examined with care the brown impurity in Bengal indigo {J.C.S. 1907,91,279). After digeating the indigo with boiling dilute hydrochloric acid to remove gluten, they extracted it with boiling pyridine. The pyridine extract contained, besides a Jittle indLubin, three substances, (a) the main constituent, $Ci_8H_{13}O_3N_a${?), insoluble in alcohol and acetic acid; (6) C_4,Hj_20_sN., (?), soluble in acetic acid ; and (c) $C_{lfl}H_{lt}O_tl4_t$ (?). soluble in alcohol.

These substances are brown amorphous powders, readily reduced by zinc dust in alkaline solution giving pale brown liquids. When heated with 50% caustic potash solution they give some anthranilic acid, indicating that they are derived from indoxyl. It wits stated earlier that Schunck had obtained from his indican, among other substances, *indihumin which* he thought might be the same as indigo brown. Perkin and JtJloxam by boiling pure indican with dilute sulphuric acid obtained a brown substance having a similar elementary composition tcthe above main constituent of indigo brown. Thus, although nothing is known of its constitution, it may be concluded that the indigo brown ia derived from indoxyl Uuring the manufacture of indigo. Analyses of indigo made by Perkin and ^^oxam gave the following contents of indigo brawn: Java indigo, new hot-water process, •6-4%; new cold-water process, 5-2%; ordinary process, 4-15%; Coventry process indigo, 8-7%; Bengal indigo, 9-6%; all these were from /. *arrecla;* Bengal indigo from *I. sumairana* contained 140%. Indigo brown seems to have little influence on the dyeing process; its presence in large amount can be taken to indicate inefficient manufacture.

Indigo-Gluten.—The gluten may be obtained from indigo by extracting with dilute acid, neutralising with chalk, evaporating to dryness and extracting the gluten with alcohol. Orchardson, Wood and Bloxain (J.S.C.I. 1907, 26, 4) describe it as a horny mass, or light bLsi uit-coloured **powder,** which evolves ammonia when heated. The quantity present may be large; Perkin and Bloxam found that crude Bengal indigo (62% indigotin) lost 21-5% of its weight by acid extraction. Whether-the gluten playa any part in dyeing has not been scientifically investigated.

Indigo Yellow.—A yellow substance in **natural** indigo was first reported by Bolley and Oinsoz (Jahresber. 18G0, 637) who isolated from Bengal indigo, by sublimation, a yellow crystalline compound, soluble in alkali, subliming at 130°. Rawson also detected in Java iiAiigo a similar compound having the properties of a mordant dye (J.S.C.I. 1899, 18, 251). Pcrkin concluded that this substance is the trihydroxyflavano), ka«nipferol,



for it was shown that the leaves of /. *arrecla,* from which Java indigo is prepare-l, contain sometimes as much as 4% of kaempferitrin, the rhamno»ide of kaempferol. This substance i-i not hydrolysed by the indigo enzyme, but the presence of kaerapferol in the Java indigo may ^result from the use of sulphuric acid in the manufacturing process, the acid hydroiysing the kaempferitrin. Since the Bengal plant does not contain kaempferitrin, Perkin suggests that the indigc examined by Bolley and Crinsoz was not of Bengal origin.

Seeth Water.—An investigation of the product obtained by evaporating the " seetli" water, the liquor from which the indigo precipitate settles out at the conclusion of the oxidation process, was carried out by A. G. Perkin {J.C.S. 1910, **109,** 210). The only definite substance isolated was a little succinic acid; the main product was an amorphous substance resembling indigo brown, and there was also obtained a protein-like substance, about 20% of the whole, containing 8-22% of nitrogen. The " seeth " water has some value aa a fertiliser.

THE ANALYSIS OF IMDIQO.

A variety of methods have been proposed for the analysis of indigo and the literature is voluminous. The object to be achieved is generally the determination of the amount of indigotin present in the commercial indigo, a problem of no small difficulty in presence of such impurities as have been indicated above. There also come into question methods of determining the quantity of indican present in the plant, and the quantity of indigotin which the plant might be expected to yieli).

Many of the methods which have been proposed for the analysis of the manufactured indigo are only of historical interest. Such are methods of extracting impurities with volatile solvents; methods of extracting indigotin with solvents sucb as aniline, phenol, nitrobenzene; or with acetic and sulphuric acid, although this has been used as a method of purification (Mohiau and Zimmermann, *Z.* Farb.-u. TextU-chem. 1903, 2, 189); sublimation of the indigotin; extraction of the indigo by various reducing agents. Methods which may sometimes be of practical use are determinations *ty* dye trials (Grossmann, J. Soc, Dyers and Col. 1897,**13,** 124) and colonmetric methods. The methods of most practical importance, however, are those by which the indigo is sulphonatcd and the indigo tinsu I phonic acid is titrated with an oxidising or a reducing agent.

Oxidising agents which have been proposed for the titration are <$l£rine water (Berzelius), chloride of lime (Chevreul), potassium chlorate and hydrochloric acid (Bolley, Dinglers Polytech. J. 1851, **119,** 114), potassium dichromate and hydrochloric acid (Schlumberger, J. nr. Chem. 1*42, [i], 26, 217), dichromate and oxalic acid, potassium ferricyanido (tJUgren, A^alen, 1865, 136, 96), potassium permanganate "(Mohr, Dinglers Polytecfc J. 1854, **132,** 363) and, in more modern times, eerie sulphate (private communication). The reducing agents which have been recommended for the titration are sodium hydrosulphite (Mfiller'a method, c/. Bernthsen and Drews, Ber. 1880, 13, 2283) and titanous chloride (Knecht, J. Soc. Dyera and Col. 1904, 20,97; 1905,. ,21, 292). Of these methods the one to which most attention has been given is the oxidation process using potassium permanganate.

The Permanganate Method.—To eliminate the errors duo to the oxidising action of permanganate on subst&nc'Js other than indigotin, Rawson devised two methods. The first depended on precipitating the indigotinsulphonic acid with salt, leaving impurities in solution *(ibid.* 1885, i, 74, 201 ; Knecht, Rawson and Loewenthal, " A Manual of Dyeing," 8th ed., C. Griffin, London, 1925, Vol. II, p. 815); the second depended on adding barium chloride, when the precipitated barium sulphate carried down suspended impurities. The results were identical by both methods (J.S.C.I. 1899, 18, 251). The process, using the salting out technique, is carried out as follows : finely powdered indigo, 0-5 g., is mixed with its own weight of ground glass*- and sulphonated in a porcelain crucible using 20 c.c. of concentrated sulphuric acid at 70° for |-1 hour; the product is diluted with water to 500 e.c. and the liquid filtered to remove insoluble impurities. 50 c.c. of this solution are mixed with 50 c.c. of water and 32 g. of common salt, and, after standing for I hour the precipitated sodium indigotinsulphonate is collected and freed from soluble impurities by washing with 50 c.c. of salt solution *(d* 1-2), The precipitate is dissolved in hot water, 1 c.c. of sulphuric acid added, diluted to 300 e.«. and titrated with *Nj5Q* potassium permanganate solution. The liquid gradually takes a greenish tint, the final disappearance of which constitutes the end of the titration. Each c.c- of *Nj50* permanganate is equivalent to 0*0015 g. of indigotin. This figure was later corrected to 0'00147.

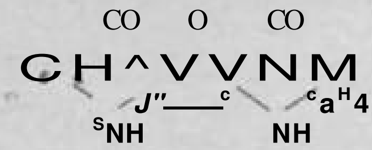
The analysis of indigo, particularly by the permanganate method, was examined critically by Bloxam (J.CS. 1905, 87, 974; JJS.CJ. 1906. 25. 735), Bergtheil and Briggs *(ibid..* 1906, 25, 729), Orchardson, Wood and Bloxam *{ibid.* 1907, 26, 4) and Gaunt, Thomas and Bloxam *(ibid.* 1907, 26, 1174).

Bloxam considered that all methods of removing impurities f&Zed when the indigotin was sulphonated only to the disulphonic acid, but found that if the sulphonation was carried to the *ieirasulpkonic acid,* this could be precipitated in a pure form by potassium acetate. The experiments were made at first with indigo purified by sublimation from tl^p Badische Company's synthetic " B.A.S.F. rein " material. The process iB carried o.*.t thus: 1 g. of indigo mixed with 2-3 g, of powdered glass, free from iron, is sulphonated with 5 c-c. of fuming acid (25% SO3) for 0-5 hour, in a water oven, and the solution,diluted to 500 c.c. with water; 100 c.c. of this solution are treated with 100 c.c. ^of potassium acetate solution {450 g. per litre), which ' causes precipitation. The mixture is warmed and then cooled in ice water when the tetrasulphonate separates completely in crystalline form. It is filtered on a Gooch crucible, and washed free from the brown supernatant liquor with a solution of 90 g. of potassium acetate and 5 c.c, of acetic acid in 600 c.c. of water. The product is dissolved in 200 e.c. of water, and 20 c.c. of this solutionare diluted with 80 c.c. of water, and after addition of 0'5 c.c. < of sulphuric acid, titrated with permanganate (1/1000). The factor ^ven is 1 0.0. of 1/1000 permanganate=000222 g, of indigotin; Rawson's figure of 1 c.c. JV/50=0-00147 when calculated to 1/1000 permanganate ia rather higher, namely 000237. It was sho^n that pure indigo when mixed with indigo brown and indigo-gluten gave accurate results by this method. Further, Perkin **end** Bloxam (J.CS. 1010, 97, 1473) have analysed natural indigo by this method, determining the indigotintetrasulphonic acid after isolation and re-solution, by titration both with permanganate and titanous chloride, and they obtained results by both methods identical within the limits of experimental error with those obtained by a method involving an initia extraction of indirubin by pyridine *(see below).*

Reduction Methods. — The reduction methods of determining indigotin depend on the fact that both hydrosulphite ($Na_2S_2O_4$) and titanous chloride reduce indigotinsulphonic acids quantitatively to the leuco-compounds. Both of these reducing agents are unstable on exposure to air, and special precautions have to be taken to protect the standard solutions from oxidation. Titanous chloride is the less unstable of the tw<\'-" moreover the technique of its use is now^o well known that it is to be preferred. Knecht *(I.e.* 21, 292) found that when the reduction of the indigotinsulphonic acid by titanous chloride took place in presence of mineral acid the end point was indefinite, but sharp results were obtained when the titration was carried out in presence of a tartrate, namely Rochelle salt. Bloxam, however, preferred to use sodium tartrate as it is more soluble than Rochelle salt. The method used by Knecht is to sulphonate 1 g. of indigo with 5 c.c. of 100% sulphuric acid at 90° for 1 hour, dilute to 300 c.c, treat with 12 g. of chalk, cool and make, up to 500 c.c.; 50 c.c. of this solution are mixed with 25 c.c. of 2-0% solution of Rochelle salt and titrated whilst boiling with titanous chloride. Bloxam sulphonatea 1 g. of indigo -with 20 c.c. of 100% Hj,SO_4; the product is diluted to 500 c.c. and 26 c.c. of this, requiring 4 g. of sodium tartrate, are titrated with titanous chloride solution containing 1 c.c. of cone, hydrochloric acid in 50 c.c.

Jones and Spaans (J. Ind. Eng. Chem. 191fi, 8, 1001) have suggested titrating sulphonated indigotin with sodium formal dehydesulphoxylate.

Unlike the above reduction processes, the oxidation of indigotinsulphonic acid by permanganate is not quantitative in the sense of consuming Btoicheiometrically related quantities of the reagent. Standard empirical conditions must be observed to obtain quantitative results for analysis. Whereas complete oxidation to ^satinsulphonic acid would require 0-4824 g. of potassium permanganate per gram of indigotin, actually only 0-45 g. is-needed to decolorise the indigotinsulphonic acid. Perkin and Bloxam (J.CS. 1910, 97, 1462) consider that two explanations are possible, either that the oxidation to the isa'tin stage proceeds iri* two steps, an intermediate compound, possibly the sulphonic acid of (*) being formed; or that two products are formed by 'two separate reactions, one being possibly a dehydroindigotinaulpbonic acid. These, however, are speculations. Later work by Heinisch (Farber-Ztg. 1918, 29, 183, 194) showed that when sulphonaied indigotin was titrated with permanganate at the very high dilution of 1 part of indigotin in 20,000 of water, the permanganate used corresponded with 9 atoms of oxygen to 5 mol. of indigotin,



I.

instead of the 2:1 ratio required for isatin formation.

ANALYSES OF INDIGOS RICH IN INDIRUBIN.

Indirubin and its sulphonic acid are less readily attacked by both oxidising and reducing agents than indigotin and its sulphonic acid; consequently when the mixed sulphonic acids are being titrated with permanganate, titanous chloride or hydrosulphite, the indigotinsulphonic acid is to some extent preferentially attacked. It has been claimed by Rawson that an approximate estimate of the indirubin present may be obtained from the colour change towards the end of the permanganate titration; and Knecht makes the same claim for the titanous chloride process. Other workers, including Bloxam and Perkin, and Koppeschaar (Z. anal. Chem. 1899, 38, 1) do not agree. Generally, for indigos rich in indirubin, it is preferable to extract the latter with a solvent before sulphonating.

For the extraction of indirubin, ether was used by Rawson, glacial acetic acid by Koppeschaar and acetone by Gardner and Denton (J. Soc. Dyers and Col. 1901,17, 170). Bloxam and Perkin re-examined the question and concluded that the solvent power observed of ether and acetone for indirubin was in reality due to their alcohol content. Acetic acid was fairly satisfactory, but pyridine was better and they devised a method based on its use (for details, *see* J.C.S. 1910, 97, 1460). The indirubin extracted by the pyridine contained some indigotin. It was sulphonated, after it had been freed from indigo brown, and the indirubin and indigotin contents were determined by comparison in a Duboscq colorimeter with mixtures of standard solutions of sulphonic acids of pure indirubin and indigotin. The residual indigotin, after extraction with pyridine, was freed from indigo-gluten and determined, for example, by the tetrasulphonate method.

Determination of Indican in the Leaves of Indigo Plants.—Considerable research was devoted to devising a means for estimating the indican content of plants, this being among the data necessary for determining the efficiency of the manufacturing process. Rawson devised a process consisting in extracting the leaves (20 g.) for 2 minutes with boiling water (260 c.c.) and simultaneously hydrolysing the extracted indican with hydrochloric acid and, oxidising to indigotin with ammonium persulphate. This process was later improved to give a higher yield of indigotin by Bergtheil and Briggs (J.S.C.I. 1906, 25, 734) and by Orchardson, Wood and Bloxam *(ibid.* 1907, 26, 4).

A better method was later devised, based on the reaction of indoxyl with isatin to give indirubin. Orchardson, Wood and Bloxam *(l.c.)* proceed as follows: to 250 c.c. of plant extract, from 5 g. of leaf, is added 0-1 g. of isatin and the mixture is boiled in a flask for 5 minutes, to expel air, whilst carbon dioxide is passed through. By means of a tap funnel 20 c.c. of hydrochloric acid are added and the liquid is kept boiling for 30 minutes. The precipitated indirubin is filtered, washed with hot 1% sodium hydroxide and then with acetic acid, dried and weighed. The indirubin obtained is practically pure (98-5%) and the weight can be taken for calculating the indican content of the sample; or for greater accuracy it can be sulphonated and titrated with titanous chloride. This method gives quantitative figures with pure indican, and higher figures both with pure indican (15%) and with leaf extract (25%) than the persulphate process, probably because persulphate has an oxidising action on indigotin.

ANALYSIS OF SYNTHETIC INDIGO.

Synthetic indigo can, of course, be determined by sulphonation and titration with permanganate as described for natural indigo, and with the synthetic product the difficulties due to the presence of so many impurities do not arise. W. Thomson (J. Soc. Dyers and Col. 1921, 37, 166) gives directions for the use of the permanganate method for the analysis of 20% indigo paste. Ceric sulphate has found application in an industrial laboratory for the determination of indigo, after sulphonating. As with permanganate, the method is empirical, and comparative titrations are carried out on a sample of pure standard indigo and the sample to be tested. The sample of indigo to be analysed is first extracted with hot hydrochloric acid (2-5 g. of indigo, 100 c.c. of water and 30 c.c. concentrated acid at water-bath temperature) for 10 minutes, filtered, washed and the loss in weight determined. About 1 g. of the dried, extracted indigo is sulphonated in a test tube with 12-0 c.c. of concentrated sulphuric acid (*d* 1-84) for 1 hour at 75°, and the mixture poured into 500 c.c. of water. After adding washings, the whole is made up to 1 litre, filtered, and 50-0 c.c. of the solution, diluted with 300 c.c. of water are titrated, in a *T>* in. porcelain basin, the ceric sulphate being run in at the rate of about 6-0 c.c. per minute until the greenish colour disappears. The end point is observed best by running in 3 or 4 drops of ceric sulphate solution and stirring slowly, a streaky effect showing that indigotin is still present.

The ceric sulphate solution used for the titration is prepared by dissolving by warming 20 g. of technical ceric sulphate in a mixture of 41 c.c. of concentrated sulphuric acid and 400 c.c. of distilled water. The solution is cooled to room temperature, filtered through glass wool and made up to 1 litre with distilled water. The strength should be adjusted so that 50 c.c. of sulphonated indigo solution (about 0-05 g. of indigotin) is equivalent to 45 c.c. of the ceric sulphate solution.

An electrometric method for determining indigotin, especially in reduced indigo preparations, has been described by Strafford and Stubbings (J.S.C.I. 1938, 57, 242). It consists in adding a known amount of hydrosulphite to reduce the indigo present, and following the electrical potential whilst titrating with Fehling's solution. The potential curve gives the amount of hydrosulphite and of leucoindigotin present, and from the former the amount of indigotin reduced by the added hydrosulphite can be calculated. For details the original must be consulted.

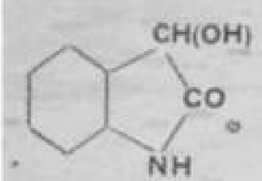
A colorimetric method for determining the indigo content of a vat is described by J. Lotichius (J. Soc. Dyers and Col. 1939, 55, 87; 1940, 56, 433). A known amount of the vat is oxidised "by hydrogen peroxide in presence of sodium protoalbinate which prevents precipitation of the indigo so that a blue sol ia obtained. Thia, alter suitable dilution, is compared colorimetrieaUy with a sol of known indigo content or with a dyeatuff solution of similar shade, such as Sinus Blue E, which has been standardised against a known indigo sol,

SYNTHETIC INDIGOTIN.

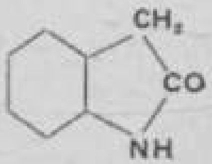
Pure indigotin *ie* a a did substance which can be crystallised from a number of solvents, especially from phthaliu anhydride, from which it separates in beautiful blue prisms, which when rubbed have a coppery sheen. It is insoluble in water, acids and alkalis and cold alcohol; slightly soluble in hot alcohol and acetone, more readily in chloroform and glacial acetic acid, readily in boiling aniline, nitrobenzene and phenol. It can be volatilised giving *u.* violet vapour, its density corresponding with the formula $C_{te}H_{1D}N_aO_a$. Its absorption spectrum shows a maximum at A59(WA. in xylune, and ACO 15A. in tetralin.

Chemical Structure and Early Synthetic Methods.—The chemical structure of indigotin was elucidated by.the German chemist Adolf von Baeyer, after he had devoted many years to the study of the dyestuff and compounds related to it. He devised, in, the course of his work, several methods by which indigotin could bo prepared artificially, but it was not his fortune to discover a process which was suitable for manufacture; this problem was solved by others.

Baeyer has hiniseti disclosed the motives which inspired his work on indigo in a paper which tells the story of his researches down to 1880 (Ber. 1900, S3, Sonderbeft, LI). In 1826 Unvcrdorben had obtained aniline by dry distillation of indigc.-and later, in 1841, Fritzache had obtained s 'thranilic acid, which was later to be of such importance for indigo Manufacture. Thus the benzenoid character of indigotin waa fully established, and in 1841 Erdnmnn, and independently Laurent (1842), had obtained isaAin by oxidation of indigo. Baeyer decided to investigate isatin, especially the problem of reducing it back to indigotin. This work led to the discovery of dioxindqle (I), oxindole (II) and eventually of indole (III), which waa



I.



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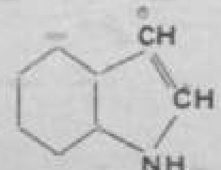
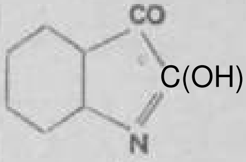


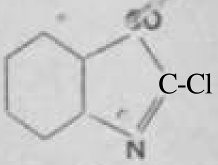
III.

obtained by Baeyer and Emmerling by fusing o-nitrocinnainic acid with potash and iron filings *(ibid.* 1869, 2, 680).

The following year the same chemists obtained some indigo by heating isatin with phosphorus trichloride and acetyl chloride in presence of & little phosphorus at 75-80° *(ibid.* 1870, 3, 514). Baeyer returned to ^the consideration of this reaction 8 years later. By then be had concluded that iaatin had the formula (IV), and

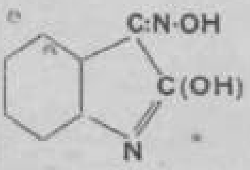


IV.

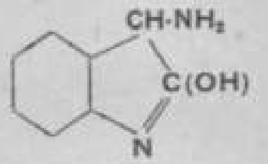


V.

he realised that, to convert isatin into indigo, he must attack the carbon atom which is attached to the nitrogen atom. He, therefore, now used phosphorus pentachloride and obtained an intermediate substance, to which he assigned formula ('/). This was readily reduced by a variety of agents, including ammonium sulphide, to indigotin. For about 8 years after 1870 Baeyer left the indigo field to Kekule, who was trying to synthesiae iaatin without success. About 1878 Baeyer took up the subject again. He succeeded in nitrating phenylacetic acid to ibe o-uitro-derivativc, and on reduction this readily gave oxindole by ring-closure. To make the indigotin synthesis complete it was now necessary to convert oxindole into isatin. This was done through nitroso-oxindole (VI) and amino-oxindolo (VII), the latter giving isatin



VI.

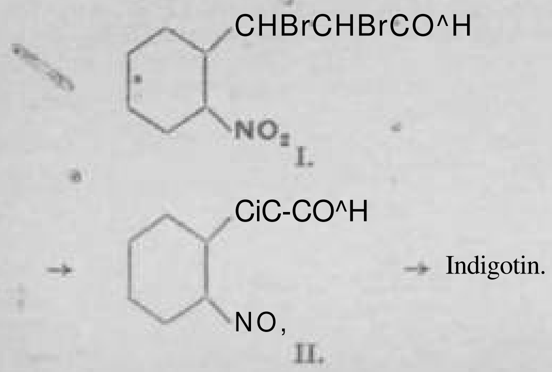


VII.

on oxidation (i'6»d.-4878, 11, 584, 1228). An independent synthesis of isatin from o-nitrobenzoyl chloride throggh o-nitrobenzoyl cyanide and o-nitrobenzoylformic acid was accomplished by CTaisen and Shadwell $&& 1879, 12, 350). When the nitre-group of this acid is reduced the resulting o-aminobenzoylformic acid undergoes ring-closure, thus confirming the suggestion made by Kekule *(Aid.* 1869, 2, 748) that isatin is the inner anhydride or lactam of this acid.

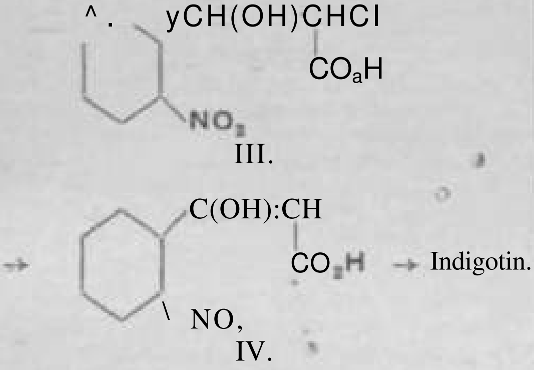
So far no synthesis of indigotin having aDy technical importance had been discovered, but wKen Baeyer turned his attention to o-nitrocinnamic acid the outlook changed; from thia time (1880) onwards, all discoveries having the slightest chance of being workable WFW patented, and the Badische Anilin- und Soda-Fabrik took an .active intorest in the search for an indigo synthesis.

A vast amount of time and trouble was expended in trying to devise a satisfactory synthesis from o-iiitro-aubstituted acids, ketoncs, *i-u•.*, of the benzene series. The methods all broke down, however^ on account of low yield or of difficulty in getting the requisite o-nitro-compound. Generally *o*-nitrobenzaldehyde was needed as a starting material, a substance notoriously difficult to get. BaeyerV first success was obtained by converting o-nitro-cinnamic acid through its dibromide (I) into o-nitropropiotic acid (II), which with **mSd** reducing agents gave indigotin *(ibid.* 1880, **13,** 2254):

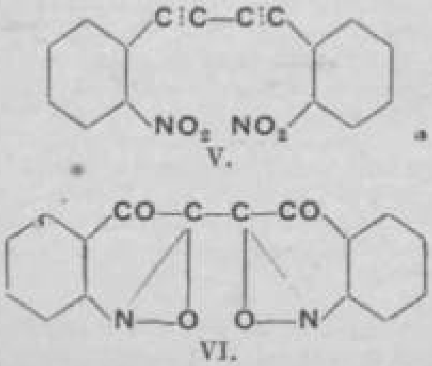


This process was patented (G.P. 11857), and was sold to the Badisehp, Co. and the HBelist FarWerke jointly.

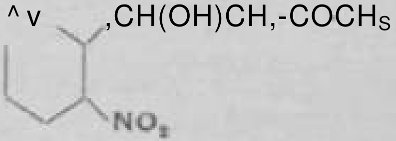
Another method devised was that involving addition of hypochlorous acid to o-nitro-cinnamic acid to give (III), followed by removal of HC! to form o-nitrophenyl-jS-hydroxyacrylic acid (IV), which on heating gave, indigotin {Ber, 1880, **13,** 2262):



Another synthesis of great theoretical interest was from o-nitrophenylacetylene, obtained by heating o-nitrophenyipropiolic acid in water. The copper compound of the acetylene when mildly oxidised with ferricymide gave dinitro-diphenyldiacetylene (V), converted by,fuming sulphuric acid **into** an isoinenc compound, di-isatogen (VI) which *by* reduction gives indigotin *{ibid.* 1882,15, 50). Baeyer's synthesis of indoxyl (which *see)* and thence of indigotin by oxidation follows similar lines,



0-Nitrobenzaldebyde was condensed by Baeyer and Drewsen with acetone to form /3-hydroxy-/?--nitrophenylethyl methyl ketone,



which is converted into indigotin by simple treatment with alkaji *{ibid.* **1882,** 15, 2856); instead of acetone, other substances such as pyruvic acid could be used.

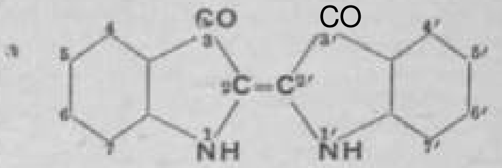
Of all the above processes, only two achieved transitory practical application. o-Nitrophenyl-propiolic acid was sold, as its sodium salt, by the Badisehe Co., to be made up into a printing mixture immediately before use* with ti thickener, a xanthate as a reducing agent and borax as a mild alkali. Its use was restricted owing to its high cost and the objectionable odour of the xanthate. Kalle and Co. marketed the bisul-phite convjound of Baeyer and Drewson'e ketone as " *Indigo Sail,"* also for calico printing, but it had a restricted use.

Structure of Indigo.—As a result of his work, extending over about *IH* years, Baeyer in a masterly paper **(t&irffl883,16,** 2188) formu-lated his views on the structure of isatin, indoxyi, the indogenides and finally of indigotin. The formulae which he advanced have stood the test Of time and have been the foundation on which a vast chapter of chemistry has been built up (flee INDIOOIP, DYE-STUFFS). The matter is referred to again, however^ u.ider structure and colour *(gee* p. 447a). •

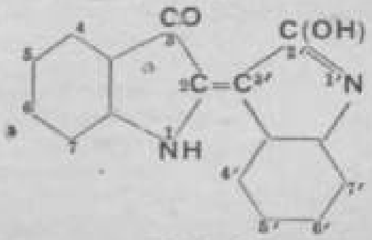
The arguments leading to this fo<ynula for indigotin were briefly:

(1) Indigotin contains two imino groups.
(2) The carbon atom next to the benzjne ring must carry an oxygen atom.
(3) The formation of indigotin friJm dimtro-diphenyldiacetylene proves the prOence of the chain **$C_sH_4CCCCC_aH$,.**

Indigotin must be closely related to indirubin; the two are isomeric, and since indirubin must be the 0-indogenide of isatm, indigotin must be the a-indogenide. The formulae with con-ventional numbering are given below ;

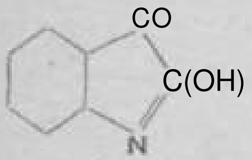


Indigotin.

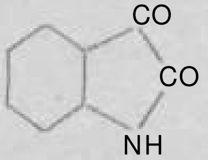


Indirubin.

Btieycr pointed out clearly in this paper that both isntin *and* indoxyi are capable of reacting in two forms, owing to the lability of a hydrogen atom. He. 'gave to the compounds and their *pseudo-forms* tho following formulae:

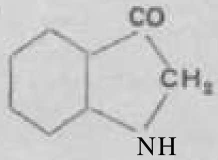


Isatin.



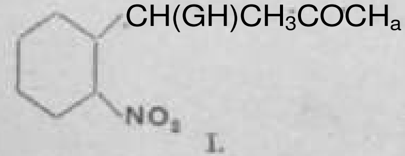
i/i-lsatiu.

Jndoxyl.

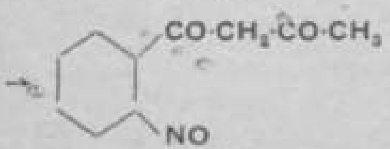


^-indoxyi.

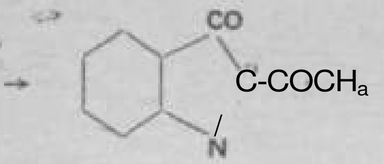
An explanation of the formation of indigotin from Baeyer and Drcwson's o-nitrobenzaldehyde-acetone condensation product lias been ad·.inced by T. Tauuscscu and A. Georgeacu {Hull. Soc. ciiim. 1932, [iv], 51, 23+). They suppose that the ketol (1) passes with loss of water into the o-nitroso-compound (II) which, in



I.



II.



III.

presence of alkali cyclises to (III), 2 mol. of •which by hydrolysis give acet'.c acid and 1 mol. of indigotin.

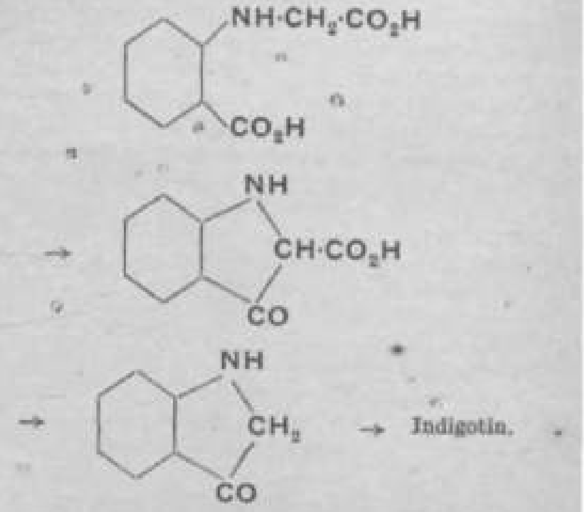
The first claim to hate Hyntheaised indigo was made by Emmerling and Engler {Ber. 1870, 8, 885), who obtained a very email quantity by heating o-oitroacetophenone with zinc and soda-ljme. Much doubt' was thrown upon their claim as for .a long, time ,the experiment could not be repeated successfully, but it was eventually admitted that a traoi of indigo can he thus obtained. Later it was shown that c-amino-acetophenone, and especially o-amino-iw(-chloro-((•romo-)acetophenone uan thus be converted into indigo. It has recently been shown by P. Kuggli and H. Rek-bwein {Helv. Chim. Acta, 1937, 20, 013) that while the free amine gives **a** very low yield of indigotin a much improved yield, as high as 73%, can be obtained by acetylating the amino group and heating the 0-acetamino-a>-bromoacetophenone with alkali in an air current.

The ketols obtained by condensing o-nitrobenzaldehyde with acetophenone and its substitution products also **gjva** imligotin with alkali. I. Tanaseacu and A, Bauiu (Bull. Soc. chim. 1937, [v], 4, Hi73) ha\'e shown that negative substituents in the benzene ring of the acetophenone favour indigotin formation, and in particular the compound from acetophenoie-4-carboxylic acid,

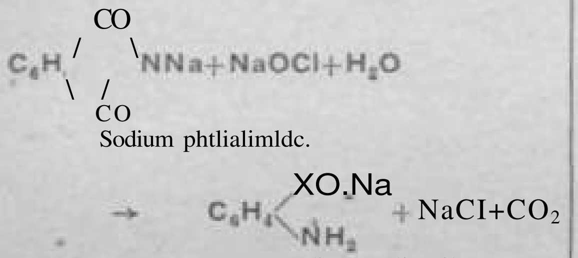
passes quantitatively into indigotin by simple dissolution in alkali.

MANUFACTURE OP SYNTHETIC INDIGO.

The discoveries underlying modern manuiacturiijg methods for indigo were made by K. Heumann, of the Zurich Polytechnic (Ber. 1890, 23, 343), who in 1890 observed that both phcnylglycine and phenylglycine-o-carboxylic acid are transformed into indoxyl by fusion with cau3tic potash. The processes were patented (G.P. 54620, 56273, and numerous additions) and **were** utmiucd **bytbfi** tvuii'-ciic Aiiilin- mi'l **Soda-**Fabrik. The yield from phenylglycine was very small; that from the phenylglycine-o-carboxylic acid was better, and it was on this process that attention was concentrated. As has been shown by ('published experimental results, yields of indigo/«s high as 80% of theory c&n be obtained by fusing phenyMycine-o-carboxylic acid with 12-10 mol. proportions of caustic potash at 260° for 10 minutes and oxidising the in doxy 1 **formed** (M. Phillips, J. Ind. Eng. Chem. 1921," 13, 759). Caustic «oda gives lower yields than caustic potash. The reactions involved are the following:



Tliis process was the one utilised by the Jiudische Co. in the first auceesuful manufacture of eynthetic indigotin, which was launched on to tli m..ket in 1807. There were many difficulties, however, to be overcome before the project became a success, and the Badische Co. alone is said to have expended £1,000,000 in research and experiment before manufacture^ succeeded. Phenylglyrine-o-carboxyhc acid, which was to be the starting-point of the synthesis, had to be manufactured from anthranilic acid and chloroacetie acid. In view ot the enormous quantities of anthranilic acid that would be required, its 1l, -nitration from o-nitrotoluene was not feasible. Fortunately, another process was available, namely, the application of the well-known Hofmann reaction to phthalimido. Sodium phthalimide is treated at a low temperature with sodium hypochlorite when the following reaction occurs:



Sodium phtlialimldc.

Sodium antliranilnte.

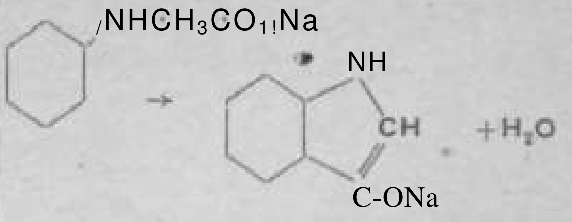
The phthahmide for this process is readily obtained by the action of ammonia on phthalic acid or anhydride- Fortunately,.at about this time there was discovered a cheap and facile process for obtaining phthalic anhydride by the oxidation of naphthalene with sulphuric acid in presence of mercuric sulphate. Thus it was possible to found the synthetic indigo industry at once on a cheap, abundant raw material, naphthalene. At the same time the success of the enterprise must turn on the economical utilisation of all materials and the recovery of by-products. The manufacture of phthalic anhydride used up vast quantities of sulphuric acid which were converted into sulphur dioxide. This large production of sulphur dioxide- was re-oxidised to sulphuric acid by the "contact" process, a process for the manufacture of sulphuric acid which undoubtedly was stimulated by the development of indigo manufacture. The ultimate success of the first synthetic indigo manufacture is attributed to the courage, inventive genius and perseverance of Rudolf Kniotsch of the Badische Co.

The next important discovery bea-ing on indigo manufacture came from a source outside the dyestuff firms. The Deutsche Gold- und Silber-Sehcidcanstalt in Frankfurt a/M. w«« manufacturers of sodamide, for sodium cyanide, and one of their chemists, J. Pfleger, discovered that the conversion of phenylglycine into indoxyl in the alkali melt goes much more smoothly, in fact practically quantitatively, when sodamide is used instead of sodium hydroxide. This discovery immediately put the manufacture of indigo in a now light, since aniline now became a competitor of anthranilic acid as starting material. It is true that the Pfleger process was also applicable to phenylglycine-o-carboxylic acid, but any improvement duo to such ft modification could hardly off-set the lower price of aniline compared with anthranilic acid. The process was acquired by the firm of Bleister, Lucius and Briining, who at about the same time discovered an important new method of manufacturing phenylglycine without using chloracetic acid. They applied some earlier work of Bender and of Miller and Ploch) on anhydroformaldehyde-anih'ne, and showed that phenylglycine-nitrile could be readily and quantitatively obtained from aniline, formaldehyde and sodium cyanide (G.P. 151538, 1901):

$$C_6H_5NH_2+CH_2O+NaCN$$
$$=C_6H_5NH\cdot CH_2\cdot CN+NaOH$$

Subsequent hydrolysis of the nitrile gives the glycine.

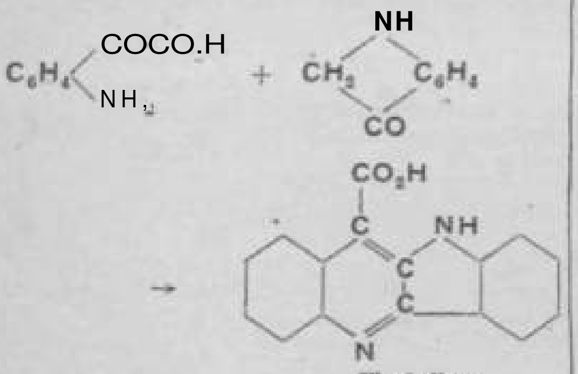
These two discoveries paved the way for what is now, probably, the only practically worked process for indigo manufacture; in brief, the preparation of phenylglycine from aniline, formaldehyde and sodium cyanide; fusion of the sodium phenylglycinate with mixed caustic potash and soda in presence of sodamide; and oxidation of the indoxyl by means of air. Water is formed during the cyclisation and it is the function of the sodamide in the fusion to counteract the destructive effect of this water at the high temperature used:



and 1 mol. proportion of sodamide should suffice for this purpose.

Details of the above fusion and oxidation processes are given by Fierz-David, " Künstliche organisebe Farbstoffe," Berlin, 1928, pp. 441-443, and by P. Henesey (J. Soc. Dyers and Col. 193fJ, 54, 105). The two descriptions differ in detail, from which one can infer that the processes employed differ in different factor^ It can be gathered from the descriptions that the phenylglycine may be used as a mixture of sodium and potassium salts; that the mixed alkali used is about 4 times the weight of the phenylglycine, and may contain KOH:NaOH in the ratio 2:1. The sodamide may, according to Fierz-David, be made *in situ,* in the fusion pot by passing dry ammonia into the vessel containing a mixture of caustic soda and potash at 350", and adding sodium whilst the mass is allowed to cool. The glycine salt is added at a temperature of about 190°. According to Henesey the fusion is finished at 220° in an inert atmosphere, and is complete in 5J hours; Fierz-David gives a fusion temperature of 190-210° and a total duration of 2\ hours. Henesey claims that the best yield is obtained using 2 mol. of sodamide per mol. of phenylglycine. At the end of the fusion the mass is discharged into ice and water, thus keeping the temperature below 50°, and is air-blown to oxidise the indoxyl to indigotin. According to Henesey the concentration of indoxyl at this stage should be about 4% and of alkali about 0% (these figures should represent the proportions of glycine to alkali used in the fusion, which Henesey does not give) and the temperature should not exceed 70°. The precipitated indigo tin is filtered in a press, washed with water, then washed in a vat with dilute acid to remove alkali, finally filter-pressed *and* washed again. It is then ready for standardising.

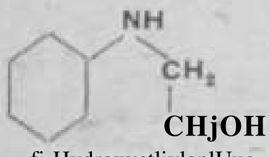
An important part of the process is the recovery of the alkali by concentration of the dilute solution obtained after the filtration of the indigotin. The yield of indigotin is given by Henesey as about (32-6% on the phenylglycine. There are, however, recoveries which bring the yield much higher. During the fusion, some 8% of the glycine is hydrolysed to methylaniline and aniline, which are recovered; and during the oxidation some anthranilic acid is formed which is also recovered. Another by-product formed in small amount is *flavindine* (o,uindolJnc-4-carboxylic acid), formed by interaction of isatin (or the corresponding acid) and indoxyl, thus:



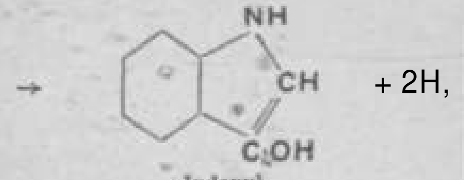
Flavindine.

Fierz-David claims that the over-all yield of indigotin by the process is about !X)% of theory.

Only brief reference can be made to two other processes which have been used for the manufacture of indigo. The Badische Co. is said to have manufactured large quantities of indigo between '"12 and 11)l4 by alkaline fusion of β-hydroxyethylaniline, obtained from aniline and ethylene chlorohydrin (see Fierz-David, *op. cit.* 443-44). The fusion follows much the same course as that of phenylglycine, except that a mixture of caustic alkali and quicklime is used:



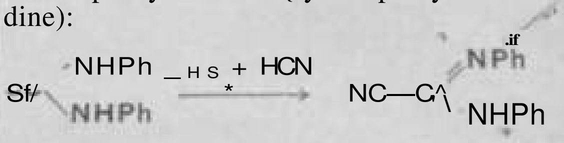
fi-HydroxyctliylanlUuc.



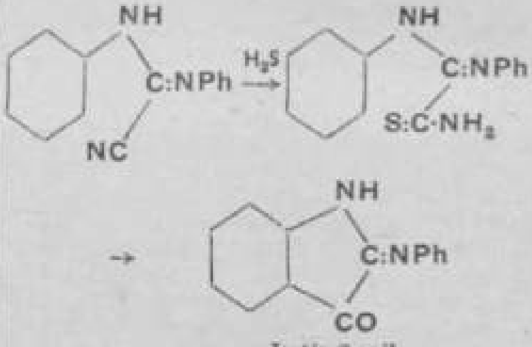
Indoxyl.

and the formation of indoxyl is accompanied by that of hydrogen.

Another synthesis is that of T. Sandmeyer (Z. Farb-u. Textil-chem., 1903, 2, 129), which, although it failed to be applied for the synthesis of indigotin itself, yet served as the cheapest process for isatin and its substitution products. Unlike the other technical syntheses it arrives at indigotin through an isatin derivative. The synthesis starts with thiocarbanilide, obtained quantitatively from aniline and carbon disulphide. This is treated simultaneously with lead oxide and hydrocyanic acid, when it is converted quantitatively into "hydrocyanocarbodiphenylimide" {fyanodiphenylforinanridine):

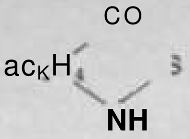


The last compound when treated with yellow ammonium sulphide is transformed by addition of H_2S into a thioamide which is converted by concentrated sulphuric acid into isatin-2-anil, m.p. 126°,

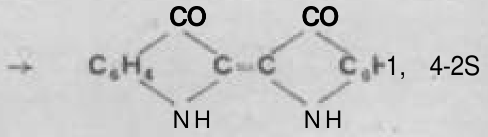


Isatin-2-anil.

The anil is readily hydrolysed by boiling dilute acid to isatin and aniline. It can be converted into indigotin by reduction with ammonium sulphide in alcoholic solution; or it can be converted by means of sodium hydrosulphide into a-thioisatin which, when treated in aqueous suspension with sodium carbonate decomposes into indigotin and sulphur;



2-thio:iatln.



(For a full description, *see* H. E. Fierz-David and L. Blangey, "Grundlegende Operationen der Farbenchemie," 4th ed., 1938.) Sandmeyer's process, which gives an over-all yield of 80% of theory, was used for manufacture for a time by J. R. Geigy & Co. of Switzerland. One of its drawbacks was its extensive use of sulphuretted hydrogen, a dangerous industrial poison.

In 1914 the manufacture of synthetic indigo was confined to two firms in Germany, the Badische Co. and Meister, Lucius und Brüning; and one in Switzerland, the Society of Chemical

Industry in Basle, The firm of **Master,** Lucius und Brüning had started to build a factory, ttnd nearly completed it, at Ellesmere Port in Cheshire, when war broke out in 1914. This factory was opened for indigo manufacture by Messrs. Levinstein Limited, and eventiuilly became absorbed into the British **Dywtuffa** Corporation and then into Imperial Chemical Industries Limited. .1

After the war of 1914-18 manufacture was successfully taken up in the United States, Francuj **Jtalyduid** Japan. Russia was reported to have started a factory in the Ukraine in li)3(i, but by 1939 this attempt waB said *U** have **been** unsuccessful. It may be that the saturation point haft been reached. Already in 1920 **Fiera-David** estimated the output at 10,000,000 kg., about 10,000 tons, of 100% indigotin per annum. It seems probable, too, that for snme of its uses indigo has been, and is being, displaced by newly discovered dyestuffs.

THE STBUCTPBE AND COLOUB OF INDIGO.

Although Baeyer's formula for indigotin is in a general way satisfactory, and no responsible chemist doubts that the component atoms of the molecule are combined as the formula shows, many chemists have felt that it docs not satisfactorily account for the behaviour and properties of the substance. There are three principal facts which the formula, a? ordinarily written, does not account for:

(1) As an ethylenio compound of the form

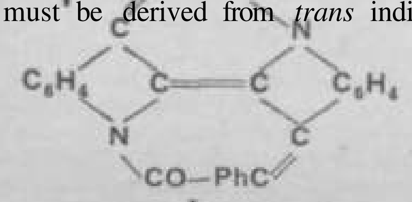
indigo should exist in two isomeric forms. *cia* and *trans;* only one form is known.

(2) The two keto- and two imino-groupa^are comparatively indifferent towards the usual reagents which attack such groups.

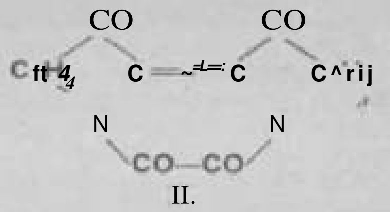
(3) On existing theories of colour the **intense** colour of indigotin is scarcely to be expected from the structure ascribed to the compound.

It seems probable that all these facts are to be ascribed to a common cause, and that a satisfactory formula should account for them all. It muat be remembered that a satisfactory theory must not only account for the colour of indigotin but also for that of thioindigo and, all the other types of indigoid dyes.

The question whether indigotin itself has the *trans* or *cis* structure may not be answerable from chemical evidence. When indigotin is condensed with 2 mol. proportions of phenylacety? chloride, the derivative (I) ia fornrd which must be derived from *trans* indigotin.

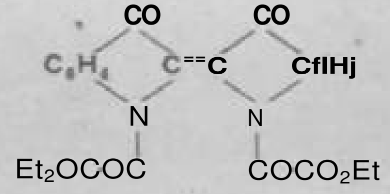


I.



II.

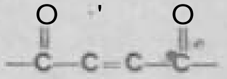
This substance has a red colour and, according toPosnerfBer. J!)2(i, 69 (lij, 1700) its absorption **Bpeetrom** is of the same type as that of indigotin, as is that of the corresponding derivative from indigotin and ethyl raalonate. On the other hand the oxaiyl derivative (11), which can be obtained from indigo tin and oxalyl chloride in **pyridine** at room temperature (Van Alpben, *ibid. 19'Sii,* 72 [Bj, 52<i), must be a *cis*-indigotin derivative. This compound is yellow, but ii^ *dianil* is red-violet and the cliethoxyoxalylindi^o (III) is also red-violet {Van Alplirn, Rec, trav.



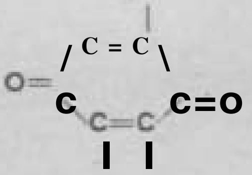
III.

chini. 1939, 68, 378). Th? crystal form of indigotin is said to indicate a *trans* structure (A. Keis and W. Schneider, Z. Krist. **1928,** 68, 547).

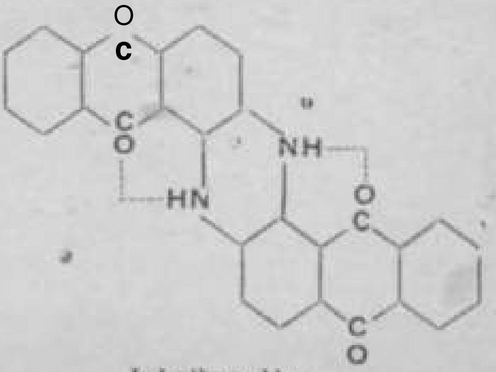
The chromophore of indigotin may bo regarded as the grouping



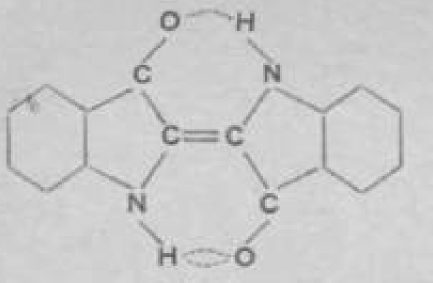
which is the grouping characteristic of all indigoid compounds. The auxochrome is to be regarded as the **NH** or **C_6H_4NH** group. .• It is to be noted that the chromophore is th^aame as that present (in a **double farm),** in Denzoquinonc



Since the group N H is a stronger auxochrome t liiiii S. indigotin (blue) has a deeper colour than



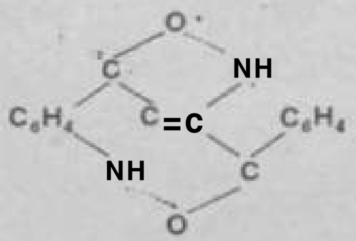
Indanthrene blue.



