COMMERCIAL ORGANIC ANALYSIS.

THE PRACTICE

OF

COMMERCIAL ORGANIC ANALYSIS

A TREATISE ON

THE PROPERTIES, PROXIMATE ANALYTICAL EXAMINATION, AND MODES OF ASSAYING THE VARIOUS ORGANIC CHEMICALS AND PRODUCTS EMPLOYED IN THE ARTS, MANUFACTURES, MEDICINE, &c.

WITH CONCISE METHODS FOR

THE DETECTION AND DETERMINATION OF THEIR IMPURITIES, ADULTERATIONS, AND PRODUCTS OF DECOMPOSITION.

BY

ALFRED H. ALLEN, F.I.C., F.C.S.,

LECTURER ON CHEMISTRY AT THE SCHOOL OF MEDICINE AND THE WESLEY COLLEGE, SHEFFIELD;
PRESIDENT OF THE SHEFFIELD LITERARY AND PHILOSOPHICAL SOCIETY;
PUBLIC ANALYST FOR THE WEST RIDING OF YORKSHIRE, THE NORTHERN DIVISION OF DERBYSHIRE, AND THE BOROUGHS OF SHEFFIELD, CHESTERFIELD, DONCASTER, WAKEFIELD, &c.

VOLUME II.

HYDROCARBONS, FIXED OILS AND FATS, SUGARS, STARCH AND ITS ISOMERS, ALKALOIDS AND ORGANIC BASES, &c.

LONDON:
J. & A. CHURCHILL,
NEW BURLINGTON STREET.
1882.

PREFACE.

THE favourable opinions expressed respecting Volume I. of my "Commercial Organic Analysis" have convinced me that such a book was really wanted by chemists, and have encouraged me to undertake the compilation of a second part.

As in the case of Volume I., I have spared no pains to render the contents reliable and complete. In many instances I have personally verified the described reactions and processes, whilst in the case of others I have received most valuable assistance from chemists of special experience in particular branches of work, whose collaboration has enabled me to enrich the test with methods and data never before published.

I have found considerable practical difficulty in giving the subject-matter an arrangement which should be at once fairly scientific and practically convenient, and can only say that the plan which has been adopted is the result of prolonged consideration and consultation. The subject-matter has grown so much during its collection and arrangement, and even while passing through the press, that the volume now published considerably exceeds its intended size, and hence I have been reluctantly compelled to omit

several important sections which it was my original intention to include. Thus, with the exception of a comparatively short notice under the head of "Basic Aniline Derivatives," I have omitted all mention of dyes and colouring matters, feeling that the properties and modes of assaying many of these bodies have already been adequately treated by Calvert and other authors. With less regret, but from a similar feeling, I have omitted all reference to the methods of examining coal-gas. "Animal Products," including methods for the examination of blood, milk, urine, gelatin, albumin, wool, &c., I had intended to treat in a separate chapter, but feeling that it would be better to ignore them than to treat the subject inadequately, I have postponed their consideration till a demand shall arise for an additional volume, or a second edition of those already published.

In conclusion, I desire to thank those friends to whom I am indebted for information, and by whose assistance the volume has greatly profited.

ALFRED H. ALLEN.

SHEFFIELD, *December* 31*st*, 1881.

CONTENTS OF VOLUME II.

HYDROCARBONS.

FIXED OILS AND FATS.

SUGARS.

STARCH AND ITS ISOMERS.

ALKALOIDS AND ORGANIC BASES.

COMMERCIAL ORGANIC ANALYSIS.

HYDROCARBONS.

THE numerous compounds of carbon with hydrogen which modern organic research has made known to chemists are classed together by the general name of hydrocarbons.

Hydrocarbons are conveniently grouped according to the relative number of atoms of hydrogen and carbon present in the molecule. In this manner they may be arranged in various natural orders or series, of which the following table contains the most important.

It will be seen that the generic formula of each series of hydrocarbons differs by H_2 from that of the preceding series. Thus, while the hydrocarbons CH_4, C_2H_6, C_3H_8, &c., are said to be homologous, the hydrocarbons C_2H_6, C_2H_4, and C_2H_2 form an isologous series. While the members of the paraffin series, C_nH_{2n+2}, are extremely indifferent to chemical agents, and refuse to form additive compounds, the "olefins" unite with Br_2, the acetylenes with Br_4, valylene with Br_6, and dipropargyl with Br_8. Thus the capacity of the hydrocarbons for combining with the haloid elements increases regularly with the removal of hydrogen.

The hydrocarbons of series I., II.*a*, III., IV.*a*, and V.*a*, constitute, therefore, a complete isologous series, the carbon atoms probably forming "an open chain." In the case of the terpenes and the hydrocarbons of the benzene series the law of combining capacity is completely altered, a fact which has led

No. of Series.	Generic Formula.	Name of Series or of Leading Member of Series.	Important Members of Series.	Chief Sources and Modes of Formation.
I.	C_nH_{2n+2}.	Marsh gas series. Paraffins.	Marsh gas, CH_4; ethane, C_2H_6; hexane, C_6H_{14}; paraffin wax.	Found as petroleum, ozokerite, marsh-gas, fire-damp. Formed by dry distillation of coal, peat, wood, bituminous shale, &c. Also producible synthetically, &c. See page 9.
II.	C_nH_{2n}.	(*a*) Ethylene series. Olefins.	Ethylene, C_2H_4; hexylene, C_6H_{12}; lubricating oil.	Found in petroleum. Produced by dry distillation of coal, &c., and largely in distillation of bituminous shale. Also producible synthetically. See page 7.
		(*b*) Paraffenes.	Hexahydro-meta-xylene.	Found in petroleum.
III.	C