Indigotin.

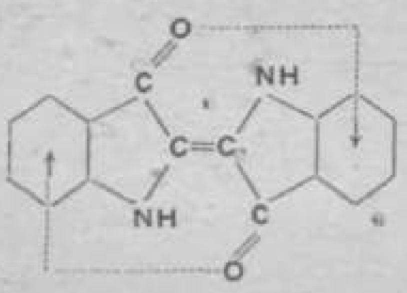
LhioindigO (red). It. Robinson (J. Sue. Dyers and Col. 1921, 37. 77} pointed out that the **blue** colours of indigotin and of Indauthrenc Blue are probably due to the same cause, the interplay of partial **valency** forces between the CO and NH groups. Forces of this kind woulc stabilise indigotin in a *traits* form and no *cis* form could exist. A Bimilnr idea was put forward by tScholl and Madelung independently *(sec* Madelung and Willielmi, Ber. 1024, 57 [BJ, 234).

In recent times the theory has been advanced that hydrogen can act as a co-ordinating elemeiit; it might play such a r6Ie **in** Indigotin, and this would account for the suppression of keto and imino-propertics; but such co-ordination can have little to do with the colour of indigotin, for the N-alkyl ar<l other derivatives of **indigotin** which have no imi no -hydrogen are also deeply coloured, as are also thioindigos, etc. Maddung *(I.e.) favours a formula* in which partial valency is active between the O of the kcto group and the N of the imino group thus:

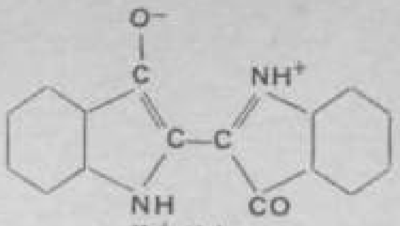


At the eame time he shows that the oxygen of the keto-group may be displaced by the :NH, **:NPh** and **:NOH** groups {by indirect methods), the resulting compounds all being spectroscopically similar to indigotin.

Posner *(I.e.)* discussed the different formula which had been proposed, and suggested a new one, in which the residual valency of the keto-grotip interacts with the far benzene *iin&* as indicated in (I). Van Alphen, on the other hand, considers that the properties of indigStin can only be tin counted for by Ihe simultaneous existence of a number of " resonance hybrids " of which (II) may be one (Rec. trav. cui'Ji. 1938, 57. 911).



Posner.
I.

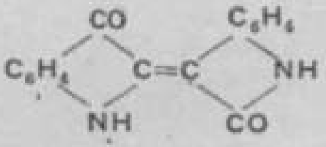


Van Alphen.
II.

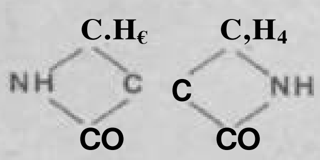
The following Table (Posner) shows **the** effect of substitution in the NH **group** on the **position** and intensity of the **principal** absorption band of indigotin. It is to be noted that all substitution lowers the intensity very considerably, even when the effect is bathochroruic- Thioindigo, however, has the same intensity as indigotin.

Substance.	urn max.	Relative Intensity.
Indigotin	591	1·00
N N '-dic-liiyliruligotin .	652	0·31
N N '-dibcn/oylindigotin	575	0-31
NN'-diacetylindigotin .	545	0-35
7:7'-dimethylindigotin .	004	0-54
N - benzoyl - 7:7' - di - mcthylindigotin . .	575	0-31
Indigotin phenylacetic ester	555	0-31
Indigotin malonic ester	550	0-31
*Thioindigo	540	1·00

The writer is of opinion that, in the consideration which has been given to the colour of iric.itjoid dyes, insufficient attention has been paid a the indirubip and i>dndigo scries. In imli;otin the auxochromic effect of the NH group is at *a* maximum; indirubin is much redder than indigotin, and wriudigo has lost all blueness.



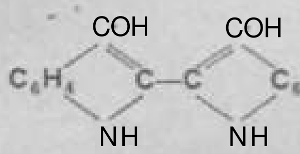
Iudirublii, viulot red.



isolndlgo, browulsh red.

The effect on the colour of indigotin of substitution in the benzene ring is comparatively simple, iubstitution generally has a bathochromic Efect, *i.e.* moving the absorption bands towards ongcr wave-lengths, except in positions 6 and 6" **for** numbering, dee p. 443d) where the effect ia hypsochromic. These remarks apply particularly when the substituent is methyl-, chloro-, bromo- or alkoxy- (see Forminek, Z. angew. Chem. 1928, 41, 1133). Although indigos containing many other substituents in different positions have been described, no exact comparisons of their absorption spectra have been published.

Leucoindigo; Indigo White.—Amongst the numerous reduction products of indigotin which are known, only one is of technical importance, indigo white or leucoindigo. This reduction product is formed by the addition of two hydrogen atoms to the two ketonic oxygen atoms of indigotin, the process being analogous to the reduction of a quinone to the corresponding hydroquinone:



Indigo white.

Indigo white and the corresponding reduction products of other indigoid dyes have the valuable properties that they form alkali salts which are soluble in water; that in this form they have affinity for textile fibres; and that they are readily re-oxidised, generally by air, into the dyes from which they have been derived. Indigoid dyes are all applied to textiles in the form of their leuco- compounds. In practice the most important reducing agent for dyeing is sodium hydrosulphite, $Na_2S_2O_4$. For printing purposes, especially for discharge printing, sodium or zinc sulphoxylate, stabilised by combination with formaldehyde, is generally used. Before the introduction of these substances, glucose in presence of alkali has been much used in printing with indigo. In the fermentation vat, which is now little used in Europe for dyeing but still persists in the East, indigo is reduced to indigo white by products of the fermentation of carbohydrates by bacteria and yeasts. A very smooth reduction of indigotin to indigo white is effected by hydrogen in presence of nickel suspended in aqueous alkali. This process is said to have been employed technically for the manufacture of indigo white. Another reaction of technical interest by which leucoindigo may be produced is that between indoxyl and indigotin in presence of alkali, whereby both are converted into the leuco-compound:

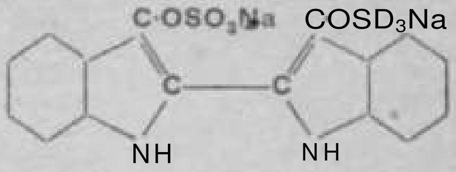
$$2C_8H_7ON+C_{16}H_{10}O_2N_2=2C_{16}H_{12}O_2N_2$$

By this reaction it is possible to convert the indoxyl melt from phenylglycine directly into leucoindigo (Imperial Chemical Industries, B.P. 417862).

Indigo white can be obtained crystalline by acidifying a hot solution obtained by reducing indigo with zinc and aqueous caustic soda and cooling. Leucoindigo is marketed both as a concentrated solution containing soda or NH_3 and in the solid form. It is more stable when isolated by acid precipitation than in presence of alkali. Numerous processes have been patented for improving pastes and other preparations of leucoindigo by addition of such substances as calcium chloride, molasses and other forms of sugar, glycerol, etc., and many devices for preparing stable dry powders have been protected by patents. Leucoindigo behaves as a dibasic acid and its acid units are much more soluble than the neutral salts, a fact which can be utilised in the preparation of concentrated solutions. The magnesium salt is sparingly soluble.

Leucoindigo can be both acylated with acid chlorides and alkylated or benzylated with appropriate reagents. The last property is utilised technically in the process of discharge printing. A quaternary ammonium compound, obtained by combining, for instance, dimethylaniline with benzyl chloride and sulphonating (marketed as "*Leucotrope W*") is used to assist the removal of reduced indigo, by forming a water-soluble benzyl derivative; in this way a white discharge can be obtained in printing.

Indigosol.—A very important step forward in the technique of dyeing with indigotin was made in 1922, when M. Bader and C. Sunder of the Swiss firm of Durand and Huguenin invented a product now marketed as "*Indigosol 0 or DH.*" Indigosol, which has the structure shown, is the sodium salt of the disulphuric ester of leucoindigo.



The sulphuric ester is formed by the action of chlorosulphonic acid or sulphur trioxide on leucoindigo in pyridine or other tertiary base such as dimethylaniline (B.P. 18G057). The advantage of indigosol is that it has the properties of an acid dyestuff and can be dyed on to wool from an acid bath; when dyeing wool from an indigo vat great care must be taken not to damage the wool by the action of alkali. It is said that dyeings of better fastness to rubbing are obtained with indigosol than by vat dyeing, owing to better penetration of the soluble dye in the fabric. The colour is developed on the cloth dyed with indigosol by treatment with an oxidising agent such as sodium nitrite or bichromate and dilute sulphuric acid. Indigosol also finds important application in calico printing. Processes for dyeing and printing with Indigosol are described in a series of patents (B.P. 202630; 202632; 203681; 218649; 220964; see *also* M. Bader, Chem. et fed. 1924, Special No., 449; F. Peterhauser, J. Soc. Dyers and Col. 192& 42, 152; 1927. 43, 251). Besides indigotin itself, many other indigoid dyestuffs are marketed as indigosols. A careful study of indigosols has been published recently by P. Ruggli and M. Stiiuhle (Helv. Chim. Acta, 1940, 23, 689).

An alternative process for preparing the sulphuric esters of leuco-derivatives of vat dyes was discovered independently by Morton. Sundour Fabrics, later Scottish Dyes Limited, who treated the dyestuff itself with sulphur trioxide and a metal such as copper in the presence of pyridine (B.P. 245587; 248802; 251491; 258626). This process is particularly suitable for vat dysa of the anthraquinone series (r. ANTHBAqDINONB DVESTtTFFS, Vol. I, 420a).

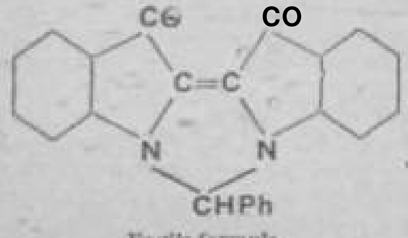
Other methods of obtaining soluble derivatives of indigo have since been proposed, particularly for use in printing. The Society o£ Chemical Industry in Basle have condensed, leuco-indigo with chloroacetic ami jS-chloropropionic acids; the products are for use in printing, being oxidised by such agents as ferric chloride (B.P. 291768/1927). The J.G. Farbenindustrie patented the condensation of leuco-indigo (B.P, 330579) or of indigo *itstif* (B.P. 324119/1928) with m-chiorosulphonylbenzoic acid. The products were claimed for use in printing (B.P. 337846). Unlike the indigosols, the indigo condensation product is hydrolysed by alkalis to the dye.

Indigo Derivatives as Dyestuffs.—Many indigo derivatives, substituted indigos which are still vat dyestuffs, are dealt with in the article INDIUOID DITESTUFFS. There are, however, a few other derivatives of indigotin of different character, which may be mentioned here.

Indigo Carmine, Indigo Extract.—It was discovered *as* early as 1740, by Barth, that indigo could be converted by sulphuric acid into a water-soluble dyestuff. The product so obtained was known'as " *Indig' Extract* " and was used as an acid dye for wool.

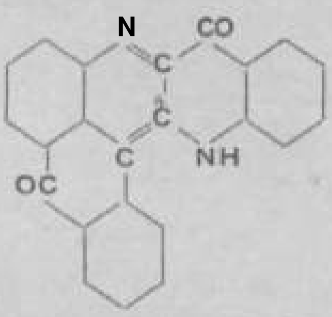
A similar product is manufactured from synthetic indigo by converting it into the disulphonic acid. As a dyestuff it has poor tightfastness and its use has declined. As a foodstuff colour its use is permitted in the U.S.A. and in Australia. The disulphonic acid of commerce (disodium suit) is the, 5*5'-derivative (Vorlander and Schubart, Ber. 1901, 34, 1860); further aulphonation gives the 5:5':7-tri- and 5:5':7:7'-tctra-sulphonic acids (E. Grandmougin, Compt. reno*. 1JJ21,173, 586).

Indigo Yellow 3G Ciba.—In 1910 it was discovered tL^t when indigo is treated with beilzoyl chlo.'ie under certain conditions *{see below)* a valuable yellow vat-dyestiiiF uus formed {B.P. 29308/1910) which appeared on the market as " *Indigo Yellow* 3'? *Ciba."* This discovery was made by Engi and Frohlich, Engi being a chemist of the Society of Chemical industry in Basle who was responsible for many important discoveries in tbe indigoid field. Engi provisionally regarded the new dyestuff as a simple derivative of indigo having the formula {:*) (Z. augew. Chem. 1914. 27, 145), but doubt was thrown on this conception and in 1926 T. Posner and R. Hofuieister (Ber. 192ti, 59 IB], 1827), on account of the intense colour of its vat and stability to oxidising agents, considered that it had lost its indigoid character and become converted into an anthraquinonn derivative (II).



Engi's formula.

I.



Posncr'a formula.

II.

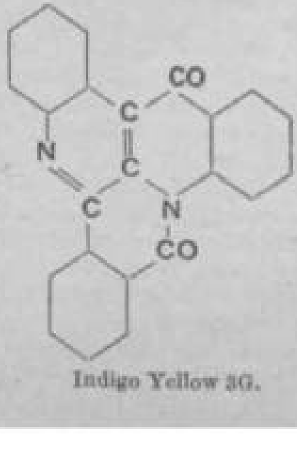
Later the question was re-investigated by E. Hope and collaborators in England (J.C.S. 1932, 2783; 1933, 1000) and by H. de Dieebach and collaborators in Switzerland (Hclv, Chim. Acta, 1933, 16, 148; 1934, 17, 113; 1936, 19, 1213; 1937, 20, 132; 1940, 23, 469). The problem involves four complex compounds obtained by the action of benzoyl chloride on indigotin.

(1) The firBt is the so-called Dessoulavy compound, obtained by acting on indigotin **with** excess of boiliug benzoyl chloride until the blue colour disappears, and adding alcohol or benzene ; it forms colourless crystals, m.p. 238°. It is also obtained from NN'-dibenzoylindigotin and benzoyl chloride and contains chlorine.

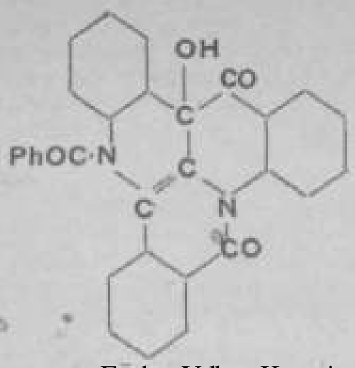
(2) The so-called *Hockst Yellow B,* which can be obtained by simple hydrolysis of the Dessoulavy compound, Cl being replaced by O H. It is isomeric with dibenzoylindigotin and is sometiiiies obtained as a by-product in the preparation of Indigo Yellow 3G-

(3) *Indigo Yellow* 30, obtained by heating indigotin with excess of benzoyl chloride in nitrobenzene in presence of copper powder at 150-160°. H. de Diesbach showed that the nitrobenzene acts as an oxidising agent and that oxygen or air increases the yield.

(4) *Hdchst Yellow U,* which is formed when Höchst Yellow R is healed with concentrated sulphuric acid on the water bath. Both Hope and de Diesbach rejected Posner's formula, for Indigo Yellow 3G and put forward alternative proposals. de.Diesbach'3 formulas for two of these compounds are given below:



Indigo Yellow 3G.



Eochst Yellow K.

Indigd (or Ciba) Yellow 3G ia brominated to give a dibromo-derivative, " *Ciba Yellow 0,"* said by Engi to[1] be a still faster vat-dye. The latter was reduced in alcoholic alkali by such reducing agents as hydrosulphite to give a redder vat-dye of uncertain constitution, "*-Ciba Yellow 5R."*

When indigotin ia condensed with 2 mol. proportions of phenylacetyl chloride it gives a brilliant red compound, " *Ciba Lake Red* B_t*"* discovered, by Engi in 1911, which is used for the manufacture of pigments of high fastness to light.

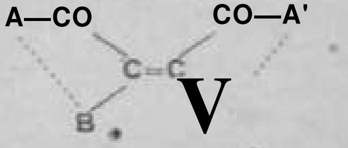
Commercial Forms of Synthetic Indigo.—Synthetic indigo is marketed in Great Britain by Imperial Chemical Industries in the following forms which correspond closely to those of Continental manufacturers; " *Indigo LL powder"* and " *Indigo LL* 20% *paste* "; " *Indigo Grains* 60%," a solid form of the Ieuco-compound; " *Indigo LL Vat I,"* a ready-prepared leuco-eolutiort for wool dyeing; and " *Indigo LL Vat II,"* a Ieuco-solution for cotton dyeing.

Literature.—Besides the references given in the iJext above, information is obtainable from* the following sources: History of the Indigo hynthesis, A. von Baeyer, Ber. 1900,33, Sonderheft, LI; H. E. Fierz-David, "Kuhstliche Organiscbe Farbstoffe," Berlin, 1926, pp. 428 *et stq.*\ J. Martinet, " Matieres Colorantes; VIndigo et sea DeriveV' Paris, 1926; Beilstein; Handbuch der organiflehen Cheinie, 4th *ei*\., 1936, 24, 417.

E. H. H.

INDIGOID DYESTUFFS. The indigoid dyestuffs comprise a lai'ge class of colouring matters which are closely related to indigjtin in then- chemical constitution and are dyed by similar methods, involving reduction to a soUiblo leuco-compound, application to t&o material to be dyed and subsequent re-oxidation thereon to the colouring matter. These dyestulTa have been discovered and developed almost entirely since 1900. Several factors contributed to their rapki[1] development after this date. The «rst was the chemical knowledge gained during the intensive study of indigo itself which culminated in its successful manufacture by the Badische Co. in 1897. When the problem of indigo was solved, the knowledge acquired was turned to the production and study of numbers of its derivatives and congeners. A second factor was the improvement and simplification of the old, uncertain and difficult indigo vat-dyeing process through the researches of the dyestuff manufacturers, particularly the introduction of stable brniB of the reducing agent, sodium hydrosulihite ($Na_2S_2O_4$). The way was thus prepared or introducing now vat-dyes to the dyers. A ;hird factor was the discovery by Frie^lilndcr in 1905 of thioindigo, a red dyestuff, which, with its derivatives, immediately extended the range of shades obtainable with vat dyes. During the decade following this discovery there was intense activity in developing this field of dyestuffs, many new dyes being marketed by Kalle and Co. of Biebrich, who first manufactured " *Tkio-indipo Red* " ia 1906; by Mcistcr, Lucius and Briining of Hochat; and by the Society of Chemical Industry of Basle. The manufacture of these dyestuffs is generally more difficult than that of indigo itself and they are not produced on so large a scale as indigo. Nevertheless their properties, their brilliance of shade and all-round fastness are so attractive that they can sell at a price which is about five or six times that of indigo. Although first introduced for dyeing wool, which they leave in a much softer condition after dyeing than do those dyes needing a chroming treatment to render them fast, **they** are now lately used also in calico printing, and provide a rapge of shades including brill inn t oranges, scarlets and blues, besides browns and greys.

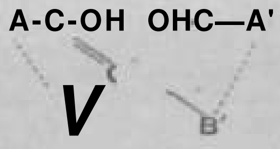
A satisfactory definition of indigoid dyes is not easily given in a few words. In the. broadeat sense, the class includes alWiyes of the general formula



where the bonded pairs A ajitf B and A' and B' respectively link the chromophoro

$$—OC—C{=}C—CO—$$
$$\quad\;\, | \quad\; |$$

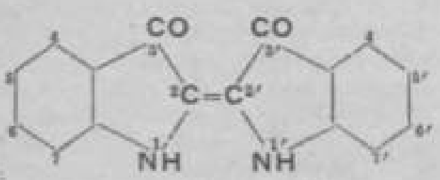
to two,-<five or six me inhered, unsaturate^d cyclic systems. By reduction of the two keto groups the system assumes the, form



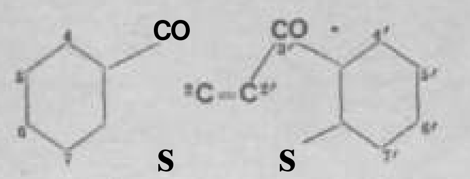
representing the "Jeuco-" compound, which is soluble in alkali and has dyeing properties. The molecule of the original dyestuff consists of two distinct cyclic systems, which may be alike or unlike, joined by the ethyleuic double boud. Obviously the number of types of compound coming under the above definition is very large; and when it is remembered that substituent groups of all kinds can be introduced in every' possible way it can ,be seen that thousands of different dyestuffs are possible.

The 7th edition of Schultz' Farbstofftab*ll -u (1931) gives the constitution of 54 different commercial indigoid dyeatuffa; there **are** in addition many of undisclosed constitution on tho market, and hundreds **are** described in the **patent** literature.

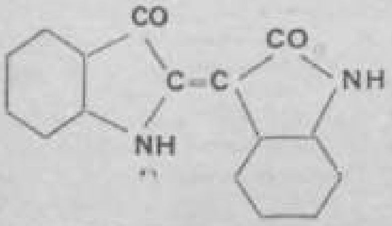
Indigoid dyestuffs are named from the ring systems from which the two portions of the molecule joined by the ethylene linking are derived. ..The following are the formulae and names of indigos which may be regarded as the parents of some dyestuffs of technical importance ; others follow the same lines :



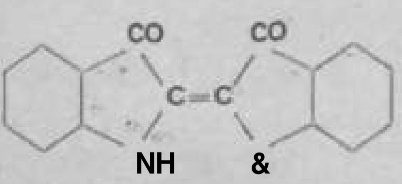
2:2'-Bis-indolei&digo (indigotin).



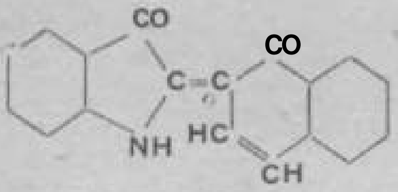
2:2'-Bis-tKionaphtlienindigo(thioindlgo).



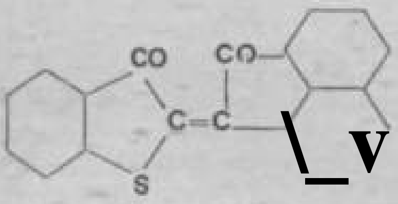
^:3'-lll3-lndoleIndigo(lndirubln).



2>1 ndole-2 '-t li lona ph t he n I n di go.



2-Indole-2'-naphthaleneindigo.



2-Thlonaphrnen-accnaj*hthenc!ridlffo.

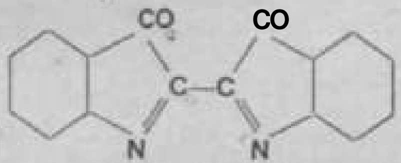
Note that three structural isomers are possible when the two components of the indigo molecule are alike, and four when they are unlike. Thus bis-indoleindigo has three isomers, indigotin (2:2'). indimbin {2:30 and tAundigo (3:3')- The 2:2'-compounds are the deepest coloured and most important; the 3;3'-compound8 are usually of little or no value as dyestuffs.

Symmetrical Bis-indoleindigos.—Indigotin has been dealt with fully in the article INDIGO, NATURAL and SYNTHETIC. Indirubin is of no technical importance. The halogenated indigotins, however, supply very valuable commercial dyestuffs, especially those containing bromine. The purple of the ancients, obtained from species of mollusc, *Alurex brandaris* and *Murex trunculus,* was shown by Friedlander to be 6:6'-dibromoindigotin. It has never been manufactured synthetically. Bromination in the (i:{>'-positions gives a product redder than indigotin, but halogenation in the 5- or 7-positions makes the shade a slightly greener blue, and brighter; halogenation in the 4:4'-positions is said to impart a much greener shade.

The commercial halogenated indigotins are manufactured by direct halogenation. " *Indigo Ciba B* " is a mixture of mono- and di-bromo-indigotins (5- and 5:5'-). which may be obtained by the action of bromine on dry indigo, or on a suspension of indigo in acetic acid, in sulphuric acid, etc. More highly brominated products are obtained by brominating in nitrobenzene solution (a process discovered by Engi), or under other conditions in which water is excluded. The most important of the products so obtained is 5:7:5':7'-tetrabromoindigotin, marketed as " *Duritidone Blue 4BC*" (Imperial Chemical Industries), " *Ciba Blue IB* " (Society of Chemical Industry, Basle), " *Indigo MLBjiB,"* etc. The importance of these dyestuffs lies in the much greater affinity of the vat for all fibres than that of indigo itself.

Higher brominated indigotins, up to penta- and hexabromo-, can be obtained by the action of bromine on indigotin, or on lower brominated indigotins, in concentrated or in fuming sulphuric acid. " *Ciba Blue 0* " is pentabromo-indiin.

Halogens also have the power of converting indigotin into dehydroindigotin by dehydrogenation, and, since dehydroindigotin is more readily halogenated than indigotin itself, the process can be continued to give highly halogenated, products. Thus by the action of chlorine on indigo in acetic acid in presence of anhydrous sodium acetate at 30°, tetrachloro-dehydroindigotin can be obtained. This with sodium bisulphite gives a compound **which** is hydrolysed by acid to tetrachloroindigotin and sodium hydrogen sulphate.



Dehydroindigotin.

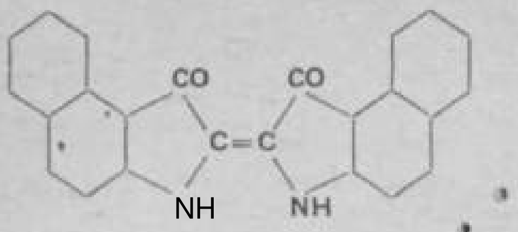
Other halogenated indigotins on the market are " *Brilliant Indigo BASF IB* " (5:7:5':7'-tetrachloro-), *BASFfZB* {5:5'-dichloro-7:7'-dibromo-), *BASFfG* (4:5:4':5'-tetrachloro-) and *BASFjiQ* (4:4'-dichloro-fi:5'-dibromoiudigolit]).

The sole derivative of indirubin **which** has been marketed, as far as is known, is " ***Ciba*** *Heliotrope B* " (S.C.I.), probably a tetrabromo-indirubin.

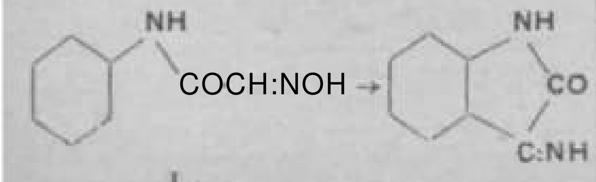
Two homoiogues of indigotin are known to have been marketed, the 7:7'- and 3:5'-dimethyl-indtgotins, respectively "*Metkylindigo B* and *R*." These may be obtained from *o*- and *p*-tolylglycine by the Heuaiaun synthesis, or perhaps from the respective niLrotolualdehydes and* acetone by the Baeyer synthesis {*v.* INDIGO, SYNTHETIC, this Vol., p. 443c).

Nitro-derivatives of indjgotin can be obtained by direct nitration if care be taken to exclude •<.T; and also by other synthetic methods, *e.g.* reduction of rutroisatin chloride with hydrogen iodide. By reduction in the vat they give leuco-derivatives of aminoindi^otin, which can ulso be obtained by direct synthesis, *e.g.* from iftninophenyiglycine. Only one iimmo-derivativc has been used technically, "*Ciba Brown R*" which is 5:7;5':7'-tetrabromo-6:6'-diaminoindigotin. For recent work on the nitration of indigotin, see J. van Alphon, Rec. trav. chim. I93S, 57, 837.

Many other substituted indigotins containing other groups such as hydroxyl, alko.vyl, carboxyl, cyano-, mcrcapto-, etc., have been described in the scientific and patent literature, but none of the bis-^ndoleindigoa of this kind are of technical interest. Four symmetrical indigos derived from naphthalene are possible and all are known. One of them, bis-jS-naphthindoleindigo is of some importance, since when brominated it gives) a very bright green vat dye, used in printing and marketed as "*Ciba Green 0*" and "*Helindone Green G,*"



Asymmetrical Bis-indoleindigos.—Substituted indigotins in which the two sides of the molecule are different are obtained by condensing an indoxyl with an isatin-2-chibride or isatin-2-anil. The isatin s them "elves condense with indoxyla to give dyes of the indirubin type, (since the 3-kuto-group of the isatin atone is active. If isatin-2-anil (or isatin chloride) is used, however, condensation gives an indigotin derivative. Isatin-2-anil is obtained by the method of Sandmeyei described under INDIGO, SYHTHBCTO {thin Vol., p, 446A). Another general method for producing isatins, also due to Sand**meyer** (Ih-lv, Chim. Acta. 191U, 2, 234) *K* an follows. An aromatic amine, such as aniline, is boiled with a solution of hydroxylamine sulphate and -.-Moral hydrate whereby ox imin (meet an.tide (I) is formed, which when merely dissolved in concentrated .sulphuric acid is converted into isut in-3-inline (II) and this yields isatin on heating and diluting the solution. In this way Sandmcyer prepared many substituted isatins from the corresponding substituted anilines.

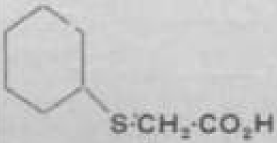


I.

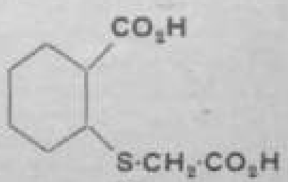
Thioindigo and Derivatives.—The discovery that a coloured compound of similar structure to indigotin could be obtained in which sulphur atoms were substituted for the imino-groups of the latter, was made by P. Friedlander (Ber. 1906, 39,1060). The resulting dyeetuff is bright red, is readily vatted, and in the form of its leuco-compound has good affinity for textile fibres.

The methods of synthesis of thioindigo and its congeners are closely parallel to some of those employed for indigotin. vThe following is a brief description of a few of these methods.

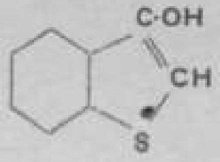
Phenylthioglycollie acid itself (I) can be cyclised to *thioiitdoxyl* (3-hydroxythionaphthen (Ill)), but in practice, *o*- car boxy phenylthioglycollic acid (II) is used. Anthranilic acid is converted through its diazo-compound by the standard method irfto thiosali^ylic acid, this is condensed with chloroaccti; acid to give (II), which is known technical^ as *0 Acid*^ The cyclisation proceeds more readily with these compounds than with the phenylglycines, and (II) is readily converted into thioindoxyl by baking,with caustic soda in a vacuum at about **205°.** Thioindoxyl is more eUble than^.idoxyl, .and although it can be oxidised to thioindig< means of air, 'in practkfc a more rapid oxidation process is employed. Technically, the oxidation is accomplished by boiling a caustic soda solution OA* thioindoxyl with sulphur, or even by the action of molten sulphur on the thioindoxyl.



I.



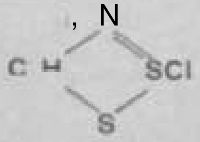
II.



III.

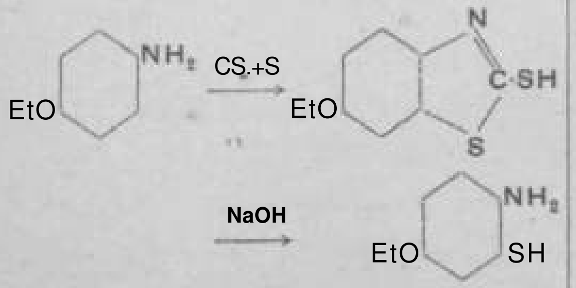
Thioindoxyl is a crystalline substance, m.p. 71°, very similar in odour and general properties to a-naphthol.

T4ie o-ammolhiopheriiiU achieved importance as starting materials for the manufacture of tluoindigoid dyes; a new and convenient method of preparing them was discovered by H. Hcrz, of L. Cassella & Co., in 1914. The method consists in a reaction between *i aromatic amine and sulphur chloride, S_2CL; a compound of the type is formed, which **can** be decomposed by alkali to give the **e-MnmothiopheooL If** the *p*-posi-



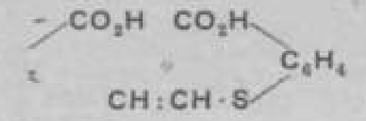
tion of the atnine is free, chlorine substitution occurs fn thia position during the reaction with sulphur chloride. The *o* - am inothio phenol is condensed with chloroacetic acid to form the o-aminophenylthioglycollic acid, which is converted by thc'diazo reaction into o-cyanophenylthioglycollic acid, whence the o-carboxy-compound can be obtained. The route to the thioindigo is then as before. This method can be employed for obtaining a beautiful pink dye-etuff from o-toluidine, and an orange from jy-phenetidine *{see* B.P. 17417, 18292/1914; G,P.. 360690, 307344, 367345, 370854),

*O'&m*inothjophenols can also be obtained by a method discovered by A. W. Hofmann (Ber. 1887, **20,** 1790), by fusing 2-mcrcapU>benzthiazoles with caustic alkali. This process has been applied by Du Pont de Nemours & Co. of America for preparing the orange thioiudigoid dye from j>-phenetidine. The base is converted into b'-etboxy-2-niercaptobenzthiazole by heating with carbon disulphide and sulphur in an autoclave at 200°, and the mercapto- com pound on fusion with caustic soda at 180-185° is converted into 2-amiTio-5-etho3tythiophenol (B.P.



423869). The route to th*> thioindigoid dye is then as de.smljd above.

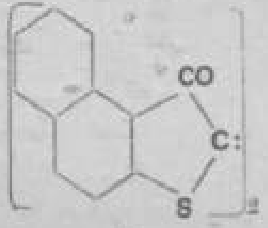
Two other method of obtaining symmetrical tliifiiir'igoid dyes niiiy **ffe** mentioned. When ti salt of thioaalicylic acid reacts with fl-dichloroqfchylene in j)resence of alkali, acetylene-bis-thio alicylic acid is formed,



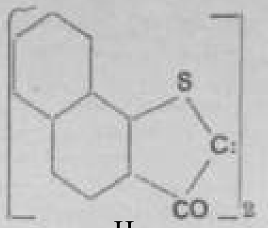
A cety tc nc- uts-tWosaUcy He a eld.

This is converted into thioindigo by treatment with a condensing agent such as sulphuric or chlorosulphonic acid (E. Munch, Z, angew, Chem. 1**908,21.2009;** G.P.*205324).

K. Dzicwofiaki *el al.* {Bull. Acad. Poloir.'.isc, 1030, A, 198) discovered that a- and j8-naphthyl methyl ketone can be converted into 1:2-napbfchthioindi«otin (1) and the 2:l-isomer (II) respectively by heating with sulphur at 230-260°:



I.



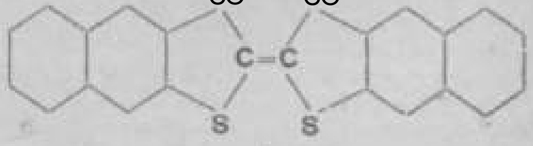
II.

The brown dyestuff (I) can also be prepared by cycliBing ^rnaphthylthioglyt^ollic acid, and is of commercial importance. AcetophenonC does not give *Thipindigo Bed* in appreciable amount by this process *(see* T. W. Jezierski, ROCK. Chem. *U>:u,* 14, 216).

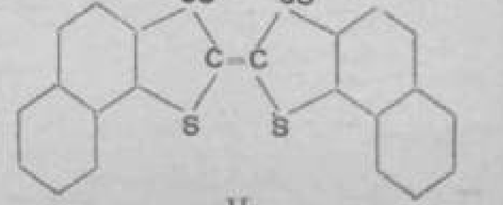
Properties of Thioindigo.—Pure thioindigo is a solid substance which ceysUtilises from organic solvents in **reddish-brown** crystals having a metallic lustre. It sublimes without melting when heated. Its solutions in chloroform, carbon disulphidc anil tulueno show a magnificent reddish-yellow fluorescence but in alooholic solutions only at the temperature of liquid air. It dissolves with a bluish-green colour in concentrated sulj. huric acid with formation of a sulphate, and is sulphonated by fuming sulphuric acid at 30-40°. Many methyl -subatitu ted thioindigOB are known, including 4:5:7:4':5';7'- and 4;6:7:4';6';7'-hexamethyl derivatives.

Thioindigo is more readily reduced to the leu co-compound than indigo, and, unlike the latter, is reduced by sodium sulphide and even by sulphur dioxide. The leuco-compound i« less readily oxidised and, therefore, more stable in air than leucoindigo. It can be isolated as **pole** yellow crystals, sparingly soluble in water; or as the sodium or magnesium salt. Thioindigo ijj also more stable to both oxidising agents and **concentrated** alkalis than indigo.

The effect on shade of substitution in the thioindigo molecule is similar to that in indigo tin. Methyl, halogen or alkoxyl in the 5- and 7-**positions** have a bathochromio elTect, changing the shade from red towards violet; in the 6-positions the effect is hypsochromic, giving pink to orange shades. Tliiuincligos cover a greater range of shades fiian indigos. Thioindigos derived from naphthalene are of many possible types; they may be symmetrical or asymmetriral. It is interesting that dyes of the linear type (I) are bluish-green in'colour, whilst those of angular type, such as (II), are brown. Com-



I.



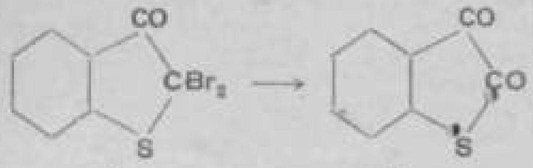
II.

pounds of tlie hybrid type, half of (I) and half of {II), are dark blue. Similarly, the linear symmetrical dye from anthracene is green, the angular dyoe brown. The linear dye from authraquinone is said to be grey-blue, the angular brownish-grey.

The following are some of the **commercial** symmetrically substituted thioindigoid dyes : " *Ciba Bordeaux"* (5r5'-dibromo-); *"**Ciba** lied B "* (G:6'-dicbtoro-); " *Durlndon*. Pink FF* " (O:t>'-di-•>chloro-4:4'-dimethyl-); " *Durivdone Orange J{* " ((i:fi'-di€th^xy-); " *Helindone Jied* 3.B " (6:5'-dich?oro-7:7'-dimcthyl-); " *Helindone Fast Scarlet R"* (5:5'-dibromo-6:6'-dietkoxy-); " *Indanthrene Crey QB* " (7:7'-diiunino-); " *Helhidon&t Orey Bll* " (5:5'-dichloro-7:7'-dianiino-): " *Helindone Orange D* " (5:.V-dibromo-li:ii'-diamino-2:2'i>i9thio]iaphthenindigo).

The Ciba dyes are manufactured by the Society of Chemical Industry, in Basle ; Durindone dyes by **Imperial** Chemical Industries Limited ; and Helindone and lndanthrene I)yes by I.G. .Farbenindustrie A.-G. The' last firm reserves the name " *Indanthrene* " for dyes of the highest fastness, and •several indigoid dyes come into this category? Most of the dyes quoted are made by more than one firm, although only one name is given here.

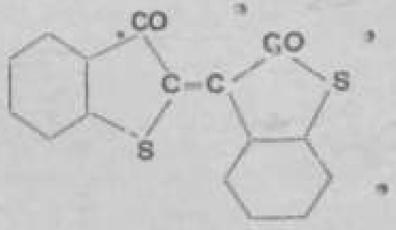
Thionaphthenquinone$ (Thioisatins).—Corresponding with iaatins in the indolc series are the thionaphthenquinoncs or thioisatins in the thionaphthen series. Thionaphthenquinone (II) can be obtained by bromiuating thioindoxyl to the 2:2-djbroruotbioiinloxyl (I) and hydrolysing. It forms intense yeilow prisms, m.p. 121°.



I. II.

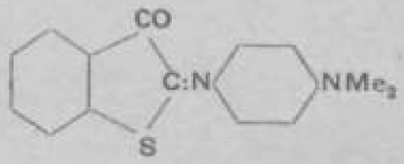
With aniline the dibromo- (or dichloro-) compound gives the 2-anil of the quinone.

When thioiButin condenses with, **for** example, a thioindoxyl, it reacts in the 3-postition, just as isatin does, giving a dyestuff of indirubin type. Thus Friedl&nder (Moyiatsh. 1908, 29, 373) condensed thioisatin with thioindoxyl to form " tliioiiKlimbiii."'



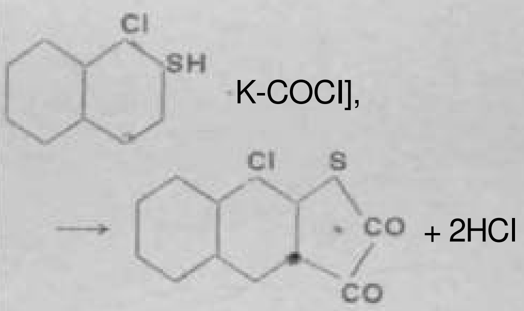
Wlien, hofrever, a 2-anil or 2-chloride of fchioiaatin is[1] used for condensation, a dye of true indigoid type ja obtained. There are unconfirmed statements in patents, however, that **tfakriaatm** it-self will condense in the 2-poaition, *e.g.* with accnaphthonone *(eee* G.P. 220244, Society of Chemical Industry in Baale), or with oxindole (G.P. 241327, Kalle & Co.), and the mutter is, therefore, in an undeejdetl state.

Anils of **She** tliionaphthenqui nones can also be obtained by the action of aromatic nitroso-compounds on thioindoxyl. From y-nitroaodimethylaniline and thioindoxyl, the »-dime thy 1-aininoatul (below) is readily obtained, and frequently figures in the patent literature us an



inter mediate for the preparation of indigoid dyes of many kinds (we B.F. 17498/1908, B.A.S.I'.; *also* **Pnmmerer,** Ber. 1'JIO, 43, 1370).

Thioisatins, especially naphththioisatins, are also obtained by condensing a thionaphthol with oxalyl chloride (B.P. 214864, Society of Chemical Industry in Basle), thus :

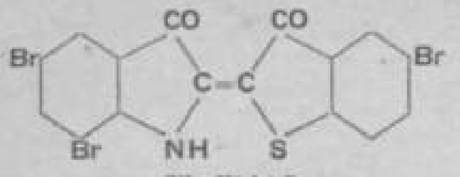


There do not appear to be any tommerciiil examples of asymmetric thioindigoid dyes, although during the last 20 years a great **many** have been patent*! by **German** and Swiss firms.

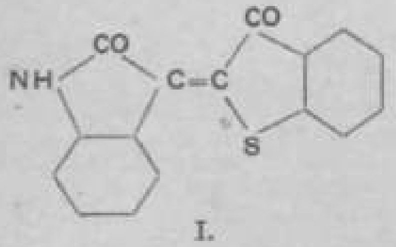
Selenoindigos.—**Dyeetuffp similar** to **the** thioindigoid dyes **anb** 'the thiophcnindole-indigos are known in which .selenium#.present in place of sulphur. I'hcnylselenoglycollic-o-carboxylic acid iB cyclised by acetic anlrydride (not by caustic alkuli) to 3-hydroxjfselenonapLthen, m.p. 76-77°, which is stable in air. In alkaline solution it reddens in air and is readily oxidised by potassium ferrieyaiffde to selenoindigo. This is reddish-violet in colour, sublimes without decomposition at 270° giving a violet vapour, and can be vatted and dyed like thioindigo. Asymmetric indigoid dyes can be prepared from 3-hydroxy.selenonaphtficn, or from selenonajihthcmjuinoiiL (a stable, red compound, m.p. 10^-103°).

Indigoid DyeJ of Mixed Types.—Just as Aatinanilide will react with an indoxyl to give u.'i indigoid dye, so it will react with a thiointloxyl to give a mixed indolethionaplittu-n-indigo, and conversely a thioisatinanilide will react with an indoxyl. More generally, the 2-chlorides and **2-anilidea** c^both isatin and **thioj** isutin will **react** w»th compounds containing reactive methylene groups, and by this reaction many new indigiJid dyes are obtained. Such dyes can also be obtained by the interaction of cyclic* 1:2-diketones with indoxyU and thioindoxyla.

2-Iadole-2'-thionaphthen indigo is a violet dye of no interest because of its lack of fastness, but its 5:5'-dibromo-derivative is " *(Jifn Violet* 3if," and a tribromo-derivative is " *Ciba Violet B*" It should be noted that the shade is intermediate between those of indigotin and thioindigotin.



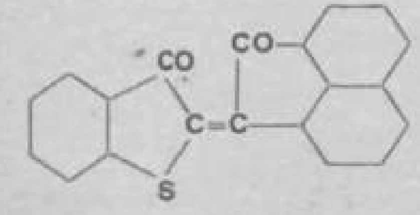
Ciba Violet B.



I.

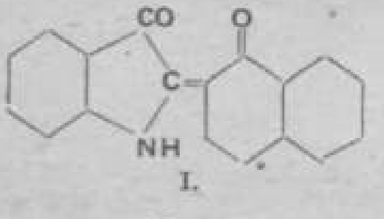
By **oaadetufcig** thioindoxyl with isatin a scarlet dyestuff (I), an analogue of indirubin, is obtained.

One of the most important dyes of this mixed series *is* obtained by condensing tliioindoxyl with acenaphtlienequinone, it has the formula

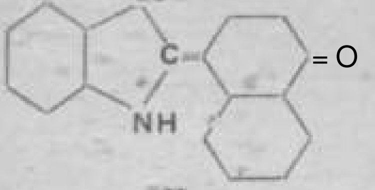


and is marketed as " *Ciba Scarlet G* " and " *Durindone Scarlet* 7." A uibro mo-derivative is " *Ciba Scarlet &.*"

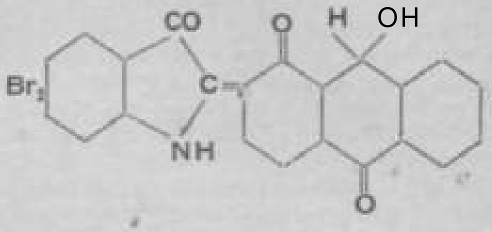
Another type of indigoid dye is obtained by condensing isatin-2-chloride or -2-aniJide with a-n&phthol or a-anthrol. P. Friedlander first discovered that indigoid dyestuffs could be obtained in this way (Ber. 1908, 41, 772). With a-nr^bthol two products are obtained in abov*[1] equal amounts, (I) and (II), but only {1) has the true indigoid structure. Dyes of type (II) are designated *fadoiiateau,* this* example being named 2-indole-1'-naphthalene-indolignone, F. Bayer *&* *Qo.* condensed bromoisatin-ct-chloride, and also brominated jS-naphthisatms, with o-naphtliol and a-hydroxyanthracene in this way (G.P. 237199), and Meister, Lucius und Bruiting, using a-hydroxyoxanthrone instead of a-hydroxy anthracene, obtained a dyestuff of presumably the following structure :



I.

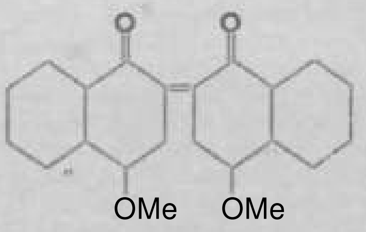


II.



[11] *Hdindone Blue SON* " is said to be a dye of this formula, whilst the above Bayer patent is said to cover " *Alizarin Indigo ZR* " and " G."

Mention may also be made of one or two dyes which fall into the indigoid class although containing neither an indolo nor a thionaphthen residue. By oxidation of 4-methoxy-a-naphthol by ferric chloride, F. Russig (J. pr. Chem. 1U00, fii], 62, *53)* obtained a blue dyestuff, having the formula (1), which can be dyed like indigo from *a* vat. The I.G. Farbenind. A.-G. have patented a process of dyeing fur in fast blue shades by oxidising 4-methoxy-a-naphthol on the fur to **this** dyestuff (B.K 4070t>6). Another dye of iudigoid- type, *Pyrazoh >3ltie* (II) was discovered by Knorr (Annalen, 1887, 238, 171) who showed its similarity to indigo.



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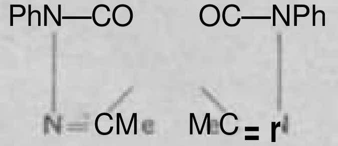
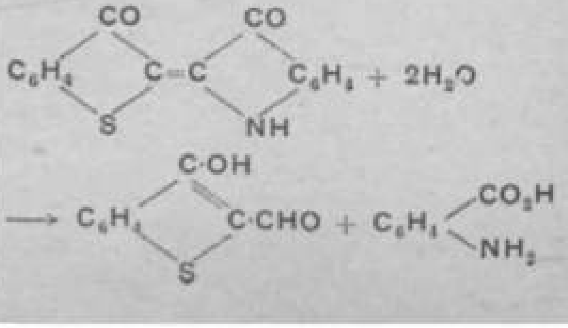


U.

Scission of Indigoid Dyes.—Many indigoid dyes can be split by heating with alkali into two components the iJcntification of which establishes the constitution of the dye.

Tlio bia-indolcindigos give by this treatment I nml. of a 3-liydroxyindolc-2-aldehyde and 1 **moL** of an anthranilic acid derivative, A thio-n;i[ilithen-indoleindigo gives the 3-hydroxythio-**naphthen-2-aldBhydB** and anthramlk ncid **thus** i



2-Naphthalene-2'-indoleindigo gives 1-naphthol-2-aldehyde. Thioindigo is more resistant than indigo to alkali fusion. With alcoholic caustic potash it breaks up giving thioindoxyl, thionaphthenquinone and the thioindogenide of 3-hydroxythionaphthen-2-aldehyde. Some of the* substituted thioindigos cannot be split in this way, the reaction being far from general.

Solubilised Indigoid pyes—Indigosols.-Indigoid dyes can be converted into sulphate e&ers of their leuco-compounds by the processes devised by Jtader and Sunder and by Scottish Dyes, Ltd., respectively, in the same way as indigotin itself *{see* Indigosols *imder* INDIGO, SYNTHETIC, this Vol., p. 449c). Different dyes-give esters of different stability, but many are stable enough to be used commercially, and they are sold under the generic names of " *Indigosols* " *(/.<?.)* and " *Soledons* " *(LCI.)* both of which ranges include solubilised indigoid and anthraquinone vat dyes. For the description of these dyes and their application, *see* F. Peterhauser (J. Soc. Dyers and Col. 1927, 43, 251), M. Bader (Chem.-Ztg. 1937, 61, 741, 763) and W. Christ (J. Soc. Dyers and Col. 1938, 54, 93). The use of these solubilised forms ttf vat dyes is continually extending. Whittaker and Wilcock, (" Dyeing with Coal Tar Dyes," 3rd ed., London, 1939, p. 172) state that it is their practice to make ever-increasing use of the Soledons and Indigosols in dyeing both viscose and cotton in the skein form on the roller type of skein-dyeing machine. Christ gives a list of 28 Indigosol dyes of which 21 appear to be indigoids, the remainder being solubilised anthraquinone vat dyes. The Indigosols from indigoid dyes* are colourless or only faintly coloured, whilst those from anthraquinone vat-dyes are deeply coloured.

Bibliography.—J. Martinet, " Matières Co]p rantes. Les Indigoides," Paris, J.-B. Baillière et Fils, 1934. H. E. Fierz-David, " Kiinstliche organische Farbstoffe," Berlin, 1926. Colour Index, edited by F. M. Rowe, 1924. Reports of Applied Chemistry, published by the Society of Chemical Industry, articles on Intermediates and Colouring Matters. For Germpyi patents, Friedlander, " Fortschritte der Teerfarbenfabrikation, 1877-1935," Theil. 1-22. '

E. H. R.

INDIUM. At. no* 49; At. wt. 114-76. Indium belongs to, the aluminium group, of the elements and was discovered by Reich and Richter in 1863'during the spertroscopic examination of some crude zinc chloride fcom a Freiberg zinc blende (J. pr. Chem. 1863, [i], 89, 441; 90, 172; 1864, li], 92, 480). The name *indium* was chosen because of the prominence of the two indigo-blue lines in its spectrum. Although occurring only in small quantities it is, like many rare metals, widely distributed in nature and is found in numerous zinc blendes, pegmatites, siderites ana in some tungsten, manganese and tin ores (Hartley and Ramage, J.C.S. 1897, 71, 533; Brewer and Baker, J.C.S. 1936, 1286; Romeyn, J. Amer. Chem. Soc. 1933, 55, 3899).

Extraction of indium is inevitably a tedious process which at some stage or other includes repeated or fractional electrolytic deposition of the metal. Separations from other metals are also based on: *(a)* the solubility of indium sulphide in 2-3N. hydrochloric or sulphuric acid and its insolubility in 0-5-0-8N. acid; *(b)* precipitation of indium sponge by means of zinc; (c) the insolubility of basic indium sulphite; *(d)* precipitation from alcohol of tha complex between anhydrous indium chloride and pyridine; (e) sublimation of indium tribromide; (/) precipitation of indium hydroxide with ammonia in the presence of ammonium salts. The most difficult impurity to remove is iron, although small amounts of it may be separated by extracting as ferric thiocyanate with ether (Reich and Richter, *I.e.;* Lawrence and Westbrook, Ind. Eng. Chem. 1938, 30, 611; Thiel, Z. anorg. Chem. 1904, 39, 119; 40, 290; Bayer, Annalen, 1871, 158, 372; Mathers, J. Amer. Chem. Soc. 1907, 29, 485; Dennis and Geer, *ibid.* 1904, 26,437; U.S.P. 1855455, 1886825, 2052387).

Physical Properties.—Indium is a silvery-white, readily malleable metal, ductile and softer than lead. It can be obtained crystalline, the X-radiogram indicating a face-centred tetragonal structure with 4 atoms per unit cell whose dimensions are a_0=4-583 (4-588)A., c_0=4-936 (4-946)A., a:c=1:1-077 (1-078) (Zintl and Neumayr, Z. Elektrochem. 1933, 39, 81; Dwyer and Mellor, J. Proc. Roy. Soc. New South Wales, 1932, 66, 234; Frevel and Ott, J. Amer. Chem. Soc. 1935, 57, 228); the atomic radius is 1-569A. (Goldschmidt, Z. physikal Chem. 1928, 133, 408), and the calculated density 7-308 (Z. and N.).

Two isotopes are known with masses 113 and 115, the relative abundances being 4-5 and 95-5%. For radioactive isotopes, *see* Lawson and Cork (Physical Rev. 1937, [ü], 52, 531).

Indium has a comparatively low m.p. (155°c.) and high b.p. (1450°c); rf" is* 7-31. Polished surfaces of the metal pocsess a high reflecting power making it suitable for mirrogs and reflectors.

Other physical properties are:

Compressibility (megabair^{1} x 10^{fl})=2-55 between 100 and 500 megabars pressure.

Hardness=1-0 Brinell. Tensile strength (99^1% metal)=15,980 lb. pir sq. in.

Average specific heat between 0° and 154° is given by Cp=0-0569+0-000013(<-18) g.-cal. per g.

Specific resistance (ohm-cm, x 10^{fl})=9 at 20° and 29 at 155°. The mean teiriperature coefficient between 0° and 100° is 490-4 x 10-^{5}. Indium becomes superconducting at low temperatures.

Spectra.—Indium* compounds colour the Bunscit flame a bluish-red while the flame, arc and spark spectra show two brilliant indigo-blue lines of wave-lengths 4101-8 and 4511·3A. respectively. Other prominent lines in the arc spectrum, are 2710-25, 3039-36 and 3256·06A. Lines due to singly and doubly ionised indium have also been mapptti (Paschen, Ann. Physik. 1938, [v], 32, 148).

For the *X-ray* spectrum, *see* Blake and Duane (Physical Rev. 1917, [ii], 10, 697), Vatesek *(ibid.* 1&29, [ii], 34, 1231) and Siegbahn (Jahrb. Radioaktiv. 1916, 13, 296).

Chemical Properties.—Indium reacts as a tri-, di- and mono-valent element, this being also the order of stability of its compounds so that only those of the trivalent series are stable in aqueous solution. The metal is unaffected by air at ordinary temperatures and is not attacked by boiling water or alkalis. Heated to redness in air or oxygen it burns with a blue flame producing the trioxide; sulphur, selenium and tellurium also combine with the heated metal, incandescence occurring in each case (Thiel and Koelsch, Z. anorg. Chem. 1910,66,315). Halogens react readily on warming. Indium is slowly soluble in cold and more readily so in hot dilute mineral acids; the attack of concentrated acids is more vigorous.

ALLOYS.

Numerous alloys containing indium have been produced largely with the desire to secure dental alloys, to impart corrosion-resistance to metals like silver and copper or to obtain fusible alloys. Indium amalgamates with mercury, and dental amalgam bases containing up to 50% indium have been patented (U.S.P. 1959668).

The silver-indium system has been closely studied, but the hope that such alloys might possess tarnish-resistance has not been fulfilled. Over 40% of indium is necessary to provide a completely tarnish-proof product aci such alloys are too hard and brittle to be of practical importance. Better results are claimed by plating the metal on to silver, but difficulties have been experienced through dull coatings and inability to secure a good polish. The addition of small amounts of indium to the precious metals improves their colour, hardness and strength. Some of the many alloys which have been made with copper possess precipitation- and heat-hardening properties (Weibke *et al.,* Z. anorg. Chem. 1934, 220, 273; 1937, 231, 197).

Indium has been recommended as a constituent of bearing-n: tals, in order to increase the res^tance to attack by organic acids derived from vegetable lubricating oils (B.P. 283862). Low-melting alloys are obtained by adding indiu*n to Wood's metal, the reduction in the melting-point of the latter being propoitional to the concentration of the rare metal, reaching a maximum with 18% indium, this alloy melting at 46-9°c.

Alloys have also been produced with magnesium, zinc, cadmium, gallium and lead as wejl as with the alkali metals.

SALTS.

Indium Trifluoride, InF_3.—Obtained as a white powder by heating ammonium indifluoride, $(NH_4)_3lnF_e$, or indium sesquioxide in a stream of fluorine; it melts at 1170° and has *d\\$^5$4-30.* It is very sparingly soluble in hot and cold water, yielding a slightly acid solution; in dilute acids it dissolves readily (Hannebohn and Klemm, Z. anorg. Chem. 1936, **229,** 337).

Evaporation of a solution of the sesquioxide in hydrofluoric acid apparently gives either a tri- or ennea-hydrated fluoride according, presumably, to the temperature of crystallisation. The trihydratc when treated witfii liquid ammonia yields the triammine **lnF_3,$3IMH_3$** (Thiel, Z. anorg. Chem. 1904, 40, 280; Klemm and Kilian, *ibid.* 1939, **241,** 93; Chabrié and Pouchonnet, Compt. rend. 11)05, **140,** 90).

Indium Chlorides.—The anhydrous *trichloride* $lnCI_3$ may be formed by the usual methods purification being by distillation in a current of carbon dioxide. So obtained it appears as white, deliquescent, lustrous plates, d^{25} 3*46, m.p. 586°. It volatilises readily above 600°, but at about 1100° dissociation to a lower chloride becomes evident. The chloride is slightly hydrolysed ire aqueous solution, crystallisation from solution being difficult; evaporation of the solution at elevated temperatures is said to yield an insoluble oxychloride. *Jndium oxychloride,* InOCI, has been made by Thiel as a sparingly soluble white powder by passing a mixture of oxygen and chlorine over the dichloride.

Indium trichloride readily forms double compounds with alkali chlorides ^ of the types $K_3[lnCI_6]$, $Rb_2[lnCI_5,H_2O]$; the caesium compound, $Cs_3[lnCl_6]$, which readily separates as octahedra, has been recommended for use in a microchemical test for indium.

Ammoniates containing 7, 5, 3, 2 and 1 molecule of ammonia per molecule of the trichloride are known, while. with pyridine in alcoholic solution there is produced a white cryotaUine precipitate of the complex **$lnCl_b$,$3C_5H_5N$.** Double salts have been obtained with many other organic bases (Ekcley and Potratz, J. Amer. Chem. Soc. 1936,58, 907). •

Indium Qichloride is formed as a yellow liquid, solidifying to white crystals on cooling, by heating indium, indium trichloride or indium sesquioxide in a current of dry hydrogen and hydrogen chloride: m.p. 235°, b.p. ~ 570°, d_4 3*64. It is probably associated in the solid state, but between 500° and .700° it exists as undissociated simple molecules. In contact with water it decomposes into indium and indium trichloride. Aiken *et al.* (Trans. Faraday Soc. 1936, 32, 1617) state that the action is one of disproportionate into I n CI + I n $C1_3$ followed by the reaction $lnCI\text{-}{>}ln{+}lnCI_3$. These authors regard the dichloride as being derived from the hypothetical " indichloric acid" $HlnCI_4$, the decomposition in water being represented thus:

$$\mathrm{In+[InCl_4]-=In++In+{*}M-4Cl-}$$

Reduction of the dichloride or trichloride by heating with the metal leads to the formation of *indium monoSdoride,* InCI, which is a dark-red solid, d_4^{25} 4-18, melting to a blood-red liquid. AH indicated above it is decomposed by water, yielding indium and indium trichloride (de Boisbaudran, Compt. rend. 1885, **100,** 701; Thiel, *I.e.*; Ber. 1904, 37, 175; Nilson and Pettersson, Z. physikal. Chem. 1888, 2, 657; Klemm and co-workers, Z. anorg. Chem. 1927,163, 225, 235, 240; 1934,219,42; Robert and Wehrli, Helv. Phys. Acta, 1935, 8, 322).

Indium Bromides.—The three bromides corresponding to the above chlorides have been prepared and resemble them in properties. The lower bromides are less easily decomposed by water, so that although the dibromido is readily converted into the tri- and mono-salts heating is necessary to change the latter into the metal and tribromkie, Double compounds are formed between the tribromide and alkali or ammonium bromides, while ammoniates containing 15, 7, 5 and 3 molecules of ammonia are known.

Indium Iodidės.—Indium di-iodide has not definitely been isolated, but the tri- and monovalent derivatives have been made. The *mo.\o-iodide* is stable to hot water but dissolves in dilute acids with evolution of hydrogen (Thiel, *l.c.;* Z. anorg. Chem. .1910, 66, 288; Klemm *et aL₉ I.e.).*

Indium Sesquioxide, ln_2O_3.—Ignition of the hydroxide, carbonate, nitrate or sulphite at comparatively low temperatures yields a pale yellow amorphous oxide which, according to Renz (Ber. 1903, 36, 1847), is converted into yellow, trigonal crystals, isomorphous with those of ferric oxide, on heating at high temperatures in air. The two modifications differ considerably in their solubility- in dilute acids, the crystalline form being so resistant that it can be separated from the amorphous variety by boiling with dilute sulphuric acid. Heated above 850° and without free access of air the sesquioxide begins tq decompose slowly and then appears white, owing to a thin superficial film of the lower oxide ln_2O. According to Thi& and Luckmann (Z. anorg. Chem. 1928,172, 353) the purest form of oxide is obtained by heating the hydroxide at 850° to constant weight and then heating in air at 1000° for half an hour. So prepared, its density is said to be C-75±0·01, but Klemm and .Von Vogel *{ibid.* 1934, 219, 45) give it as 7·04 while other values up to 7*18 have also been reported.

Indium Hydroxide, $In(OH)_3$.—White, colloidal precipitate produced when solutions of indium salts are treated in the cold with aqueous ammonia, alkalis or hydroxylamine; heating the mixture or precipitating from hot solutions yields a dense, granular precipitate. The freshly deposited amorphous form is slightly sdluble in excess of ammonia and readily 8(5 in excess of alkali hydroxide; reprecipitation occurs on boiling or adding ammonium salts. Both the colloidal and granular forms show the same .X-ray diffraction pattern ar/i are the hydrous trihydrate or hydroxide (Weiser and Milligan, J. Physical Chem. 1936, 40, 1; J. Amer. Chem. Soc. 1937, 59, 1670).

In addition to its* basic properties, indium, hydroxide also possesses weakly acid Junctions; the product obtained by careful drying at about 150°, which has the composition $InO(OH)$, may be regarded as metaindic arid, $HlnO_2$. A magnesium mctaindate, $Mg(lnO_2)_2,3H_2O$, was obtained by Renfc (Ber. 1901, 34, 2763) by boiling a solution of indium and magnesium chlorides; the white powder so produced is Lisoluble in water but dissolves in dilute*acids.

Lower Oxides of Indium.—Winkler stated that on heating the sesquioxide in hydrogen at 300° a.Jriack oxide, ln_3O_4, was formed, while the preparation of intermediate oxides, ln_7O_9, ln_4O_6, etc., was also claimed. Thiel and Luckmann (I.e.) found, however, that there was no interaction at 300°, but that at 500° a bluish-black material was formed consisting of crude ln_2O. This substance could be purified by subliming in a high vacuum at a temperature of 650-700°, and in thin transparent films bad a yellow colour although thicker layers formed a black, brittle ajid fairly hard mass of density 6·34 (Thiel and Luckmann) or 6·99 (Klemm and Von Vogel). This oxide is stable to cold water but dissolves in hydrochloric acid with evolution of hydrogen. Heated in air it glows suddenly and is converted into ln,O«; it does not melt below 1000°.

The residue left after subliming the ln_2O is a dirty-white powder the composition of which agrees with the formula InO, but it has not been obtained sufficiently pure for its identity as an oxide of bivalent indium to be established.

Indium Sesquisulphide, In_2S_3.—Prepared by heating the metal with excess sulphur, by passing hydrogen sulphide over the heated oxide or by precipitation with alkali or hydrogen sulphide from neutral or faintly acid solutions of indium salts; in the last method it is necessary to remove excess of sulphur by heating the product in an indifferent gas. According to the method of preparation it is yellow to brown in colour. It is appreciably volatile at 850°, but some decomposition takes place as the sublimate contains free sulphur and a brownish-black substance, presumably ln_2S. Heated in a sealed tube the sesquisulphide melts at 1050°, the melt solidifying on cooling to a black mass, density 4·89, which is red when finely divided. The sulphide dissolves in concentrated acids and is converted to the oxide on roasting in air.* Double salts, $KlnS_2$ aifd $NalnS_s,H_2O_f$ have been made.

Lower Sulphides of Indium.—ln_2S is formed by subliming *in vacuo* the orude slate-grey material obtained by heating indium with a slight excess of the theoretical amount of sulphur at 450° i? carbon dioxide. It is yellow in thin layers but thicker films are black with a metallic lustre; m.p. C93°,>/ 5-951 (5-87).

Sublimation *in vacuo* at 850° of ttoB product made by heating molecular proportions of indium and sulphur yields only ln_2S and S. The slate-grey colour of the crude Material differs from that of the reddish-bro^9, soft mass formed by passing hydrogen sulphide over the heated metal and which Thiel and Koelsch (Z. anorg. Chem. 1910, 66, 314) stated was InS. Klemm and Von Vogel *(l.c.)* give 5-18 as the density of this sulphide (Meyer, Annalen, 1869, 150,137; Thiel, *l.c.;* Thiel and Luckmann, *I.e.).*

Indium Sulphite.—A basic sulphite,

$$ln_2(SO_3)_3,ln_2O_3,8H_2O,$$

is obtained as a crystalline powder on boiling a Solution of an indium salt with sodium bisulphite.

Indium Sulphate, $In_2(SO_4)_3$.—Concentration of a solution of the metal or hydroxide in a large excess of sulphuric acid yields diamond-shaped crystals of an acid indium sulphate, $ln_2(SO_4)_3,H_2SO_4,7H_2d$: The salt is stable under ordinary conditions but evolves sulphuric acid above 250° leaving a residue of the anhydrous normal Sulphate. Slow evaporation of an aqueous solution of this residue leadf to the sepaAtion of small prismatic crystals of $ln_2(SO_4)_3,9H_2O$. Addition of alcohol to the aqueous solution precipitates a basic salt, $ln_2O(SO_4)_2,6H_2O$ (Seward, J. Am«r. Chem, Soc 1933,55,2740).

A number of double sulphates have been prepared, including the ammonium, rubidium and caesium alums, $M_2SO_<,ln_s(SO_4)_3,24H_3O$ (M==NH^, Rb or Cfi). These crystallise in the usual regulaf octahedra and have low melting points, that of the rubidium salt being 42° and of the ammonium aiuro 36° (37-38°). Solutions of the alums react acid and deposit basic sulphates or indium hydroxide on heating.

The soHinm and potassium alums have not been made, but double sulphates of the type $Na_2SO_4,ln_{:!}(SO_i)_3,8H2O$ are known, as are also the corresponding thallous n,nd ammonium compounds. The ammonium double salt is the stable modification above,, the melting-point of the ammonium indium alum in the system $(NH^)_2SO_4$-$ln_2(S0_4)_3$-H_2O. The melting-point of the alum is also the transition point. Double salts with certain organic baRes have been made (Reich and Richter, *I.e.;* Meyer, *I.e.*; Nilson and Pettersson, Compt. rend. 1880, 91, 232; Chabrie" and Eengade, *ibid.* 1900, 131, 1300; 1901,132,472; Roessier, J. pr. Chem. 1873, [ii]$_f$ 7, 14; Soret, Arch. Sci. phys. nat. 1885, [iiij, 13, 5; 1888, [iii], 20, 520; 'Hnttnx and De Vries, J. Amer. Chem. Soc. 1936, 58, 212fi; Ekelpy and Potratz, *ibid.*, p. 907).

Selenium and Tellurium Compounds of Indium.—A complete range of tri-, di- and ^mono-valent selcnides and telluridee has been **obtained** by synthesis, while the sesquiselenide ln_2Se_3 is also formed as a brown precipitate on passing hydrogen selenide into a solution of indium acetate (Thiel and Koelach, *I.e.*; Klemm and Von Vogel. I.e.).

Hydrated selenites and selenatcs have been prepared, and the formation from the selenate of a caesium selenium alum, •

$$Cs_2SeO<, In_s(fieO_4)_{ai}24H_aO,$$

has been»..ported although this compound is said to crystallise in tetragonal pyramids (**Mather** and fiehluederberg, J. Amer. Chem. Soc. 1908, 30, 215).

Indium Nitride, InN.—Raid to be formed on heating ammonium indium fluoride at 600°. X-ray analysis indicates that it has an hexagonal, wurtzite lattice, the calculated density being 6-91 (Juza and Hahn, Z. anorg. Chem. 1338, 239, 282; Angew. Chem. 1938, 51, 189).

Indium Nitrate.—A solution of indium nitrate produced by dissolving the metal, oxide, hydroxide or carbonate in nitric acid de**posits** crystals on concentration with greater **difficulty** the more nearly neutral is the solution. In the presence of nitric ficid the hydrate $ln(NO_3)_3,41HjO$ separates fairly readily as colourless, deliquescent necdleB readily soluble iti **WSter;** tin's salt loses two-thirds of its water of crystallisation when heated at 100°. Attempts at complete dehydration, using higher temperatures, result in Bome decomposition of the nitrate (Winkler, J. pr. Chem. I8B7, fi], 102, 292). A white double nitrate has been obtained with ammonium nitrate (Dennis and Geer, J. Amer. Cii.Mi. **Boe. 190*.** 26. 437). ';

Indium Carbonate.—Addition of alkali earbonnte to aqueous solutions of indium salts precipitates u white compound, insoluble in exce38 of precipitant but soluble in ammonium carbonate solution. This precipitate is stated to be indium carbonate but the substance has not received careful study (Winkler, J. pr. Chera. 1807, [i], 102, 273).

OBOANIC COMPOUNDS OF INDIUM.

Indium Trimethyl, $In(CH-)_3$.—Obtained when indium, mercury dimethyl and a little mercuric chloride are treated together in dry CO_S at 100° for 8 days. Excess mercury dimethyl is distilled off and the residue purified by sublimation. The indium trimetjiyl forms colourless acicular crystals, m.p. 89-89·5°, which are easily decomposed by water, air or oxygen. Cryoacopic measurements in benzene indicate molecular association to $[ln(CH_s)]_4$ altluugh it is monomeric in the vapour state {Dennis ***a** al.,* J. Amer. Chem. Soc. 193-}, 56, 1047; Laubengayer and Gilliam, ***ibid.*** 1941, 63, 477).

Indium Triphenyl, $ln(Ph)_3$.-—Formed by heating indium and mercury diphenyl at 130° in a scaled tube, extracting the mass with chloroform, filtering and concentrating until colourless needles are obtained. Schumb and Crane *(ibid,* 1938, 60, 300), carrying out the operations in an atmosphere of CO_a, found ^heir product melted at 291° but Gilnian and Jones *(ibid.* 1940, 62, 2353) using nitrogen give 208° as the melting-point and, moreover, they show that indium triphenyl is slowly decomposed by COg. It also reacts with water, oxygen and a number of organic compounds. Successive addition of bromine leads to the formation of diphcnylindiura bromide, pheny I indium dibromide and indium tribromide; similar reactions occur with iodine. The halogen derivatives are buff-coloured powders. Diphcnylindium chloride and pheny]indium oxide hav? also been reported (Goddard in Vol. XI of Friend's " Text-book oflnorganic Chemistry ").

Indiurn Acetylacetone, $ln(C_5H_7O_2)_3$.—**Obtained** by heating indium hydroxide with alcoholic acetylacetutic and concentrating **the** solution. It is dimorphous, one forin being isomorphous with ^-gallium and scandium acetylacetones and the other with ferric acetylacetone. It can be sublimed at 140°under 10 mm. pressure; the melting-point is 183° (Chabrie and Eengadc, Compt. rend. 1900, **131,** 1300).

Numerous salts of organic acids have been made of vhich indium t.irtrate.js said to possess preventive and curative properties against certain forms of experimental trypuiKisomiasis (Meyer, *'I.e.*; Ekelcy and Johnson, J, Amer. Chem. Soc. 1935. 57, 773; Levaditi *el al.,* i'<.$_m$pt. rend, 1932,**194,** 325).

G. R. D.

INDOCYANINES (Vol. I, *Slid;* Vol. I1l, 519c). .

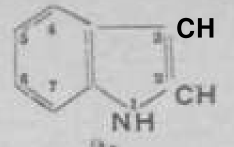
INDO1NE BLUE (Vol. I, 576c).

INDOLE (as perfume). This body, a parent of the indigo group of compounds, is a, liquid of powerful and disagreeable odour, but in minute quantities acts, like civet and ekatole, as & strong fixer of perfumes, and the odour disappears on dilution. Por its determination in essential oils, aee Parry's " Chemistry of Essential Oils," Vol. 11, p. 292.

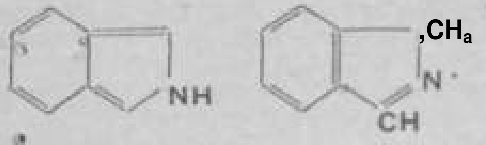
K. J. P.

INDOLENINE YELLOW (Vol. Ui, 519</}.

INDOLES. Compounds containing a 5-membered pyrrole ring fused to a benzene ring. Two structures are thus possible, indole and



I.

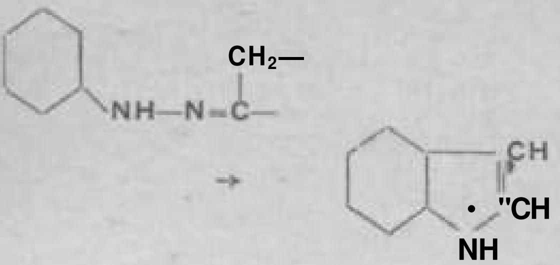


(a) II. (b)

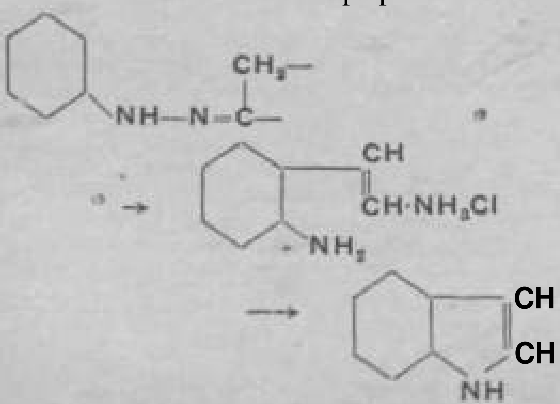
isoindole, (I) and (IIb) respectively; the second possibility is not encountered among simple compounds and even the isomeric pseudo-isoindole system (IIa) is unstable in its simple representatives.

The indole group is of considerable importance in natural economy—indigo, tryptophan and skatole are naturally occurring indoles—and is becoming increasingly important in **technical** practice.

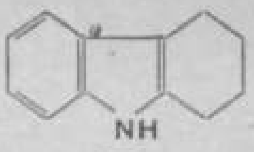
General Syntheses.—(1) The phenylhydrazones of carbonyl compounds containing the grouping —CO—CH_2— are treated with condensing agents such as zinc chloride, copper chloride or acid:



and the elimination of ammonia may in some cases be effected catalytically (Arbusow, Saize w and Rasumow, Ber. 1935, 68 [B], 1792). The reaction is thought to involve (1) the transformation of the hydrazone into an unsaturated hydrazine; (2) the benzidine-type rearrangement of the resulting hydrazine; (3) ring formation by elimination of ammonium salt from the product (Robinson and Robinson, J.C.S. 1916, 113, 630; **1924,** 125, 827; *cf.* Campbell and Cooper, ibid. 1935, 1208), although many other mechanisms had been proposed earlier:



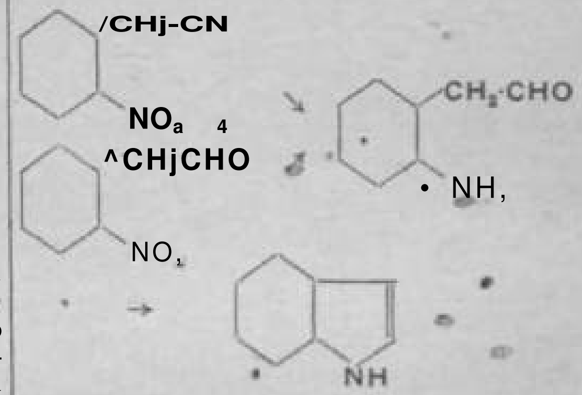
The reaction cannot be applied to the formation of indole itself, but the phenylhydrazone of acetone affords 2-methylindole in moderate yield. Generally the carbonyl component may be aldehydic or ketonic, even a-ketoacids reacting in this way; a variety of substituted aryl hydrazines and secondary hydrazines have been employed, the reaction usually proceeding still more readily with the latter. When the ketonic compound is a cyclic ketone the final product is trinuclear; thus the phenylhydrazone of *cyclo*hexanone yields 1:2:3:4-tetrahydrocarbazole **(III).** For recent applications of the synthesis,



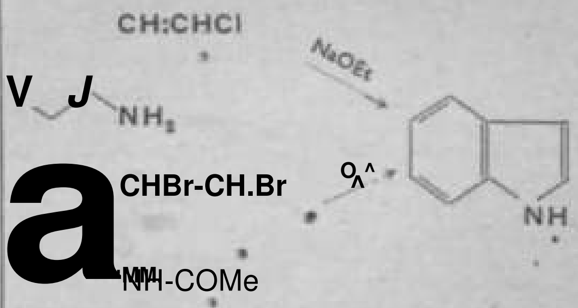
III.

see Julian and Pikl (Proc. Indiana Acad. Sci. 1935, 45, 145); Moggridge and Plant (J.C.S. 1937, 1125); Hughes and Lyons (Proc. Roy. Soc. New South Wales, 1937-38, 71, 475).

(2) Many synthetic reactions depend upon the internal reaction of an aromatic amine with a reactive or the **—C-C-X** group. Thus reduction of o-nitrophenylacetonitrile, o-nitrophenylacetaldehyde (Stephens, J.C.S. 1923, **127,** 1874; Weerman, Annalen, 1913, **401,** 12) results in ring-closure. Indole is also formed by ring



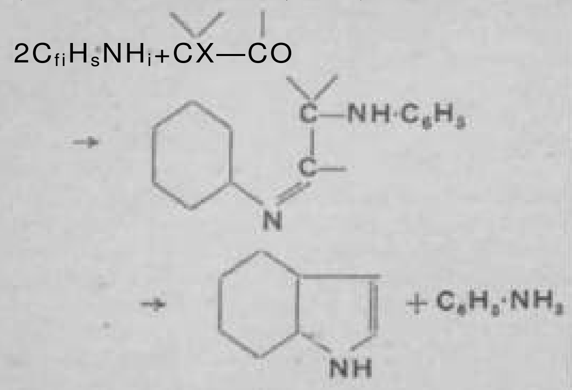
closure of o-amino-ω-chlorostyrene or o-acetaminostyrene dibromide (Lipp, Ber. 1884, 17, 1072; Taylor and Hobson, J.C.S. 1936, 181):



(3) The calcium salt (Mauthner and Suida, Monatsh. **1889,** 10, 252), or better the alkali salts of phenylglycine, afford indole on fusion, preferably in presence of reducing agents (G.P. 152083).

(4) The reaction of aromatic bases with

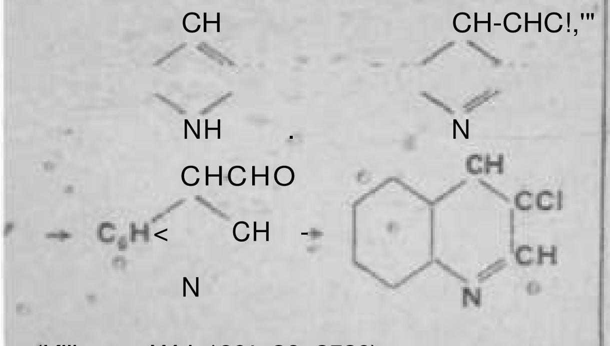
a-halogenated ketones is of general application (Bischler, Ber. 1892, **25,** 2860):



A similar reaction ia the production of indole by reducing o:tLi-dinitrostyrene with iron, zinc dust or aluminium amalgam (Van der Lee, Rec. trav. chim. 1925, 44, 1089). A recent method consists in nitrating phenylethyl chloride, reducing the o-nitro-compound with hydrosulphite and finally treating the amine with hexamethylenetetramine {Russ. P. 48309).

Properties.—Indoles are feebly basic, in nature and participate in most of the reactions of pyrroles although they are less sensitive than the simpler compounds. Thus they form alkali metal compounds (Weissberger, Ber. 1910, 43, 3521) and can be poly nerised in contact with acids, tri-indoles being well characterised products (for constitution, *see* Schmitz-Dumont *et* ol., *ibid.* 1630, 68 [B], 323 j 1933, 66 [B], 71; 1935, 68 [BJ, 240; *3.* pr. Chem. 1931, [ii], 131, 146; **132,** 39; 1934, [ii], **139,** 167; Annalen, 1933, **504,** 1; 1934, **514,** 267).^

Towards strong .substituting reagents indoles usually react abnormally, but with weaker reagents substitution occurs in the 3-position when that is free. Thus iodination or chlorination (using sulphury! chloride; Pauly and Gundtrmann, Ber. 1908, 41, 4007; Mazzara and Borgo, (iazzetta, 1905, **35,** ii, 564, 566) affords. 3-halogenoiIdoIes and alkyl nitrites or nitrates yield " nitroso- or 3-uitro-derivatives (Angeli and Marchetti, Atti. II. Accati. Lincei, 1907, [v], 16,1, 381; Angelico and Velardi, *ibid.* 1904, [v], 13, I, 242). 1-Acetyl- and l:3-diacetyl-indoles are obtainable by direct acetylation (Zatti and Ferratini, Ber. 1890, 23, 1359). Indoles undergo typical pyrrole reactions with chloroform and alkali to yield 3-formyl-indoles and, by intermediate rearrangement, 3-chloroquinolines:



(Kllinger. *Wd.* 190^, 39, 2520).

Indoles containing a free 3-pouition react with diazonium salts and also with Grignard compounds, and from the products of the latter reaction 3-substituted indoles can be obtained. Aldehydes of the indole series are readily prepared by the action of methylformylanilide on indoles in the presence of a condensing agent (I.G. Farbenind. A.-G., F.P. 773255), 1933).

Indoles are readily hydrogenated first to 2:3-dihydroindoles (G.P. 623693), then to perhydroindoles and finally on d.^stic hydrogenation ±he 5-membered ring suffers fission with production of o-alkylanilinea; this fission is less readily effected when the pyrrole ring is highly alfcy-Jatcd (*see* Von Braun and Bayer, Ber. 1925, 58 [B], 387). ' "

Jndole forms 2-5% of the oil extracted by fat from picked jasmine flowers, and 100 g. df the flowers liberate es much as 5-6 nig. of indole in a confined space (CerigheUi, £k>mpt. rend. 1924, 179, 1193); it has also been detected in several other plant products, *e.g.* in M longoza " oil (Madagascar) (Trabaud and Sabetay, Perf. and Essent. Oil Rec. 1938, 29, 142; *see also* GiJdemeister and Hoffmann, "JJie Aetherischeu Oele," 3rd ed., Vol. I, p. 677). Indole is also found in coal tar (Weissgerber, Ber. 1910, 43, 3520), and together with akatole is a constant product of biological degradation of protein by pancreatic or bacterial digestion (*literature*: EUingerin Abderhalden, "Handb.d. biol. Arboitsmethoden," Abt. I, Teil 7, 1923, p. 779) ancl is therefore frequently found in products of animal origin, *e.g.* normal perspiration contains 0^003-005% of indole (Labhardt, Zentr. Gynak. 1924, 48, 2626) and sewage and sludge may contain 0-25 parts per billion and 0-8 p.p.m. respectively [Rudolfs and Ingols, Sewage Works J. 1938, 10, 653). As tryptophan *(v. infra)* is also a constant constituent of protein it is not surprising that it is also degraded by bacterial action ty indole. With some strains of bacteria (''' indole negative ") degradation only proceeds as far as indole-3-acetic acid and the positive Ehrlich reaction is only observed if " indole positive " bacilli are employed (*literature*: Mckel in Abderhalden, " Biochem. Handlexikon," Bd. XII, 1930, p. 234).

In addition to methods indicated above, indole may be obtained by extraction from coal tar [G.P. 223304, 454696) but **jje** usually prepared by sing phenylglycine o-carboxylic acid with caustic a^ah" at 280-290° (G*». 85071) or at 250° under reduwd pressure (G.P. 152548, 260327],(.

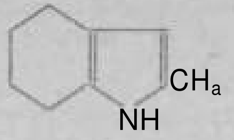
Indole forms leaflets, ni.p. 62°, b.p. 253-254°, which are volatile in steam. In addition to chemical transformations indicated above, indole may be directly oxidised to indoxyl by activated oxygen and eventually to indigo (G.P. 1306291.

In ***vtnr*** of the occurrence of indole in body luids a large number of qualitative tests for it have been proposed (*literature:* Hoppe-geyler and Thierfelder, " Handb. d. phvsic\- und mtholog.-chem. Analyse," 9th ed,, 19*24, pp. 307, t3£S; Oppenheimer, "Handb. d. Biochem. d. Menschen u. Tiere," 1924, Vol. I, p. 255; Abderbalden, "Handb, d, biol. Arbdtsmethoden," Abt. I. Teil 4, 1923, p. 831; **Tail** 7,). 783). Tosatti (Biochim. Terap. Bperim. 1935, KB, 286) Btates that the Ehrlich- reaction with >-dimethylaminobenzaldehyde, which Happold and Hoyle (Biochem. J. 1934, 28, 1171) have used in the colorimetric assay of indole, surpasses all other known reactions and will detect 1 part in 5,000,000.

Pure indole may be titrated with iodine (Pauly and Gundermann, Ber. 1908, 41, 4007)' but there would seem to be no methods for its exact determination in mixtures. Larger quantities are estimated approximately aa the picrate (Hesse, Ber. 1899, 32, 2612); smaller amounts, e.0. in bacterial cultures, are distilled in steam and **es^matod** colorimetrit-ally by the nitrite method {Moraczewski, Z. physiol. Chem. 1908,55, 45), by naphth&quinonesulphonic acid (Herter and Foster, J. Biol. Chem. 1906, 1, 257; BergeiuV *ibid.* 1917, 32, 17), or by Ehrlich's reagent (p-dimethyiaminobenzaldchyde) (Fellers and Clough, J. Bact. 1925,10, 105).

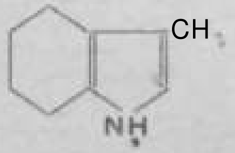
Indole has little direct application but is used in compounding artificial perfumes ((!.]'. 139822, 139869). Its presence in jasmine is said to be the prime reason for adding jasmine to tea, and indeed its detection in aromatic teas has been claimed aa an indication of quality (Wang, Ni and Chen, J. Chem. Eng. China, 1937, 4, 218),

2-*Mel kylijidole*



ia obtained from acetone phonylhydrazone (0.1?. 238138; Fischer, " Anleitung zur Darst. org. Praparate," 1922, p. 68), or from aniline and chloroacetone (G.P, 40889). It forms needles, in.p. 59°, b.p. 272°. Like **tndole** it is suitable for use as a perfume base (G.P. 139869), for the pi&-duction of azo colours (G.P. 141354, K-i>674, 163141) and of medicinal areenicals by direct reaction with arsenic acid (G.P. 240793}.

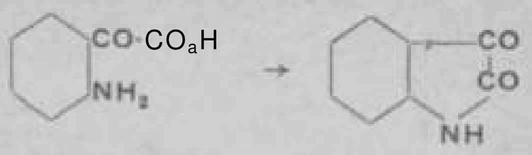
3-Afcthylindole, akatole,



which accompanies indolu jn nature? may be separated by its non-reactivity towards l:2-naphthaquinone-4-suIphonic acid (fferter and Foster, J. Biol. Chem. 19(16, 2, 267). Skatolo forms leaflets, m.p. 95°, b.p. 265°. It gives a purple or violet-red coloration with vanillin in concentrated hydrochloric acid (Blu men thai, Biochem. Z. 1909, 19, 527) which unlike that given by tryptophan is extracted by tohiene (KrauH, J. Biol. Chem. 1925. 63, 167) thus allowing a quantitative separation.

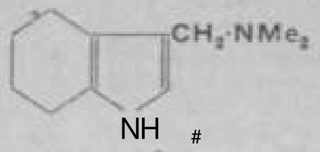
Hydroxjvderivatives of indole having hydroxyl groups in the pyrrole ring are of significance in that they arc intermediates in almost all syntheses of indigo (t. IKDOXYI. COMPOUNDS).

Isatin, 2:3-diketoindoline, behaves in many reactions as the laetam of isatinic acid, in which form it exists in alkaline solution; its formation by reducing 2-nitrophenyl-propiolic, -glyoxylic and -pyruvic acids (Reinsert, Ber. 1904, 37, 1038) is then readily understood. It is obtained aa sodium isatinate by allowing limited



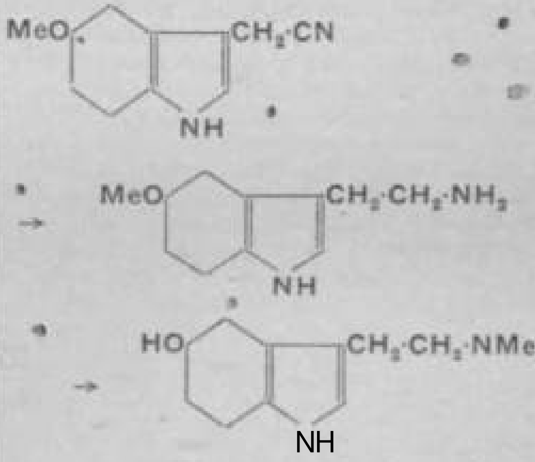
access of air during the fusion of phcnylglycme with alkali (G.P. 105102) or preferably by the action of hot sulphuric acid on oxiuiino-acetanilide {Sandmeyer, Hclv. Ciiiin. **Aota,** 191B, 2, 234; G.P. 320647 ; Organic Syntheses, Coll. Vol. I, 321) or iaatiq-2-anil (G.P. 113979). Isatin forms orange-red prisms, m.p. 200-201°. In addition to its direct interest in connection with indigo, isatin has also been used in the production of tluoindigoid colours (G.P. 182260; Bezdzik and Friedlaender, Monatsh. 1908, 29, 376; *cf.* the colour reaction with thiophen in concentrated sulphuric acid with formation of indophenin) and other *(e.g.* halogenated) indigos.

Qramine, donaxine (q.v.),



is an alkaloids directly derived from indole.

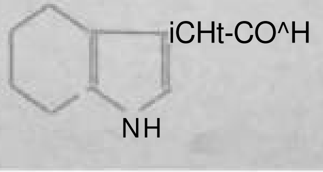
Bufotmine.—Of higher indolea bufotenine with **a** hydroxy] group in the aromatic ring is interesting as occurring in the secretion of the akin of toads (Wieland, Konz and Mittasch, Annalen, 1934, **513,** 1; Jens-m and Chen, Ber. 1932, 65 [B], 1310). It was synthesifved'by reducing 5-methoxy-3-cyanomethylirJHole, methylating the resulting base and deme thy luting the" pftenolic methoxyl with aluminium chloride :



ilufotenIn?

(r/. Hoshino and Shimodaira, Bull. Chem. Soc. Japan. 1936, 11, 22?; Annalen, 1935, 520, 19).

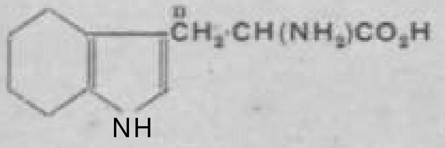
0-Indolyl-<l'(icetic acid.



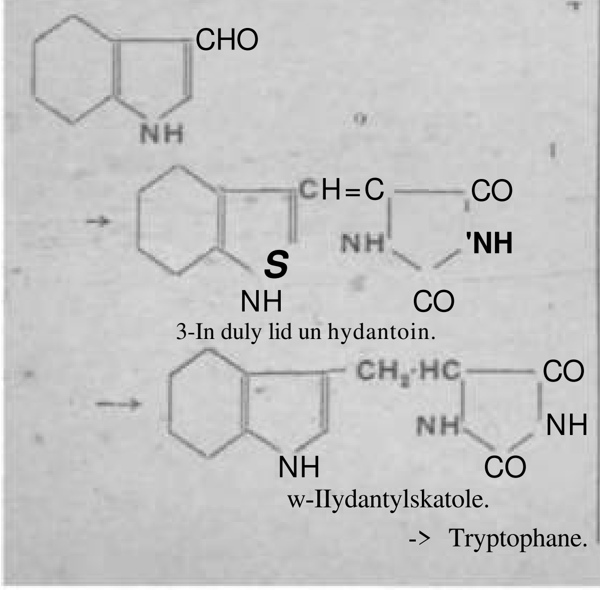
This acid has m.p. 1(54°, and is obtained by boiling the phenylhydrazone of 0-formylpropionie phenylhydrazide with dilute alcoholic sulphuric acid and hydrolysing the product (EUinger.'Ber. 1904, 37, 1806). It has for long been known to occur in normal and pathological urine, in the products of putrefaction of albumin, etc., and was for some time thought to be the chromogen in urine giving rise to " ururosein," the red pigment formed in presence of nitrous acid (EUinger and Flamand, Z. physiol. Chem. 1909, 62, 285; c/. Ewins *et aL,* Biochem. J. 1913, 7, 24; Homer, J. Biol. Chem. 1915, 22, 353). A number of micro-organisms grown under controlled cond'*,ions were observed to elaborate a factor which influences cell elongation in the *Avena* coleoptile. This compound, *heteroauxin* was isolated by KogI and his coworkers (Z. physiol. Chem. 1934. 228, 113) and shown to be identical with indolyl-3-acetic acid from urine *(ibid.,* p. 104). *v.* AUXIN and GROWTH PROMOTERS.

A number of 5:7-di-iodoindole-3-acetic, -propionic acids and other iodinated indole and oxindole acids have been prepared by the Fischer hydrazone method and used as X-ray contrast media for therapeutic purposes *G.V.* 425041, 459361, 436518; U.S.P. 1656239; Swiss P. 122243).

Tryptophan



is a constant constituent of protein, *e.g.* comprises 6-11% of the protein of human milk (Boccadoro, Pediatria, S9£J,30,257; see Abderhnlden, " Biochem. Handlexikon, Bd. XII, p. 693). • Its isolation by hydrolysing lactalburain with baryta is described by Waterman (J. biol. Chem. 1923, 86, 75), and it is conveniently synthesiaed by causing indole to react with ethyl magnesium iodide iifanisole; the indole magnesium iodide is .den converted into itidole-3-aldehyde by formic ester and thence through 3-indolylidenehydantoin and tu-hydantylskatole (Majima and Kotake, Ber. 1922, 55, 3859) to tryptophan:



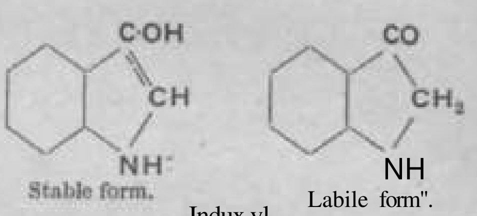
Racemic tryptophan has m.p. 289° and is slowly deaminated by acids with the formation of hum in-like materials,

Hypaphorine. is the betaine of tryptophan. *(v.* Vol. I, 6S6rf),

A. H. C.

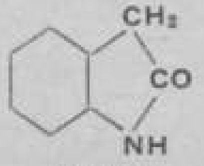
INDOXYL COMPOUNDS. *Indozyl* is a nitrogenous organic compound of both industrial and biological importance j industrial, because it is* an intermediate product in the technical synthesis of indigo; biological, because it occurs as a glucoside, *indkan,* in indigo-yielding plants (see INDIGO, NATU&AL), and also as a sulphuric ester in human urine.

Chemically, indoxyl is 3-hydroxyjndole, and is related to indole as o-naphthol is to ruphthalene. Indoxyl is a tautomeric substance, in that it behaves chemically as if it hadbUh structures (I) and (II). The stable form is the phenolic form (I)



Indux yl.

I. II.



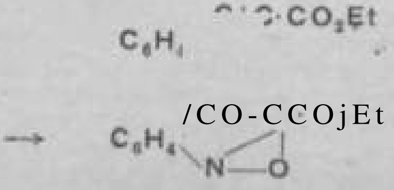
Oxindole.

III.

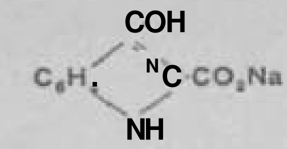
Whilst the isomeric oxindole is stable in the keto[1] ic form (III).

The plant glucoaide indican has been fully discussed under INDIOO, NATURAL. The first observation that human urine deposited a blue colouring matter under certain conditions is attributed by Thudichum (" A Treatise on the Pathology of LVine," London, 1877) to Janus Plancus, 1767. The &lue colouring matter was identified as indigo by Heller and Kletzinaki, and Baumann (Pflugc-a Archiv, 13, 291) with Brieger (Z. phyaiol. Chem. 1879, 3, part 4) isolated the chromogen froin urine and showed it to be the potOtssium salt of indoxyl sulphuric acid, decomposed by dilute acids into indoxyl and sulphuric acid (Baumann and Ticmann, Ber, 1880,13.415).

Indoxyl was first synthestsed by Baeyer (Ber. 1881, 14, 1741) from ethyl o-nitrophenylpropiolate, which with concentrated Htiljiburic acid undergoes rearrangement to ethyl isatogenate.



The latter by reduction yields ethyl indoxyUte, hydrolysed by caustic soda to sodium indoxylate (IV); with dilute acids this loses carbon dioxide to give indoxyl,

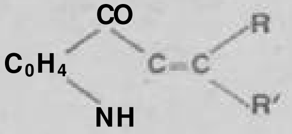


IV.

Alkali iudoxylates are also formed by alkali fusion "of phenylglycine-o-carboxylic acid; and phenylglycine itself forms indoxyl when fused with caustic alkali and sodamjde (see INDIGO, SYNTIJETIC). Many other syntheses are now known, for which textbooks should be consulted.

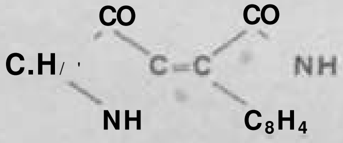
Indoxyl crystallises in bright yellow prisms, ra.p. 85°. It was obtained crystalline for the first time by Vorlander and Drescher *(ibid.* 1902, 35, 1702) by decomposing indoxylic acid with warm water iu an atmosphere of coal gas. It is soluble in water with a green fluorescence, which is destroyed by acids and strong alkalis. It forms alkali salts which can be isolated in presence of excels of alkali. It can be distilled with slight tleeo in position in steam, and has a fecal odour. It is very unstable, being oxidised in air, especially in presence of alkali, to indigotin, and it reunifies in presence of acids.

Indoxyl and indoxylic add react with aldehydes and ketones to form indogenidea of the general formula (I):



I.

Indogenide.

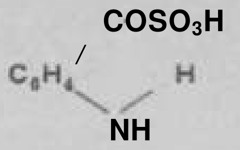


IntJirubin.

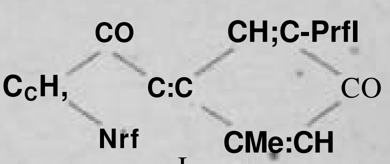
A special case of tin's **reaction** is the formation of indirubin (II) from indoxyl and isatin. Asymmetric indigoid dyes can be obtained similarly using a-anilidea of Matins or thionaphthenquinonc3 *(see* IKDIOOID DYES-TUFFS). Indoxyl also couples with diazo compounds, like a phenol, to give azo compounds (J. Martini* and 0. Dornier, Compt. rend. 1920,**170,** 502). These may be regarded as phenylhydrazine derivatives of isatir\ *Benzeneazoindoxyl* forms orange prisms, m.p. 240°. *H-Methi/Undozyl* has m.p, 57°. *N-Accttjliitdoxyl,* m.p. KHi°.

Indoxylic Acid is obtained as a white crystalline powder, m.p. 122-123°, by adding a solution of the sodium salt to ice-cold dilute sulphuric acid. It decomposes on melting with evolution of carbon dioxide. The *N-acetyl* derivative has m.p. 17fi° (deco'mp,).

Indozylsulphuric Acid,



occurs, as stated above, in human urine, as its potassium salt, which is referred to in the literature as " urinary indican," The free acid ia unstable but the *potassium* salt forms glistening leaflets from alcohol, in which it is sparingly soluble. Dogs fed on indole excrete the substance to a considerable extent in the urine. The indole is transformed into indoxyl in the liver, Houssay, Deutofen and llazzocco (Compt. rend. Soc, Biol. 1935, **119,** 875). Indoxyl may originate in the intestine, be stored in the blood and excreted by the kidneys (Houasay, Mazzocco and Potick, *ibid.* 1934,**117,**1235,1237). A method for the detection and colorimetric determination of urinary indican is given by A. Jolles (Monatsh.' 1915, 36, 457), depending on the oxidation of indoxyl with ferric chloride in fuming hydrochloric acid in presence of thymol, when a violet colouring matter is formed which can be extracted with chloroform and determined quantitatively by colorimetric comparison of the chloroform solution with a standard. Jolles considers that the violefc colouring matter.is 4-eyniol-2"indoleindolignone (I), An improvement on Jolles' method has been described by H. Sharlit (J. Biol. Chem. 1933, 99, 537), who uses potassium persulphate as oxidising^agent (which prevents pigment formation with sSatolo) and extracts the colouring matter **Witt** ethyl **tdohloroacetate.** The indican is detertuned colorimetrically by Viewing the solution so obtained through a green filter, and comparing with a 1-5% solution of **$CoSO_4,7H_aO$** which Has been standardised aguin.st a known amount of indican. A determination can be made on 10 c.c. of urine, and leas than 0-0025 ing. of indican can be detected. Jolles' method has also been examined by C. 0, Guillaumin (Bull. **Swc.** Chim. biol. 1935, **17,** 403) and T. Kuraon (Z. pbyaiol. Chem. 19:)5, 231, 205) has **faacxibed a** violet **compound of fndozy] with ninhydrin which** can be used for the colorimetrio deterniination of urinary indican.



I.

Indoxykulphuric acid c*i be prepared synthetically by the action of potassium pyro-" sulphate on potassium indoxyl {Baeyer, Bef. 1S81, 14, 1745), a«d by the action of chlorosulphonic acid on N-acetylindoxyl **in p^dina** (A. Jolles and E. tichwen'k, Bioc'hem. Z. 1914, 69,347}.

E. H. R.

INDUCTIVE EFFECT—The m^nifuuuee of the electronic theory of valency as a basis for the development of an electronic theory of organic chemical reactions is that it limits, by *tho* principle requiring the prpsorvflHoti flf stable electron groups, the forms of electron displacement which it is permissible to assume in **the interpretation of intramolecular clecti-ii-nl** interaction. Two methods have been suggested by which electron duplets may undergo displacement with the preservation ol" the atomic octets and without alteration of the original arrangement of atomic nuclei. The first method is characterised by the circumstance that the displaced electrons remain bound in their original atomic octets; displacements of this type were postulated in 1923 by G. N. Lewis,[1] who showed how the electrostatic dissymmetry, arising from the unequal electron attraction of two different atoms linked together, could be propagated along a molecule by a mechanism analogous to electrostatic induction. This mode of electron displacement was considered to apfly to a permanent molecular condition, therefore producing a permanent polarisation of the normal molecule: it has been called the *ht-ditctive effect."* It is commonly represented by the *use* of arrow-headed bond signs indicating the direction towards which the electrons are concentrated:

$$Cl \leftarrow CH_2 \leftarrow CH_2 \leftarrow CH_3.$$

Complementary to this mode of electron displacement is that which is characterised by the substitution of one electron duplet for another in the same atomic octet. This source of polarisation of the normal molecule is called the *vie&omeric effect.*[3] The two effects form the main pillars of the theory of the polarisation of normal molecules, which hat[1] direct application in the **interpretation** of the physical properties {dipole moment, iSagr'.etie susceptibility, refractivitv, nuclear and electronic spectra) of organic molecules, and the thermodynamics {heats and equilibria) of organic reactions. The same theory requires only to be supplemented by a closely analogous theory of polarisation accompanying activation in order to deal with the kineii)(:s (activation heats and rates) of organic reactions.

In the theory of the polarisation of normal molecules, and, in particular, in that part of the theory which deals with the inductive effect, electron repulsion and attraction are regarded as relative phenomena: by convention the standard of reference is hydrogen. A group X would be described as repelling electrons if in X—CR_3 the electron densities in tho residue CR_S are greater than in H—CR_a. Similarly Y is said to be electron-attracting if in Y—CR_3 the electron densities in CR. are reduced by «omparison with H—CR_3. Electron repulsions **are** conventionally 'distinguished by positive signs and attractions by negative signs, so that the inductive effects illustrated may be represented briefly by the .symbols +1 and - I :

X-*CR_3	H—CR_3	1' ← **CR_3**
(-t-I-effect.)	(Standard.)	(-I-effect.)

It is inherent in the idea of intramolecular electrical interaction that the inductive effect exerted by groups must be influenced to some extent by molecular **environment,** and although this offact is usually insufficient to change the qualitative behaviour of a substituent, it is convenient when **commencing** the task of classifying ittoniH and **groups** to set up the problem in a form in which the disturbance mentioned is minimal. Thia will be true if the groups considered are imagined to be singly present as substituents in a parar*n framework:

A major distinction must be drawn bctwei-r charged and neutral groups. Anionic groups, *e.g.* O -*, S -+•, as a whole are expected to repel electrons in comparison with neutral groups considered as a whole; and similarly cationic groups, *e.g.* R_aN •«-, R»S «-, as a class should attract electrons relatively to neutral groups as a class. The reason is that in anionic centres the atomic nuclei are over-compensated, and in cationic centres they are under-compensated, by the electrons of their own octets. Groups consisting of, or containing, forma] dipolar ions, *e.g.* -*• $\overset{+\ -}{NO_a}$, ->-$\overset{+\ -}{SOR}$, -*$\overset{+\ -}{NC}$, should attract electrons relatively to neutral groups, since the former are invariably joined through their cationic centres to the remainder of the molecule. The electron-attracting effect of such a forma] dipole should obviously be less than that of the corresponding free positive pole. It should be emphasised that these are general relationships, and that they take no account of the individual variations which may lead to occasional overlapping between the various series.

Individual **distinctions** depending on chemical type become apparent on considering a series of neutral groups. In the series -CH_3, **-NHj,** -OH. •F,, the total nuclear and electronic charges are the same, but the distributed (protonic) port inn of the''nuclear charge in 'CH_3 becomes progressively centralised in -NHjt **-OH, *F, which** therefore attract electrons from an attached atom successively more strongly in comparison with the methyl group (the polarity of alkyl groups is conside .-ed below). Again an atomic field is expected to suffer more loss through internal electronic deformation in larger than in smaller atoms, and thus inductive electron attraction should diminish along the series -F, •*Cl,* Etc 'I. A regular connection between the inductive effect and position in the periodic table of the elements is indicated in this reasoning, and if R is a non-polar or feebly polar group <H, Alkyl), then all groups such ad -NR_a, -OR, •SR, -Hat. :NR, :O, ˙.N, should attract electrons relatively to the methyl group. The extent of the attraction should increase with the **number** of thfl periodic group and decrease witth Increasing number of the period; it should also be greater in multiply-linked atoms than in the corresponding singly-linked atoms.

it can be deduced from the premises stated that the polarity of all alkyl groups is zero. **Thia** conclusion is, however, *a,* formal one, directly connected with the choice of the paraffin framework as a means of standardising the effect of molecular environment. A more significant conclusion conrrxnyij: alkyl groups is that, unlike the groups already considered (the intrinsic polarity of which renders their classification at least qualitatively insensitive to the dioturbance of molecular environment), alkyl groups will essentially exert those polar effects which are impressed upon them by the other groups presant in the molecule. In this connection the important property of alkyl groups is that they are much more polariflable than hydrogen, and thus -CH_3, although ft has no polarity in CH_a—CH_a, becomes an electron-repelling group in CH_3 -+ CO;H, and, in particular, it becomes so ii'hen * comparison is made between H P d CH_3-+CO_aH and H—CO_2H. Since the majority of substituents commonly encountered in organic molecules are attractors of electrons, alkyl groups generally function as weak electron-repelling gro(jps. They do this also in hydrocarbon structures such as toluene, though the cause in this case is more appropriately classified **with** the mcsoineric effect.

The conclusions reached in the preceding discussion are assembled for convenience in a table, in which the " greater than " sign, >, is used to indicate inequality.of magnitude of the inductive effect: *

Electron Repulsion. (+1):—

•NR>-6; •O>-8>*8e; Alkyl groups.

Electron Attraction (—**I**):— *t*

•ORj>-NR_3; •NR_3>-PR_a>-AsR_a>'SbR_s;

OR_2>SR_2>-SeRj>TeR_a;

•NR,> NOj; •86ıR>-S6R;

+- +-

•SO_1R>-SO_S; •

+ + •

•NR_3>NR,: OR_a>OR; -$8R_S$>-SR;

•F>OR>NR_{2i} F>Cl>-.Br>-I;

:O>:NR; :N>-CR;

:O>-OR; ;N>:NR>NR_a

REFERENCES.

1. G. N. Lewis, " Valence and the Structure of Atoms and Molecules," Chemical Catalogue Co., 1923, p. 139. *

2. C. K. Ingoldt Chem. Soc^ Annual Rep. 1926, 23, 129.

3. C. K. Ingotd and E. H. Ingold, J.C.S. 1926, 1310; c/. C. K. Ingold, *ibid.* 1933, 1120.

INDULINE SCARLET {Vol. **I**, 575d).

iNDULINES. (Colour Index NOB? 859-863.) Dale and Caro in 1863 and Coupier in 1867 observed that on heating ami no azo benzene hydroch!t>ride with aniline and its hydrochloride dark blue colouring matters were formed to which the name *IndttHnes* was given ; these are in soluble in water but dissolve in alcohol *(Spirit-solnbh Jndulines),* whilst the free bases are soluble in oils and fats. Sulphonation yields water-soluble acid dyes known under a large variety of names such as *Fast Blue, Solid Blue, Cotton Blue,* etc.

The first induline was prepared empirically by Dale and Caro (iJ.P. 3307. ISM) by **heati** iuiilme hydrochloride with sodium nitriU[1], but it was soon appreciated that amiripazobenzene was an **intermediate** product and tlmt by varying the conditions of formation different products could be obtained. The initial product is the so-called Azophenine (dianiliiiocjuinone dianil) which forms dark red crystals melting at 240°C, and on further heating yields successively Induline B, 3B and n'naBy 6B. On heating the spirit-soluble indutines first formed with aromatic bases other blue dyes of greater value are formed ; thus with jj-phenylenediamine the water-soluble *ParaphenyUne Blue* *is formed and with *p*-toluylenediamine water-soluble *Tolu.yle.ne Blue* is obtained.

Such water-soluble indulines may also be prepared by a modification of the induline melt by allowing ami noazo benzene, aniline and aniline hydrochloride to react together in concentrated aqueous solution, or by heating azobenzene with aniline hydro chloride, *p*-phenyl^ncdiamine and a little ammonium chloride,. Indulines are also formed as by-products in,other processes such as the oxidation of crude aniline in the magenta melt.

Alternative methods of preparation arc («) from phenols or quinones ami **amino&zo-compounds,** *(b)* from hydroxyazo-compounds and aniline, (c) from azobenzene an* aniline hydrochloride at 200-230°C, *id) by* the action of p-diaminea upon azo dyes derived from naphthylencdiumines, (e) by melting aminoazobenzene or preformed indulines with benzidine hydrochloride to produce substantive cotton dyes.

By the addition of nitrobenzene or nitrophenois to the melt greyish-IJue ***Nigroainea*** are produced ; following *tijtf* suggestion of Caro the name Induline is now reserved for those colouring matters produced from amines anaazo-compounds whilst the name Nigrosine is reserved for those produced from nitrobenzene or **Ditrapheojols.**

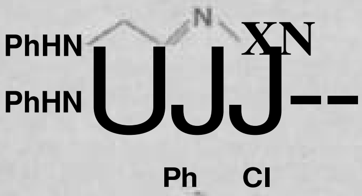
On a large scale the dyes are prepared by heating the required base dissolved iuQ-niline together with anilirftr hydrochloride (the " Indutinc melt "), the apparatus required consisting essentially of an enamelled still with oil heating, and provided with a suitable stirrcr and condenser. Some details of the process may be found in Ficrz-David, " Kuustlichc Organiwcho Farbstoffe " (1926), pp. **333~334,**

The uses of the spirit-soluble indulines are •ainly confined to the **preparation of** s-pirit lacquers and varnishes whilst the free bases are used for colouring candles, waxes, etc. For textile purposes some use is **made of the** indulines for cotton printing, the colour dissolved in acetin being known as 4fce(in., **fiftta,** *Printing Slue,* etc., and in ^()ite of **the** coin petition 01 newer and faster dyes the indulinea still retain some measure of importance since the dyeings on silk and cotton on a tannin mordijpt aro fairly^ast.

The constitution of the dyes formed in the induline melt remained long in doubt, but the researches of 0. Fischer and Hepp (Annalcn, 1893,272,306; 189f>,286, 187) and in **particular** the classical investigations of F. Kehrmnnn and his pupils (<•/. Kehrniann and Klopfenstein, Ber. 1923, 56 [Bj, 2394} have now solved the problem.

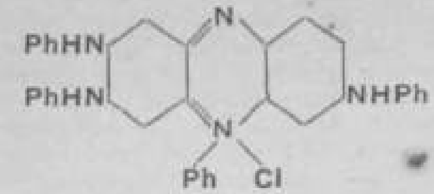
The essential components of the melt have been Bhown.to consist of various anilinophcnylphenosafranines:

Anilinopiienyl-'pkenosafranine, $C_{30}H_{24}N_6Ct$,



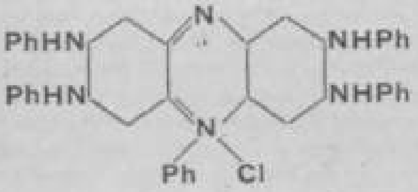
Indullue It.

AniUnodiphtnyl-j)he.noaafranine, $C_{36}H_{28}N_5Cl$,



Induline 3B.

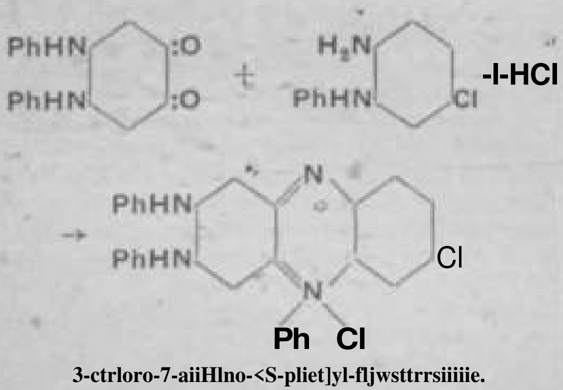
Dianilinodiphenyl-phenosafranine, $C_{42}H_{33}N_6Cl$,



Indulge 6B.

It is of course difficult* to carry out the melt in such *a* manner as to obtain homogeneous products and the commercial dyestuffs are therefore mixtures of the above substances in varying' proportions.

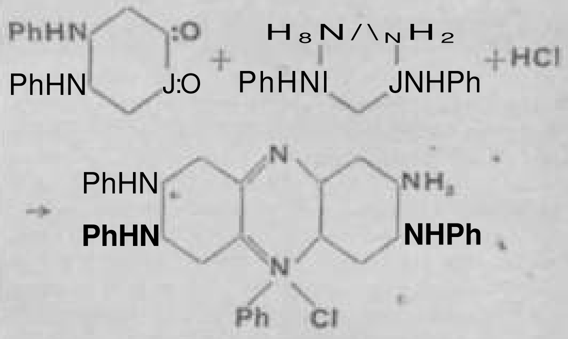
The pro>:f of tho accepted constitutional formula has been given by Kehrmann (Helv. Chira.'Acta, 1924, 7. 471;. 1925, 8, 661; Her. 1923, 56 [B], 2394), who by boiling 3-chloro-7-&nilino-6-phenyl-ap0safranine (from dianilino-o-quinone and 2-amiiio-5-chlorodiphenylanii!i'-hydrochloride) with aniline obtained 7-aniIiuo-3:6-diphenyl-phenosafranine, which is identical with Induline 3H,



3-ctrloro-7-aiiHlno-<S-pliet]yl-fljwsttrrsiiiiie.

$\xrightarrow{PhNH-}$ Iiiiliiliin- ail.

Using dianiliao-o-quuioue **and** aym-dianUinc* Mi-phenylenediamine the product is 2-amino-7-anilino-3:ti-diphenyl-phenosafranine which on heating with aniline and aniline hydrochloride yields Iuduh'ne 6B:

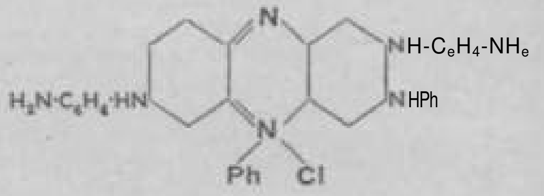


2-aralno-7-aniUiLO-3:6-dlplienyl-pheno3afranlne.

$\xrightarrow{PhNH_2\text{-}HCl}$ Induline OB.

Indutinc UB *in* also formed on heating Induline 3B with aniline, aniline hydrochloride and mercuric oxide.

The water-soluble dyes such as Faraphenylene Blue probably have atnino-groups attached to the side nuclei:



which **would account for tlicir solubility and increase basicity,**

F. A, M.

INDURITE **(Vol. IV, 46fi6).**

INFUSORIAL EARTH (Vol. **III,** 570a).

INHIBITORS, ANTIOXIDANTS. Although isolated examples of the effect of small amounts of compounds in retarding the onset of atmospheric oxidation had been known for over a hundred years, tlf is subject did not attain scientific or technical significance until 1917-18 with tho work of Moureu and Dufraisae on the cause and prevention of'the polymerisation of acrolein. They showed that tSe polymerisation was due to chemical reaction **with** the oxygen of the air and that both oxidation and polymerisatJ'on couU be **markedly** delayed by traces of compounds termed by them " antioxygenea " which were themselves sensitive to atmospheric oxidation {Moureu and Dufraisse, Compt. rend. 1922, **174,** 258).

It bM now been fully established that aiitoxidisable substances of the moat diverse type, both inorganic and organic, can be protected by a small amount of a reactive extraneous substance. These protective substances do not belong to any one cluss, but include elements such as iodine, salts such as sulphides and sulphites, derivatives of the non-metals and metalloids, and a wide variety of organic compounds, particularly phenols and aromatic amines (Aloureu and Dufraisse, Chem. Rev, 1926, 3. 113}. Indeed, Dufraisse goes so far as to say that every chemically reactive substance should be capable, under suitable experimental conditions, of functioning as an antioxidant.

The technique used by the French workers in their researches was simple, and is still the basis of most methods of detecting antioxidant action. The autoxidisable substance is confined in an atmosphere of air or oxygen under suitable experimental conditions? and the rate of oxygen absorption measured manometrically in the presence and absence of the compounds being tested as ahtioxidants.

Antioxidant action is an example of negative catalysis, the antioxidant not only prolonging the Induction period before oxidation becomes noticeable and rapid, but also reducing the steady oxidation rate which is attained in some oxidising systems. Even minute amounts of the catalyst may be effective, 1 part in a million of hydroquinone being sufficient to improve the stability of benzaldehyde to air.

Although antioxidants have been used to protect inorganic compounds such as sodium sulphite, their chief industrial outlet is in the preservation of organic compounds. Their first technical use was for the protection of vulcanised rubber, and this is still their biggest field. They are also used in petrol (v. INHIBITORS, GUM), mineral oils such as transformer and lubricating oils, fatty oils and waxes, aldehydes, etc. Anti-knocks for*fuels function by an antioxidant mechanism, and the growing realisation of the significance of antioxidants in biological phenomena may be mentioned.

In practice, antioxidants are used at concentrations varying from 0-001% (petrol, aldehydes, etc.) to 1-2% (rubber) by weight on the autoxidisable substance. Technical antioxidants are usually organic compounds, the most widely used being aromatic compounds with* a free phenolic group or a basic nitrogen atom. Among the phenols may be mentioned /J-naphthol, catechol, hydroquinone and pyrogallol. Bases include N-phenyl-a- and' 0-naphthylamine (Du Pont, B.P. 276968); N N'-diphenyl-p-phenylenediamine (Goodyear, B.P. 305195); condensation products of aniLne with acetone and of a-naphthylamine with acetaldehyde, and substituted amines such as pp'-dimethoxydi-^ phenylamine andp-benzylaminophenol.

It has been stated above that antioxiaants are reactive substances which art themselves sensitive to oxygen. Ah antioxidant for one* system may act as a pro-oxidant for another system, and even a change in concentration may change an antioxidant into a pro-oxidant. The first explanation of their action was the antagonistic o: ide theory put forward by Moureu and Dnfraisse in 1923 (Compt. rend. 1923,**17ft** 624). On this theory, the first reaction is the formation of an unstable peroxide of the autoxidisable substance; this reacts with the antioxidant to give two unstable oxides, which decompose to regenerate the original substance, the antioxidant and molecular oxygen.

$$A+O_2\rightarrow A[O_2]$$
$$A[O_2]+B\text{-*}A[O]+B[O]$$
$$A[O]+B[O]\text{-*}A+B+O_g$$

A is autoxidisable substance.
B is antioxidant.

This theory is not now generally accepted. The present view is that autoxidation proceeds by a chain mechanism, the unstable peroxide first formed initiating reaction chajns throughout the autoxidisable substance. The antioxidant functions by reacting with the unstable peroxide to give deactivated products, thus breaking the chain-propagating mechanism *(see,* for example, Christiansen, Trans. Faraday Soc. 1928, 24, 714). Each time a chain is broken, an antioxidant molecule is destroyed. This mechanism has been shown to hold for the autoxidation of substances as varied as benzaldehyde (Bäckström and Beatty, J. Physical Chem. 1931, 85, 2530) and rubber (Morgan and Naunton, Proc. Rubber Tech. Conf., London, 1938, p. 599).

R. F. G.

INHIBITORS, GUM. The term "gum-inhibitors*' has been applied to numerous organic compounds' that have the power of preventing the formation of resinous or gum-like material in motor spirits during storage. Gum [1] formation in motor spirits is a liquid-phase oxidation process and gum-inhibitors are a special class of antioxidants (v. INHIBITORS, ANTIOXIDANTS)•»

Attention was drawn to the formation of gum in motor spirits as a result of the development, since about 1910, of the cracking process for the conversion of gas oil and other high-boiling fractions of petroleum Into motor spirit. The petrol produced, particularly by vapour-phase cracking processes, was found to be highly unstable, readily formed gum, and darkened in colour on storage. Its use in internal-combustion engines caused the choking of jets, and the formation of reshjous deposits in the induction manifold and inlet-valve pockets, and on the inlet-valve stems, causing tlytm to stick in the guides with consequent loss of engine power ajid erratic running. These objectionable properties were considered to be due to the high proportion of unsaturated hydrocarbons (olefins) present in this*type of petrol. 'Although these disadvantages could be largely overcome *" by drastic refining treatment with sulphuric acid *C2* other reagents, this was costly owing to the considerable losses of material, as well as the expense for plant, labour and reagents.

The subsequent demand for motor fuels of increasing anti-knock value further emphasised the importance of this problem, since it was found that the highly unstable petrols produced by vapour-phase^cracking processes had a high Jnti-knock value, but this was reduced to a considerable extent by the refining treatment necessary to render them sufficiently stable.

A somewhat similar position arose in connection with the increasing use of benzole as an anti-knock blending agent in petrols after the 1914-18 war. The*rude benzole produced at coke ovens and gas works contains up to 10% or more of unsaturated hydrocarbons, and unless these constituents are removed almosfc completely, the benzole is liable to cause troubles due to gum when used in engines.

Attention was first drawn to an **alternative**

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[1] The terms " gum " and " resin " have been used In this article synonymously and in a purely degcriptiva sense.

and much more satisfactory method of treatment for fuels of this type by the publication in 1030 of the investigations on gum formation of the Research Committee of The National Benzole Association (Great Britain). These investigations showed (1) that engine troubles due to the use of unstable fuels are caused almost entirely by non-volatile gum already present in the fuel at the time of use (Rept. of of Research Committee, Nat. Benzole Assoc. 1926, p. 97; V. Voorhees and J. 0. Eisinger, J. Soc. Automotive Eng. 1929, 24, 584; E. B. Hunn, H. G. M. Fischer and A. J. Blackwood, *ibid.* 1930,26,31; S. P. Marley and W. A. Gruse, Ind. Eng. Chcm. 1932, 24; 1298), and (2) that the deterioration and gumming of the fuel prior to its use in an engine can be prevented by the addition of very small quantities of certain substances, such as phenols and aromatic amines. These conclusions were supported by large-scale storage tests and fleet trials (Repts. of Research Committee, Nat. Benzole Assoc. 1927-30; W. H. Hoffert and G. Claxton, Fuel, 1930, 9, 359, 440, 476).

The use of such substances enabled the drastic refining treatment hitherto found necessary to be considerably reduced or almost entirely eliminated, thus not only effecting considerable economics in the expense of reagents, etc., but also avoiding the destruction of material having valuable anti-knock properties. These advantages have led to the wide use of gum-inhibitors in connection with the production of cracked petrols, benzoles and other motor fuels containing unsaturated hydrocarbons.

General Nature of the Gumming Process.—When motor fuels containing unsaturated hydrocarbons ar» stored, the non-volatile material, known as gun? is produced at a rate depending both on the nature of the fuel and the conditions of storage. There is often a preliminary period when the rate of gum formation is small, followed by the production of gum at an increasing rate. At first the gum remains dissolved in the fuel, but when the saturation limtt, ';vhich varies considerably with different fuels, has been reached, the gnm separates out.

The gumming process is accompanied by a marked fall in the anti-knock properties of the fuel. E. W. J. Mardles and H. Moss (J. Inst. Petroleum Tech. 1929, 15, 657; *see also* J. C. Morrell, C. D. Lowry, C. G. Dryer and G. Egloff, Ind. Eng. Chem. 1934, 26, 497) have attributed this to (1) fouling of the interior of the engine, (2) the presence of peroxides *(see below)* whic> are strong knock-inducers, and (3) the partial removal of hydrocarbons of high anti-knock value. Gum formation is also often associated with an increase in colour, although this is by no means a definite indication of gumming. Thus, extensive gum form?tion occurs in some motor fuels without any noticeable deterioration of colour, whereas with othe* fuels increase in colour occurs with practically no increase in gum content (B. T. Brooks, *ibid.* 192fi, 18, 1198; Rept. of Research Committee, Nat. Benzole Assoc. 1926, p. 41).

It has now been definitely established that gum formation does not occur in the absence of air, and it is generally agreed that it is primarily an air-oxidation process, *i.e.* the polymerisation reactions giving rise to the formation of gum are initiated by oxidation.

As early as 1918, B. T. Brooks and I. Humphrey (J. Amer. Chem. Soc. 1918, 40, 822) suggested that the diolefins rather than the mono-olefins were the chief cause of gum formation. B. T. Brooks, " The Non-Benzenoid Hydrocarbons," New York, 1922, p. 427, also drew a parallel between the oxidation of pinene and of unsaturated petroleum oils, and advanced the view that the first step in the production of gum from cracked petrols is the formation of peroxides of the diolefins, which break up with the formation of aldehydes, ketones, water and carbon dioxide, and yield organic acids on further oxidation. The pale yellow fluid gum formed from cracked petrols on exposure to air consists mainly of organic peroxides, aldehydes and ketones, whilst the resin that remains after prolonged evaporation consists largely of resin acids. N. A. C. Smith and M. B. Cooke (U.S. Bur. Mines Rept. Invest. 1922, No. 2394) similarly concluded that (1) gums are caused by oxidation, but have •io relationship to the unsaturation as determined by sulphuric acid absorption, and (2) gums are polymerised aldehydes formed by olefin oxidation.

That diolefins which readily form peroxides are mainly, although not entirely, responsible, has been confirmed by D. T. Flood, J. W. Hladky and G. Edgar (Oil Gas J. 1930, 29, No. 18, 40; Ind. Eng. Chem. 1933, 25, 1234) and by H. A. Cassar *(ibid.* 1931, 23, 1132; *see also* P. N. Kogerman, Trans. Second World Power Conf. (Berlin), 1930, 8, 33), who have compared the relative stabilities of various pure unsaturated hydrocarbons, and by S. M. Martin, Jr., W. A. Gruae and A. Lowry (Ind. Eng. Chem. 1933, 25, 381) w'o^found that when diolefins were removed from cracked petrols by maleic anhydride, by sulphuric acid or by partial hydrogenation, gum was no longer formed.

The connection between peroxides and gum formation has since been emphasised by L. G. Story, R. W. Provine and H. T. Bennett *(ibid.* 1929, 21, 1079). J. A. C. Yule and C. P. Wilson *(ibid.* 1931, 23, 1254), E. W. J. Mardles and H. Moss (Z.c), G. Egloff an4 his co-workers *(ibid.* 1934, 26, 497, 655, 885; 1936, 28, 465), and other investigators. Peroxide^ can be detected at a very early st^ge of oxidation at which no aldehyd3 or acjd and practically no gum is to be found. The rate of formation of peroxides accelerates with time. Gum is formed in considerable amounts as soon as much peroxide is present, and before the formation of any appreciable amounts of aldehydes or acids, whifh appeal" therefore to be secondary reaction products. According to Yule and Wilson there is a relation between the gum content and "peroxide number " of cracked petrols.

Although the general character of the gumming process is now well established and there is strong evidence that the first step is the formation of organic peroxides, the mechanism of the further reactions finally leading to the formation of gum is still obscure. Since the general nature of the process is one of oxidation, it is to be expected that under normal storage-conditions gumming will depend on the accessibility of air to the fuel. It is also influenced by a number of other factors, such as temperature, actinic light, material of the containing vessel, and the presence of substances which may either promote or retard the reactions involved.

Action of Gum-Inhibitors.—Any peroxides and gum already present in a raw motor spirit are removed during fractional distillation, which 13 usually an essential feature of any refining process. Thereafter, formation of peroxide and gum may * recommence immediately or, as already stated, there may be a short delay or "induction period" before gumming commencgs* The effect of adding an inhibitor is to cause a very prolonged induction period before oxidation commences, apparently by preventing the initial formation of peroxides as postulated by C. Moureu and C. Dufraisse (Chem. Rev. 1926, 3, 113) for antioxidants in general. During this period the further reactions leading to the formation of gums, to darkening in colour and to fall in anti-knock value are suppressed. A very wide range of organic compounds has been found to be capable of prolonging the induction period, some being much more effective than others. The most efficient are those containing a phenolic group, and the property appears to be possessed to the greatest degree by substances that are themselves readily oxidised.

Gum-inhibitors do not prevent gum formation indefinitely, they only delay the commencement of the process. However, since efficient gum-inhibitors in suitable concentrations, which may vary from one-thousandth to a few hundredths of 1%, are capable of prolonging the induction period under normal storage-conditions for many months, or years, this is not of any practical consequence.

Gum Tests.—In connection with thetstudy and application of inhibitors, it is necessary to consider the tests available for determining the quantity of gum in a fuel at any particular time, i.e. the so-called *preformed or existent gum,* and those used for determining the tendency of a fuel to form gum on further storage, *i.e.* the so-called *potential gum.* Clearly, the relative tendency of fuels to form gum can be determined by storing them for a definite period and then determining the existent gum. Such storage tests, however, ta&e too long to be of practical use, and it has been found necessary to devise much more rapid laboratory tests.

(i) *Determination of Existent Gum.*—Numerous tests have been suggested for this purpose, all of them involving evaporation of the fuel under defined conditions and measurement of the non-volatile residue. The chief difficulty has been to prevent further oxidation and gumming of the fuel during evaporation. Clearly, the method of * evaporation that gives the lowest result will approximate most closely to the true gum content of the fuel.

The earliest tests consisted of merely allowing the fuel to evaporate from a glass or copper dish heated on a boiling-water bath (100°C). Sometimes the gum obtained in this way was subsequently " dried " by further heating at a higher temperature. It was found, however, that further gumming occurred during the tests, particularly with fuels containing high-boiling constituents. Moreover, with certain fuels the copper apparently catalysed the formation of gum *(see below).* N. A. C. Smith ^nd M. B. Cooke (U.S. Bur. Mines Rept. Invest. 1922, No. 2394; M. B. Cooke, *ibid.* 1925, No. 2686) proposed a steam-bath method and porcelain dishes to eliminate these effects. Attempts were also made to simulate engine-manifold conditions by subjecting the fuel to flash evaporation (W. S. Norris and F. B. Thole, J. Inst. Petroleum Tech. 1929, 15, 681), or passing the vaporised air-fuel mixture over a hot plate (E. B. Hunn, H. G. M. Fischer and A. J. Blackwood, J. Soc. Automotive Eng. 1930, 26V 31). Methods involving vacuum distillation were also tried (W. Littlejohn, W. H. Thomas and H. B. Thompson, J. Inst. Petroleum Tech. 1930, 16, 684; and O. C. Bridgeman and E. W. Aldrich, J. Soc. Automotive Eng. 1931, 28, 191). All these methods have now been superseded by " air-jet tests." These have been developed from a procedure originally proposed by Hunn, Fischer and Blackwood, which consisted in allowing a stream of air to impinge on the surface of the fuel during evaporation on 'a water bath. Under these conditions the fuel evaporates much more rapidly and further oxidation is almost entirely eliminated, no perceptible differences being observed when the air is replaced by nitrogen or carbon dioxide. Various* modifications of the original method, in which higher temperatures are employed and the air is preheated, have been suggested (M. J. Mulligan, W. G. Lovell and T. A. Boyd, Ind. Eng. Chem. [Anal.], 1932, 4, 351). A conventional air-jet test has now been adopted tentatively as a standard by the Institute of Petroleum in Great Britain (" Standard Methods of Testing lj?trdleum and its products," 1935, p. 206) and a more elaborate method employing a hot air-jet, by the American Society for Testing Materials in the U.S.A (" A.S.T.M. Standards on Petroleum Products and Lubricants," 1939, p. 150).

(ii) *Determination of Potential? Oum.* — Numerous tests have similarly been devicid for determining potential gum. Practically all of them, although differing in the conditions used, depend on. the same principle, viz., intensifying the conditions of oxidation. In some of the tests, the gum formed during a definite period of oxidation is measured, in others the length of the induction period, as indicated by oxygen absorption.

ffhe earliest test, which was first developed as a test for corrosion, involved evaporating the fuel from a polished copper dish. The copper was considered to catalyse the formation of gum. Subsequently, further work cast considerable doubt on the significance of the results, since they were ofte% at variance with those of engine and storage tests (Rept. of Research Committee, Nat. Benzole Assoc. 1926, pp. 41 *et seq.*; V. Voorhees and J. 0. Eisinger, i Soc. Automotive Eng. 1929, 24, 584; and E. B. Hunn, H. G. M. Fischer and A. J. Blackwood, l.c.).

A test which has been standardised internationally for benzoles (W. H. Hoffert and G. Claxton, Gas J. 1932, 200, 494; Nat. Benzole

Assoc. " Standard Specifications for Benzole and Allied Products," J938, p. 109) consists in bubbling oxygen through the fuel whilst it is heated at lO0°C. in a flask with reflux condenser, the gum formed during a definite period being finally determined. This test, however, is unsuitable for **highly** volatile fuels owing to loss of fuel in the oxygen stream. For petrols, a better procedure, and one which is particularly suitable for the study of inhibitors, is that originally proposed by V. Voorhees and J. 0. Eisinge'r (J. Soc. Automotive Eng. 1929, 24, 584) and recommended by T. H. Rogers, J. L. Bussies and P. T. Ward (Ind. Eng. Chem 1933, 25, 397). It consists of heating the fuel with oxygen in a flask in a steam bath {fig. 1) and observing the rate at which oxygen is absorbed, by means *of* a manometer connected to the flask. In this way the induction period is measured or, if desired, the gum content of the fuel may also be determined after a definite period of oxidation. Numerous tests have also been devised in which the fuel is heated under pressure with oxygen in a metal bomb (E. B. Hunn, H. G. M. Fischer and A. J. Llackwood, *l.e.*; E. W. Aldrich and N. P. Robie, J. Soc. Automotive Eng. 1932, SO, 198; 0. C. Bridgeman, Oil Gas J. 1932, 31, No. 3, 55; G. Egloff, J. C. MorreL\ C. I). Lowry and C, G. Dryer, Ind. Eng. Chem. 1932, 24, 1375; J. W. Ramsay, ***ibid.*** 1932, 24, 539; B. P. Ward, Oil Gas J. 1932, 81, No. 1?, 16; C. Winning and R. M. Thomas, Ind. Eng. Chem. 1933, 26, SU j W. H. Tho.uas, Proc. **World** Petroleura Congr. 1933,2,122), the size of bom'j, material, quantity *of* fuel and technique, however, varying considerably.

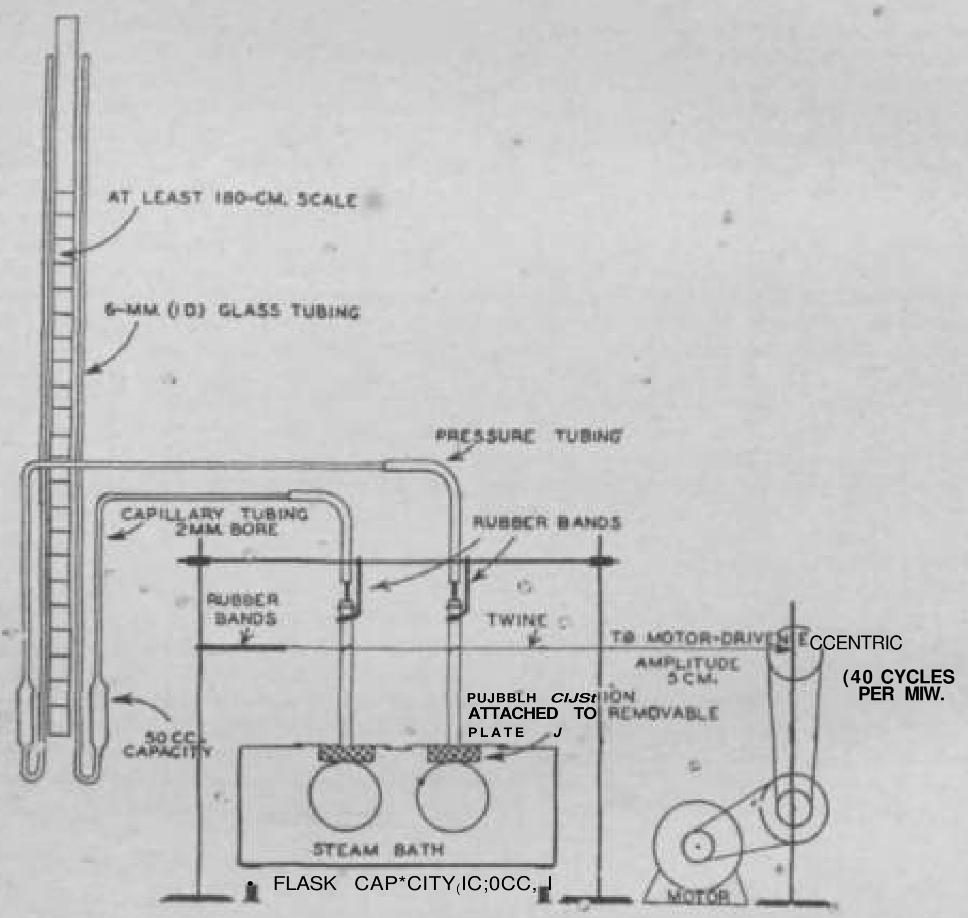


FIG. 1.

The standard test adopted tentatively by the Institute of Petroleum in Great Britain consists in heating the fuel with air in a flask immersed in a steam bath for a definite time, and subsequently determining the existent gum ("Standard Methods for Testing Petroleum and its Prodi.-jU," 1035, p. 208). The A.S.T.M. him' standardised tentatively a metal bomb test, in which the induction period is measured, as in the Voorhees and Eiaingcr test, by a recording manometer {" A.S.T.M. Standards on Petroleum Products and Lubricants," Committee D.2,1939, p. 153).

Correlation of these tests with actual storage tests has proved extremely difficult, and only a rough relationship has been established {W. H. Hoffert and G. Claxton, *l.c.;* T. H. Rogers, J. L. Bussies and P. T. Ward, *l.c.*; C. G. Dryer, JvC. Morrb'J, G. Egloff and C. D. Lowry, Ind. Eng. Chem., 1935, 27, 15; " A.S.T.M. Standards on Petroleum Products and Lubricants," Committee D.2, 1939, p. 9). Hence it is advisable to check any conclusions drawn from them by iintiial fltorngo touts. Moreover, owing to *the* fact that it is impossible to cover in a single test the many storage conditions used in practice, it is desirable to allow a high factor of safety with regard to the stability requirements of motor fuels.

A further limitation with regard to potential gum tests has been pointed out by E. W. J. Mardles (Proc. World Petroleum Congr. 1933, 2, 67, 116). At the high temperature used (100°C.) the relative efficiencies of inhibitors may differ considerably from their relative efficiencies under normal storage-conditions. A substance may even exhibit practically no inhibiting effect under the conditions of a potential gum test, although quite effective at atmospheric temperatures. An example of this is afforded by hydroquinone, which has little or no inhibiting effect under the conditions of a bomb test (G. Egloff, J. C. Morrell, C. D. Lowry and C. G. Dryer, Ind. Eng. Chem. 1932, 24, 1375), but is quite effective under normal storage-conditions. For this reason Mardles prefers incubation tests on samples of the fuel at 35°C. to oxidation tests at 100°C. However, most of the substances that give rise to these anomalies have only feeble inhibiting power, and no examples appear to have been reported in which the converse occurs, the substance having a much lower inhibiting effect than that indicated by potential gum tests.

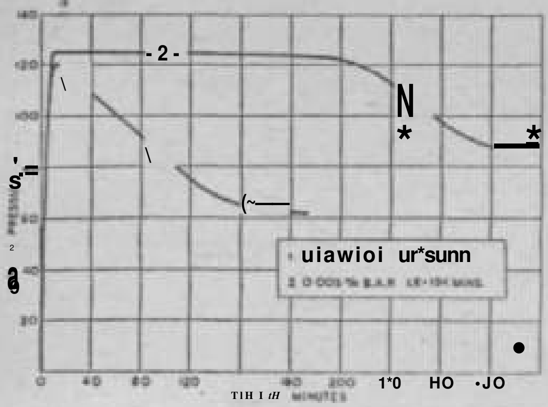
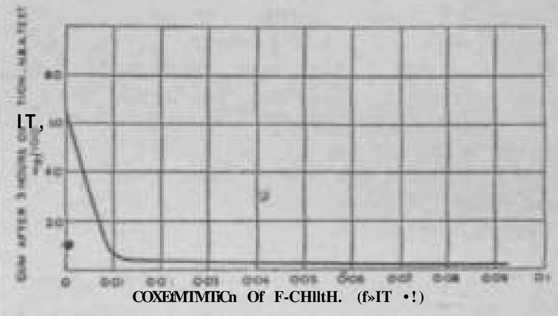


FIG. 2.

Effect of Concentration of Inhibitor.—As already mentioned, the effect of adding an inhibitor to a motor fuel containing unsaturated hydrocarbons is to cause an induction period before gum is formed on storage or under the conditions of potential gum tests. Typical results are shown in figs. 2 and 3.

With an efficient inhibitor in low concentration in a moderately unstable fuel, the increase in the induction period, as indicated by oxygen absorption, is directly proportional to the concentration of inhibitor. Typical results due to T. H. Rogers and V. Voorhees (*ibid.* 1933, 25, 520) are given in fig. 4. With very unstable fuels, however, or when high concentrates of inhibitors of low efficiency are used, considerable deviations from this simple relationship are found (Du Pont de Nemours & Co., "Gasoline Antioxidants," Tech. Bull. No. 4). Thus, when the induction period is plotted against the inhibitor concentration, a curve is obtained which may become horizontal. In other words, further addition of inhibitor gives no increase in induction beyond this point, and it may be entirely impossible to obtain a satisfactory induction period.

If the induction period is measured with respect to gum, it is often found that a small amount of gum is formed during the induction period, either from the fuel itself or from the inhibitor, by secondary reactions. Moreover, the inhibitor may be non-volatile, thus increasing the residue left on evaporation (W. H. Hoffert and G. Claxton, J.S.C.I. 1933, 52, 25T). Hence the problem of determining the amount of inhibitor to use in practice resolves itself into either (1) a potential gum test to determine the quantity of inhibitor that will give a required induction period, *e.g.* 400 minutes by the Voorhees and Kisinger test, which is claimed to be equivalent to a storage life of about 1 year under temperate climatic conditions, or (2) determination of the concentration of inhibitor that will reduce to, *e.g.* 10 mg. per 100 ml., the quantity of gum formed during a definite time of oxidation in a potential gum test. When either of these



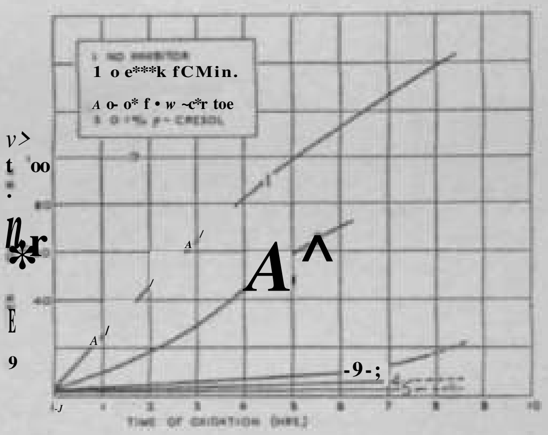


FIG. 3.

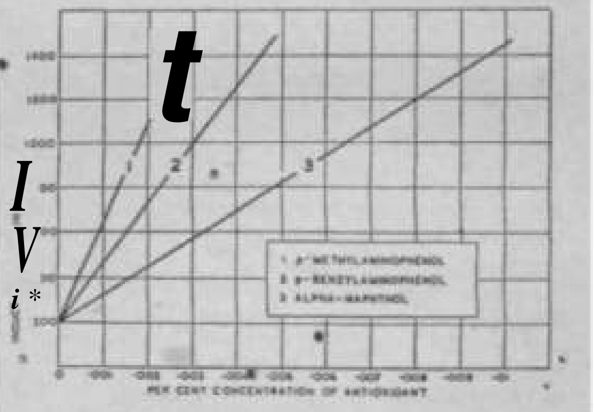


FIG. 4.

methods is applied, it is found that the concentration of inhibitor required varies considerably according to the particular substance used, and rlso according to the character of the fuel to which it is added.

Relation of Chemical Composition and Inhibiting Power.—Data concerning the relative inhibiting efficiencies of various organic compounds have been published by G. Egloff, J. C. Morrell, C. D. Lowry and C. G. Dryer (*l.e.*; Proc. World Petroleum Congr. 1933, 2, 50; *see also* G. Egloff. W. F. Faragher and J. C. Morrell, Refiner, 1930,9, No. 1,80), T. H. Rogers and V. Voorhees (Ind. Eng. Chem. 1933, 25,520; Oil Gas J. 1933, 32, N6\ 11, 13; Proc. World Petroleum Congr. 1933, 2, 63) and other investigators. The method usually adopted has been to compare the increase in the induction period, determined with respect to oxygen absorption, when the same concentration of the various compounds has been added to different portions of the same fuel. Unfortunately, the actual concentrations of the added substances, the types of fuel and the conditions of oxidation used by different investigators have varied considerably. Moreover, owing to the fact that the relationship between concentration and the induction period may not be linear, it is not always safe to reduce the results to the same concentration of the added substance.

Some observers ha to merely compared the quantities of gum obtained with a single concentration of the various substances after a fixed time of oxidation. Since the relative quantities of gum will differ considerably, depending on whether this time is longer or shorter than the induction period, such results give little or no indication of relative inhibiting power.

Further difficulties Kve arisen owing to the instability of the base fuels and to differences in the stability of distillates from the same stock of raw material, since T. H. Rogers and V. VoorVes (Oil Gas J. 1933, 32, No. 11, 13) have shown that the relative effectiveness of inhibitors depends to a certain extent on the initial stability of the fuel used. Thus it is not surprising that widely different relative efficiencies have been reported, and that there is disagreement as to whether certain substances^ have any inhibiting effect. However, certain conclusions can be drawn as to the types of compounds that are most effective, and a number of generalisations have been brought to light with regard to the effects of the introduction of substituent groups into different classes of orgaific compounds. The effect of substitution is important not only because it indicates the direction in which improvement in inhibiting efficiency may be made, but also because it influences the solubility relationships of inhibitors with regard to motor fuels and watery which are important under practical conditions *(see below).*

There is general agreement that phenols and aminc phenols are by far the most effective classes of organic compounds. Certain aromatic amines have high inhibiting efficiencies. On the other hand, aliphatic alcohols and aliphatic amines have little or no inhibiting effect.

(i) *Phenols.*—Data on phenolic compounds are given in table I—A. It will be noted that phenol has only moderate inhibiting action under the conditions used. The inhibiting property of the hydroxyl group, however, is intensified by the introduction of alkyl groups into the ortho- or para-positions, whereas these have little or no effect when introduced into the meta-position. Thus, the *ortho-* and para-cresols are considerably more effective than phenol, whilst *meta-cresol* has only aixmt the same efficiency. Two alkyl groups are considerably more effective than a single group. Again they are most effective when they are in the orth6- and para-positions to tfre hydroxyl group. This superiority of an ortho- or para-substituted compound over the meta-compound has also been encountered in a number of other series. On the other hand, the substitution of the hydrogen *in* the hydroxyl group by an alkyl group, *e.g.* anisole and phenetole, causes entire loss of inhibiting properties.

When additional hydroxyl groups are introduced into a phenol, the inhibiting action is increased. As with alkyl radicals, a hydroxyl group in the ortho- or para-position is much more effective than one in the meta-position. Catechol, for example, has powerful inhibiting properties, whereas resorcinol is only slightly more effective than phenol. Again, pyrogallol is one of the most powerful inhibitors known, whereas phloroglucinol, in which the hydroxyl groups are in the meta-position to one another, is far less effective.

The ethers of poly phenols have no inhibiting effect, but the presence of both an ether group and a hydroxyl group in the same molecule, *e.g.* eugenol and guaiacol, confers moderate inhibiting properties.

Among hydroxynaphthalene compounds, *a*-naphthol is very effective, whilst the j3-compound is much less so. This difference may be compared- with the effects of ortho- and meta-substitution in the phenols. 1:5-Dihydroxynaphthalene is a powerful inhibitor.

In general the introduction of a nitro-group into a phenol decreases inhibiting efficiency, as illustrated by th£ fact that nitrophenol is less effective than phenol. The introduction of a nitroso group, however, increases the effect, p-nitrosophenol being a highly effective inhibitor,

(ii) *Amines.*—As a claps, the aromatic amines are not^so effective as the phenols or aminophenols (table I—B). Aniline and the toluidines have onlyTeeble inhibiting action. The diamiifes and,secondary amines, however, are considerably more powerful. a-Naphthylamine has moderate inhibiting properties, but the 0-compound is much less effective, a relationship similar to that exhibited by the naphthols.

(iii) *Aminophenol8.*—An amino-group in Miy position in a compound containing a phenolic hydroxyl group increases inhibiting power, the effect again being usually most marked when the amino-group is in the ortho- or paia-position (table I—C). The replacement of one of the amino-hydrogens also results in a considerable increase in inhibiting efficiency, but when both hydrogens of the amino-group are replaced, as in p-benzalaminophenol, the activity falls off considerably. This substitution in the amino group has also been used to increase the solubility of aminophenols in motor fuels,

TABLE I.—INCREASE IN INDUCTION PERIOD (MIN.) CAUSED BY ADDITION OF 001% o» VABIOUS SUBSTANCES.

Reference.	(G. Egloff, J. C. Jliirrell, C. D. Lowry and C. U, Dryer ')•	(T. U. Rogers and V. Voorhees V	(W. H.-Hoffert. G. C'liixton and E. G.Huncock').*
Test	D.O.P. Bomb test.	Voorhce3 and Eistnger test.	Voortiees and Eisinger test.
Fin'!.	Pennsylvania cracked putrol (induction period 45 mlDutca).	Cracked petrol (induction period varied and given In brackets).	Benzole (induction period 0 minutes).
A—AROMATIC HYDHOXY-COM FOUNDS			
AfanoRydroxtf-			
Phenol	30"	3 (55)	20
o-Cresol	&0	9 (55)	100
wi-Cresol	*SO*	—	—
p-CresoJ	165	9 (55)	—
Trioresol (tech,)	90	—	—
Butylphenol (o- and *p-)*	150	—	—
ferf-Butylphenol (o- and *p-)*	165	—	—
Butylcresol	—	40 (230)	—
4-Hydroxy-l:3-di!nethylbcjizenc	375	—	—
SJ-Hydroxy-ljH-dimetliylbtiiizeiie	375	—	ISO
6-Hydroxy-l:3-dijjiethyIbonzene	—	—	20
4-Hydroxy<l:2-di methyl benzene	**210**	—	—
2-Hydroxy-l:4-diineth.ylbenzene	240	—	—
o-Benzylphenol	—	—	30
jj-Benzylphenol	—	—	30
p-Pheny I phenol	—	95 (335)	—
p-cyeiotlexylphenol	—	<I0 (230)	—
3-Methyl-4- benzyl phenol	—	—	30
4-Methyl-2-benzylphenol	—	—	11'
Thymol	255	—	—
Carvacrol	135	—	—
2-Hydroxydiplit'nyl	15	—	<20
3-Hydroxydijihenyl	90	—	<20
^j-Nitroso phenol	—	690 (907	—
Pohjhytlroxy-			
Catcchol	2,356	—	2,050
Kesorcinol	105	—	—
Orcinol	105>	—	—
Hydroquiuone	40	75 (55)	210
4-Butylrcsorcinol	315	—	—
4-Hexylresorcinol	345	170 ?230)	—
4-Heplylre8orcinol	255	—	—
Toluhydroquinoue	1 25	—	—
Pyrogallol	2,140	975 (90)	6,800
Phloroglufinol	45	—	—
3-MethyJcatcchol	—	—	3,400
Butylcatcchol	—	—	3,000
Benzylcntwhol (mixed isomers)	—	—	1,550
4:4'-I>ihydroxydiijhenyl	—	500 (335)	500
Mono- and *di-hydmxycyclk-*			
tt-Naphthol	**2,205**	—	710
^-'Naphthol	285	15 (55)	—
1:;>-lJihydroxynapht)lalene	1,680	**190** (135)	1,250
1;4-Dihydroxyanthraquinone	—	—	<20
1;5-Dihxdroxyanthraquinone	—	—	<20
Nitroao-jS-naphthol	90	—	—
Wood tar phenols	—	no (ii5)	**230**

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[1] Ind. Eng. Chcm. llKiU, 24, ia"5 ; Proc. World Petroleum Congr. 1B33, 2, 50.

» Ind. Eng. CheiiL. 1033,25, 5iiO ; Oil Gas J. 1933, 32, No. 11,13 ; Proc. World PeUokum Con$_K$r, 1»33, Z, 63.

* Int. (Jonf. Benzole Producprs, 1030, nod unpublished resultB.

* RcHUlta at 001% of added substance calculated asmi mlng linear relationship between Induction period and concentration.

TABLE I.—INCREASE IN INDUCTION PERIOD (MIN.) CAUSED BY ADDITION OF 0·01% OF VARIOUS SOBSTANCJES—*continued.*

Reference.	(tt.'Egloff, jr. C. Morrell, C. D. Lowry antl C, G. Dryer •).	(T, H. Rogers and V. Voorhera*).*	(W. H. HofTert., O. C lax Ion and E. G. Hancock [3]).
Test.	U.O.P. Uomb test.	VoocbbiH and Kisingcr test.	Voorhees and £1 singer test.
Fuel.	Pennsylvania cracked petrol (induction potto 45 minutest).	Cracked petrol (Induction period varied and given in brackets).	Benzole (Induction period 0 minutes).
B—AROMATIC AMINES			
Mono-amines			
Aniline	0	2 (55)	—
o-Toluidine	15	—	—
7n-Toluidine	J5	—	—
p-Toluidine	15	—	—
Xylidine	0	—	—
Dimethylaniline	0	—	—
Ethyl-o-toluidine	0	—	—
o-Nitro-aniline	0	—	—
Diphenylamine	60	'JO (55)	—
4-Aminodiphcnyl	0	—	<20
Polyaimnea			
o-Phenylenediamine	405	—	—
«t-Phenylenediamine	1-JIJ	50 (55)	—
jj-PhenylenedianYltie	915	385 (55)	SID
tN-ToIuyleuediamine	]!(.-)	—	—
p-Aminodimetliylaniline	590	—	—
JJ-Aminodiethylaniline	330	—	—
pp'- Diaminodiphenylarnine	900	—	—
lienzidine	150	6 (55)	—
o-ToIidine	7/5	—	—
2:4-Diaminoiiplienylamine	835	—	—
Dibutylbenzidine .*	—	135 (90)	—
p-A^ninodiphenylaminc	—	—	2,250
Naphthylamines			
a-Naphthylamine	tin	17 (.IS)	—
β-Naphthylamine	30	—	—
Ethyf-a-naphthylamine	121)	—	—
Phenyl-a-naphthylamine	U75	—	—
Phenyl-jU-naphthylamitae	150	—	—
G—AMIKOFHEMOLS			
O'Aminophenol	1,275,	450 (55)	—
m-Aminophenol	285'	—	—
jp-Aaiirioplienol	2,295	"430 (55)	—
2:4-Diaminophenol	—	800 (90)'	—
2-Amino-5-hydroxyto]uene[f1]	1,740	—	—
2-Amino-4-nitrophenol	1,215	—	—
^-Methylaminopbenol	—	1,745 (55)	—
j)-Ben2ylaminophenol ("*B.A.P.*")	—	1,100 (120)	2,800
p-Phenylamino]>henol	—	860 (120)	—
p-Benzaiaininoplieno!	—	200 (80)	—
Cinnanaal-j'-arninophenol	—	150 (80)	—
1-Hydroxy-2:6-dimethy>4-aminobenzene.	—	—	<7,720
jj-DibenzylaminophenoI(di "*B.A.P*")	—	—	1,820
4.Amino-4'-hydroxydiphei.yl	—	—	100
4-Amino-)3-naphthol	—	350 (135)	—

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[1] Ind. Eng. **Cham. 1932,** 2*, **1878**; Proc. World Petroleum Coiigr. 1933, 2, CO.

* Ind. KtiL'. Chcin. 1033,25, G20 ; Oil Gos J, 10:«, 32, Ko. 11, 13; Proc. World Petroleum Congr. 1033, 2, (13.

* int. Cow. Benzole Producers, 1930, and anpnbnahed results.

* **Btolt** nt 0·01 % of added substance calculated assuming linear relationship between induction period and coucc filiation.

TABLE L—INCREASE IS INDUCTION PERIOD (MIN.) CAUSED BV ADDITION or 0-01% OF VARIOUS SCBSTANOES—*continued.*

Eefercnce.	{«, Egloff, J. C. Ttforrell, G, B. Lowry and C. G, Dryer[v]).	(T. H. Ilogcis ant! V. Voorhecs *).•	(W. H. Hoffcrt, (i, (Unxton and B. G. Hancock[3]).*
Test.	U.O.P. Bomb test.	VoorhecB and Els In per test.	Voorhees and Eislnger test.
Fuel.	Pennsylvania cracked petrol (induction period 45 minutes).	Cranked petrol (induction period varied and given In brackets).	Benzole (Induction period 0 mill 111<-»).
5—MISCELLANEOUS COMPOUNDS			
Anthracene		0 (125)	—
Phtrsanthrenci	0	0 (126)	—
Urea	0	2-5 (60)	—
Furfuramidc	—	40 (90)	—
Aldol-a-naphthylamino	—	40 (55)	—
Phenylhydrazine	195	0 (55)	—
Benzalphcnylhydrazine	G	0 (90)	—
Cmnatnal phenylhydrazine	—	**no (30)**	—
Hydrazobenzenc •	0	2 (56)	—
•*pp'*-lyaminohydrazobenzenV	—	420 (90)	—
jj-Aiuinoazobenzene	—	0 (90)	100
Diazoaminobenzene	—	—	20
•*p*-1)ydroxyazobenzene	—	0 (90)	—
Thiourca	10	5 (60)	<20
j)-Thiocresol (0-05%)	0	0 (90t	
o-Thiodplienylamine	1.395	150 (13$	Z
Nicotine	(J	0 (00)	—
Brucine	—	0 (80)	—
8-Hydroxyquinoline	—	—	120
^-Hydroxyphenylmorpholine	—	—	1,240
Tirbutylaniine	0	—	120

[1] Ind. Eng. Chem. 1032, 24,1375 ; Proc. World Petroleum Congr. 103a, 2. 50. *

[2] Ind. Eng. Chem. 1933,25, 520; Oil Gas J. 1*33, 82i No. 11,13; Proc. World Petroleum Congr. 1933, 2,03.

* Int. Conf. Benzole Producers, 1836, and unpublished results.

• Results at 0-01% of added substance calculated assuming linear relationship between Induction period and concentration.

jj-benzylaniinophcnol being one of the beat nhibitors so far discovered.

(iv) *Compounds of Other Types.*—Table I—D gives the results for a miscellaneous group of compounds, some of them of interest owing to patent claims for inhibiting properties. Aromatic nitro-compounds Save only slight fectton. Chloro-compounds are ineffective, but the introduction of a chlorine atom into an inhibitor molecule makes little change in its "effectiveness, 1:2-Naphthaquinone possesses inhibiting effect, but 1:4-naphthaquinone and other quinonea and ketones havo little or no effect. Of a number of m'trfffen compounds, mostly cyclic, studied by Eglort', only phenyihydrazino and 8-hydrSxyquinotirte had inhibiting properties. Of the sulphur compounds thiodiphcnylaminc Bhowed marked inhibiting power. The thiocresols, however, were ine(furtive. The alkaloids havo been reported as antioxidants, but Rogers and Voorhees found that they had no effect. Of the hydrazincs and hydrazobonzenes, only <li-aminohydrazobenzene was effective. Certain dyes, *e.g.* indophenol, are quito effective (C. D. Lowry, G. Egfoff, J. C. Mom-11 ami 0. G. Dryer, Imi. Eog. Cbom. 1935, 27, 413; C. L. Gutzeit and Standard Oil Development Co., B. 1>: 385066; C. Winning, L. E. Sargent and J. F. I>-(dley and Standard Oil development Co., B.P. 383511).

Hydrocarbon Standard for Evaluating Inhibitors.—Since the publication of the data on relative inhibiting efficiencies, given above, a method of overcoming difficulties caused by changes **in** the base fuel has been proposed by (J. G" Dryer, **0. D*£owiy, G. Egloff** ami J. 0, M(*rell (Ind. Eng. Chem. 1935, 27, 315), who have described a standardised method of rating the efficiencies in terms of c^cfohexene, as a primary standard. The efficiency of an inhibitor is expressed as a " *cyc\okexene number,*[1]' *i.e.* the number of minutes by which the induction period of e;i/cZohejfene 13 increased by the addition of 0^002% of the inhibitor. It may bo* calculated from tssta on reference petrols (secondary standards), the relationship of which to cyclohjjxene has been determined by standardisation with a-naphtho]. Inhibitors with a low solubility in the standard petrols may bo dissolved first in an organic solvent, *e.g.* **betuena** or hcxane, that does not affect the imiuntion period.

Correlation of Inhibiting Action and Oxidation-Reduction Potential.—C* D. Lowry, G. Egloff, J. C. Morrell and C. G. Dryer (*ibid.* 1933, 25, 804) have drawn attention to the fact that the " critical oxidation potentials " of inhibiting substances can be correlated with their value as inhibitors, as determined by an accelerated oxidation test. The term " critical oxidation potential " introduced by L. F. Fieser (J. Amer. Chem. Soc. 1930, 52, 5204), is the potential at which the rate of oxidation of the reductant of an oxidation-reduction system becomes so small as to be jiiBt detectable.

The correlation is Bhown in table II for & number of aromatt'c hydroxy -compounds selected to cover a wide potential range and tested in equimolecular concentrations in a cracked petroL It will be noted that as the potential decreases, the induction period lengthens, shows a sharp peak between 0-800 and 0*700 volt, and drops slightly at Btill lo~,-er potentials. The variations in induction period with changes in structure, to which attention has already been drawn, are paralleled by similar relationships between oxidation potential and structure. Thus tlie eupcriorit}' in inhibiting effect of ortho- or para-substituted compounds bver their meta-isomers—shown by catechol nvt-r resorcinol or in the cifsols and xylenols—is accompanied by corresponding differences in oxidation potentials. Similarly, the suneriority of a- over /3-naphthnl is related to the lower potential of the former compound.

TABLE II.—COMPOUNDS CONTAINING HYDBOXYL GKOUPS

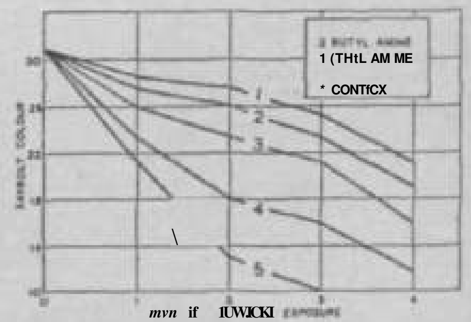
(0-OOOOS g.-mol. per 100 g. petrol.)

	Critical oxidation potential (volts).[1]	Induction period (minute).
Pennsylvania cracked gasoline alone	—	45
henol	1-433	45
o-Nitrophennl	1-433	n
wt-Nft.roiihcnol	1-147	60
Phenol	1-086	40
m-Cresol	1-080	t'>
o-Cresol.	HMO	120
p-Cresol	Hr;s	165
2-Hydroxy-1 :i-dtmethyl-benzene	1-038 (Cftlc.)	1B0
[redacted] Hydroxy-3:2-d!methyl-bcnjene	1-036 (Calc.)	150
[redacted] Hydroxydipbeiiyl	1-030	150
[redacted] Naphthoi	1017	255
[redacted] Hydroxy-1:3-dimethyl-baaene	0-895 (Cnlc.)	255
4-Hydroxy-l :3-dimct.hyl-benzene.	0-895	255
Phloroglucinol	0-799	75
a-N»)ilit|[i'l	0-797	1,320
Cwtochol	0-742	1,800
t:S-Dihydroxynaphthalene	0478	1,380
Hydro<jnlnonc	0-831	ISfi
Pyro(;;t||()l	0-600	1,440

It will be noted that two of the compounds, phloroglucitiol and hydroquinone, have shorter induction periods than would be expected from their oxidation potentials. The weak inhibiting action of the former compound ia possibly due to its existence in the ketonic form (C. Moureu and C. Dtifraissc, Compt. rend. 1922. 174, 258), whilst attention has already been drawn to the anomalous behaviour of hydroquinone in accelerated oxidation tests, this compound being a highly effective inhibitor at normal temperatures.

A similar relation rbetween inhibiting action and critical oxidation potential was found wi'h the amines. However, this relationship represents a, general trend, rather than an .".bsolute index of inhibiting value.

Colour btab)Iity.—Certain inhibitors, as already mentioned, give rise to colour formation in motor fuels, particularly when exposed to light. This colour formation, which usually increases with the concentration of the inhibitor, is probably due to " parasitic" reactions whereby the inliibitor is gradually destroyed during the induction period. It has been found that certain substances termed " secondary stabilisers" exert a protective or colour-stabilising action on gum-inhibitors. The aliphatic amines, particularly the butyl- and amylamines appear to be the most effective (L. V. Sorg, Ind, Eng. Chem. 1935, 27, 156), and have t>een used for preventing colour formation in certain types of cracked petrol stabilised with d-naphthol or " *B.A.PJ"*[1] (H. W. Steininger, *ibid.* 1034, 26, 1039). Th" optimum amount varies from 0-002 to 0004% by wt. regardless of the original cnlour of the petrol, larger quantities giving no additional improvement. The effect of sul\,tituent groups on tLe amines as colour stabilisers is shc;vn in fig. S.



Em, 5.

According to J. B. Rather and L. C. Beard ;Oil Gas J. 1U36, 34, No. 52, 209) the following inhibitors have been used for preserving the colour of cracked distillates and keronenes: thiocarbanilide, hydroquinone, resorcino], catechol, pyrojialiol, phloroglucinol, 1:2:4.trihydroxytxsnzene, butylpyrogallol, alkyl-substituted jolyhydroxybenzenes, ethanolamines, urea and thiourea. Many of these compounds possess the additional property of deeoloriskg cracked 3etrola and kerosenes that have gone off colour on storage. The usual procedure is to agitate :he off-colour oil with a solution of the reagent n alcohol at the rate of 1 lb. of reagent to 2,000-15,000 gallons of oil, according to the nitial colour.

Requirements for Gum-Inhibitors.—The various properties that have been stated to

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[1] Data from Fiescr (J. Amer. Chem. Soc. 1930, 5H, 5204) except calculated values.

govern the suitability or otherwise of a substance aa a gum-inhibitor for motor fuels may be summarised as follows (P. G. Somerville and W. H. HofTert, B.P. 289347, **1928;** W. **H.** Hofltrt and *G.* Claxton. **Proa World** betroleum Congr. 1933, *2,* 69; T. H. Rogers and V. Voorheea, Ind. Eng. Chem. 1933, 25, 620; Oil Gas J. 1933, 32, No. 11, 13 ; C. G. Dryer, J. C. **Morrell** and G. Egloff, *ibid.* 1937, 35, No. 45. US, 110):

(1) It should possess a high efficiency for perform fng its primary purpose—the stabilisation of the fuel.

(2) It should he soluble in the fuel at atmosphcrie temperatures to an appreciably greater extent than that required for effective stabilisation.

(3) The quantity required, or its **volatility,** must be such that little or no residue ia left when the fuel is evaporated.

(I) It should be more soluble in the fuel than in water, so that it is not removed by any water the fuel may come into contact with during storage and distribution.

(5) It should not of **Itae&canse** discoloration of the fuel and should inhibit discoloration in both light and durk storage.

((j) It must not affect adversely the normal combustion of the fuel or lead to obnoxious combustion products.

(7) It should not cause the fuel to have any corrosive properties.

(8) It should not be unduly volatile nor possess any offensive odour, and should not be detrimental to the health of operators aod workmen handling it.

(9) It must be available in adequate commercial quantities at a reasonable cost.

Owing to the fact that motor fuels are often stored in contact with water, the solubiftty of inhibitors in water is an important factor. The differences in the ease with which certain inhibitors nre removed by water ia shown in **table HI,** which gives the decrease in the induction period caused by shaking **benzole** containing 0'01% by wt. of various inhibitors with water (W. H. HofTert, G. Claxton and E. G. Hancock, *unpublished Itept.* Int. Conf. Benzole Producers, 1936),

TABLE III.

Inhibitor.	Induction period, minutes per 0·01 % of inhibitor.	
	Before **trashing** with water.	**After** washing with *i* vol. water.
N-Benxyl-p^ii ill no plie nol	**2,80(1**	**2,600**
CatechoJ	**2,050**	CO
N-Dlbfrnssyl-jJ-aniiiioplicii ol	**1,620**	**1,500**
1:5-Dihydroxy naphtha IPHC	1,250	**Mfl**
JI- Hytiroxy eth morph- oline	1,240	**210**
a-Naphthol	730	730
WootMur (Istillate	260	lill)
1 - Hydroxy • E:ft-dimethyl-benzene	150	ISO
a-Crcsol	100	**n**

Owing to these stringent requirements, only a relatively few compounds have been nsed commercially.

For cracked petrols, catechol was one of the first to be tried, but was found to be too easily removed by water. a-Naphthol was more satisfactory in this respect, but tended to cause discoloration. Both these inhibitors were replaced by mono- and p-dibenzylaminophenol (Antioxidants Ltd. and Standard Oil Co. (Indiana), B.P. 350438) and certain wood-tar acids (Universal Oil Products Co., C. D. Lowry and C. G. Dryer. B.P. 410115; *see also* U.O.P. Booklet No. 224,1938). woPropylmonomethyl-, monobutyl- and monp- *wo* butyl-derivatives of y-aminophenol have also been used recently (Kodrfk. Ltd., B.P. 503310, 503401). For benzoles and coal spirits, cresol (P. G. Somerville and W. H. Hoffert, B.P. 289347) has been used in Great Britain, a« well as both cresol and cateehol, whilst p-benzylaminophenol haa been used in the U.S.A.

The following particulars with regard to p-beiv/ylnTiiinopncnol (" *B.A* J*."), one of the best inhibitors so far developed, are of interest. It is produced commercially as an odourless, **light-brown** powder, melting between 84* and 90°C The quantities normally required for stabilising motor fuels vary from 0*0005 to 0-006%. It is of high purity and less than 20% is insoluble in petrol or benzole. At 25°C. its solubility in anhydrous methanol is about 60%, mid in 95% ethyl alcohol about 65%. It is soluble in water to about 006% at 25°C, whilst its solubility in petrola at this temperature varies from 0-1 to 0-5%, depending upon the nature of the petrol. It has a higher solubility in aromatic-type spirits and dftsolvea in qiotor benzole at 25°C. to the extent of ah^ut 1-35%. Hence its distribution **coefficient** between motor fuels and water ranges from 1 -7 to 22-5. Provideffit is not used in excessive quantity, it does not discolour motor fuels in the absence of alkali, and generally impr(vvea their colour stability.

The comparative effectiveness of "B.A.P." ami a wood-tar distillate are illustrated t/ the following results (**taMfc** IV), (V. Voorhees, Proc, World **Petroleum** Congr. 1933, 2, 63).

TABLE IV.

Fuel.	Induction period (minutes).	K:it ii> of ILUIoUElt.S Of Inhibitor r«ialrad to 3VB too minutes induction period.
Low Stubitity Petrol		
Unstabilised	US	
"Bji.p." **o-ooi%**	285	
"il.^-P." 0-0023%	600	
Wood-tur distillate 0 0025%	120	**21:1**
" " 0 01%	225	
" " O-0&%	Wu	
ModtmU Stability Pttrol		
Unstablllacd	**275**	
"B.A.P." 0·001%	**BSD**	
" 00025%	**B3Q**	**10:1**
Wood-tar dlstilliite 0005%	**450**	

Correlation of Inhibiting Action and Oxidation-Reduction Potential. — C. D. Lowry, G. Efcloff, J. C, Morrdl and C. G. Dryer *(ibid,* 1933, 25, B04) have drawn attention to the fact that the " critical oxidation potentials " of inhibiting substances can be correlated **with** their value as inhibitors, as determined by an accelerated oxidation teat. The term " critical oxidation potential " introduced by L. F. Fieser (J. Amer. Chem. Soc. 1930, 62, 5204), ia the potential at which the rate .of oxidation of the reductant of an oxidation-reduction system becomes BO small as to be just detectable.

The correlation is shown in table II for a number of aromat'-c hydroxy-compounds selected to cover a wide potential range and tested in cquimolecular concentrations" in a cracked petrol. It will be noted that as tlte potential decreases, the induction period lengthens, shows a sharp peak 'between 0-800 and 0-700 volt, and drops slightly at. still **lofra** potentials. The variations in induction period with changes in structure, to which attention has already been drawn, are paralleled by similar relationships between oxidation potential and structure. Thus tke superiority in inhibiting effect of ortho- or para-substituted compounds over their meta-isomera—shown by catechol over resorcinol or in the crnsols and xylenols—is accompanied by corresponding differences in oxidation potentials. Similarly, the superiority **trf** a- over /9-naphthol is related to the lower **potential** of the former compound.

TABLE II.—COMPOUNDS CONTAINING HYDROXYL GROUPS

(0-00005 g.-mol. per 100 g. petrol.)

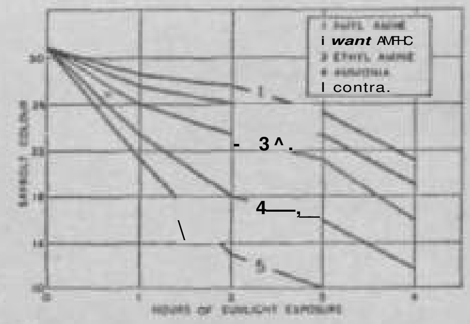
	Critical oxidation potential*" (volts).[1]	Induction period (minute).
Pennsylvania cracked gasoline alone . . .	—	45
p-Nttrophennl . . .	1-433	45
0-Nitraphenol . . .	1-433	00
m-Nltrophenol . . .	M47	60
Phenol	1-089	TO
jn-Cresol	1-080	ti
o-Cresol	1 ·<!·!<!	I2U
p-Cresot		105
2-Hydroxy-1: 4-d [mcthy 1-benicnc	1-038	160
4-Hydroxy-1:2-dimet,hyl-benzrne . « . .	1038 (Culc.)	150
Jj-Uydroxydiphenyl .• ,	1-ofo (Cntc.)	150
0-Nnplit.tml . . . . .•		255
2- Hydro^y-1 :3-dimetliyi-benzene	1017	255
<-Hydroxy-1:3-dlmetliyl-benzene	0895 (Catc.J	
	0-805	255
Phlorc-tfuHnol . . .	0-790	75
a-Nfipfithol	0-707	1/920
Cateehol «>	D-74S	i **,890**
t:5-DJhyt}roxynftpht)ia-lene	tt-073	**1,380**
Hydroquinonc . . .	fftei	135
Pyrogallol	o-oon	1,440

[1] Data from Flcser (J. Amer. Chem. Soc. 1930, 6a, 5204) except calculated values.

It will be noted that two of the compounds, phloroglucinol and hydroquinone, have shorter induction periods than would be expected from their oxidation potentials. The weak inhibiting action of the former compound is possibly due to it« existence in the kctonic form (C. Moureu and C. Dufraisse, Compt. rend. 1922, **174,** 258), **whilst** attention has already been drawn to the anomalous behaviour of hydroquinone in accelerated oxidation tests, this compound being a highly effective inhibitor at normal temperatures.

A similar relation .between inhibiting action and critical oxidation potential was fouud wi/.b the amines. However, this relationship represents a general trend, rather thar. an absolute index of inhibiting value.

Colour Stability.—Certain inhibitors, as already mentioned, give rise to colour formation in motor fuels, particularly when exposed to light. This colour formation,^ which usually increases with the concentration'of the inhibitor, is probably due to " parasitic" reactions whereby the inhibitor is gradually destroyed during the induction period. It has been found that certain substances termed " secondary stabilisers" exert a protective or colour-stabilising action on gum-inhibitors. The aliphatic amines, particularly the butyl- and amyi-atnines appear to be the most effective[1] (L. *V.* Sorg, Ind. Eng. Chcm. 1935, 27, 156), and have been used for preventing colour formation in certain types of cracked petrol stabilised with o-naphthol or "'/3.4./V' (H. M. Steininger, ***Aid.*** 1934, 26, 1039). The optimum amount varies from 0-002 to 0-004% by wt. regardless of the original colour of the petrol, larger quantities giving no additional improvement. The effect of BuK,tituent groups on tLe amines *as* colour stabilisers is shofvn in fig. 5.



Fio. S.

Aceording to J, B. Rather and L. C. Beard (Oil Gas J. l'i»36, 34, No. 52, 209) the following inhibitors have been used for preserving the colour of cracked distillates and kerosenes: thiocarbanilide, hydroquinone, resorcinol, catechol, pyrogallol, phloroglucino], l:2:4.trib,ydr. oxyUnzene, butylpyrogallol, alky 1-substituted oolyhydroxybenzenes, ethaaolamines, urea and thiourea. JIany of these compounds possess the additional property of decolorising cracked petrols and kerosenes that have gone off colour >n storage. The usual procedure is to agitate ihe off-colour oil -with a solution of the reagent n alcohol at the rate of 1 lb. of reagent to 2,000-15,000 gallons of oil, according to the nitial colour.

Requirements for Gum-Inhibitors.—The various properties that have been etated to govern the suitability or otherwise of a substance as a gum-inhibitor for motor fuels may be BiimnwiBed ns follows (P. O, Somerville and W. H. HofTert, B.P. 280347. 1920; W. H. Hoflfert and G. Cla.xton, Proc. World Petroleum Oongr. 1933, 2, fi!?; T. H. Rogers and V. Voorhees, Ind. Eng. Chem. 1933. 25, 520; Oil Gas J. 1933, 32. No. 11, IS; C. G. Dryer, J. C. Morrell and G. Egloff, *ibid.* 1037, 36, No. 45, U8, 110):

(1) It should possess a high efficiency for per-(formifng its primary purpose—the stabilisation of the fuel. ,

(2) It should be soluble in the fuel at atmospheric temperatures to an appreciably greater extent than that required for ;) effective stabilisation.

{3) The quantity required, or its volatility, must be sueh that little or no residue is left when tho fuel is evaporated.

(4) It should be more soluble in the fuel than . in water, so that it is not removed by any water tiie fuel may eome into contact with during storage and distribution.

(5) It should not of itself* cause discoloration \pf the fuel and (should inhibit discoloration in both light and dark storage,

(0) It must not affect adversely the normal combustion of the fuel or lend to obnoxious combustion products.

{7) It should not cause the fuel to have any corrosive properties.

(8) It should not be unduly volatile nor possess any offensive odour, and should not be detrimental to the health of operators and workmen handling it.

(9) It must be available in adequate commercial quantities at a reasonable cos£.

Owing to the fact that motor fuels are often stored in contact with water, the solubility of inhibitors in wate is an important factor. The differences in the ease with which certain inhibitors are removed by water is shown in table III, which gives the decrease in the induction period caused by shaking benzole containing 0-01% by wt. of various inhibitors with water (W. H. Hoffert, G. Claxton and E. G. Hancock, *unpublished liepL* Int. C'onf. Benzole Producers, 1936), *

TABLE HI.

Inhibitor.	Induction period, minutus per 0-01% of Inhibitor.	
	Beforo washing with **water.**	**After** wasI with *i* vol. Wilt IT.
N-Ittmzyl-p-amlnciphcnol .	**2,800**	2,000
Catechol	’	60
N-DilieiLzyl-p-amlnniili- ti"I	1,820	1,500
1:5-Dihydroxynaphthatene	1,250	520
y-HydroxyphfMiylniorph-olinc.	],240	210
a-Nanhtliol.	**780**	730
Wwd-tftr dlstiJlHtc . . .	**2Q0**	150
1 - Hydroxy - 2:« - dunctiyl-benzene.	150	150
0-CrCBOL	HHI	**u0**

Owing to these stringent requirements, only a relatively few compounds have been used commercially.

For cracked petrols, catechol was one of the first to be tried, but was found to be too easily removed by water. o-Naphthol was more satisfactory in this respect, but tended to cause discoloration. Both these inhibitors were replaced by mono- and jj-dibenzylaminophenol (Antioxidanta Ltd. and Standard Oil Co. (Indiana), B.P. 350438) and certain wood-tar acids (Universal Oil Products Co., C. D. Lowry and C. G. Dryer, B.P. 410115; *see also* U.O.P. Booklet No. 2'24, l(t3S). *iso*Propy 1monomethyl-, nionobutyl- and moi>p~M0 butyl-derivative* of 75-amjnophenol have also been used recently (Kodrfk, Ltd., B.P. 503316, 503401). For benzoles and coal spirits, cresol (P. G. Somerville and W. H. Hoffert, B.P, 289347) has been used in Great Britain, as well as both cresol and catechol, whilst *p*- ben 7.yJ ami no phenol has been used in the U.S.A.

The following particulars with regard to jB-benzylaminophenol (" *B.A.P"),* one of the best inhibitors so far developed, are of interest. It is producpd commercially aa an odourless, light-brown powder, melting between 84° and 90°C. Tho quantities normally required for stabilising motor fuels vary from 0-0O05 to 0-00fl%. It is of high purity" ivnd less than 20% is insoluble in petrol or kenzole. At 25°C. its solubility in anhydrous mcthanol is about 60%, and in 05% ethyl alcohol about 65%. It is soluble in water to about 00G% at 25°C., whilst its solubility in petrols at this temperature varies from 0-1 to 0-5%, depending upon the nature of the petrol. It has a higher solubility in aromatic-type spirits and dissolves in mntor benzole at 25°C. to the extent of ajput 1-35%. Hence its distribution coefficient between motor fuels and water ranges from 1-7 to 22-5. Provideffit is not used in excessive quantitj', it does not discolour motor fuels ii\ the absence of alkali, and generally improves their colour stability.

The comparative effectiveness of ** *S.A.P."* and a wood-tar distillate are ilhtstrated *by* the following results (tabffl IV), (V. Voorhees, Proc. World Petroleum Congr. 1933, 2, (J3).

TABLE IV.

Fuel.	Induction **period** (minutes).	Ratio of amounts *n(* **inhibitor required to** give 400 **mlnntct** induction period.
Low Stability f'rtrol		
triatablllsod	115	
"BJL.P." 0001 % , . * .	**285**	
"HAP." 00025% . . .	**000**	V -o i +1
Wood-tar distillate 00025%	*Vhi*	
,, ,, 001%		
,, ,, 005%	000	J *
Moderate Stubilitu I'tteol		
Unstnblllscd	875	
tfj.r." 0-001% . . .	080	> JD:1
,, 0-0025% . . .	990	
Wood-tat distillate 0 005%	tGQ	

Influences of Material of Containing Vessel and Suppression of Metal Catalysts.—Metals and metallic compounds have long been recognised as oxidation catalysts. In paints ana varnishes, for example, oxides and soaps of inctjils, particularly those possessing multiple valence states, are used as driers {W. M. **MscKay** and H. Ingle, J.S.C.I. 1916, 35, 454; 1917, 36, 317; *set also* DKYINO OILS, Vol. IV, p. 916). The autoxidation by metallic catalysts of unsaturated hydrocarbons (It. Willstiitter and E. Sonnenfekl, Ber. 1913, 46, 2952; 11. Criegee, Annalen. 1930, **481, 263),** of petroleum hydrocarbons (C. E. Wagner and •). Hvman, J. Amer. **Chfm.** Soc. 1930, 52, 4345; 1931, 53, 3019} and of phenols (W. Treibs, Brennstoff-Chem. 1933, 14, 81) has als. been studied. Hence some effect of the material of the containing vessel on gum formation is to be expected.

W. H. Hoffert and G. Claxton {Repts. Research Committee, Nat. Benzole Assoc. 1927, p. 128; 1928, p. G3; 1929, p. 58) have shown that, compared with glass, copper containers reduce the quantity of gum formed from benzoles when phenols are abflent (fig. 6), but increase gum formation in their presence. Iron and tin also appeared to reduce gum formation in the absence of inhibitors. **Similar** results were obtained when these metals were introduced into the fiVikin the N.B.A.[1] oxidation test, or when gumming was promoted by the action of ultra-violet light. E. \V. J. oUardlea and A, Mosa (J. Inst. Petroleum Tech. 1929, 15, 637) have confirmed that copper and other metals can have an inhibiting effect on gum formation from cracked petrols during incubation teats at 35°C. Oi^gano-metallic compounds have also been patented as inhibitors for preventing the oxioation of lubricating and transfoiuicr oils (H. L. Callendar, R. O. Kin^ and K. W. J. Mardks, B.P. 295230, 1927; 4V. Helmore and E. W. J. Mardles, B.P. **398222,** 1932 ;""E. A. Evans and C. C. Wakefield^ B.1'. 2C7174, 1925). These results indicate that the effect of metals on the gumming of motor fuels depends on whether certain constituents other than hydrocarbons are present. Metals have a deleterious effect on *inhibited* motor fuels, causing a decrease in induction period both on storage and during potential gum testa. The decrease of induction period of inhibited benzoles caused by introducing strips of various metab ((i-5 sq. in.) into the Haak in the Voorhees and Eisin^er potential gum test is shown in table V (W. H. Hoffert, G. Cla.xton and E. G. Hancock, *unpublished Kept.* Int. Conf. Benzole Producers, **1036).**

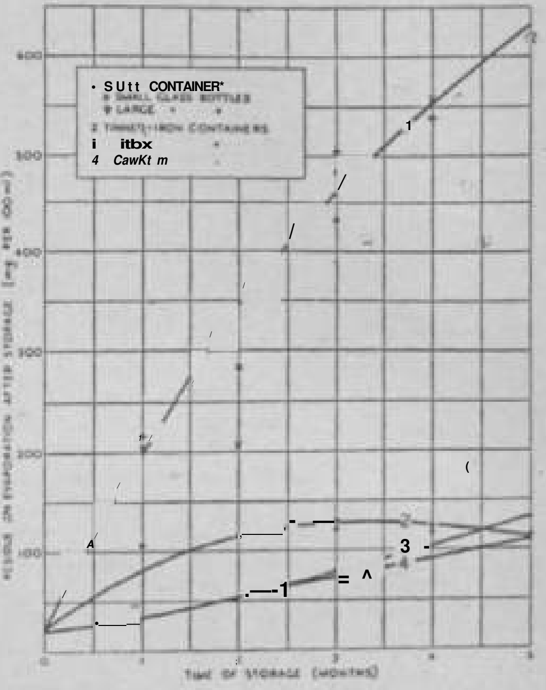


FIG. C.

Copper and rusty steel considerably reduced tin.' length of the induction period with most of

TABLE V

Inhibitor.	Induction period {minute per 0-01%).							
	Glass.	Copper.	Ziuc.	Tin. ,	Al.	Clwin steel.	Susty HIT].	Hust.
PyrogaHo]	**6,800**	**1,380**	—	—	—	1,170	**S0**	—
'•'B.A.P.".	**2,800**	**780**	**2,840**	1,430	1,770	1,320	**350**	900
Catediol	2,050	**41(1**	**2,120,**	1,230	1,840	**1,180**	**120**	**100**
di-"Ii.A,P:'	1,820	800	—	—	—	—	47U	—
2>-Hydroxyphcnyliiiorpli oline . . . .* .	**1,260**	350	1,320	**MM**	**10,00**	1,000	560	**1,300**
I •"•-Uihydroxynaphtlmlcnc	**1,240**	**280**	— .	—	,—	—	**260**	—
^-l'henylencdiamine . '.'	810	220	OtiO	**590**	**690**	570	7U	400
a-K'aphtho]	710	**ISO**	—	**580**	Tin	3UQ	**S70**	910
Wond-tar distillate . .	200	i 00	3C0	**280**	—	**120**	70	90
1 Hydroxy-2:(j-dimethy!-benzene	**ICO**	**90**	[CO	**120**	m i	90	**190**	170
o-Cresol	100	50	90	80	80	50	**B0**	100

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[1] National Den zoic Association.

the inhibitors. Zinc, tin and aluminium had only a minor effect. In general, monohydric phenols were less affected than polyhydric phenols and amines. The effect of rust is important, because most inhibited motor fuels are stored in mild steel or wrought-iron vessels Hydrated ferric hydroxide appeared to be the reactive component. In the teats with copper and Bteel, copper and irop could be detected in "olution in the benzole at the end of the induction period. The metal probably reacts with the inhibitoir, thus reducing the quantity available. Similar results were obtained when samples of inhibited benzoles wore incubated at 35°C. in containers of different metals and the time to form 10 mg. of gum per 100 ml. of benaole was determined-

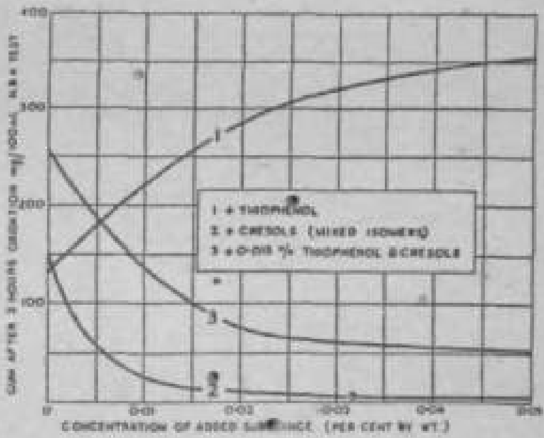
TLiae tests,* carried out under much more drastic conditions than normal, indicate the direction in which the various metals, etc., affect inhibited motor fuels, rather than the extent, since experience has shown that under normal storage conditions—lower temperatures and larger ratio of volume to surface area—the effect of the material of the containing vcsae] is mush loss than indicated by laboratory-scale **tests.**

It has been claimed that certain compounds are capable of suppressing the effect of metal catalysts. According to Hariseatische Miihlenwerke A.-O. (B.P. 409353, 1932) jphosphatidcB of animal or vegetable origin, *e.g.* lecithin, stabilise petrols in the presence of cobalt oleate, which normally acts as an accelerator. Petrols which have been treated with copper salts for removal of mercaptans are liable to contain traces of copper, the catalytic effect of -which is not counteracted by some of the usual inhibitors. According to F. B. Downing, R. G. Clarkson and C. J. Pederson (Oil Gas *3.* 1939, 38, No. 11, 97) the catalytic effect of the copper can be counteracted by the addition of certain organic compounds (metal de activators), e.p. disalicylidene ethylenediamine, which ate effective in concentrations as low as 5 parts per million.

The greater difficulty experienced in applying inhibitors successfully to blended motor-fuels containing alcohols, such -aa are used in many continental countries (R. Weller, Oel u. Kohle, 1934, 2, 527; Benzol-Verband, *ibid.* 1937, 13, 935) is admittedly due to the greater tendency of such blends to become contaminated with metallic catalysts (W. H. Hoffert and G. Chiton, 14me. Congr. *Ohim.* ind. Paris, 1984).

Preliminary Treatment of the Fuel.—Although the direct addition of gum-inhibitors to some freshly-produced crude fuels stabilises them effectively, some mild preliminary treatment is usually necessary in order to obtain the best results. Moreover, treatment may be required for removing sulphur compounds, coloured «and colour-forming, or malodorous constituents, etc.

Many crude fuels already contain phenolic and other compounds with inhibiting properties (W. H. Hoffert and G. Claxton, J.S.C.I. 1933, 52, 2BT; E. Vellinger and G. Radulesco, Compt. rend. 1933, **197,** 417; Ann. Off. nat. Comi>. Jiq. 1934, 9, 499; F. Sager, J. Inst. Petroleum Tech. 1934, 20, 1044 j E, Field, F. H. Dempster and G. E. Tilson, Ind. Eng. Chem. 1940, 32, 489). These so-railed "natural inhibitors," however, are usually far lcss effective than commercial inhibitors, and moreover, they may be present in excessive quantities and possess' other disadvantages indicated above. Accelerating impurities, which are often present, are definitely objectionable, since the direct addition of inhibitors to such Fuels may produce little effect or even increase gum formation. An example of the effect of accelerating impurities is given in fig. 7, showing the separate effects of increasing concentrations of cresol or thiophenol in a crude benzole, as well as the effect of adding increasing amounts o£ cresol to the benzole when it already contained a definite amount of thiopfcenol (0015%) (W. H. Hoffert and G. Claxton, Proc. World Petroleum Congr. 1933, 2, 69; *see dho* C. D. Lowry, C. G. Dryer, C. Wirth and R. E. Sutherland, Ind. Eng. Chem. 1938, 30, 1275). Hence both inhibiting and accelerating impurities should be removed from the fuel aa completely as possible during the prelijainary treatment.



Fra. 7.

(i) *Cracked Petrols.*—The following methods of treatment before addition of inhi bi tor ac 3 uaed (C. D. Lowry, C. G* Dryer, J. C. Morrell and G. Egloff, OU Gas J. 1934, 33, No. 12, 8; W. B. Ross and *L.* M. Henderson, *ibid.* 1939, 37, No. 45, 107; W. W. Scteumann, *ibid.* 1939, 38, No. 25, 41):

(1) Production of cracked petrol directly from cracteng unit, and sweetening, *i.e.* removal of mercaptans.
(2) Light acid-treatment of raw stock followed by redistilling and Bweetening.
(3) Splitting raw stock into a light and a heavy fraction, acid treating and redistilling the heavy fraction*and sweetening the combined redistilled heavy and lighfr fractions.
(4) Clay-treatin§;the raw etock to polymerise only the most unstable constituents and sweetening {M. R. Mandelbaum, *Proc. *World Petroleum Congr. 1933, 2, 21).

When a preliminary vapour-phase clay treat* ment is given, it is possible to run the clay much longer, giving a greatly increased yieJd. The clay treatment removes colour, and polymerisation and removal of certain of the more active gum-forming constituents usually reduce considerably the quantity of inhibitor required (N. M. Stcfcninger, Ind. Eng. Chem. 1934, 26, 1039).

(ii) *Benzoles and Coal Spirits.*—For these types of spirit, the preliminary treatment may consist of one of the following (W. H. Hoffert and G. Claxton, J.S.C.I. 1933, 52, 25T; Proc. World Petroleum Congr. 1933, 2, 69):

(1) Treatment with (a) caustic soda for removal of phenols and (6) dilute sulphuric acid (10-15%) for removal of pyridine bases, etc., and redistilling.
(2) Treatment with 75-80% acid, for removal of colour and colour-forming compounds, and redistilling.
(3) Treatment with fuller's earth, clay or other adsorbent (V. Voorhees, Oil Gas J. 1935, 34, No. 30, 36).

When the sulphur content of the crude material is high, additional treatment for the removal of sulphur may be required. Carbon disulphide can be removed with negligible loss by (1) fractionation (Barbet column^, (2) chemical processes {*e.g.* methanol-soda or ammonium poly sulphide processes). When high amounts of thiophen, sulphides or disulphides are present, treatment with stronger acid may be necessary.

Effect of Peroxide Formation on Inhibitors.—Experience has shown that for maximum effectiveness, an inhibitor should be added to a fuel as soon after its preliminary treatment and redistillation as possible. If an unstable fuel is exposed to air without the addition of inhibitor, an inh^itor subsequently added is less effective. Some unstable fuels decrease in their respoili-e to inhibitors in a few days or cc/en hours.

The first indication of the deterioration of a motor fuel is the formation of peroxides, their concentration having a direct relationship to the effectiveness of an inhibitor (J. A. C. Yule and C. P. Wilson, Ind. Eng. Chem. 1931, 23, 1254). The deleterious effects of peroxides can be offset to some extent by increasing the amount of inhibitor. It is also possible to remove peroxides from some fuels and thus improve their "-inhibitor response" (C. G. Dryer, C. D. Lowry, J. C. Morrell and G. Egloff, *ibid.* 1934, 26, 885). If the fuel is kept longer, however, intermediate polymerised products or even gum may be actually formed, and it becomes impossible to stabilise the fuel effectively.

Precautions and Methods of Adding Gum-Inhibitors (Du Pont Tech. Bull. No. 4, 1934).—Gum-inhibitors are of three physical types: (a) liquids, which are readily niiscible with motor spirits; (6) solids, which may be in the form of powder or granuLs; and (c) solutions of solids in inexpensive solvents, such as anhydrous methanol, cresylie 'acid, etc.

In "/iew of the small quantity of inhibitor required (0·001-0·05%), care must be taken to obtain thorough solution and uniform distribution throughout the fuel.

In general, and regardless of whether the quantity of fuel to be treated is large or small, experience has shown that the most satisfactory results are obtained by batch addition, that is adding a definite quantity of inhibitor to a given quantity of fuel followed by agitation or circulation of the contents of the storage tank. This is*true whether or not the method of adding the inhibitor is of a proportioning type {*see below).*

Liquids.—Any system that is suitable for blending miscible liquids may be used. For example, the inhibitor may be added directly to the fuel in a storage tank, and the contents are then agitated or circulated by pumping out at the bottom and into the top or into a second tank. Alternatively, the liquid inhibitor may be run from a stock tank by means of a proportioning pump or other device into a stream of the fuel immediately after distillation, as it is delivered to a storage tank.

Solids.—For small batches of fuel, the solid inhibitor may be introduced directly into the storage tank of freshly-prepared fuel. Small portions of the total quantity required are added at a time, and the contents of the tank are thoroughly agitated by circulation or other means between each such addition. For larger batches, the inhibitor can be added on tin suction side of the circulating pump, either in the form of a slurry with the fuel, or by means of a suitable mechanical feeding device, to a stream of fuel as it is pumped to storage. For these methods, the quantity of solid added should be well below the maximum that will dissolve in the fuel. In the second method, the pipe line to the storage tank should be sufficiently long to provide an opportunity for the inhibitor to dissolve in the fuel before reaching the storage tank. It is desirable to avoid solid inhibitor being carried into the tank, as it is difficult to agitate the contests sufficiently to pick it up again from the bottom.

The best method of dissolving the solid inhibitor in a fuel, when production is large enough to permit of more or less continuous operation, is to by-pass a stream of the fuel from a circulating pump upwards through a small tank containing the inhibitor and rccirculating the fuel until all the inhibitor is in solution. A suitable apparatus is shown in fig. 8.

Solutions of Solids in Liquids.—These may be treated as already described for miscible liquids. Greater.difficulty may be experienced, however, when using solutions owing to the fact that they contain materials that are sparingly soluble in the fuel. Wh^n such solutions are introduced into the fuel, precipitation of the inhibitor may occur initially, followed by re-solution in the fuel, and it is essential therefore that the solution be added uniformly and accompanied by rapid agitation. The best method is to inject the solution into the main fuel stream at a high pressure by means of a proportioning device with a small orifice.

The only other precaution necessary is to avoid leaving any residual alkali in the fuel to which the inhibitor is to be added, because, particularly with phenolic and aminophenolic inhibitors, it is apt to promote discoloration. This is probably due to the fact that the alkali catalyses the oxidation of the inhibitor, with the production of coloured secondary oxidation products. Hence before milling inhibitors, all traces of alkali should be removed from the fuel by thorough **washing** with water or dilute acid. Similarly, when fuels are stored over water, the latter may be sufficiently alkaline to **cause** discoloration. In such cases it has been found beneficial to add to **the** water about 0·1% by wt. of sodium bisulphite or aluminium sulphate.

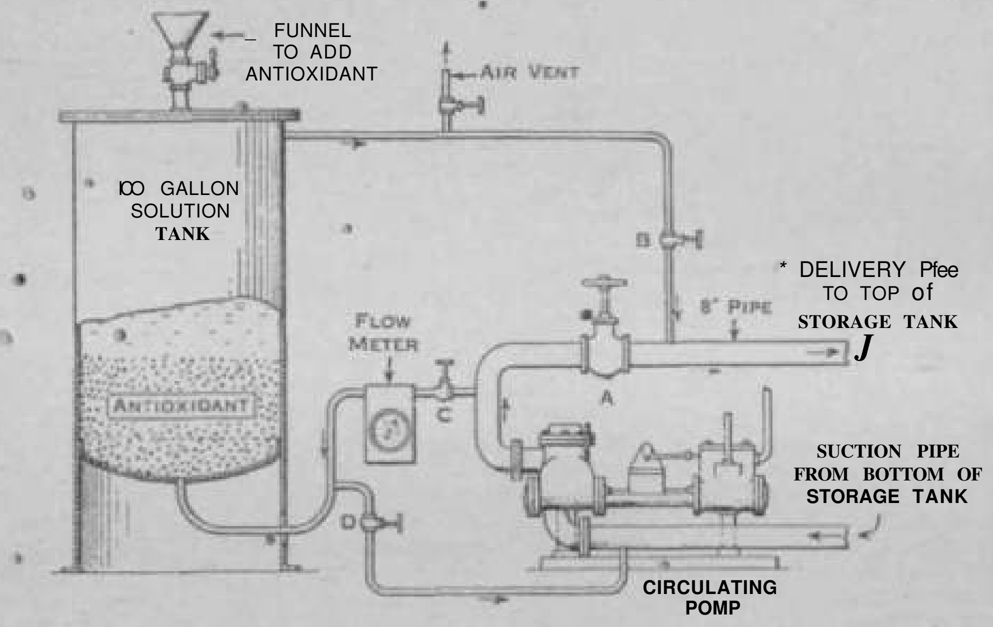
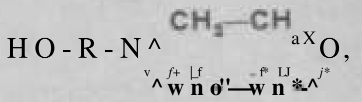


FIG. 8.

Patents.—The following **incomplete** list of British patents, relating to the use of inhibitors for stabilising motor spirits against gum and colour formation, is indicative of the **wide** variety of compounds that have been protected. For a survey of the U.S. patent literature, up to February, 19.17, *see* J. H. Byers {Nat. Petroleum News, 1937, 29, No. 11,157; No. 15, 58). Up to the end of 1938, about ISO patents relating to gum and colour stabilisers for cracked petrols, benzoles, etc., had been issued in the U.S.A. Very few of the substances claimed, however, have been used commercially, and many of them appear to have little effect on the usual types of fuels and under ordinary conditions of storage.

Patent No,	**Date.**	Patentee.	**Inhibitor covered.**
289347	27.10.26	P. G. Somerville and W. **H?** Hoffert.	Phenols and aromatic amines.
312774	30.4.28	Standard Oil Co.	Phenol, aromatic amine, urea or alkaloid.
318521	4.0.28	W. K. I*wis (Standard Oil Development Co.).	Aromatic amines, phenols and **nit.m-i ompfjunds,** *e.g.* **pyro**gallol.
319362-3	21.9.28	H. G. M. Fischer and 0. E, Gustatson (Standard Oil Development Co.).	a-Naphtho], a-naphthylamine, etc.
350438	5.3.30	Standard Oil Co.	Substituted aminophenol, *e.g.* j)-benzylaminopheiiol.
354533	28.7.30	J. Hyman and G. W. Aycrs.	Catechol and NH_3 or organic substituted ammonia.
.183511	24.4.31	(’. **Willing, L.** E.Sargent and J. F. Dudley (Standard Oil Development Co.).	Inhibitor and a coloured inhibitor, *e.g.* Jndophgnol Blue.
385060. *	**21.11.30**	C. L. Gutzeit (Standard Oil Development Co.).	Dyes such as indophenols, oxazines, etc.
388KL'I.	9.fi.;il	W. **8. Calcott** *Mid* H. \V. Walker (E. 1. L>u Pont de Nemours and Co.).	jec-Afj-lamine, *e.g.* **$NHPh_s$.**
394511	2«. 10.31	E. Ay res (Gull **Refining Co.).**	Oxidation product of o-naphlhol.
398219	7.3.32	**F. B. Downing** and **H. W. Walker** (E. 1. Du Pont de Nemours and Co.).	Amine salts of phenols.

Patent No.	Date.	Patentee.	Inhibitor covered.
399733	26.10.31	E. Ayres (Gulf Refining Co.).	Peri • mono-oxynaphthalene.
404033	8.7.32	W. S. Calcott and H. W. Walker (E. I. Du Pont de Nemours and Co.).	NN' - diarvlguanidine salt of a higher fatty acid.
406195	18.7.33	A. H. Stevens (Texaco Development Corpn.).	C-alkylat*d polyhydric phenols.
406668	8.9,31	E. Ayrea (Gulf Refining Co.).	Mixed inhibitors, *e.g.* a-naphthol and NHPh..
408229	29.8,32	F. B. Thole and W. H. Thomas (AngkvPersian Oil Co,, Ltd.).	Polyhydric phenol dissolved in cresol.
40S353	28.10.81	Hanseatiache Miihlenwerke A.-G.	Animal or vegetable phosphabides.
410U5	/18.12.31\ \ **11.3.32/**	C. D. Lowry and C. G. Dryer (Universal Oil Products Co.).	Hardwood tar.
417653	30.3.33	E. W. J. Mardles and W. Helmore.	Aminu-compounds, *e.g.* methanes, glyeine with or without a phenol.
420371	26.5.32	J. W. Orelup.	Dinaphthylene oxide or perylene.
423938	10.8.33	E. W. J. Mardles and W. Holmore.	Derivatives of hydrazines or amines.
424582	24.8.32	£, I. Du Pont de Nemours and Co.	p-Hydroxyphenylaminoacetonitril› and homologues.
430335	7.12.32	Wingfoot Oorpn.	p-Methylamino-p'-aminodiphonyl ether, etc.
432121	20.1.33	E, I. Du Font de Nemours and Co.	Dihydroxynaphthalenea, *e.g.* 1;5-$C_{10}H_6(OH)_2$
444026	24.1.34	E. V. Bereslavsky.	Pine oil treated with pyrogaHol.
444585	21.9.33	E. I. Du Pont de Nemoura and Co.	 HO-R-N O, R=arylene nucleus.
444394	26.9.34	Universal Oil Products Co.	Lignite tar fraction.
459722	12.7.35	Universal Oil Products Co.	Alkali -soluble fraction from tar, preferably L. T. tar.
459923	I8.7.S5 „	Universal Oil Products Co."'	Inhibition of one fraction of fuel only.
462593"	8.8.34	E. I. Du Pont de Nemours and Co.	ij-Cyc/ohexylaminophenol.
467056	6.9.35	Wingfoot Corpn.	flec-Naphfchylamine, *e.g.* phonyl- or tolyl-a- or /9-naphthylaminc, at least partly hydrogenated.
470072	/ 5.2.36 \ \ 7.10.36/	I.G. Farbenind. A.-G.	OrgjiN compound and a phenol.
477745	25,4.36	IV. V. Nieuwe Octrooi Mij.	Inhibitor after doctor treatment, alkali being removed by $NaHSO_3$ or $Al_2(SO_4)_3$.
501844	17.8.36	Kodak, Ltd.	80-85% N -atkyl-p-aminophenol and 20-15% ' N:N'-dh»lkyl-p-pLanylenediamine.
503316	3.4.37	Kodak, Ltd.	Compounds of "type $RCH_2NHR'OH$, where R=alkyl and R'=phenylene with or without mibstituents.
503401	17.8.36	Kodak, Ltd.	Products from polyhydric phono's containing at least two OH groups in *o*- or *p*-positions, and primary or «ec-alkyl-primary amine containing at Last 4 C atoms.

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W. H. H.

INITIATORY EXPLOSIVES (v. Vol. IV, 335a).

INK. The word " ink " comes to us through the Latin *zncauslum,* the name given to the pigment used for colouring baked tiles, and it is significant of this origin that the Ancient Egyptians wrote in carbon ink on potsherds which were afterwards baked (Fr. *encre;* Ital. *htchiostro;* tier. *TinUi).* From this primary meaning the connotation of the word " ink " has been extended to include fluids that arc employed foj producing characters in writing or printing upon any material.

Writing Inks.—The earliest kind of writing ink was Indian or Chinese ink *(q.v.),* a solid prepamtion consisting of lampblack and glue. Liquid preparations containing carbon in suspension or colloidal form were afterwards introduced and were in use all over the world. In the West, carbon inks were gradually replaced by iron-gall inks; in this country the change occurred about the eighth or ninth century A.D. In the East, carbon inks are still in use, although in the principal cities, such as Cairo, they have practically disappeared. Lucas (Ajiiilvst, 1922, 47, 9) has published analyses of modern Egyptian carbon inks.

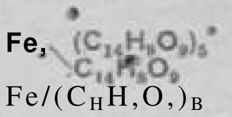
Iron-Gall Inks.—As first made, about the eighth century A.D., these consisted of an infusion of crushed galls or other form of tannin, mixed with a solution of copperas and sufficient gum arabic to keep the resulting colloidal iron tannate in suspension. Although spent tanbark, sumach and other sources of tannin are sometimes used in the manufacture of ink, galls have been found to be the most suitable raw material for the purpose.

Aleppo or nut galls contain from about 60-80% of gallotannin, with amounts of gallic acid vafring with the conditions of storage. Chinese galls usually contain about 60% of tannin (tometimes as much as 75%). Myrobalans (used for copying inks) contains 40-50% of tannin. For analyses of different kinds of galls and other tannin-producing materials, *tet* Mitchell *(ibid.* 1923, 48, 2). Experiments rmde by Mitchell (I.e.) point to the conclusion that the pyrogallic group is the tinctogenii agent in both gallotannin and gallic acid; he has also shown *(ibid.* 1903, 28, 146; 1920, 49! **126)** that the groupings (three hydroxyl groups in juxtaposition found by ScbJuttig and Neumann J" Die Eisengallustinten," Dresdei^ 1890, p. 10) to form iron inks will also yield inks in whirfi ammonium vanadate or osmium tetroxide replaces the iron salt.

The tinctogenic value of galls or other sources of tannin thus depends upon the combined amount of gallotannin and gallic acid. Fo$ this reason determinations of tannin by the standard gelatin method used by leather manufacturers do not afford a true criterion of the value of the product for ink-making. It is necessary also to take into consideration the gallic acid present, determined, *e.g.* by Mitchell's colorimetric method (Analyst, 1923, 48, 2), in which the reagent consists of a solution of 1 g. of ferrous sulphate and 0-5 g. of sodium potassium tartrate in 100 ml. of water. The standard «olution for tfee comparison consists of a, solution of pure pyrogaliol or gallic acid, and the total tinctogenic value of the substance under examination is expressed in terms of either pyrogaliol or gallic acid. The tannin in the original solution is then precipitated with quinine hydrochloride and a colorimetric comparison is made with the filtrato; the difference between this result and that originally found gives the amount of gallic acjd.

The old literature gives very divergent formulae for the relative amounts of galls and copperas to be ustd to obtain a permanent ink. Thus, Caneparius (" De Atramentis," 1660) prescribed 3 parts of galls to 1 of the iron salt, and Lewis {" Commercium Fbilosophico-technicum." 1763, p. 377) agreed with this. Other proportions recommended were 4:1 (Eisler, 17701.5:1 (Reid, 1827), 1-5:1 (Brande), 2-4:1 (Urey, etc. All these proportions were obtained empirically with galls which probably contained very different proportions of tannin, and by methods in which different amounts of tannin were dissolved. But after allowance has been made for these factors, the balance of opinion is in favour of a proportion of about 3 parts of galls to 1 part of ferrous Bulphate (c/. Mitchell, "Inks," 4th ed^, C. Griffin &, Co., London, 1937, p. 127/.

This conclusion is supported by the experiments of Sctluttig and Neumann *(op. cit.,* p. 44) and of Mitchell (Analyst, 1920, 45, 255) on the composition of th<j insoluble iron tannato formed on exposing a solution containing gallotannin and ferrous sulphate to the air. The deposits yielded from 7-8 to 8-6% of ferric oxide (=5-5-6-6% of iron). The formula that agrees best with fi-5-6-6% of iron is that suggested by Schiff (Annalen, 1875,175, 176):



$$\mathrm{Fe}_2\begin{matrix}(C_{14}H_9O_9)_5\\ C_{14}H_9O_9\end{matrix}$$

$$\mathrm{Fe}/(C_H H,O,)_B$$

In Mitchell's experiments the ratio between the agnounts of iron and gallotannin in tlft spontaneously dried deposits was **1:16.** Chis corresponds with a ratio of 1:3-22 between the^rrous sulphate and gallotantiin.[1] Since, however, the amount of tannin varies with the substance employed, the table given on the next page will afford a guide to the approximate proportions of different tannin materials to be used with 1 part of ferrous sulphate.

A typical recipe for the manufacture of iron-gall ink of the old-type is as follows: galls 120, cqpperas 80, gum arabic 80, water 2,400, phenol 6 parts.

The crushed galls are repeatedly extracted with water and the extracts are united and then mixed with the other ingredients. After mixing, the ink is allowed to iimtuie in vats for severa months.

Iron Salts for Inks.—Ferrous sulphate (copperas) has long been used as the most suitable salt for ink-making, but ferric chloride is used for gallic acid inks, and ferric sulphate chloride, FeSOjfcl,6H_8O (patented by Rohm and Haas

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[1] For a discussion of the composition of the Iron tannaU'B formed when iron-gall ink dries on paiter, see Mitchell, " Into," 4t|i e<J., p, Griffin & Co.. London, 1937.

Tannin material.	Containing imre eiillot.an- jiiii per cent. *(circa)*.	Parts by weight required.
Commercial gaUotannic acid	86	3-8
Aleppo gulls.	62	50
Chinese galls (best) . . .	75	4-3
Japanese galls	02	50
Acorn gulls (Knoppem) .	30	110
English oak-apple galls. .	2(i	12-5
Chestnut wood'	9	360
Chestnut wood extract L .	2U	160
Sumach.	22	*U-5*
Valonia.	30	**no**
Divi-disTi.	40	8-0
Myrobalana.	30	110

A.-G., Chem.-Ztg., 1921, 46, 842) is employed to a limited extent. The advantages claimed for it are **that** it is not hygroscopic or deliquescent; that unlike ordinary ferric salts it does not act on aniline dyes, and, unlike ferroun salts, docs not throw down a deposit when oxalic arid is used as the acid to render the ink stable.

Commercial copperas, as used for ink making, varies in colour from bluish-green or whitish-green to a bright grass green. On exposure to the air it grit dually absorbs oxygen and becomes coated with a white layer which soon changes to yellowish-brown, owing to the formation of basic ferric sulphate. In this condition it **ifl** technically known as rusty and is usually regarded as of more value by ink manufacturers, probably because it accelerates the preliminary darkening of the ink in the vats. **

The a- ***Want*** of iron in commercial copperas varies considerably. Fourteen samples examined by Mitchell *{op. tit.,* p. 121) contained from 11H4 *Ao* 25-92% of iron, and practical tests showed tlrt an ink prepared from copperas **with** 18'#% of iron contained too tittle iron when the calculation had been ba<«ed upon the use of copperas containing the theoretical 20%.

Commercial copperas is almost invariably acid. Thus five samples showed an acidity (in terras of >*.-alkali solution) ranging from **0-11** to 0-37 ml. per gram. It is obvious that this acidity increases the amount of strong acid in the final ink and accounts for the acidity of inks to which DO mineral acid has been added.

Blue-Black Inks.—The use of indigo to improve **the** •otour of ink was mentioned by Eifller in !77u (" Das Eislerisehe Dintefaas," HelnisUdt, 1770, p. 28) and waa used by Stephens in this country in 183f». In **1856** Leonhardi of Dresden patented an ink containHg tmtigo and madder solution, and these inks were therefore termed " alizarine " inks, even after the madder had been discarded as superfluous. The new principle introduced was that of retarded oxidation. Whilst in the old type of i i on-gall ink colour was given to the ink by partial oxidation in the vat, in " alizarine " inks a **colouring** matter is introduced to give a temporary colouring matter to the writing pending the formation of the insoluble violet-black iron tannate upon the paper. As mentioned above, indigo **was** at first the principal colouring matter used, but has **now** been partly or com**pletel;** replaced by aniline dyestuffs, especially Soluble Blue. Gum, which was a constituent of the older type of ink, in not used in the rnore fluid modern blue-black inks.

The British Specification (H.M. Stationery Office) 1934, specifics for a Record 1 Slue- Black Ink, that it must be a gallo-tannate ink containing not less than 0-5% nor more than 0-0% of iron, and that the ratio of iron to tannin substances shall be such as will ensure the highest degree of **permanence** in written characters.

A blue-black ink for general service and fountain pens must contain not less than 0-25% of iron. Like the record ink, >t must y:->ld a good blue-black colour after being blotted and give a deep **black** ui'ter 14 days. Both types of ink must remain clear and without appreciable deposit when evaporated to a fourth of the **volume** by exposure to the atmosphere. The acidity must be»the least possible having regard to satisfactory performance of the inks.

Gallic Acid In if.—The advantage of gallic acids inks over ordinary iron-gall inks is' that, being already oxidised, they remain clear in the bottle. Hence they do not require the addition of acid to stabilise thorn, and so have little, if any, corrosive action upon steel pens. On **(he** other hand, owing to the limited solubility of gallic acid (about 0-9% at IS'C.). these acid-free inks lack " body," and do not penetrate the paper so readily as the normal blue-black inks, **which** often contain more than 0-1% of free acid.

Originally gallic acid inks were prepared by liydrulysiug Chinese galls to convert the gallotannin into gallic acid, but these were essentially mixed gallotuiinin and gallic acid inks, and gallic ai'iil i> now more generally used, Ferric chloride is used instead of copperas, and about 3% of an aniline dye and 0-1% of phenol are added.

Copying Inks.—These are concentrated iron-gall (blue-black) inks to which un ingredient, such as glycerin ior dextrin, has been added to retard atmospheric oxidation of the ink upon tho paper. Speaking generally, iron-gall copying inks should contain about 30-40% less water than inks *o$* the same formula intended for ordinar- writing purposes. The British Specification (H.M. Stationery Office) for blue-black copying inks requires the sa-.nple to contain **not** less than 0(i% of iron and to dry without stickiness and give a good clear copy 48 hours after writing. The ink must produce a good blue-black colour after being blotted and give a deep black after 14 days. Other requirements are the same as for ordinary blue-black inks *{supra)* *

Logwood Inks.—Inks in which part of the galls is replaced by logwood chips or logwood extracts were at one time extcnshjely used, especially on the Continent, but have'now to a large extent been displaced by cheap blue-black and aniline inks.

Chrome logwood inks (Dingli-rs I'olytech. J. 1850, **151,** 80) are also practically **Absolete,** at all events in this country, although still used in Germany. Walther (Chem.-Ztg. 1921, 45, 432) gives the following formula for a cheap ink of this type: Logwood extract 24, hydrochloric acid (20° Be.) 15, potassium dichromate 3, phenol 1, water 1,000 parts.

Ink from Ammonium Ammonoxyferrigallate.—**Sflberaann** and Ozorovitz (Chem. Zentr. 1908, II, 102-1} found that gallic *aStd* reacts with ferric chloride to produce a chloroferrigidlic acid,

$$HO_tC(HO)C\}lS \overset{O}{} \ \text{^FeCI}$$

and that this acid, when treated with ammonia, forms **ammonium** ammonoxyferrigallate,

This compound in a 7 or 8% solution can be used as a writing ink. The writing is **violet-black** at first, but becomes black in a few hours, and is sufficiently oxidised in 30 minutes not to be removable by water. According to Ziinmermanii, Weber and Kimberly (J. Hes. Nat. Bur. Stand. U.S.A. 1935, 14, '405) a solution of ammonium ainmonoxyfeAigalhite (20 g, per litre)*forins an ink that flows well and leaves no sediment after exposure to iho air fur a month. It 19 rccoimm'mlcci **ofl** a satisfactory record ink,

Lignone Sulphonate Inks.—The lignonc sulphonates in the waste liimor from the manufacture of cellulose pulp by the sulphite process combine with iron salts to form black compounds which resemble iron tannatcs and dry on paper as insoluble black pigments. Hence, black and blue-black inks can be made from these waste liquors, and during the last few years Bud) inks have become commercial products. Whilst they have many excellent qualities, the experiwee of many years will be necessary to prove that these inks will be as permanent as properly made iron-gall inks,

Coloured Writing Inks.—Formerly these inks consisted of suspensions or solutions of pigments, such as verdigris, and natural colouring matters such as cochincaj. They arc now almost exclusively made from aniline dyestuBs. The following are coloured writing inks of the old type:

Red Ink was fornidrly prepared from lirazil wood or extract ofJSrazil wood, with the#.ddition of alum or stannous chloride, e,</.

1I) Brazil wood *80, tin-aalt 10, gum 20 parts ; boiled with 3,500 parts of water and evaporated duwn until the required depth of colour ia attained.

(2) Extract of Brazil wood 15, alum 3, tin-salt 2, tartaric acid 2, water 120 parts.

Cochineal or carmine inks are prepared by boib'ng cochineal in water, precipitating the carmine with alum and tin salt and **dissolving** this in the requisite amount of strong ammonia. Another method is to dissolve 2 parts of ammonium carbonate in ^00 parts of water and macerate ibr 'i-4 hours with 40 parts of cochineal and 2 party of uluiw.

Most of tho red inks now used arc solutions of magenta or eosin in water, together with u little gum. Glycerin also its added if the ink js to be used for copying.

Blue Ink.—In the older typo of blue ink Prussian blue was the colouring matter commonly employed. The **pigment** was placed in an earthen vessel and either strong hydrochloric ncid, nitric acid or sulphuric acid was added to it. After the mixture had remained 2 or 3 days, much water was added, and after settling, tho supernatant liquor was drawn olf from tliB sediment. The sediment was well washed until the wash licjuor was free from iron and free acid, after which it was dried and mixed with oxalic acid in the proportion of 8 parts of Prussian blue to 1 part of acid. The **pigment** was dissolved in sufficient water to bring it to the required **intensity.**

An excellent blue "tnk can be made by dissolvj^ig 10 parts of indigo-car mine and 5 parts of gum in 50-100 parts of water. Solutions of blue aniline dyes may be used, but are easily effaced by bleaching agents and some fade on exposure to light.

Typical modern coloured writing inks consist of solutions of the following dyestuffg ;

Blue.—Soluble Prussian Blue (0-5%), sodium indigo sulphonate (O'l^,), Uethylene Blue (0-5%), Bavarian Blue DSK (1-2%).

Green.—Acid Green (I'-%*),* Malachite Green (0-2%).

Red.—Macarate S (0-5%), Fuchsin *V* (0-2%), Eosin A (1-5%).

Violet.—Methyl Violet<0-3%).

Brown.—Alizarin (2-5%) and ammonia solution (!%). Dries brown.

For table of systematic, tests for these and other coloured inks, see Lunge, " Technical Methods of Analysis," li)14, iii, 1,529, and Mitchell *{<>[>. t.Lt.).*

State of Massachusetts Official Ink.—This is a standard ink for comparative tests, and contains the follow ing^ng re dients : Dry gallotannin, 234; gallic acid **crystals,** 7-5b; .ferrous sulphate, 30; gum arable, 25; dilute hydrochloric acid, 25; phenol, 1, in 1,000 parts of water. Thin formula; is based on that given by Si'hlüttig and Neumann *{op, cit,).* **o**

" League of Nations " Ink.—At a meeting of the **National** Ke^.arch Council at ftttawa, September, 1932, a **Report** by the League of Nations on the Permanence of Papere was accepted ; thid Report included recommendations as to the requirements of a permanent ink. These comprised the following, *inter alia :*

(1) The ink must be thin and Ho wing, and keep in a non-stoppered^ bottle.

(2) It must dry.quickly and must not be sftcky, even **immediately** after drying.

(3) It must not be acid enough to attack pen or paper, or show any tendency to spread over the paper.

(4) It must contain sufficient iron and tannin, SQ that when dry it will turn black, will not fad« in light, and will resftt water and alcohol.

" *Art.* 4tt.—Ink for documents shall be black, - free from aniline *or corrosive materials, and resistant to light and decolorising substarfbes.

" Ortiy tho ferro-gallic inks are accepted as **'normal,'** and they must comply with Die following conditions:—

" (1) Be clear, fluid, not acid enough to attack the pen, nor have a tendency to spread on tliu paper; have, a lasting colour, and produce a writing which dries quickly without stickiness.

" (2) Contain not less than 5 g. of iron per litre.

" (3) Be completely indelible in 15 days.

" (4) Produce a dark colour and be as resistant to light, air, water and alcohol as an ink composed of 23*4 g. of tannin, 7*7 g. of crystallised gallic acid, 30 g. of iron sulphate, 10 g. of gum arabic, 2-5 g. of concentrated hydrochloric acid and 1 g. of carbolic acid, made up to 1 litre. The inks are tested according to the regulations of the Bureau of Control and Standards."

It may be pointed out that some of these requirements are contradictory. An ink containing 0-25% of conc. aqueous hydrochloric acid will attack pens, and an acid-free ink (which will not corrode pens) will not comply with the requirements for tannin and gallic acid.

Prussian Regulations for Official Tests of Ink.—According to the Prussian regulations of May 22, 1912, inks are classified into (1) " documentary," and (2) " writing inks," the latter being subdivided into (a) iron-gall inks, and (6) logwood and dyestuff inks. (1) A " documentary ink " is defined as an iron-gall ink which gives dark writing after 8 days' exposure to light and air. It must contain at least 27 g. anhydrous gallotannic and gallic acids, and 4 g. iron (calculated as the metal) per litre. On the other hand, the amount of iron must not exceed 6 g. so that the ratio of gallotannic plus gallic acid to iron must lie within the limits 4-5:1 and 6-75:1. The ink must not alter for at least 14 days in the ink-pot, and must flow readily from the pen. The writing done with it must not be sticky immediately after drying; and after 8 days it must remain deep black when washed with water and with alcohol (85 and 50%). (2) Iron-gall " writing inks " must contain at least 18 g. gallotannic and gallic acids, and at least 2-6, and not more than 4 g. iron per litre (ratio 4-5:1 and 6-75:1). In other respects they must comply with the requirements of " documentary inks." Inks of Group (6) are not officially tested.

For the American standards for iron writing, duplicating and cancelling inks, their composition, manufacture and methods of testing, *see* U.S.A. Bureau of Standards, 1920, Circular No. 95 (for Abstract, *see* Analyst, 1921, 46, 61).

Examination of Writing Inks.—*Acidity.*—A rapid method of determining corrosive acids in ink has been devised by Mitchell (*ibid.* 1921, 46, 131). 10 ml. of the ink are repeatedly distilled with excess of sodium acetate and the acetic acid in the distillates is titrated with standard alkali.

Another method of determining both the added mineral or oxalic acid and the weak organic acids is to bleach the pigments in the ink with boiling hydrogen peroxide and titrate the liquid with N.-alkali (phenolphthalein as indicator). The alkalinity of the glass bottles used for ink may sometimes neutralise the acidify of the ink and cause deposits to form (Mitchell, *op. cit.*, 184, 224).

Ash.—Iron-gall inks differ considerably in the readiness with which the carbon can be burned off. Cautious addition of a few crystals of ammonium nitrate facilitates the ignition. Typical English inks have been found to yield from 0-42 to *2-52%* of mineral matter.

Iron.—The ash is dissolved in dilute hydrochloric acid, and the iron is oxidised with hydrogen peroxide and precipitated with ammonia. Or the volumetric method prescribed in the Prussian Official Tests may be used: the ash from 10 ml. of ink is dissolved in 1-2 ml. of hydrochloric acid (sp.gr. 1-124), the solution is evaporated to dryness with 1 to 2 ml. of chlorine water, the residue is treated with 0-5 ml. of hydrochloric acid to dissolve basic iron salts, and the solution is cooled and diluted with 20 ml. of water. About 1 g. of potassium iodide is added, and the iodine liberated at 55° is titrated with N./10 thiosulphate solution, the solution being cooled before the starch indicator is added.

Mitchell (Analyst, 1908, 38, 81) analysed a large number of English writing-inks and found that, although the composition of any one manufacturer's ink remained fairly constant over long periods, there were marked differences between the inks of different manufacturers. The total solid matter ranged from 1-89 to 7-94%, the ash from 0-2 to 2-52% and the iron from 0-18 to 1-09%.

Gallotannin and Gallic Acid.—A mixture of 10 ml. of the ink with 10 ml. of concentrated hydrochloric acid is shaken with successive portions of 50 ml. of ethyl acetate until the aqueous layer gives no reaction for gallotannin or gallic acid after treatment with sodium carbonate and addition of ferric chloride and ferrous sulphate. A special form of shaking apparatus, devised by Rothe, is suitable for the extraction. The ethyl acetate extract is shaken several times with semi-saturated potassium chloride solution (10 ml. each time) to remove iron salts, and then evaporated *in vacuo;* the residue is taken up with a little water, transferred to a weighed crucible and dried at 105-110°, or preferably *in vacuo* at about 60°, until constant in weight. In the Prussian Regulations the residue is regarded as gallotannin and gallic acid when 0-1 g. thereof absorbs in the presence of 2 g. of sodium bicarbonate at least 0-5 g. of iodine. If less iodine is absorbed the ink is not up to official requirements. In determining the iodine absorption about 0-1 g. of the residue is mixed in a stoppered flask with 2 g. of sodium bicarbonate and 25-50 *ml.* of a standard solution of iodine (about 50 g. per litre), and the flask is closed and allowed to stand overnight, after which the unabsorbed iodine is titrated with standard thiosulphate.

A more accurate determination of gallotannin and gallic acid may be made by Mitchell's colorimetric method (Analyst, 1923, 48, 1).

Gums and Dextrin.—10 ml. of the ink are treated with 20 ml. of 95% alcohol, and the precipitate is collected on a counterpoised filter, dried and weighed.

Glycerin.—The total solids of the ink are treated with 96% alcohol and the alcoholic extract is evaporated and tested for glycerin, *e.g.* fumes of acrolein on heating with potassium bisulphate (*v.* Vol. V, 302c).

Phenol and Salicylic Acid.—The residue from the ink is mixed with sand and extracted with ether. On evaporating the ethereal extract phenol may be recognised by its odour and by giving a precipitate with bromine water. Salicylic acid ia detected by the violet colour obtained with ferric chloride (». Vol. II, 6706).

Dyestuffa—The ink is slightly acidified with hydrochloric acid and boiled for 15 minutes with a thread of wool or cotton. The threads are thoroughly washed with hot water, and if they have been dyed they are boiled in sodium carbonate solution or acidified water, and the dyestuffe are again fixed %n cotton or wool and identified by systematic testa for dyes (e/. Vol. IV, 156-172).

Indigo Carmine in- fixed upon wool and re-dissolved by an alkaline bath., In alkaline solution it remains bright blue after addition of sulphuric acid, but is changed to green by hydrochloric acid.

Te ying the Waiting,—Pieces of standard paper are stretched in a frame inclined at an angle of 45°, and a definite amount of ink made to flow down them from a pipette fixed in & special position with regard to the paper. At the same time a parallel test is made upon the same paper with Schluttig and Neumann's standard iron-gall ink **containing** 23*4 g. gallotannic acid, 7*7 g. crystalline gallic acid, 30 g. ferrous ani-mate' 10 g. gum arabie, 2'5 g. hydrochloric *acid,* and *I* g. phenol per litre. This ink is allowed to stand for at least 4 days at 10-15°, and decanted from any deposit. For comparison in the test it is coloured with a suitable dyestuff to match the ink under examination. The paper with the colour Btripes of tho two inks upon it is exposed to the air for 8 days in diffused day-light, and is then cut horizontally into strips which are immersed in water, 50% alcohol and 80% alcohol respectively. No perceptible bleaching of the ink should take place (Hinrichsen, Chem.-Ztg, 1913, 37, 265; Mitchell, <>. *rjt.,* p. 207). •

Age of Ink in Writing.—The change«n the colour of ink on paper proceeds rapidly at first, then very slowly, and is usually complete in the course of a few months. If the colour of tbe writing changes in tho course of a. few days, the ink is comparatively recent *(set* Mitchell, *op.cit.,* p. 207).

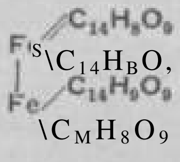
Another test depends upon the fact that as the ink becomes oxidised it in gradually converted into a res in oil* tan n ate, which retains the ilyestuff. Thi^s if a dilute acid is applied to writing a few months old the ink will run, whereas if the ink* is some y£ars old it will be hardly affected by the reagent. • *

Mezger, Rail and Heess (Chem.-Ztg. 1931, 65, 481) have devised a method based on the gradual diffusion of the salts in tho **ink-writing** into the adjacent paper. Their "chloride pictures " and " sulphate pictures " enable a judgment to be formed of the relative age of the ink. Tha precautions to be observed in drawing conclusions "from the " pictures " have been diB-cussed by Heeas (Arch. Kriminol. 1935, 96, 13; *also* Mitchell, *op. cit.,* p. 213)*

It is probable that in oxidised ink the iron exists as the first in the series of tarmatea,

$$\begin{array}{l}Fe(C_{14}H_9O_9)_3\\ |\\ Fe(C_{14}H_9O_9)_3\end{array}$$

described by Wittstein (Jahreaber. 1848, 28, 221) and by Schiff {Annalen. 1875, 175, 176). *(See also* Silbermann and Ozorovitz, I.e.)- As the oxidation proceeds the successive precipitates contain more iron, and eventually approximate in composition to



$$\begin{array}{l}Fe\begin{array}{l}/C_{14}H_9O_9\\ \backslash C_{14}H_BO,\end{array}\\ |\\ Fe\begin{array}{l}/C_{14}H_9O_9\\ \backslash C_MH_8O_9\end{array}\end{array}$$

obtained by Pclouze by prolonged exposure of a solution of ferric sulphate and gallotannic acid to air (Mitchell, Analyst, 1920, 45, 247).

Ink Powders.—Owing to their convenience for u^e by travellers, ink powders and tablets are being increasingly used. Some, when dissolved, approximate in composition to gallotannate inks, whilst others consist of aniline-dyestuffs.,

A violet logwood-ink powder described by Dietcrich (" Pharmazeuti aches Manual," 10th ed., 1900, p. 646) consists of logwood extract 100, aluminium sulphate 40, potassium oxalnte 00, potassium bisutphatc 20, potassium chroroate, 4, salicylic acid 1-5 parts.

Aniline Ink Powders.—Viedtin 1875recommended the use of Nigrosine, which was to be dissolved in SO parts of water.

Dieterich *(op. cit.)* gives the following formula for ink powders of differ^t colours ;

Black Ink Pomder.-—Aniline Green D 9-0 Ponceau 2R 80, Phenol Blue I part.
Red Ink Powder.—Ponceau Red 2R,
Green Ink Powder.—Aniline Green.
Violet Ink Powder.—Phenol BIuo *l-S,* Ponceau 211*2 parts.
*Violet Copying-Ink Powder**—Methyl Violet 20, sugar 10, oxalic acid 2 parts.

The British Specifications (H.M. Stationery Office) for Blue-Black Ink Powder, require the ink made up from the powder to contain not less tfmn 0-2I>% of iron, and the ratio of Iron salt to tannin substances to be such as w\ll ensure a satisfactory degree of permanence. ILe ink must produce a goo*d blue-black colour after being blotted, and give a deep black after 14 jJays.

Gold and Silver Inks are prepared from gold and silver, or from cheaper substitutes such as bronze powder and Dutch leaf. The leaf metal, mixed with honey, is carefully ground down to the fincstf possible condition; it is then well washed and dried. A suitable medium preparation consists of 1 part of pure gum Arabic and 1 part of soluble potash glagg in 4 parts of <liHtilled water. As a rule, 1 part of the powder is sufficient for 3 or 4 parts of the medium.

^Imitation silver **ink** is Hfest made by rubbing up nluminium foil ortpowder with gum.

Sympathetic or Secret Inks.—These preparations are deviled to traco words or figures which are invisible when written but become visiblei when subjected to heat or appropriate chemical reagents. Examples: a weak infusion of galta is colourless ou paj>er, but becomes black when moistened with a solution of copperas; and if **a** weak solution of copperas be used, tbe writing will be invisible, until the paper is moistened with a weak solution of galls. Equal parts of copper sulphate and sal ammoniac dissolved in water form a colourless ink, the writing of which turns yellow on the application of heat. Weak solutions of silver nitrate or of auric chloride when exposed to the sunlight become dark brown and purple respectively. Solutions of cobalt chloride or nitrate give tracings which become green or blue when heated and disappear again as the paper cools.

Ink for India-rubber Stamps.—The following preparation produces ink adapted for this purpose. It does not easily dry upon the pad, and is readily taken up by the paper: Aniline colour in solid form ,blue, red, etc.) 16, boiling distilled water 80, glycerin 7 ,Darts. The colour is dissolved in the water, and the other ingredients are added whilst agitating. The "*carbon papers*" used for giving two or more copies of written or typed matter are coated on one side with a mixture of, for example, yellow wax and tallow containing a suitable pigment such as lampblack or Prussian blue, or some aniline colour.

Indelible or Safety Inks.—Compositions passing under these names consist of finely divided carbonaceous substances, such as Indian ink or lampblack, held in suspension in a glutinous or resinous liquor. They are devised so as to resist the action of strong acid or alkaline solutions. Ah ink having these properties may be made of Indian ink rubbed into ordinary writing ink.

A suspension of lampblack in sodium silicate solution makes an excellent safety ink, but has the disadvantage that it must be kept in airtight bottles.

Vanadium ink is prepared very simply by adding a small proport^n of ammonium vanadate to altered decoction of galls. It is a deep black ink, which flows freely from the pen and isrfiot easily removed without destruction of the paper.-L

Copying, Ink or Indelible Pencil's (*v.* Vol. III, 339).

Hektograph Inks are used to give a large number of copies, and must therefore contain a concentrated colouring matter. The original is written on ordinary paper with the ink and is laid face-down on a sheet of a composition of glue and glycerin (about 1:5) until the ink has been absorbed into the surface of the composition. By applying sheets of paper with slight pressure, 60 to 100 copies can then be obtained.

A typical ink contains: a water-soluble blue dye 10, glycerin 10, water 50-100 parts.

Dyes not easily soluble in water or glycerin are first dissolved in alcohol and then mixed with the other ingredients. Thus a red hektograph ink may contain: nfagenta 20, alcohol 20, acetic acid 5, gum 20, water 40 parts; or magenta 10, alcohol 10, glycerin 10, lAter 50 parts.

Ticitet-Writer's Ink is made of good black ink, with liquid gum added to produce *sf* gloss.

Ink for Writing on Glass is a solution of gum arabic in strong hydrofluoric acid coloured with some matter which can withstand the action of the acid: cudbear is used for this purpose.

For Enamelled Cards ordinary printing ink (mainly a mixture of lampblack and oil) is mixed with a few drops of equal parts of copal varnish and mastic varnish.

Lithographic Ink ought to conform to the fallowing requirements. It should be flowing on the pen, not spreading on the stone; capable of forming delicate tracings, and very black to show its delineations. The most essential quality *of* the ink is to sink well into the stone so as to reproduce the most delicate outlines of the drawing and to afford a great many impressions. It must therefore be able to resist the acid with which the stone is moistened in the preparation, without letting any of its greasy matter escape.

Lithographic ink may be prepared as follows: mastic (in tears) 8 oz., shellac -12 oz., Venice turpentine 1 oz.; melt together; add wax I lb., tallow C oz.; when dissolved, add a further 0 oz. of hard tallow soap in shavings; and when the whole is perfectly incorporated, add 4 oz. of lampblack; lastly, mix well, put .in moulds, and when cold cut it into square pieces.

Another recipe is as follows: melt together wax 18, soap *1%* shellac 14, resin 6, tallow 10 parts. Then stir in 2 parts of india-rubber dissolved in 5 parts of oil of turpentine, and 0 parts of lampblack. Heat the whole until the smell of turpentine has nearly disappeared and then cast into sticks.

Autography is the operation by which a writing or a drawing is transferred from paper to stone. For autographic ink: mix white wax 8 oz. and white soap 2-3 oz.; melt and add lampblack 1 oz.; mix well, heat strongly, and add shellac 2 oz.; again heat strongly and stir well. On the mixture cooling pour it out as before. With this ink lines may be drawn of the firest and fullest class, without danger of spreading; and the copy may be kept for years before being transferred. These inks are rubbed down with a little water in the same way as Indian ink.

Printing Ink.—Ink prepared for use with type, copper-plat?s, etc., consists of a medium and pigment. The chief properties required in a good printing ink are:

(1) A perfectly uniform syrupy consistence.

(2) Must be easily transferred from the ink-rollers tp the type, and from the type to the paper.

(3) Must not smudge types, and must be easily washed off them wjth printer's lye.

(4) The ink must not dry so quickly as to set on types or rollers, but must not dry so sluwly on the paper as to hinder folding, etc., of sheets.

(5)gWhen dry, the ink must not "set off" from the paper on to anything with which it comes in contact.

(G) The printed characters should.not show a greasy margin.

(7) The ink shoind not have a strong odour.

The ink which most nearly fulfils all these requirements is composed of the finest quality of lampblack incorporated with a pure linseed oil varnish. (For methods of examining lampblacks and carbon blacks, *see* Neal and Perrott, U.S. Dept. of the Interior, Bureau of Mines

Bull. No. 192,1922, 72; *also* British Standards, Nos. 284, 286, 287, 288.) The demand for cheap inks for the printing of newspapers and cheap books has been met by using cheaper qualities of lampblack and substituting for the varnish various mixtures of oils and resins with soap, which may or may not contain a proportion of linseed oil.

The linseed-oil varnish used for good ink was formerly prepared by heating linseed oil in a boiler until the vapour evolved could be ignited. A light was then applied and the whole allowed to burn for about half an hour, until a trial showed that the oil was of the right consistence. The practice of burning the oil gave a dark-coloured product and has now been discontinued.

The present practice is to heat the oil to about 38(>-^)0°, taking every precaution to avoid its ignition. The boiler is provided with a closely fitting lid, or, better, with a cover of wire-gauze, which extinguishes a flame while allowing the vapours to escape.

Provision is made for lifting the boiler from the fire or withdrawing the fire from the boiler, or, in some apparatus, for running off the oil into a cold vessel. A gutter round the furnace above the fire-door prevents any chance of the oil reaching the fire, even should it boil over the top of the pot. In some modern plant the oil is heated by means of superheated steam. A varnish so prepared is insoluble in water or alcohol, but mingles readily with fresh oil and unites with mucilages into a mass diffusible in water in an emulsoid form. The oil loses from one-tenth to one-eighth of its weight by boiling into the thick varnish.

Letterpress ink of average quality may be made by reheating a varnish produced as described above and adding for each gallon of the original oil 4 lb. of rosin and 1 lb. of brown soap in slices. This is then mixed with the requisite quantity of pigment—for lampblack rather less than one-third of its weight—and the whole is thoroughly ground and incorporated in a suitable machine, usually between rollers of polished granite or steel, as in Lehmann's apparatus. The presence of soap in the ink causes it to " lift " well, *i.e.* to be completely transferred from the type to the paper. The following recipes are typical of inks of a cheaper class:

Linseed Oil and Rosin Vehicle.—Rosin 50, boiled linseed oil 100, rosin soap 10, partly boiled oil 6 parts by weight.

Rosin Oil Vehicle.—Rosin oil 50, rosin 50, boiled linseed oil 50, rosin soap 5, thin boiled linseed oil 6 parts.

Cheap Mineral Oil Vehicle.—Rosin is dissolved in about an equal weight of heated mineral oil (petroleum of sp.gr. 0·880-0·920s Wass, F.P. 322298, 1902).

Composition Vehicles.—Venice turpentine 5, castor oil 15, white wax 1 kg. These are mixed at 100° (Kncchl); then 9 kg. of thick turpentine, 10 kg. of soft soap and 4 kg. of " *oleine,* " mixed hot, are added (Rosl).

The lampblack used is of various qualities according to the price of the ink, The proportion should be just sufficient to give a full black impression; it is less with the better qualities of lampblack. The ink for rotary machines contains about 28% of lampblack, that for high-speed newspaper-printing about 24%, that for book printing about 21%, and that for illustration work about 19% with 2% of Prussian blue and 1% of indigo.

Other inks consist of 25 parts of paraffin oil, 45 parts of fine colophony and 15 parts of lampblack. The amount of colophony is reduced in soft inks for high-speed work.

It has been proposed to use oxides of iron or manganese as black pigments for printing ink (*see e.g.* Fireman, U.S.P. 802928, 1905). Paper printed with such ink could be bleached and subsequently made into white paper. This could not be done with the lampblack inks now used.

It is said that so extremely thin is the layer of ink on small type that 1 lb. wt. even of cheap newspaper ink will cover no less than 7,000 sq. ft. of type matter.

Coloured Printing-inks.—These inks are made from the varnishes above described by the addition of dry colours, taking great care that the colours are thoroughly well ground and assimilated with the varnish, since lumps of any kind not only clog the type but alter the tint. Some tints which are exceedingly light will require an admixture of white powder to give the necessary body to the ink.

The following pigments are eligible for incorporation in printing inks:

White.—Heavy spar (barium sulphate), zinc white and titanium white.

Red.—Orange lead, vermilion, burnt sienna, Venetian red, Indian red, lake vermilion, orange mineral, rose pink and rose lead.

Yellow.—Yellow ochre, gamboge and lead chromate.

Blue.—Cobalt blue, Prussian blue, indigo, Antwerp blue, Chinese blue, French ultramarine and German ultramarine.

Green.—Usually mixtures of yellow and blue, but sometimes chrome green, cobalt green, emerald green or terre verte.

Purple.—A mixture of those used for red and blue.

Deep Brown.—Burnt umber with a little scarlet lake.

Pale Brown.—Burnt sienna; a rich shade is obtained by using a little scarlet lake.

Lilac.—Cobalt blue with a little carmine added.

Pale Lilac.—Carmine with a little cobalt blue.

Amber.—Pale chrome with a little carmine.

Pink.—Carmine or crimson lake.

Shades and Tints.—A bright red is best obtained from pale vermilion with a little carmine added; dark vermilion when mixed with the varnish produces a dull colour. Orange lead and vermilion ground together also produce a very bright tint, and one that is more permanent than an entire vermilion colour. Cheaper substitutes are orange mineral and rose pink, and red lead. Lead chromate affords the brightest colour. For dull yellow yellow ochre is used. Indigo is excessively dark and requires a good deal of trouble to lighten it. It makes a fine showy colour when brightness is not required. Prussian blue is useful, but it dries very quickly, hence the roller must be frequently cleaned. The objection to Prussian, Antwerp and Chinese blues is that they are hard to grind and likely to turn greenish with the varnish when used thin. For green any of the yellows and blues may be mixed: The varnish itself having a yellow tinge will produce a decidedly greenish tint with a small quantity of Antwerp blue. Emerald green is made by mixing pale chrome with a little Chinese blue, and then adding the mixture to the varnish until the tint is satisfactory.

In using painter's colours it is advisable to avoid the heavy ones as much as possible. Some colours require less oil in the varnish than others.

A bronze of changeable hue may be given to inks with the following mixture (Southward): gum shellac 1£ lb. is dissolved in 1 gallon of 95% alcohol or Cologne spirits for 24 hours and 14 oz. Aniline Red then added. After standing for a few hours the mixture will be ready for use. When added to good blue, black or other dark ink, it imparts a rich hue. The quantity must be carefully apportioned.

Reflex Blue Lakes.—The pigment known as " Reflex Blue " is prepared from the carbonium dye, Alkali Blue, by precipitation from an aqueous solution with hydrochloric or. sulphuric acid in presence of lead acetate. The moist precipitate is incorporated with a lithographic varnish, and after standing for the water to separate, the lake is ground into ink. These lakes get their names from the bronze effect obtained when they are mixed with lithographic varnish.

Monastral Fast Blue BS.—An insoluble blue dyestuff pigment of a new type has been introduced under this name (*see* R. P. Linstead *et. al*, J.C.S. 1934, 10^5-1039). It is insoluble in water, oils, alcohol and many organic solvents. The same pigment is made in Germany and sold under the name of Heliogen Blue B (Chem. Ztg. 1936, 60, 375). It can be used in admixture, with yellow pigments to produce greens brighter than the ordinary Brunswick greens. "Unlike cobalt blue, it is relatively opaque to infra-red rays" (Mitchell and Ward, Analyst, 1936, 61, 754).

Rotagravure Inks.—The principle of the " rotagravure " process is the reverse of that used in half-tone work, the printing surface being an intaglio composed of minute rectangular cells of varying depth. These cells, numbering about 40,000 to the sq. in., are filled with the ink, the excess of which is removed by means of a steel blade or " doctor," so that films of graduated depth are left in the cells on the cylinder of the rotary press. When the web of paper is pressed against the mouths of the cells the ink is lifted from them and transferred to the surface of the paper, and the density of the deposited pigment corresponds with the amount of ink in the respective cells. The ink required for the process differs in its properties from ordinary printing ink. It must be capable of being removed completely from the cells, must be fairly transparent, and must not yield deposits. These requirements are met by using special media containing balanced proportions of fixed and volatile ingredients, and by the use of pigments which are thoroughly ground. Special mills are required for grinding the mixture of pigment and medium, and the ink is passed through a hair sieve before being used *in* the printing machine.

Rotagravure inks made with an oil basis require thinning with benzine or carbon tetrachloride, whilst those with a water basis have the drawbacks that they smudge readily and are not waterproof. A waterproof ink prepared by Albert (Penrose's Annual, 1932) is free from these drawbacks; the medium consists of water and water-soluble organic pigments incorporated with a solution of rosin soap.

An asphalt ink particularly suitable for "intaglio printing has been patented by Winship (B.P. 334370, 1929). The asphaltic base (e.g. from gilsonite *q.v.)* is diluted with a petroleum solvent and an oily resin; the emulsion is stabilised with glue and finally incorporated with water and a suitable pigment.

Patent Inks for Cheques.—Numerous printing inks for cheques have been made with the object of revealing any attempt to remove writing from the surface of the paper. One of the best known of these inks is that of Hehner and Dupré (B.P. 375, 1881). The preparation used for printing the note consists of a sulphide (insoluble in water, but acted on by dilute acids, *e.g.* zinc sulphide), with lead carbonate or other salt of a heavy metal. The mixture is made into a paste with glycerin, treacle and gum arabic, and can be used for printing invisible characters on the cheque, or added to the coloured paste used for printing the groundwork. Dark stains are immediately produced when acid, alkali or a cyanide solution is applied to the cheque.

In the ink patented by Waterlow & Sons and Cliffolti (B.P. 292393, 1927) a substance fluorescing in ultra-violet light, but the fluorescence of which is destroyed by ink-erasing agents, is claimed. In a later patent (B.P. 417488) claim is made for the use of water-insoluble substances for this purpose.

Examination of Printing Inks.—The behaviour of a printing ink in practice is of much more importance than its composition. For methods of analysis, *see* luttle and Smith, J. Ind. Eng. Chem. 1914, 6, 659. Specifications for the tests to be applied to inks used in the U.S. Government Printing Office have been published. These include tests for the following properties: (1) non-separation of oil from pigment; (2) cleanliness of transfer; (3) hardness; (4) drying properties; (5) offset or smudging; (6) colour; (7) quantity required for an average 5,000 printed pages.

Arsenic in Printing Ink.—As a result of the detection of arsenic in the printing on wrappers used for bread (Elsdon, Analyst, 1924, 49, 336), Barry (*ibid.* 1927, 52, 217) suggested limits for the proportions of arsenic to be permitted in the pigments used in printing inks, and classified these pigments into three groups:

(I) those to be used unconditionally, containing less than 1 part of arsenic in 50,000 of pigment;

(II) containing between 1 in 20,000 and 1 in 50,000, to be used in conjunction with those in Class I;

(III) those containing more than 1 part in 20,000, which are to be rejected.

These suggestions were adversely criticised by Morrell and Smyth *(ibid.* 1927, 52, 339) as too stringent in view of the amount of arsenic tfrat would be present in die final ink.

Bronzing.—The production of printed matter having the colour and lustre of gold or silver, is carried Wt by printing with a varnish which remains " tacky " for a time, and then dusting over the whole surface with bronze powder or alumiifium powder or similar substances. The powder adheres only to the varnish and thus prodiTOS the dJsired effect.

Such a varnish may be produced by melting into a good linseed oil varnish sufficient beeswax to give it the consistence of lard or tallow. *{See* lire's Diet, of Arts, Manufactures, etc.; Cooley's "Cyclop, of Practical Receipts"; Lehner's "Ink Manufacture"; Southward's " Practical Printing "; Noble's " Principles and Practice of Colour Printing "; L. E. AndeV ", Oil Colours and Printer's Inks "; Mitchell's " Inks: Composition and Manufacture"; Seymour's " Modern Printing Inks.")

Marking Inks.—Natural marking inks, such as Chose prepared from the juice of the *Coriaria thymifolia* (the ink-plant of New Granada) and the juice of the Indian marking nut *(Semecarpus anacardium),* are not only used locally, but also form the basis of commercial preparations. The juice of *Rhua toxicodendron* (" the poison ivy ") and that of *Rhus venencUa* ("the poison sumach ") are also employed in the manufacture of black varnish and of marking inks.

Chemical Marking-Inks.—The inks of this type most commonly used are those containing a silver salt the reduction of which within the fibres of the fabric leaves an insoluble black pigment. In the earliest inks of this type the linen had first to be treated with a *pounce* (e.g. sodium carbonate in gum mucilage) add then dried, but these have been completely superseded by inks in which the reduction is effected by heat.

Redwood's marking ink, which is still the prptotype of certain modern marking inks, was prepared by adding a solution of 31 'parts of silver nitrate in water to an aqueous solution of 50 parts of sodium carbonate, collecting and washing the precipitated silver carbonate, triturating it with tartaric acid, and adding sufficient ammonia to dissolve the silver tartrate. The ink was then completed by the addition of *15* parts pf archil extract, 16 parts of white sugar and 50 parts of gum arabic.

An analysis by Mitchell of a British silver marking ink of this type gave the following results: twater (containing 4-87% of ammonia), 76-93; total solio>, 23-07; mineral matter, 12-30; silver, 9-98; platinum, 0-26; tartaric acid, 6-83; gum, 3-94%. The ink contained archil as a temporary pigment.

Various modifications of silver marking-inks have been published, and the addition of certain other metals to the ink has been claimed in different patents.

Aniline Marking- Inks.—Two types of these marking inks are sold. In the older type there are two solutions which are kept separate until just before use. These are to a large extent similar to Jacobsen's aniline ink (Ditglers Polytech. J.'1867,183, 78) :

(a) Copper Solution.—Copper chloride, 8-52 g.; sodium chlorate, 10·65 g.; ammonium chloride, 5-35 g.; water, 60 ml.

(b) Aniline Solution.—Aniline hydrochloride 20 g., dissolved in 30 ml. of water and. mixed with 20 g. of a solution of gum arabic (1:2) and 10 g. of glycerin.

For use, 1 part of *(a)* is mixed with 4 parts of *(b).* The writing, which is green at first, gradually blackens as aniline black forms within the fibres of the fabric. Steaming accelerates the blackening, but dry heat tends to make the marked place brittle. Finally the marked place is washed with soap and water which renders the ink a deep blue-black.

As this process is relatively tedious, there has been an increasing demand, especially by laundries, for one-solution writing and stamping inks which do not necessitate preliminary mixing, and produce markings which do not require to be steamed or washed.

In some of these inks the aniline salt and oxidising agent are so balanced that oxidation does not take place within the bottle. Several inks made on this principle were patented by Grawitz (F.P. 276397, 1898). One of them contains: (a) aniline oil, 110 ml.; hydrochloric acid (20 Be*.), 100 ml.; water, 100 ml.: (6) potassium ferrocyanide, 150 g. in 300 ml. of boiling water. The two solutions are mixed, cooled and added to a solution of 60 g. sodium chlorate in 400 ml* water.

In some of these inks the stage of retarded oxidation has not been ftached, for after keeping fluid for months they may suddenly gelatinise in the bottle.

Other one-solution inks contain an aniline blacl^ dyestuff dissolved in aniline oil or«n mixtures of aniline and its homologues** The exact composition and methods of preparing these inks are carefully guardedtas trade secrets.

Examination of Marking Inks.—The composition of a marking ink is of subsidiary importance to its behaviour in practical tests. The main requirements of a good marking ink are: (1) it must not injure the fibres of the fabric; (2) it must flow smoothly from a pen, but not " run " v4ien applied to linen; (3) the marking must darken'rapidly when treated with a moderately hot iron or otherwise; (4) the marking must not fade when repeatedly washed with soap and water, and must resist the action of acids, alkalis and bleaching agents; (5) the ink must be stable in the bqf.tle and not gelatinise OP form deposits if the cork is not replaced fos some time.

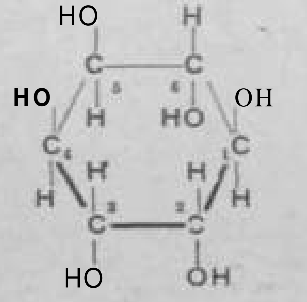
Marking Ink Pencils.—The earliest type of pencil devised for marking linen consisted of a silver salt incorporated with a suitable? basic material and a provisional colouring matter (Dunn, B.P. 2316, 1858). In other pencils (Hickisson, B.P. 9149, 1884) one end had a marking point composed of a mixture of silver nitrate fused with gum and potassium nitrates whilst the other end was a mordant *(e.g.* borax wax and pyrogallol) wliieR was applied to the writing to fix it.

Aniline dyestuffs soluble in oil are claimed by **Hlefciuon ^BJP.** 5316, 1893) as the colouring matter in marking-ink pencils. For this purpose they are incorporated with a suitable medium such as gum tragacanth, kaolin and borax. Some of the aniline marking-ink pencils now sold produce characters that are very fugitive.

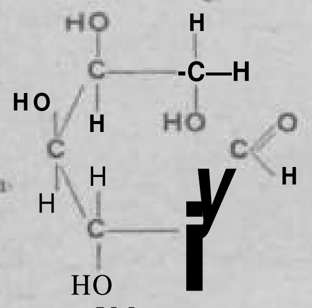
Organic pigments are now to be obtained rivalling the most permanent mineral pigments in fastness. Thus Indanthrene Blue G, after exposure to the air for 18 months was found to bo as permanent, though not quite so brilliant, as cobalt blue.

INOSINASE **(w. VoL IV, 316a).**

IN OS 1 TO **L.—**Several po ly hydro *Ky-cyclo** hexanes occur naturally, and of these the inositolfl are the best known. They are hexaliydroxycyc/ohexanea (hexitols). Nine stereoisomers of this formula are possible, according to the positions of the hydroxyl groups on each carbon atom, relative to each other and to the planB of the ring. For convenience, the above structure of (-inositol is expressed by the symbols $\frac{1\ 4\ 5}{2\ 3\ 6}$, indicating that the hydroiyl groups attached to carbon atoms 1 4, and 5 **tie** above **the** plane of the ring, and those attached to carbon atoms 2, 3 and ti lie below the plane. Using this shorthand the theoretically possible afereoisomers arc: $\frac{1\ 2\ 3\ 4\ 5\ 6}{0}$, $\frac{1\ 2\ 3\ 4\text{-}5}{6}$,
{"1 2 3 4 1 2 3 5 1 2 4 5 1 2 3 1 3 5 2 3 (1
4 **1!** **3 6** '4 5 C' 2 4 0' 1 4 5
1 4 5 / Z o " Other variations will be found upon examination to be identical with one of these structures. In particular, it should be noticed that in **one** case only is the mirror image non-coincident ; $\frac{2\ 3\ 6}{1\ 4\ S}$ cannot be made to coincide with $\frac{1\ 4\ 5}{2\ 3\ 6}$- and theso two are therefore optical boincrides. The other isomers are inactive.



Muusitol.



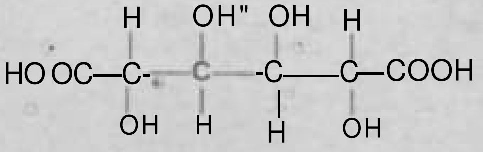
J-Maunosc.

Of these nine possible structures, four only liave been isolated. These are *d-* and /-inositol, meso- or i-inositol, and seyllitol. All occur naturally, either fret? or combined. All hav,e closely similar chemical properties. They are white crystalline solids, readily soluble in water, sparingly soluble in alcohol. Like th» sugars they have a nweet taste, and in fact are **isomerio** with the hexoaes, having the **molecular** formula $C_0H_{12}°B$. *"rom tne "formula! of J-nw-nnose and J-inositol given above, the transformation of a hexose to an mositol would- appear *tp* be *a* simple aldol change, but such a reaction has not yet been carried out *in vitro.* A reaction of this type is, however, postulated in *a.* series of changes recorded by Micheel, Ruhkopf and Suckfiill (Ber. 1935, 68 [B], 1523).

d-lnositol *(matezodambose).*—M.p. 247-248°, $[a]_D$ -j-65° {in water), occurs as the monomethyl ether in ***Pinua Umburtiana.*** DemcthyLttion with hydriodic acid yields d-inositol. Its'chemical properties are typical of other inosttols. Thus, it forms hexa-acetyl and **hexahgoxoyl** derivatives. It reduces ammoniacal "silver nitrate but not Fchling's solution, and doe3 not mutarotate.* The monomethyl ether, *pinitol,* found in *P. lamhertiana,* occurs also in senna **leaves** and in **Madagascar** rubber latex and has m.p. 188°, Mo +65*- The structures of *d-* and J-inositol are discussed immediately below.

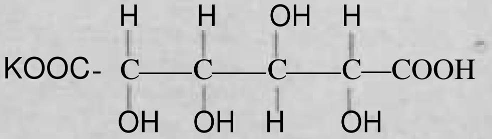
Mnositol.—M.p. 247^U_T $[a]_D$ -65°, occurs as **a** monomethyl ether, *qucbrachito],* in quebracho bark and in rubber latex. Demcthylation with hfdriodic acid yields J-inositol (Tanret, Compt. rend.* 188!), 109, 908). Qtiebrachitol is a white crystalline solid, m.p. 190°, $[a]_D$ -80°.

The structural formula? of *d-* and f-inositol are readily assigned, since of tho nine possible stereoisomers two only are optically active and enantiomorphs. -One of these is shown above (/-indsitol); the other is its mirror image. **These** structures are in agreement with the isolation of both mucic acid,



$$HOOC—\underset{OH}{\overset{H}{C}}—\underset{H}{\overset{OH"}{C}}—\underset{H}{\overset{OH}{C}}—\underset{OH}{\overset{H}{C}}—COOH$$

and <t-saccbartc acid,



$$KOOC-\underset{OH}{\overset{H}{C}}—\underset{OH}{\overset{H}{C}}—\underset{H}{\overset{OH}{C}}—\underset{OH}{\overset{H}{C}}—COOH$$

on oxidation of i-inositol with jir-rmanganate (Posternak, Helv.Thim. Acta, 1930, 19, 1007). The configurations assigned are not absolute but are dependent upon the convention used in the sugar aeries.

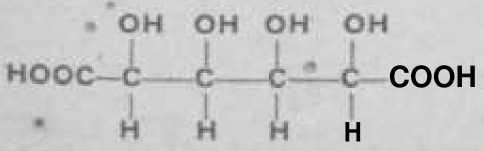
Racemic, **rii-lnositol.—ftLp. 283°,** can **be** formed by mixing **equal** weights of *d-* and /-inositol, and occurs naturally in mistletoe berriea and "in blackberries. It ia, of course, inactive (Tanret, Compt. rend. 1907, 145, 1196}.

I- Inositol *{mQBoinositol, dambose, nueite)* is the isomer most commonly found in nature. It occurs in muscle, heart, lunga find liver and many other human and animal organs. ITi plants it ia also widespread, especially in leaves (asparagus, oak, ash, walnut, etc.), frequently esterified with phosphoric acid *(e.g.* phytin). The large-scale isolation from the steep-waters from the preparation of corn starch has been described by, Hoglart and Bar tow (Ind. Eng. Chem. 3939", 31, 749). A monomethyl ether, *borneaiiol* (m.p. 199°) is found in Bccneo rubber; a dimethyl ether, *dambonitol* (m.p. 195°) has been isolated from Gaboon rubber. An icomerk monomethyl ether, *sequoyite,* has been isolated from redwood fSherrurd anrl Kurth, J. Anier. Chem. Soc. 1929,51, 3139).

t-Inositol is a white crystalline solid, m.p. 225°, optically inactive and non-reducing. The following derivatives have been described : the /texa-a«.(ii(e, m.p. 212°, the *wonobronw-inositol penta-acetate,* m.p. 240°, *iHbTOMoinositul tetra-acetate,* m.p. 140° or 235°, nnd the *inoaitotdi-bromofydrin,* m.p. 210° (Miilier, J.C.S. 1907, 91, 1780; *see also* Griffin and Nelson, .1. AIIHT. Chem. Soe. 1915, 37, 1555); the *hexapropionaU,* m.p. J00°, the *hexa-n-bulyrate,* m.p. 81°, the *kexa-mobidyrate,* m.p. 181°, the *hexa-n-valera(e,* m.p. fi3°, the *hexa-iacrvalerate,* m.p, 147°, and the *kczw-3:5-dinUrobenzoate,* m.p. 86" fHogfan and Bartow, *I.e.).* On oxidation with nitric acid *(d* 1-4) it yield* the ketone *inosose* (penta-hydroxycyctohextwone), m.p. 198-200° (Vostcr-nak, Helv. Cliim. Aeta, HI3U, 19, 1833).

The allocation of a structural formula to t-inositol is difficult. Since it is optically inactive, the structures $\frac{2\ 3\ 0}{1\ 4\ 0}$ and $\frac{1\ 4\ 5}{}$ *(see ab<fce)* may he ruled out; in fact, they bclon^*to </- and (-inositol. Seven possibilities remain, and these'are reviewed by Posternak (Comfit, rend. 19:29, 188, 121)0). The following considerations enable a formula to be suggested:

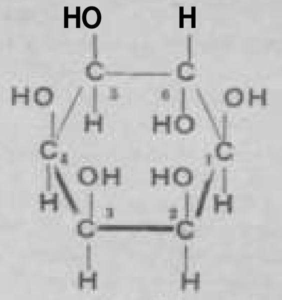
(a) A tctraphosphnte of fcfnosjtol with a negative rotation lias becjj prepared. This fact excludes structure $\frac{1\ 2\ 3\ 4\ 5\ \circ}{0}$. *(b)* An in-adive monophosphate is known (AncWsott, J. Biol. Chem.]<J15, 20, 480, 405). ?tiis ex-eludes structure $\frac{1\ 2\ 3\ 4}{}$. *(cf* The action of fuming nitric acid on mono- and di-phosphates of t-inositol gives both raccmie and inactive tartaric aeida. These could not be obtained froiV the structure $\frac{}{0\ 4\ 6}$. *(d)* Oxidation with alkaline permanganate at 0° gives among other products, allomucie acid,



$$HOOC-\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{OH}{C}}-COOH$$

Of the remaining structures, this acid cftn only be obtained from $\frac{*\ 2\ \wedge\ 4\ 5}{0}$.

The structure of Mnositol would therefore appear to be :



i-Inositol.

This configuration is supported by more recent work'fty Postemak (Arch. Sci. phys, nat. 1941, [v], 23, Suppl. 44). *Acetoixtcter suboxydana* oxidises i-inositol tn give a keto group at C_a, and on further oxidation ($KMnO_r Na,CO_3$) df-sacclumc acid is formed, establishing the structure of the ketone. The latter oil i :tt,ih tic reduction (H_4-PtO_a) yields i-inoaitol quantitatively. If sodium amalgam is used for the reduction, *acyllitol* is also formed *(see belvir).*

Mnositol ias been found to promote the growth of bacteria and other organisms, including yeast. In this connection it ha.s been cull^il " *bios I."* A review of these accessory growth factors has been given by Eosor and Saunders (Bact. Revs. 193K, 2, 9N) *[v.* QBOWTH-PBO-MOTDto SUBSTANCES, this VoL,]). 138).

A hexaphosphtite of i-inositul, *pin/tic, acid,* occurs as an alkali salt *(phytin)* in pUnts arxl plant seeds («ee Posternak, Compt rend. 1919, 169, 139; Helv. Chim. Acta, 1921, 4, 150; Anderson, J. Biol. Chem. 1915, 20, 490).

Scyllitol *(cocositol, querciniiol),* m.p. 3-19°, is a fourth siereoisonie^ of the inositol group. It has been found in organs of the dog-fish *(Scyllium canicula)* and in the cocoaffut palm *[Cocoa* species) and in *Acanthus vulgarUf C'orntu jlorida,* etc. Recent work by Poatemak *[lx.* 1941)* indicates that scyllitol ditlers* from t-inositol only in the configuration aiffuml C_a.

The preparation of other isoincrs liar been reported from the aclion of acids on t-inositol (Muller, J.C.S. 1912,101, 2393) and by reduction of the ketone iiio.«o^fl (Posteniak, fietv. ('him. Xetft, 1930, 19, 1333). Little ia known of these products.

An A'-ray examination *of I-* and i-inositol and of quebrachitul has been made (Patterson and WI lite, Z. Krist. 19X1, 78, 70 ; White, *ibid,* 80, 1).

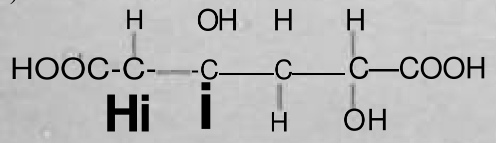
iSfor the detection of inositols, Scherer's reaction is used (Annalcn, 1852,81, 375). Evaporation with nitric acid and then with ammoniacal calcium chloride yields a rose-red coloration if 0-0005 g. of inositol is present. The estimation of inositols in the presence of yhicose, using periodic acid, is described by I^leury and July (J. I'harm.' Chim.,. 1937, 26, 341, 897). D. W. Woolley (.I'. Biol. Chem. 1941, 140, 453) determines i-inositol by its growth-promoting pBfect.apon y< :ist {\f(jut rat ions.

PEKTITOLS.

Owing to their close relationship to tlx-inositols (hesitob), the pentahydroxyc^c/o-hexanes (pentitols) may be mentioned here. Of the sixteen possible sterepisomers of thia formula, two only are known, both optically active. They are named d- and *l-qutrriial,* but they are aot enantiomorphous. This nomenclature is therefore unfortunate, since enantiomorrihs may well be found.

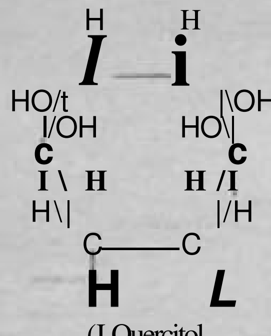
d-Quercitol, $C_8H_{1S}O_S$, m.p. 234°, $[a]_D$ +24° (in water), is found in acorns and to a email extent in the leaveB and bark of the oak. It -has also been isolated from the leaves of *Cha&maervpshumilis* Linn., the European member of the palm family (H. MiiUer, J.C.S. 1907, 91, 1766). The presence of five hydroxyl groups is shown by the formation of a penta-acetate and pentanitrate. It is reduced by hydriodic acid to a mixture of aromatic derivatives, including benzene, phenol, pyrogallol and quinone, and also to hexane.

The structure of d-quercitol has been the subject of communications by Karrer (Helv. Chim. Acta, 1926, 9, 116), Kiliani and Scheibler (Ber. 1889,22, 517 ; 1931,64 [B], 2473) and Posternak (Helv. Chim. Acta, 1932,15,948). The isolation of mucic acid from the products of oxidation by nitric acid (Kiliani) agrees with structures expressed by the arrangements 2 5 6 •r-j't 2 5 6 „ T-» or their mirror images, 1 4 ,;--^ 2 u U 3 4 » v 5 2 O D ("«« *above* for explanation of the LJtation). Posternak (1.0.) oxidised tf-quercitol with alkaline permanganate at 0° and isolated metasaccharonic acid (yield 19%) from among the products. This acid he identified by degradation of the corresponding aldono-lactone (metasaccharin) to d-2-deoxyxylose (Levene and Mori, J. Biol. Chem. 1929, 83, 803).



$$HOOC-\overset{H}{C}-\overset{OH}{C}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}-COOH$$

Metasai'chiironic add.



(J-Quercitol.

The structure of d-quercitol follows, but it is, of course, dependent upon the convention wb,ich allocates the configuration of d-gluco»e. It may be noted that d-quercitol is a deoxy-rf-inositol.

/-Quercitoi.m.p. 174°, $[oj_B$ -74° (in water), occult in the leaves of *Oymnema sylvettre.* It is not the cnantiomorph of tZ-quercitol >and *Us* structure ifl not known.

G. T. Y.

INSECT WAX (Chinese Wax, Chinese Insect Wax) is the secretion of an insect. *Coccus ceriferw* Fabr. *(0. pela* Westwood), which infests the bark and twigs of the " evergreen tree," *Ligustrum luciduvi* Ait. growing in Western China. It should not be confused with the so-called " China wax," the Chinese variety of oriental beeswax, *v.* GHEDDA WAX.

E. L.

INSECTICIDE EMULSIONS (i>. Vol.IV, 301*d*).

INSULARINE. Insularino has been isolated together with a second base from the root of *Cissampelos irwutt&ria* Makino (Fam. Menispermaceae) by Kondo and Yano {J. Phu,m. Soc, Japan, 1927,47, 107). *C. ochiaiana* Yamamoto also contains insularine (Kondo and Tomita, Arch. Pharm. 1936, 274, 76).

Itisvlarine, C_a,$Hj_8N;_.O_6$, [a]^ +27-95°, m.p. 160°, ia amorphous and easily soluble in Et_2O (thus weparated from accompanying base). It contains three methoxyl and two N-methyl groups, the three remaining oxygen atoms occur probably in ether linkages. The Hofmann degradation of the methiodide yields an o-*meihine,* m.p. 115°, to]" +110-6°, and a *B-methint,* m.p. 185°, Further degradation yields a N-free compound, m.p. 208° and [a]J?+ 73-37°, needles from ether.

The constitution of insularine is still unknown ; for absorption spectrum, see Ochiai, J. Pharra. Soc. Japan, 1929, 49, 425.

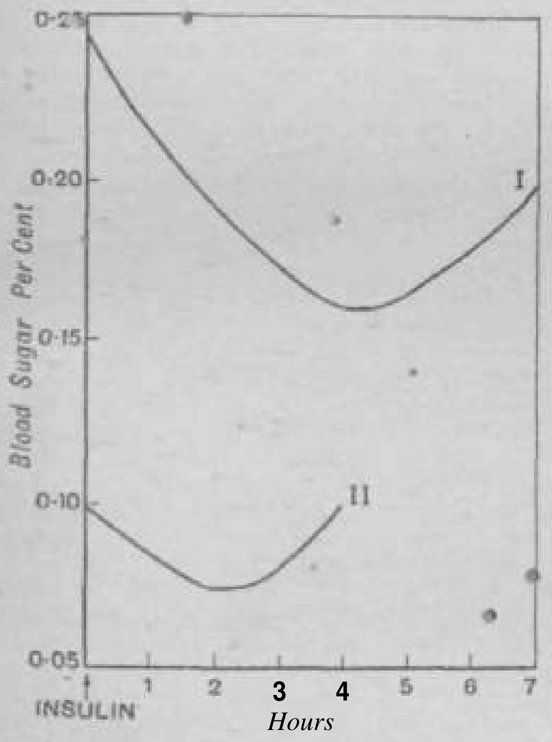
Insularine belongs to the group of the bisco* claurine alkaloids {*v.* Vol. I11, 230c) which contain 2 mol, of substituted t*enzyltetrahydroi«o-quinolines joined together by one or several oxygen^bridges. To the same chemical group belong *dauricine {q.v.), oxyacantJiine {v.* Vol. I, 683c), *berbamine, telrandrine, ph&nlhine,* etc. For survey on this group, see Kondo and Tomita(l.c).

Schl.

IN3ULIN, THE ANTID1ABETIC HORMONE. Insulin is a protein hormone from pancreas and b an important factor in the metabolism of carbohydrate in the body. When injected into the normal (curve II) or diabetic (curve I^nimal it produces a temporary decrease in blood sugar.

It ia used for the amelioration of the symptoms of *diabetes indlitus,* the causa of which may be a failure of the pancreas ta supply enough insulin for the_ needs of the body. Symptoms of this disease include hunger, thirst, polyuria and muscular weakness. The Mood sugar is high, and glucose, often accompanied by acetoacetic acid, acetone and jS-hydroxybutyric acid, is excreted in the urine.

Removal of the pancreas was shown by von Mering and Minkowski (Arch. exp. Path. Pharju. 1890, 26, 371) to cause diabetic symptoms. The occurrence of diabetes when the main gland was removed was prevented by grafting a portion of the pancreas on to the abdomen. They postulated that *diabetts mellitus* IB caused by the'absence from the body of a principle essential for carbohydrate metabolism. In mammalian pancreas there co-exist .zymogenous tissue, supplying an exocrine secretion which passes through the pancreatic duct into the duodenum, and a number of microscopic islets, first described by Longerbans, whose cells are the source of the endocrine secretion of insulin into the blood stream. These islets are frequently in anatomical continuity with the zymogenous tissue. Until 1921 many unsuccessful attempts were made to obtain pancreas extracts which would be active by oral R<1 ministration or by injection to diabetics. These failures may have been due to the destruction of insulin by the proteoytie enzymes of panCTeatic juice which are present in aqueous extracts of the whole gland. On this assumption Banting and»Best (J. Lab. clin. Med. 1921-22, 7, 251, 464) ligated the ducts in dogs, thus bringing about the degeneration of the* zymogenous tissue. The dogs were then killed and their pancre&B ground with sand and Ringer's solution. The extract was heated and the liquid filtered and when injected into^ depanereutised dogs produced a rapid decrease in glycsemia or glycosuria. Banting ajjd Best also succeeded in preparing active extracts from fcetal calves' pancreas at a stags before the fifth mdnth of gestation when the$_a$endocrine (insulin secretion is already active iWiilo the exocrine enzyme accretion has not yet been formed. In certain fishes *(TeUoslei)* the islet tissue occurs apftrt from the zymogenous tissue and Macleod (J- Metab. Research, 1922, 2, 149) prepared active extracts from this tissue.



Tho use of aqueous alcohol by Collip (J. Uiol. Chem. 1923, 55, xl-xli) and aqueous acid nlcohol by Doiay, Ssmogyt and Shaffer *(ibid.* 1923, 55, *xxxi),* madft possible a, commercially practicable process for the production of vistilin from whole ox-pancreas. Salting out.and iaoelectrio precipitation of the insulin protein to the partial exclusion of other proteins provide methods of purifying it. Moloney and Kindlay (J. Chem. Physics, 1924, 28, 402) adsorbed insulin on charcoal and then digested the charcoal with bensofa acid in 60% alcohol. The more easily adsorbed benzoic acid replaced the insulin, which was recovered by evaporating the alcohol and extracting the aqueous insulin solution with ether to remove excess benzoic acid.

Dudley (Biochem. J, 1923, 17, 3Y6) purified crude insulin by precipitating the active material from aqueous solution by picric acid and subsequently regenerating the hydrochloride from the picrate by alcoholic hydrochloric acid.

PREPARATION.

A typical method of preparing insulin is that employed by the Toronto workers, Scott and Parker (Trana.l Roy. Son. Canada, 1032, [iii], S6,V,3U)i.

100 1b. of fresh ox pancreas freed from excess fat a*1 connective tissue are cooled to 4^{D}o. as soon (is possible after slaughter. The g Ian da are minced and dropped into 25 gallons 95% alcohol (ethyl, denatured with 10% methyl alcohol), 5 gallons water and 1,200 ml. cone. HCI. The mixture is agitated for 1 hour and then allowed to stand overnight. The liquid is then drawn off by centrifuging and the residue re-extracted with an amount of 80% alcohol equal in volume to the liquid removed during the centrifugation. The combined extracts are adjusted to p_w 8 with ammonia, filtered and the filtrate rc-:uidified by adding 140 ml. of cone. HjjSO^ to each 50 gallons of solution 300 gallons of such acidified filtrate are evaporated to about 40 gallons in a vacuum still at a vapour temperature not exceeding *2-~S.* After distillation, the concentrate, at p_u 2, is quickly heated to SO^0 and filtered to remove the coagulated lipoid. After filtering and cooling to 30" the active material is then salted out by the addition of sodium chloride to *n* concentration of 25%. The crude. protein from fiffO 11). pancreas is then dissolved in 30 litres of water and reprecipitated by sodium chloride at a concentration of 1.1%. The precipitate, weighing about 150 g., is readily dissolved in 5 litres water containing 10 ml. of S.-HG1. Tricresol to 0^{P}3% concentratSon is ridded to four such combined lots eff solution, the reaction is adjusted to p_H 5 by ffdding 5s.-NaOH and the mtsture is kept at 2^e for one week. The active precipitate which separates is removed utd dissolved in 7 litres of distilled #ater containing sufficient H_SSO_4 to make the reaction p_H *2.* To this liquid 4 vol. of absolute alcohol are added slowly with stirring. After standing at room temperature for 2 days, the precipitate is separated and rejected, and to over, 6-5 litres of liquor are added 3-5 litres of absolute alcohol and 10 litres of ether. The precipitated insulin, alter standing with the solution at room temperature for 2 days, is removed, dissolved in 8 litres of distilled water and the solution .uljlisted to^p_H 5. The resulting aciive precipitate is amoved and dissolved in *16 litres of* distilled water containing enough HCI to make the reaction of the solution pj, 2-8. * This solution is sterilised by means of aijeitz filter agd the potency assayed. The yield of insulin is about 2,000 units per kg. pancreas, but varien according to the quality of pancreas employed.

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[1] A more recent inotliod 1B deMrlbad by Roman*. Scott and Usher in Intl. Eng, Chem. 1040, 32, 9U8.

Kiaber and .Scott (J. Biol. Chem. **1984,** 106, 305) found that the inmilin content of cattle pancreas decreases with in'Tv:istng ago *vi* the animal.

Animal.	Age.	Uni.i per kg.
Fœtal calves .	5 months	29,200–38,800
" " .	5–7 "	**21,100 24,900**
Calves . . .	6–8 weeks	10,400–12,800
Cattle . . .	2 years	3,90<!-<U00
Cows . . .	9 "	I.7OQ-2.0OO

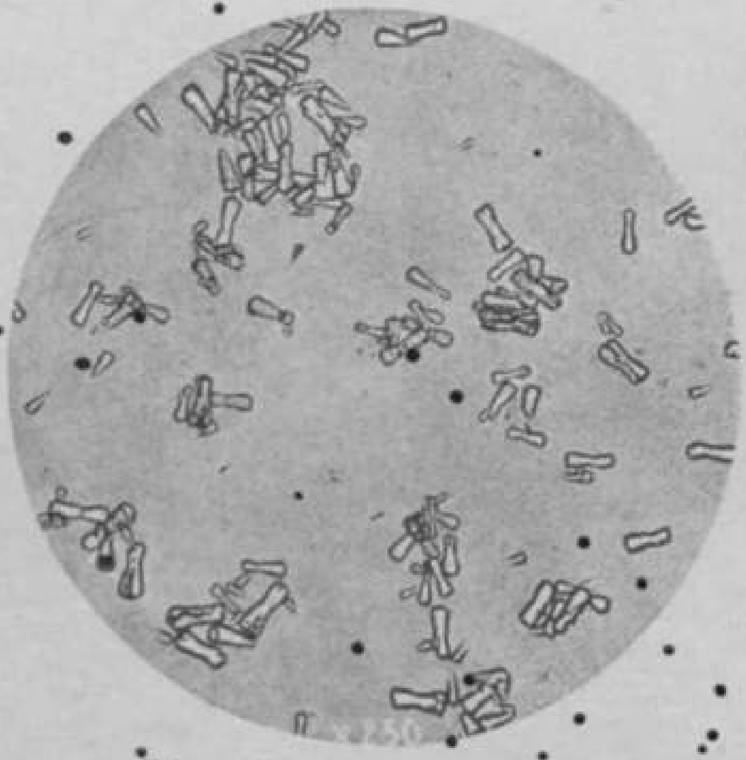
PROPERTIES.

Crystalline Insulin.—AM (Prwc, Nat Acad. H<i. **1026,** 12. **182)** fintt described eryslallino iuiwlin which he **obtained** in tho form of microflcopic rhomuobedra by **djaolving** insulin in weak iicetic **add** and *moating* rontAmg imparities by precipitation *with* brudn<. After adding ai,/6 pyridine **to Uu dear** solution there **rwM** produced on standing a predpitate of crystalline and anlorphoug insulin. Haringion and Scott (Bioc''™- J- 1»-9. 23, 384) descriiU- an improved method of **preparing** insulin ery- »UU by the u» of 8(1ponin **and pndpftting**

arington and Sec
ethod were submi.

,i t 'fhr WCd variati™ ^cording to ibe mttlrnd **OM)** fn,m 20 to 27 intentional unite per mg.

lmulin aafc. su.h as hydrochloride, sulphate, picrate have not been crystallised but are readily obtained <w **aawrphooa** i».wdcrs. • Scott *[ibid.* **IBM,** 28. 1592) found tnat the cry- **nateia** z.inc and thnt tra<* of ^ of zinc, cadmium, nickel «nd cobalt facilitate crystallisttion and showed, moreover, that electrodialysed insulin -flow ash content could not **be** mdueed to eryiulliw without the addition of trace* of **the« metajg.** H<-elaborated a method of crystalliwition I>v **adding** insulin to a



WEDGE-SHAPED INSULIN CRYSTALS.

phosphat.J ImlTcr contain UK *M%* acetone and a salt of sbio, the insulin **concentration** in the mixturc Iwing ftbfjut 0-1%; adjustment of the mixture to /iJt 0 **Atahed** invariably in proJuction of crystals or (.'ryxLals and amorphuuit .'haultn (in the latter ca.se the crystals can be 'separated from the amorphous by gontlt < <•ntri-

Si-ott (Trans. Uoy. Soc. Canada, I9S2, lijjl * ^)-™> Receded in obtaining two ibms of cryatallme insulin, a **wadae-ahaped** form from «<lueonB acetone acetate buffer at »„ fi-2 and the more uaual rhombohedra from the same procedure at p_H 0. The erj-atals were idenUeS in composition and potency. Insulin is, therefore, dimorphous.

Physical.—Insulin hydrochloride forms' a white powder, non-deli soluble in water. AdJ«^ment of the aqueous solution to p_H 5·5 isoelectric precipitate which Wint H laiid er Abramson (J. Biol. Chem. 1 found to Jmw. a constant solubility in **M./30** acetate buff! t p_H 4·8–6·5 «rf<WK»4%. The isoelectric precipitate is tMdiJJ' ^"We in all acids and alkalis although hih concentrations **of tJie** former reprecipitat P«it **witil** Ion of potency. Crystalline insulin dissolvea readily

in dilute acid and with difficulty in alkali. Insulin is soluble in phenol, cresol, formamide, strong aqueous solutions of amides, anhydrous liquid ammonia and aqueous acetone and alcohol below 80%. It is insoluble in pyridine, alcohol, acetone, ether, chloroform, ethyl acetate, xylene, benzene, toluene, propyl, butyl and amyl alcohols, petroleum and most other anhydrous organic solvents. High temperatures in aqueous solution cause inactivation and it is more unstable in alkaline than in acid solution. Heating to 100° in the dry state has little effect. According to Krogh and Hemmingsen (Biochem. J. 1928, 22, 1231) the half-life period of insulin at p_H [illegible] at various temperatures is :

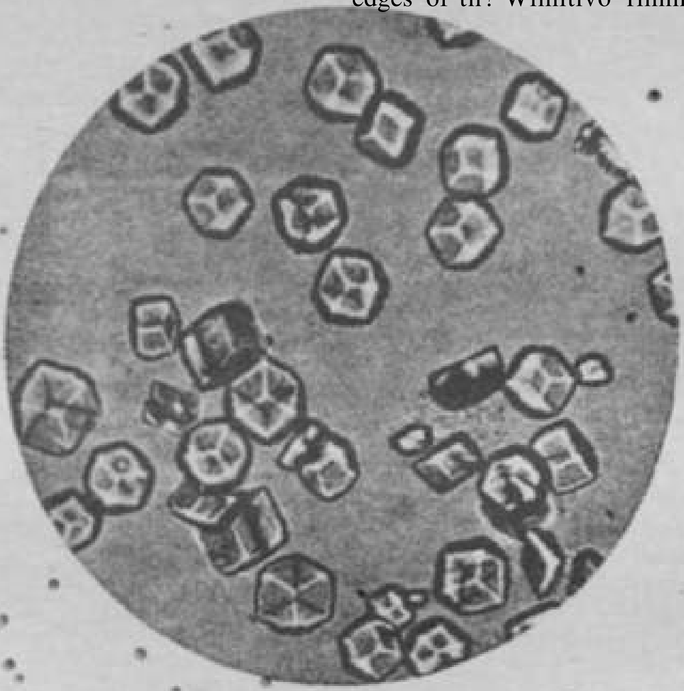
Temperature.	Half-life period.
40°	6 months
30°	2 years
20°	10 "
10°	66 "
0°	377 "

Insulin does not dialyse readily through collodion membranes.

In solution, insulin is lævo-rotatory, the degree of rotation depending on the reaction of the medium, thus:

Medium.	Insulin strength.	[α].
0·02n. HCl	0·5%	-40°
10% acetic acid	0·5%	-18° to -30°
N/50 ammonia	0·5%	-64°

Insulin has a characteristic absorption band lying between 2,700 and 2,900 Å, which has been ascribed to the cystine and tyrosine content. Ultra-violet light of various wave-lengths in the presence of oxygen inactivates insulin. Crowfoot (Nature, 1935, 135, 591) by X-ray photographs of single insulin crystals showed that they had simple rhombohedral cells with a=44·3 Å. and α=114°. Their density was found to be 1·306. The crystal unit cell contains 1 mol. of insulin only, and each molecule is surrounded by eight others, one each at 30 Å. above and below along the trigonal axis and six at 44 Å. along the edges of the primitive rhombohedron. Insulin is adsorbed from water by fuller's earth, charcoal, kaolin, benzoic acid, salicylic acid and aluminium hydroxide.



RHOMBOHEDRAL INSULIN CRYSTALS.

Chemical.—Isoelectric or crystalline insulin can be converted into the hydrochloride or sulphate by dissolving in dilute hydrochloric or sulphuric acid and adding 1½ vol. of acetone, when the salt separates as a flocculent white precipitate. Crystalline insulin exhibits the usual properties of a protein giving the biuret, Millon, Pauly, ninhydrin and xanthoproteic reactions. It does not contain phosphorus, however, and the tests for tryptophan and carbohydrate are negative. On heating, the crystals turn brown at [illegible] and melt with decomposition at 233°. Apart from its isoelectric insolubility in aqueous solution from p_H 4·5–6, insulin may be precipitated from solution by all the usual protein precipitants such as picric, tannic, flavianic, tungstic, trichloroacetic, phosphotungstic and Reinecke's acids, heavy metal hydroxides, etc. It *may* be salted out of acid solution completely by half saturation with neutral salts such as sodium chloride or ammonium sulphate, and in this respect more closely resembles a globulin than an ovalbumin. Attention has recently been directed to the precipitation of insulin in neutral solution by basic substances such as histones, protamines or their degradation products, and by spermine and guanidine derivatives in attempts to produce complexes having more prolonged hypoglycsemic action.

The nitrogen and sulphur contents of crystalline insulin are variously given as 14-4-15-4% and 3-15-3*44% respectively. Miller and du Vigneaud (J. Biol. Chem. 1937, 118, 101) accounted for 95% of the sulphur as present in cystine when the hormone was hydrolysed by a mixture of formic and hydrochloric acids, while previously with ordinary hydrochloric acid hydrolysis it had been possible thus to identify only three-fourths of the»total sulphur. Sullivan and Hess *(ibid.* 1939, 130, 745) showed that recrystallisation of insulin from an amnftmium acetate-pyridine buffer, while leaving the total sulphur content of the compound unchanged, affects a part of the cystine components in such a way as to lead to losses of sulphur in volatile form during hydrochloric but not hydrochloric-formic acid hydrolysis. Insulin recrystallised from a phosphate buffer showed no such evidence, of labile cystine. No difference could be detected in the physiological assay value of the two products. Scott and Fisher (Biochem. J. 1935,29,1048) found 0-52% of zinc in crystalline insulin, corresponding to 3 atoms of zinc per mol., assuming a molecular weight of about 37,000. Cohn *et ah* (J. AmerfChem. Soc. 1941, 63, 17) have used radioactive zinc to prepare insulin crystals so that analysis of zinc content could be carried out with reasonable accuracy on 0-2 g. After repeated equilibrations with conductivity water at reactions between p_a 5 and 6-4, which would be expected to remove occluded zinc salts, a zinc content of about 0-3% corresponding to 2 zinc atoms per mob was obtained even from crystals containing initially 0-6% zinc. Sahyun (J. Biol. Chem. 1941, 138, 487) has, however, described a crystalline insulin with a zinc content ofonlvO-15%.

When insulin is heated in N./10 HCI at 100°, a flocculent inactive precipitate forms which is solublf in dilute alkali at ©H 11 and then regains its solubility in acid and also 80% of its activity.

Inactivation of insulin is brought about by HCHO, strong acids and alkalis, dilute HNO_2, N./2 NH_4OH, N./10 NaOH, acetic anhydride; 0-75N. HCI in 75% EtOH, cysteine, glutathione, thioglycollic and thiolactic acids, I_2, H_2O_2, Na_2SO_3, $K_3Fe(CN)_8$, H_2S, H_2S_2, diazome'thane, Na and Mg amalgams, Mel, leuco-Methylene Blue, hydrocyanic acid, ketae, ascorbic acid and quinol. These reagents may bring about inactivation by either : (1) reduction of the disulphide groups; (2) esterification or acetylation of the amino-, imino- or phenolic hydroxy-groups; (3) hydrolysis of peptide bonds; or (4) destruction of amino-groups, *e.g.* by HNO_2. Reduction by specfic reagents of —S—S— groups, as in cystine and gluta/'hione, irreversibly inactivates the hormone and in proportion as SH groups are *get* free, although the degree of inactivation increases much more rapidly than that of reduction. The reduced insulin has also lost the characteristic heat-precipitation reaction. Insulin may be acetylated with acetic anhydride in the cold (Freudenberg *et aL9* Z. physiol. Chem. 1928,175, 1; 1932, 213, 241), producing an inactive substance which may regain a large part of its activity on hydrolysis with dilute alkali. More recently, Stern and White (J. Biol. Chem. 1937-38,122, 371) have shown that the interaction of ketene and insulin produces acetylation of the amino-groups only, with no inactivation if the time of contact is short;. After this, the phenolic hydroxy-groups are acetylated with loss rff activity. Carrè* *al. (ibid.* 1929, 23, 1010) found that insub'n became inactive *when.* al]pwed to stand in acidified alcohol for several hours and was partially reactivated by dilute alkali. Inactivation also occurs with other solvents such as acetone in the presence of hydrochloric acid so that the process may be due to a reversible intramolecular rearrangement (Scott andftsher, *ibid.* 1935, 29, 1050) rather than to esterification. Hydrolysis of peptide bonds by acids or alkalies leads to irreversible inactivation accompanied by a decrease in cystine or amino-nitrogen content or both. Reversible inactivation is generally produced by reactions involving a blocking of the amino- or phenolic groups. The hypoglycaemic activity of insulin is thus apparently associated with certain dithio-, phenolic and probably amino-groups which are, however, found in most proteins. The activity is either a property of the molecule as a whole or is due to»some labile unit which has hitherto escaped detection.

ENZYME ACTION.

Irreversible inactivation is produced by pepsin, trypsin and papain, but Hot by trypsin-free erepsin, non-activated kinase-free trypsin, amino-polypeptidases, dipeptidase, protaminases or carboxypolypeptidases. Any proteolytic or other degradation with a view to obtaining a smaller molecule with the same physiological actions has always resulted in less activity.

Harington and Neuberger *(ibid.* 1936, 30,809), from results of electrometric titrations in aqueous and 80% alcohoj solutions, deduce that insulin has an acid-binding capacity of 43 ±2 groups per mol. and a base-binding capacity of 60-70 groups per mol.

Insulin has been found to have a molecular weight of 35,000 and 37,000 by ultra-centrifugal and Jr-ray measurements respectively with a spherical molectfie of the o^albumin type.

The followjng table, b/ du Vigneaud (Cold Spring Harbor Monographs, 1938, Proteins, p. 279) of the distribution of aminoacids and other constituents is based on Bergman's theory of the presence of 288 mol. of aminoacid in the Svedberg unit of molecular weight 35,100.

Winch (Proc. Roy. Soc. 1937, A, 160, 59; 161, 505) in her cyclol theory suggested that the arrangement of these 288 residues in a closed cage molecule in the form of a truncated tetrahedron may be the appropriate structure for globular-type proteins like insulin, pepsin and egg albumin of molecular weight 35,000.

PHYSIOLOGICAL ACTION.

Insulin when injected lowers the blood sugar and, if the dose is large, may cause hypoglycaemic coma, convulsions and death. Intra-

Aminoacid.	Per cent, aminoacid residue.		Molecules aminoacid residue.		Molecules calculated as 2>n x 3n.
	Found.	Calculated.	Found.	Calculated.	
Lysine	1-98	2-2	5-4	6	$2^1 x 3^t$
Arginine	2-88	2-06	6-5	6	$2' x S^1$
Histidino	710	7-0	18-2	18	$2^1 x 3^8$
Tyrosine	11-00	11-2	23>ti	24	2^3x3»
Cyatine	10-70	10-8	366	36	2^1x3*
Ghitamic acid	26-30	26-4	**71-6**	72	$2^3 \times 3^2$
Leuci.Je	25-90	23-2	80-4	72	2^sx3*
Phenylalanine	1-0?	—	—	—	—
Proline	100?	—	—	—	—
Total accounted for	85-86?	83-16	242-3	234	—
Theoretical	—	100-00	—	288	—

Constituent.	Per cent.		Molecules or groups.		Molecules calculated as 2m *x* 3°.
	Found.	Calculated.	Found.	Calculated.	
Zinc	0-52	0-56	2-8	3	$2^0 \times 3^1$
Amide ami no	1-55	1-64	34	36	$2^2 \times 3^2$
Sulphur	3-2	3-28	35	36	$2^2 \times 3^2$

venous injection produces the quickest response, and then subcutaneous, with iiitrathecal and subarachnoid the slowest. Although depression of blood sugar continues for several hours after intravenous injection, yet only 10% of the insulin remains in the blood after 50 minutes. For small doses in rabbits (^-£ U. per kg. body weight) the ratio dose/fall in blood sugar is logarithmic. Mice show little response at 18" but go into convulsions at 30°. The speed of action of insulin is dependent on the metabtjic rate of the animal itself. Frogs react very slowly to doses of insulin. Insulin produces*hypoglyuEDmia but no convulsions in the fowl. In man symptoms include hunger, fatigue, mental distress and delirium, and in cats salivation. Decreases in sugar of lymph and cerebrospinal fluid are also recorded. Insulin secretion occurs early in fœtal life. Injection of insulin causes increases in acidity and chloride content of gastric juice in normal humans. Briggs *et al.* (J. Biol. Chem. 1923, 58T 721) showed that insulin caused a decreases in concentration **oft** blood-phosphorus and •potassium Jn animals, and Kay and Robison ^Biochem. J. 1924, 18.11.19) conclude that insulin brings abotft synthesis of esters of phosphoric acid in the corpuscles from the blood-glucose and inorganic phosphate. The blood of depancreatiaed animals contains 10-20 tinv s as much acetaldehyde as normals and in**jectkun** of insulin restore it to normal. Insulin counteracts adrenaline hyperglyeseraia and simultaneous injections of insulin and adrenaline may produce no change in blood sugar. Bilaterally adrenalectomised .animals are hyperecnaitivo to insulin. Burn {J. Physiol. 1923, 57, 318) found that pituitrih reduced adrenaline hyperglycaemia, but found an unexpected antagonism to insulin action by pituitrin. Burn and Marks *(ibid.* 1925, 60, 131) found that thyroidectomy greatly increased the sensitivity of animals to insulin. Insulin injection provokes a fall in body temperature. Houssay (New England J. Med. ^936, **214,** 961} found that diabetic symptoms following pancreatectomy were considerably ameliorated by hypophysectomy performed either befpre or*after the removal of the pancreas. Young (Lancet, 1937, ii, 372) has found that injection of an anterior pituitary diabetogenic extract into dogs produces a condition simulating human diabetes, **and** further (Marks and Young, *itM.* 1940, i, 493), that a " pancreotropiff" extract prepared in another way from the same gland produced on injection an increase in the insulin content of rat pancreas. The exact rôle of insulin in carbohydrate metabolism is still obscure thjmgh a specific *in vitro* effect has been described by Krebs *et al.* (Biochem. J. 1938, 32, 913) where the oxidation of citjic acid by pigeorrbreas muscle is catalytically increased by insulin.

ADMINISTRATION OK INSDLIN.

Insulin is usually administered in solution as the hydrochlorido by subcutaneous injection. Intravenous or .pther parenteral injections, however, produce a blood-sugar-lowering effect. The requirements vary widely in different cases of diabetes and normally range from 5 to 100 units per person administered daily in 2-3 injections. Attempts made to obtain insulin preparations which could be given by mouth or arinunctions have not proved successful. Sinc^ insulin is destroyed \fy proteolytic enzymea, oral administration must be designed to protect it against the digestiv% action of pepsin and trypsiu. In general large amounts of insulin mixrtt with alkali.*oil-, saponin- or try pain-in hi biting substances have some slight effect when given orally, but this method of administration remains uncertain. Ointments of insulin and lannlino have little effect on an intact skin, whereas a recently abraded skin allows appreciable absorption to take place. Insulin may be applied to the mucous surface of nose and mouth with slight action. Administration by the oral route, by inunction or by endonasal application requires large amounts of insulin and does not permit accurate quantitative dosage.

Attempts have been made to prolong the action of insulin by retarding its absorption when injected (1) as an oil suspension or emulsion, (2) with a vasoconstrictor substance, and (3) as an insulin compound sparingly soluble in body fluids. Tho last has proved very successful. Hagedorn *et al.* (J. Amcr. Med. Assoc. 1930, **106,** 177) showed that insulin may be combined with some basic group so that the compound may have its isoclcctric point or zone of insolubility nearer to the reaction of tissue fluids than that of insulin itself. Kyrin, histories, globins and protamincs were tried but only the compounds of insulin and protamincs were found to have sufficiently low solubilities at p_u 7. In particular the compound of insulin with the pro tarn i no derived from rainbow trout, *Salmo irideus,* was found to have the very low solubility of $10\sim^{5}$ in water at p_H 7-3. 'The amount of protamine combining with insulin is about 1:10. Injections of the insulin-protamine suspension have a considerably prolonged action when compared with insulin hydrochloride. Scott and Fisher (J. Vharm. Exp. Ther. 1936, 58, 78) further showed that when a small amount of zinc (1 mg. per 500 units of insulin) is added to an insulin solution prior to the addition of protamine, the hypoglyc&mic action of the resulting suspension is even more prolonged than that of protamine-in^ulin without zinc. This protamine-iiinc-insulin suspension is now frequently administerecWin preference to insulin hydrochlgride, since one single daily injection of the suspension each morning may control glyciemia and glycosuria where 2 or 3 injections of hydfochloride were previously required.

Parkês jyid Young (J. Endocrinol, 1939, 1, 108) have reported that the implantation of pellets* of solid crystalline insulin has a prolonged action. Insulin has recently been used with success in tho " shock" treatment of catatonic stupor and schizophrenia in which a coma-producing dose is given (I)ussik and Sakel, Z. ges. Neural, u. Psychiat. 1936, **155,** 351).

STANDARDISATION.

Despite what *is* known of the chemical native of insulin no chemical property or properties can bo used as a true criterion of potency. Even its crystalline form is not necessarily a criterion of homogeneity, since crystals have been obtained of potency 70% of the standard. In 1935 the League of Nations Health ^Organisation adopted as standard a sample of insulin recrystallised 10 times under tho supervision of Dr. Scott at Torooto. To this pure insulin there has been attributed after numerous biological frsts in different laboratories the value 22 units per mg. All insulin is assayed in terms of this standard which has been distributed to various centres throughout the world. All the methods of assay are, therefore, biological. In the rabbit test the animals arc divided into two groups, one injected with the standard and the other with the unknown. Some days later the test is repeated with the same animals-but with the groups reversed. The reductions of blood sugar in the rabbits injected with the standard insulin are then compared with the reductions produced by the sample of unknown potency. In the mouse test, carried ofit in a thermostat at 38°„ the number of mice sent into convulsions by a certain dose of the solution to be tested is compared with the number convulsed? by varying doses of the standard solution. The assay of a suspension of protaminc-zinc-insulin made from a previously standardised insulin solution#by the addition of zinc and protamine is carried out on rabbits against cither a standaroVprotamin/j-zinc insulin-suspension or against an ordinary standard insulin hydrochloride solution, tho shape of the prolonged-action curve falling within certain prescribed limits.

T. F. I).

INTERATOMIC DISTANCES.— The distances between the atoms in a molecule may be determined by too entirely different methods, generally known as (a) the spectroscopic method, and *(b)* the diffraction method. Each of these general methods may be subdivided. The first of the spectroscopic methods is based on the evaluation of the moments of inertia of the molecule from the fine structure in the molecular spectrum due to the rotation of the molecule; the second is based on an empirical relation between the interatomic distance (or bond) in question and its associated force constant, the latter being deduced from the vibrational frequencies in the spectrum. In this article these two spectroscopic methods will be denoted by the respective symbols Sj and S_2. The first of the diffraction methods is based on the theory of the diffraction of X-rays by a crystal lattice; the second is based on the theory of the diffraction of electrons by a gas. It is possible also to obtain interatomic distances by the diffraction of X-rays i? gases and the diffraction of electrons by crystals, but the accuracy in each case is very low and these methods need not be considered. The two diffraction methods will be denoted by D_x and P_E according as -X-rays or electrons arc being diffracted.

The Sj method is applicable when the individual rotation*' lines of tbe spectrum can be resolvtd, and ,'s by far the 'most accurate of all the four methods, the error being generally less than 0001A. Unfortunately this method has not a wide range of applicability, for the rotation lines become more difficult to resolve as the size of the molecule increases, since the spactigs between them depend on reciprocals of the moments of inertia of the molecule. Moreover it is obviously not possible to determine all the interatomic distances and angles in a complex molecule from a knowledge of the three moments of inertia. This last difficulty may be overcome to some extent by using different isotopic forms of the same molecule and by making assumptions regarding certain of the interatomic distances and interbond angles well established from other molecules.

H (0·30)	[illegible]	0·741 $^3H^2H$ S_1	0·742 $^2H_2$ S_1											
Li	[illegible]	1·595 Li^2H S_1			2·672 Li_2 S_1									
[illegible]	[illegible]	1·343 Be^2H S_1												
B [illegible]	1·233 B^1H S_1	1·231 B^2H S_1	1·27 B_2H_6 D_{2h}								1·86 B_2H_6 D_{2h}	1·594 B_2 S_1		
[illegible]	1·120 C^1H S_1	[illegible]	1·057 C_2H_2 S_1	1·04 CH_2O S_1							1·56 $B(CH_3)_3$ D_{3h}			
N (0·70)	[illegible] N^1H S_1	[illegible]									1·44 $B_3N_3H_6$ D_{3h}	1·281 BN S_1		
[illegible]	0·971 O^1H S_1	0·96[illegible] O^2H S_1	[illegible]					[illegible]			1·205 BO S_1			
[illegible]	0·917 ^1HF S_1							1·362 BeF S_1			1·309 BF S_1	1·30 BF_3 D_{3h}	1·29 BF_3 S_1	
Na	1·888 Na^1H S_1	[illegible]												
[illegible]	1·731 Mg^1H S_1	1·730 Mg^2H S_1												
Al	1·646 Al^1H S_1										2·14 AlB_3H_{12} D_{3h}			
Si (1·17)	1·52[illegible] Si^1H S_1		1·47 Si_2H_6 D_{3d}											
[illegible]	[1·43] P^1H S_1	[illegible]												
S (1·04)	1·3[illegible] H_2S S_1													
[illegible]	*1·275 $^1H^{35}Cl$ S_1	[illegible] ^{35}Cl									[illegible]	[illegible]		

	C (0·77)								N (0·70)				[illegible]			
[illegible]	1·542 Diamond	1·55 C_2H_6 D_E	1·39 C_6H_6 D_E	[illegible]	1·312 C_2 S_1	[illegible]	1·46 MeC:CH S_1	1·52 [illegible]								
(0·70)	1·172 CN S_1	[illegible]	[illegible]	1·47 $N(CH_3)_3$ D_E	1·39 Glycine D_X	1·37 Urea D_X	[illegible]	1·47 $C(NO_2)_4$ D_E	1·095 N_2 S_1	[illegible] N_2	1·47 N_2H_4 D_E	1·6–1·7 N_2O_4 D_E				
[illegible]	[illegible]	1·16 CO_2 S_1	1·20 CH_2O S_1	[illegible]	[illegible]	1·26 Glycine D_X	[illegible]		1·15 NO S_1	[illegible] NOCl D_E	1·21 NO_2 D_E	1·18 N_2O_4 D_E	1·208 O_2 S_1	1·48 H_2O_2 D_E	1·26 O_3 D_E	
[illegible]	1·39 CH_3F S_1	1·42 CH_3F D_E	1·36 CF_4 D_E	[illegible]									1·41 F_2O D_E			
Na																
[illegible]																
[illegible]	2·05 $Al_2(CH_3)_6$ D_E												[illegible]			
Si (1·1[illegible])	1·93 $Si(CH_3)_4$ D_E								1·572 SiN S_1				1·510 SiO S_1			
[illegible]	1·562 CP S_1	1·87 $P(CH_3)_3$ D_E							1·491 PN S_1				1·447 PO S_1	1·56 POF_3 D_E	1·67 P_4O_6 D_E	
S (1·04)	1·536 CS S_1	1·52 CS_2 S_1	1·5[illegible] CS_2 D_E	1·82 $S(CH_3)_2$ D_E									[illegible]	[illegible]	1·43 SO_3 D_E	[illegible]
Cl	1·69 CH_3Cl S_1	1·77 CH_3Cl D_E	[illegible]	[illegible]					[illegible]				1·68 Cl_2O D_E	1·53 ClO_2 D_E		

	F (0·64)			Na			Mg		Al		
F (0·64)	1·44 F_2 D_E										
Na											
Mg											
Al									2·02 $Al_2(CH_3)_6$ D_E		
Si (1·17)	1·54 SiF_4 D_E										
P (1·10)	1·52 PF_3 D_E	1·57 PF_5 D_E									
S (1·04)	1·56 SO_2F_2 D_E	1·58 SF_6 D_E									
Cl (0·99)	1·64 ClF D_E			2·51 $NaCl$ D_E					2·14 $AlCl$ S_1		

	Si (1·17)				P (1·10)				S				Cl		
Si (1·17)	2·32 Si_2H_6 D_E														
P (1·10)					[illegible]	2·21 P_4 D_E	[illegible]	2·84 P_4O_{10} D_E							
S (1·04)					1·85 PSF_3 D_E	1·94 $PSCl_3$ D_E			1·89 S_2 S_1	1·92 S_2 D_E	2·08 S_8 D_E	2·05 S_2H_2 D_E			
Cl		2·02 $SiCl_4$ D_E	2·01 $SiHCl_3$ D_E	1·98 $SiHCl_3$ D_S	2·00 PCl_3 D_E	2·2 PCl_5 D_E			[illegible]	2·07 $SOCl_2$ D_E	1·99 SO_2Cl_2 D_E		1·989 Cl_2 S_1		

The S» method is only applied when the rotational structure of the spectrum is smeared nut, either because the moments of inertia of tho molecule are very Urge (around 100x10-*° g.-cm.*) or because the molecules are not in the gaseous state. By using only the vibrational structure of the spectrum it is possible in many cases to deduce the values of the force constants which characterise the resistance of the various bonds in the **molecule** to stretching. Denoting the force constant of a bond by k_e then the restoring force brought into play when the bond is stretched by an amount *x* from its equilibrium value is *lc_tx,* and it has been found that k_e can be related to the equilibrium bond distance, r_t, by various empirical loptiuliu. The constants in these formula depend on the positions of the two atoms in the periodic table and are Setermined from molecules investigated by the S_t **method.** The formulas can then be applied to more complex molecules to estimate interatomic distances with an error varying between 001 and 005A. Although this method does not at present possess the accuracy of the other apectroscopio method, it has a potentially muck wider field of application.

The D_x method depends on th£ fact that a crystal acts towards a beam of *X-r&yn* as a three-dimensional reflection grating and that the resulting diffraction pattern can be computed from the relative positions of the atoms in the lattice and a knowledge of their scattering powers. It is not possible to compute the positions of the atoms in the lattice directly from the *X-ruy* pattern although recent developments have made it possible to locate the heavier atoms in a structure. The probable errors in this method lie between 0-01 and 0-05A. except in cases where the interatomic 'distance is determined directly by the ere of the unit cell (e.j. **diamond) ^rhan** it may be reliable to 0 001A.

Thff I>E method suffers from the same disadvantages as the Dx method, in that the interatomic distances cannot be deduced directly from the dill ruction pattern of the electrons 'after passing through the vapour of the compound. The patterns to be expected, from various models of the molecule can be computed and by trial and error a model is. arrived at which gives the correct diffraction pattern. The accuracy of this, method is much the same as that of the X-ray method, an average figure for the error being 003A. It should be added that both the diffraction methods are practically useless in locating hydrogen atoms.

In the preceding chart have been collected most of the interatomic distances for atoms in the first two periods for which reliable values are now available. Below each distance' is given the molecule in which this particular distance was found, and bulotv that a symbol (defined above) indicating the method employed in the determination. In parentheses below each atom ia given the Pauling-Hug~ins eovaient radius for tha*, atom. According to Pauling (L. Pauling " The Nature of the Chemical flond," ' 1st ed., Cornell University Press, 1939, p. 153) any single bond interatomic distance can be predicted by taking the sum of the relevant eovaient radii; for a double bond this sum should be reduced by the factor 0-87, and for a triple bond, by the factor 0-78. Interatomic distances which lie between single and double bond, or double and triple bond distances are then taken to indicate the existence of two or more resonating structures for the molecule. Thus the C—C distance in benzene is I-39A., compared with a single bond distance of 1*54A. and a double bond distance of 1 -33A., indicating that resonance exists in benzene. However^the Pauling-Huggins radii are not reliable enough to be applied generally in this way and modifications have recently been suggested by Schomaker and Stevensonto take account of tbe electronegativity of the atoms.

The distances given in the chart were compiled from the following sources, which fhould bo consulted for further details, and for interatomic distances between the heavier ajwme:

Spectroacapic.—G. Herzberg, "Molecular Spectra, of Diatomic Molecules," Prentice-Hall, 1939; Articles on SpectroBcopy by G. B. B. M. Sutherland (Chem. Soc. Annual Rep. for 1936 and 1938); Papers by Herzberg, Douglas and others on B_a, BH, $BC!_3$ and P_s (Canad. J, Rea. 1940 and 1941); N. H. Davidson, J. A. C. Hugill, H. A, Skinnlir and L. E. Sutton (Trans. Faraday Soc. 1940, 36, 1212) for Al—Al and Al—C distances.

Electron Diffraction.—Review article by L. R. Maxwejl (J. Opt. Soc. Amer. 1940, 30, 375); V. Schomakor and D. P. Stevenson, on some revised value's of the eovaient radii (J. Amer. Chem. Soc. 1941, 63, 37).

X-ray and Oeneral.—L. Pauling, " The Mature of the Chemical Bond," Cornell University Press, 1939; R. B. Corey, on interatomic distances in proteins (Chem. Reviews, 1940, 26, 227).

G.B.B.M.S.

^NTERFACIAL ANGLES. The contact angle *8* (fig. 1) between a liquid and a .solid surface is defined as the angle, measured in the liquid, at which the liquid rests in contact with tbe solid. By resolving tho surface tensions parallel to the solid surface, it is Been that

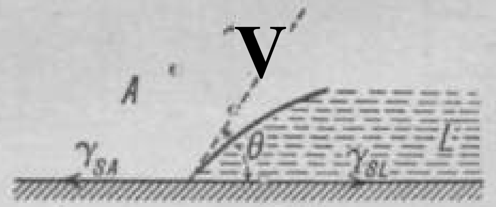


FIG. 1.

ysA=ysL+yLA °os *8* . , . \(1)

r.

»tf ysL> *YM>* heing the solid-air, solid-liquid, and liquid-air tensions. If (1) is combined with the well-known equation of Dupre, which gives a necessary relation between the surface tensions and W_SL, the " work of adhesion " between soh'd and liquid, or the work required per square centimetre to separate solid from liquid, against the adhesive forces between the™, we have

$$W_{SL}=\gamma_{LA}+\gamma_{SA}-\gamma_{SL} \quad . \quad . \quad . \quad (2)$$

We also have what is now usually known as Young's equation (3), discovered by Thomas Young in 1805,

$$H'_{fl}L=nA(l+co8\ 6) \quad . \quad . \quad . \quad (3)$$

This equation shows what are the essential forces which determine the magnitude of the contact angle. If the work of adhesion, WSLI equals (or exceeds) 2$y_{I>A}$, which is the ••ork required to break a*column of the liquid of 1 sq. cm. cross-section, or the " work of cohesion " *of* the liquid, the contact angle *0* must *bo* zero. The angle will be 90° if the adhesion of the liquid to the solid is just half that of the liquid for itself; and if the adhesion between liquid and solid could be diminished to zero, the contact angle would become 180°; this frinot, however, possible.

The term " wetting," of a solid by a liquid, which has always been recognised as intimately connected with the contact angle, is now usually defined as follows: if the contact angle is zero, the wetting is complete or perfect; if the contact angle is finite, wetting is incomplete or imperfect. More loosely, surfaces are sometimes said to be unwettable*, or to repel water, if the contact angle is large, greater than 90°; there is always, however, some degree of adhesion between any solid and any liquid in contact with it. If wetting is perfect, the liquid spreads easily in a film over the whole surface; if wetting is imperfect, the liquid gathers itself into separate drops and for a given quantity of liquid the area of contact of the drops with the solid is smaller the greater the contact angle and the poorer the wetting.

Contact angles much greater than 90° are rare; paraffin wax and water form an angle 6f about 105°, which is about the largest contact angle ever found between an organic substance and water. This large angle is due to tike adhesion between water and the hydrocarbon groups forming the surface of the wax being rather small, while the surface tension of water is unusually large, and consequently the adhesion of the water to the wax is very much less than the cohesion of the water;. Liquid metals form a very high contact angle with glass or silica; mercury ordinarily rests at about 140°, though the angle depends a gdbd deal on the condition of the glass, and iroy occasionally become acute if the glass be carefully bakeg out under high vacuum. These high angles are due to the exceptionally high surface tension and cohesion of metals; their surface tension is usually several hundred dynes per cm., and may exceed 1.000 dynes per cm., so that the cohesion of medals is much higher than their adhesion to almost all surfaces, except to other *clean* mptals.

Contact angles are extremely sensitive to the state of the solid surface. It is possible, by depositing a layer of oleic acid on clean glass, which is perfectly wetted by water, to reduce the adhesion so much that' the contact angle rises to about 90°, and the^urface is thus changed from a strongly hydrophilic to a hydrophobic surface. Sometimes small amounts of water, or other liquid, can soak into a surface which forms a large contact angle and considerably reduce the angle.

Most solids and liquids show a phenomenon called hysteresis of the contact angle, which may have any value between two extremes; a liquid advancing over a solid generally gives a larger angle than the same liquid receding from a previously wetted part of the same surface. Hysteresis, *i.e.* the difference between the advancing and the receding angles of contact, is often very large with water, amounting sometimes to 60° or more, the liquid being able to rest on the solid at any angle between the two extremes of the advancing and the receding angle. Ablctt (Phil. Mag. 1923, [vi], 46, 244) found that the amount of hysteresis depends on the speed of the advancing or receding motion,- but usually >the angle at which advancing motion first begins is considerably greater than that at which the liquid can be induced to start receding from a wetted surface. The appearance is as if the edge of the liquid tended to adhere to the solid surface. While hysteresis is greatest with water, most liquids show it to some extent; some writers claim that its amount can be substantially reduced if the solid surface is very thoroughly cleaned. Its practical importance is considerable, but there is not yet universal agreement as to its cause, which may indeed vary in different cases. Very small amounts of grease might account for the hysteresis with water and such hydrophilic surfaces as glass and some minerals, the grease being displaced after the*water covers the surface ; alternatively some of the liquid may soak into, or be adsorbed on to, the solid, increasing its attraction for the liquid after wetting. Langmuir has suggested that the molecules of a very thin film of grease may actually be overturned by contact ^vith the water so that their hydrophilic terminal groups arc outwards, and the attraction for we*er is increased. After drying, the molecules are supposed to^ revert to their normal position, with the hydrophilic terminal groups downwards, and thus the attraction for water decreases because the surface consists* of hydrocarbon groups. Wljatever the precise cause of hysteresis, it is clear that it is the result of a variation in the amount of adhesion of the surface for the liquid, according to whether or not it is being wetted by the liquid.

% Methods of measuring contact angles are numerous. If the solid can be obtained in the form of a flat plate, or even a wire or a straight fibre, a good method is to fix the solid in a holder which can be sef^ at any angle to the liquid surface, and to dip it into the liquid and adjust th% angle until the surface of the liquid remains accurately horizontal right up to the point of contact with the solid. Then the angle between the liquid surface and the solid is the contact angle. It is necessary to provide means of raising and lowering the ft>lid in the water, to find the advancing %nd the receding angles;* also, if the angle with clean water is required* means must be provided of cleaning the liquid' surface, since the surface of water is veryneasily contaminated by grease, with lowering of the surface tension and of the contact angle. Other methods depend on observing the direction of a ray of light reflected from the liquid and the solid surface very near to the line of contact between them. These methods are accurate to a very few degrees, which is usually sufficient, since the contact angle of a solid surface generally varies by this amount in different parts. Direct observation under the microscope of the angle at which solid and liquid surfaces meet is sometimes possible, and reasonably accurate; or a magnified image may be projected on a screen and the angle measured with a protractor. Another method is to measure the height to which the liquid rises in a capillary tube of known radius; if the surface tension of the liquid is known, the contact angle between the liquid and the tube can be calculated from the formula

$$h = \frac{2\gamma_{LA}\cos\theta}{gr(D-d)}$$

h is the height of rise, r the radius of the tube, *D* the density of the liquid and *d* that of the air. Alternatively the pressure required just to prevent the liquid from entering a capillary tube may be measured. This is the foundation of Bartell and Osterhof's method for finding the contact angle of a substance available only in powder form; a highly compressed plug is made of the powder, liquid is put in contact with the powder at one side and the pressure required to balance its tendency to penetrate into the plug is measured. A difficulty in this method is the determination of the " radius " of the capillary tube equivalent to the plug of powder; but at present it is almost the only method available for a quantitative determination of the contact angle of a fine powder against a liquid.

The practical importance of contact angles and wetting is very widespread. Sometimes the best possible wetting is desirable, sometimes the least possible The precise conditions to be attained vary slightly according to whether good *spreading* of the liquid over a large area of solid, or good *penetration* of the liquid into the pores of a porous solid or heap of powder is required; conversely, the prevention of spreading of a liquid over a solid surface, or hindering its penetration into pores, are not exactly similar problems.

Good spreading over the largest possible area of solid surface is required for all insecticide and disinfectant sprays and dips, so that a small quantity of liquid shall cover the largest possible area of the plant, animal or other surface to be treated. The windows of gas-masks, goggles or other transparent windows where there is a warm, moist atmosphere on one side and a colder one on the other, mist up or " dim " after a time, often so badly that it becomes impossible to see through them, unless the moisture can be condensed in a continuous thin film instead of in separate droplets. In many types of chemical plant, such as gas absorption towers or film evaporators, where a rapid interchange of a Substance between vapour and liquid is required, the liquid is made to trickle over a large area of solid surface so as to expose the largest possible area and the smallest possible thickness to the vapour. Unless the liquid spreads perfectly, wetting the solid everywhere, the area will be reduced and the thickness increased, so that exchange of gas between liquid and vapour, or evaporation, is slower than it should be; very serious loss of efficiency may result if wetting is poor. In cases where the maximum spreading is required, the contact angle must have a minimum value; unless the receding angle is zero, the liquid will not remain spread even if mechanically forced to cover the whole surface; and for the liquid to spread itself without the expenditure of much energy and careful control of the direction at which the liquid impinges on the solid, the advancing angle also must be zero, a condition which is more difficult to attain.

Few surfaces give a zero contact angle with water for long, since minute traces of grease produce a finite angle even on such surfaces as glass, which do wet completely if absolutely clean. There are now many wetting agents available, water-soluble substances which often enormously improve the wetting. They operate either by diminishing the surface tension of the liquid, or by increasing its adhesion for the solid, sometimes in both ways. Inspection of equation (3) shows that cos θ is increased and therefore θ is diminished, either by increasing W_{SL} or by decreasing γ_{LA}. Most wetting agents have the general constitution RX, R being a hydrocarbon group of considerable size, generally a long aliphatic chain, but sometimes an aromatic or alicyclic group. X is a strongly water-attracting group, and the variety of such end groups is now very great, the COONa group of soap being one of these. Alkyl sodium sulphates $ROSO_3Na$, many other sulphates or sulphonates, and amides variously substituted and generally sulphonated are common wetting agents. Some very successful modern wetting agents are polyphenols substituted with one or more alkyl chains and sulphonated. Other wetting agents are un-ionised substances such as polyglycerol esters or polyethylene oxides.

The decrease of surface tension is mainly due to the hydrocarbon part of the molecules; all substances containing long hydrocarbon chains tend to be adsorbed at the surface and to form a layer in which they usually lie flat in the surface ; this reduces the field of attractive force at the surface, and consequently the surface tension. One hydrocarbon chain containing over six carbon atoms in a soluble compound can usually, at a sufficient concentration, reduce the surface tension of water to between 20 and 30 dynes per cm. instead of 73 for clean water, and very low concentrations of substances with twelve or more carbon atoms in an aliphatic chain achieve a similar decrease in surface tension. The great majority of wetting agents are powerful depressants of surface tension.

Whether the wetting agent actually increases the adhesion of the water to the solid depends on the constitution of the solid surface and on the end-group X of the molecule of the wetting agent; any increase in such adhesion will improve the wetting. An interesting, though not particularly important, phenomenon is shown by the salts of some quaternary bases with long aliphatic chains, such as cetyltrimethylammonium or cetylpyridinium hydroxide. In extremely dilute solution these long-chain cations are adsorbed on glass (which has a negative electric charge when immersed in water) with their hydrophilic end-groups inwards and their hydrocarbon chains outwards; and the effect of washing clean glass with these dilute solutions is to reduce the adhesion and produce a contact angle of some magnitude, causing a greasy appearance on a previously clean surface. Increase in concentration reduces the surface tension so far that the contact angle again falls to zero. In general, it can be said that if a soluble substance contains groups which tend to combine with the material of the solid surface, or to dissolve it, wetting will be assisted as a result of increasing the adhesion of the liquid for the solid; but at present our knowledge of the adsorption of molecules at solid-liquid surfaces is much less complete than that of the structure of films at air-water surfaces.

Good wetting of metals by oils is desirable in lubrication. There is usually little difficulty in obtaining a low or a zero contact angle between ordinary oils and metals, but it is often useful deliberately to increase the adhesion between them by adding fatty acids, the end groups of which attract and sometimes combine with the surface of the metal. This helps to prevent the layer of molecules in the liquid next to the solid from being easily rubbed off, and thus improves " boundary " lubrication, or lubrication under conditions such that the film of lubricant is reduced to molecular thickness. Glycerides (animal or vegetable oils) are better boundary lubricants than mineral oils, because they adhere more closely to the solid.

Perfect wetting of a metal by molten solder is essential for successful soldering or brazing. Molten solders will not spread on greasy or oxidised surfaces, but spread excellently on clean surfaces; hence the surface must first be thoroughly cleaned, and also protected by a suitable flux against surface oxidation during heating.

Good penetration of a liquid into the pores of a porous solid also requires good wetting, but here the quantity $\gamma_{LA} \cos \theta$, usually termed the "adhesion tension," should be a maximum, not merely the contact angle a minimum, as for simple spreading. Spreading on a smooth solid surface will not take place unless the contact angle is zero, but penetration into a capillary space will occur to some extent if the adhesion tension, $\gamma_{LA} \cos \theta$, is positive, i.e. if the advancing contact angle is less than 90°. Two important cases in industry are the " wetting-out" of textiles by water, a necessary preliminary to scouring, bleaching or dyeing operations, and the laying of dust by water, especially in mines. The cloth may be difficult to wet from natural causes, or because of the size used in weaving; coal dust and many stone dusts are also quite difficult to wet. Wetting agents are useful in both these cases, indeed often almost essential.

Good dispersion of a solid in a liquid requires good wetting. Here it is necessary for the adhesion between the liquid and solid to be sufficient for the liquid to spread over the whole solid surface, and the larger this adhesion, probably even in excess of that required to give zero contact angle, the less chance there will be of the solid particles adhering to each other and settling out in lumps or hard masses which cannot be redistributed evenly through the liquid merely by stirring. Poor wetting of the pigment by the oil is a frequent cause of defects in paints. Here, suitable wetting agents have to act by increasing the adhesion of the solid to the liquid; the surface tension of paint media is usually not high.

There are some processes in which wetting must be reduced to the minimum possible amount, as in the flotation of minerals (v. FLOTATION PROCESS, Vol. V, 2ft3t/), and the showerproofing of textiles (v. FINISHING TEXTILE FABRICS, Vol. V,]ff:W-H)8a).

It has been suggested that condensers in steam engines could be made much more efficient if the steam could be condensed in the form of separate drops covering a small fraction only of the condensing surface. This is because the principal resistance to rapid conduction of heat seems to be the liquid film which is stagnant up to a small thickness on the condensing surface; if condensation could be made to occur so that this film did not form, a much increased rate of heat conduction and therefore of condensation could theoretically be achieved. Nagle, Drew *et al.* (Trans. Amer. Inst. Chem. Eng. 1933-34, 30, 217; 1933, 31, 593) have obtained some success in this field, but as yet the difficulties attendant on large-scale utilisation do not seem to be overcome.

The contact angle formed by the interface between two liquids, and a solid, is also of practical importance. It may be finite or zero in one liquid and 180° in the other. In the latter case, a powdered solid will tend to pass wholly into the liquid in which the angle is zero and preferential wetting by this liquid may be said to be perfect. If the contact angle is finite, the powder will tend to remain at the surface between the liquids, just as a powder with a finite air-liquid-solid contact angle can float at the air-liquid surface. Powders thus retained at a liquid-liquid surface by surface forces help to stabilise emulsions of the two liquids, since the powder naturally hinders the contraction of the surface, which accompanies breaking of the emulsion by coalescence of the drops (v. EMULSIONS AND EMULSIFICATION, Vol. IV, 284e).

The action of soap and other similar detergents in removing grease is largely due to their effect in changing the contact angle made by the surface between the grease and the water. Microscopic observation (Adam, J. Soc. Dyers and Col. 1937, 53, 124) has shown that, in water, grease on wool forms a thin film with practically zero contact angle in the grease (fig. 2, a). In dilute cetyl sodium sulphate solution, a very efficient detergent for wool, the angle changes

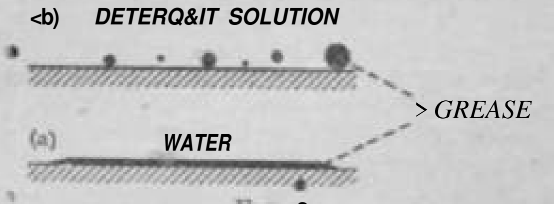


FIG. 2.

to 180° in the grease and zero in the water, and thus the grease becomes detached (Fig. 2, b) on very slight mechanical agitation.

The displacement of one liquid, such as oil, by another liquid such as water, from a porous sand is analogous to the penetration of a single liquid into a dry porous solid. It will occur if the (advancing) contact angle of the surface between the liquids is acute in that liquid which advances and displaces the other; for the most rapid displacement the adhesion tension of the water for the solid must exceed that of the oil by the largest possible amount. This property is probably of great importance in underground oil deposits.

Contact angles between two liquids and air, no solid being present, are important fr" the spreading of oils on water, which is used on a large scale in the control of malarial mosquitoes. The angle here is that in the oil, between its upper and lower surfaces, where they meet the water surface. To ensure spreading this contact angle must be zero; for this it is necessary that

$$\gamma_{WA} > \gamma_{OA} + \gamma_{OW} \quad . \quad . \quad . \quad (4)$$

γ_{WA}, γ_{OA} are the surface tensions of the water and the oil, and γ_{OW} the interfacial tension between the oil and the water. It can easily be shown that (4) is equivalent to the condition that the work of adhe^'on of the oil to the water must exceed the work of cohesion of the oil for itself; the difference should preferably be as large as possible, to provide a margin of spreading power and give the greatest chance of spreading on a slightly contaminated surface. The difference $\gamma_{WA} - \gamma_{OA} - \gamma_{OW}$ is often called the "spreading coefficient"; it should be at least 16 dynes per cm. and preferably more. *Pure* mineral oils do not spread, and have a negative spreading coefficient; the sign can be reversed mainly by increasing the adhesion between oil and water, with quite small amounts of oil-soluble substances containing hydrophilic groups; among the most powerful of these are sulphonic acid groups. The oxidation products of unsaturated oils, formed by the action of air and light, also assist spreading. Most commercial oils have a positive spreading-coefficient. Initial high spreading-power is not, however, the only requirement, for the films of oil, once spread, are usually unstable and tend to break up into films of molecular thickness, probably one molecule thick and too thin to affect the larvae, the remainder of the oil collecting into small drops which form a finite contact angle and do not spread. The phenomena of break-up of spread oil films are complex and not yet fully understood (*cf.* D.R.P. Murray, Bull. Entomol. Res. 1938, 29, 11; 1939, *W,* 211).

For further information, and references to original papers, *see* Harvey, "Wetting and Detergency," Chemical Publishing Co., New York, 1937; and Adam, "The Physics and Chemistry of Surfaces," 3rd ed., Oxford. 1941, pp. 178-215, 413-414.

N. K. A.

INUKAYA OIL (Inugaya or Bebe oil) is prepared by steaming and pressing the seed-kernels (which contain about 67% of the oil) of the Japanese evergreen inukaya tree, *Cephalotaxus drupacea* Sieb. and Zucc. (Fam. Taxaceae).

The cold-expressed oil prepared in the laboratory by Tsujimoto (J. Coll. Eng. Tokyo, 1908, 4, 85; Chem. Rev. 1908, 5, 168) was pale-yellow in colour with a faint, resinous odour, and had the following properties: *d*\\ 0-925 ;• ?£° 1-4760; f.p. below -15°C; saponification value 188-5; iodine value (Wijs) 130-3.

Commercial inukaya oil resembles Kaya oil with which it has been occasionally confused in the literature, but has inferior drying properties; it is used for similar purposes, viz. as a burning oil and for the manufacture of oiled paper, varnishes, etc., but cannot be employed as an edible oil, on account of the resinous odour which is present in even the cold-drawn product.

lL\ L. and L. I.

INULASE (*v.* Vol. IV, 3146).

INULIN (v. Vol. II, 303a).

INULO-COAGULASE (*v.* Vol. Ill, 31a).

INVAR, a 36% nickel steel.

INVERTASE (Sucrase, Saccharase) is an enzyme which hydrolyses sucrose (cane-sugar) to *d*-glucose (1 mol.) and *d*-fructose (1 mol.). It occurs in the small intestine of mammals, in the tissues of certain animals and plants and in numerous moulds and fungi. One of the best sources is yeast, invertase being present in all species except *Saccharomyces oclosporus, S. capsularis* and *S. membran&faciens* Hans. Active preparations may readily be obtained by allowing the yeast to hydrolyse at 37° in the presence of a little toluene, when liquefaction occurs. Alcohol is added to the aqueous extract and the precipitate extracted with water (O'Sullivan and Tompson, J.C.S. 1890, 57, 834; Euler *et al.,* Z. physiol. Chem. 1910, 69, 152; 1911, 73, 335). Willstatter and Rackc (Annalcn, 1921, 425, 53) carried out the autohydrolysis in a neutral, instead of acidic, medium. Various methods of purification have been used. Hudson (J. Amer. Chem. Soc. 1908, 30, 1564) removed soluble proteins and gums by the addition of lead acetate; excess of lead was removed by potassium oxalate and the latter by dialysis. Finally the enzyme was precipitated by alcohol and dissolved in water. More recently, adsorption on kaolin or aluminium hydroxide has been used for purification (Lutz and Nelson, J. Biol. Chem. 19?4, 107, 169; Kosaki, A. 1938, III, 6fi5). Weidenhagen (*X*\ 1936, 1555) used strontium hydroxide, Richtmcyer and Hudson zinc sulphide and Adams and Hudson bentonite as adsorbents. In the last two cases the extract was adjusted to p_H 4-5, and the elution carried out at p_n 61 (J. Amer. Chem. Soc. 1938, 60, 9$3). Willstätter has investigated the adsorption of invertase by aluminium hydroxide and by kaolin, finding it most efficient in dilute solution or in the presence of 10% acetic acid (& physiol. Chem. 1922, 123, 181; with Schneider, 1924, 133, 193). Invertase may be kept for several years without losing activity.

The activity of these preparations may be measured by observing the rate at which sucrose is hydrolysed under standard conditions. In their classical researches, O'Sullivan and Tompson determined the time in minutes required by

50 mg. of the enzyme to reduce to zero the rotation of 25 c.c. of solution containing 16%' of sucrose at the optimum p_B, at 15-5°. Willstätter and Racke *(I.e.*; Willstätter and Kuhn, Ber. 1923, **56** [B], 509) adopted a similar procedure. On this basis, brewer's yeast requires 150-4(%) minutes. Purified specimens can now be prepared with a time value of 0-1-0-2 minutes. Sumner and Howell (J. Biol. Chem. 1935,**108,** "31) use the dinitrosalicylic acid method for the estimation of reducing sugars formed. Sufficient invertase is,used to obtain about 10 mg. of invert s&gar by the hydrolysis of 6 c.c. of 5-4% sucrose in 5 minutes, at 20° and *p$* 4*5. Under these conditions the velocity of hydrolysis is great,*and the assay is therefore rapid. The reaction is stopped by the addition of 5 c.c. **N.-NffOH,** and the invert sugar determined colorimetrically with dinitrosalicylic acid.

There has been considerable divergence of views as to the chemical character of invertase, but it appears that both protein and carbohydrate reactions can be obtained (c/. Euler and Josephson, Ber. 1925, 57 [B], 859; Willstätter and Schneider, Z. physiol. Chem. 1924,**133,**193). The fprmer authors detected tryptophan in their preparations, and this was confirmed by ultra-violet absorption spectrum measurements (Albers and Meyer, *I.e.,* 1924, **228,**122; *see also* Lutz and Nelson, *I.e.;* Tauber, "Enzyme Chemistry," J. Wiley & Sons, 1937, p. 127). Ultra-filtration experiments upon invertase isolated from the intestinal juices of dogs indicate that it is just retained by a membrane of porosity 10 nip. (Grabar, Compt. rend. Soc. Biol. 1935,**118,**455).

The activity of invertase is maximum at 55-60° *(cf.* 35-40° for maltase), but it is destroyed at 65-70° *(see* Chaudun, Bull. Soc. Chim. bpl. 1936, **18,** 1467). Below 0°, the velocity of inversion decreases only slowly (Kertesz, Z. physiol. Chem. 1933, **216,** 229). The kinetics of the process are discussed by Nelson (Chem. Rev. 1933,**12,**1) and by Weidenhagen (Ergebn. Enzymforsch. 1932, 1, 168). T. A. White has examined the kinetics in the light of the theory that sucrose and water are adsorbed by the enzyme before reaction, the adsorbed products inhibiting the hydrolysis (J. Amer. Chem. Soc. 1933, **55,** 556). The thermal changes have been measured by K6saki (A. 1937, III, 180; 1938, III, 695).

The optimum p_H for yeast invertaso is 4-5 (Michaelis and Davidsohn, Biochem. Z. 1911, **35,**386), whereas maltise (also present in yeast) is inactive at this jp_H. Even minute amounts of alkali may inhibit the action, and care is necessary to buffer the p_H during quantitative work. The retarding effect of CN' and of pectin is ascribed to the increased jp_H (Manchester, J. Biol. Chem. 1939, **130,** 439). The action of basic and acidic dyes is discussed by Quastel and Yatcs (Enzymologia, 1936,1, 60).

Invertase will hydrolyse fructofuranosides other than sucrose. The trisaccharides raffinose and gentianose and the tetrasaccharido stachyose are also attacked by yeast invertaso (Kuhn and Münch, Z. physiol. Chem. 1925, **150,** 220; 1927, **163,** 1). Weidenhagen has shown that large amounts of the enzyme will hydrolyse the polysaccharides irisin and inulin to fructose (A. 1933, 1080). The activity with regard to these substrates varies considerably according to the source of the invertase *(e.g.* from *Aspergillus oryzx, Penicillium glaucum).*

The chemistry of invertase has been reviewed by J. M. Nelson (Cliem. Rev. 1933,**12,**1).

G. T. Y.

INDEX TO VOLUMES I—VI·

THE Index contains about 17,550 entries arranged alphabetically, and familar inversions and abbreviations have been employed. For reasons of economy many inverted entries have been printed without a final " of," and the word " dyes " has been indexed instead of "dyestufis." The letters a, *b,* c, *d* attached to references indicate consecutive quarters of a page. Titles of articles are located by clarendon numerals.

Ths space available did not allow of indexing all the synonyms, italicised words and technical terms to be found in the text, but it is hoped that the choice made will be acceptable.

The Index is not intended to solve all relevant questions of spelling, hyphening and nomeralaturepbut when the text has not been fallowed it is believed that the reason for the alteration will be evident.

Preliminary work on the indexing of Vols. II and III was done by Dr. A. H. Cook, to whom acknowledgment is made. Acknowledgments for skilled assistance are made to Miss B. Wilkinson, Miss V. Goring Thomas, Miss B. Whiteing, and Mr. 6. Bird.

J. N. GOLDSMITH.

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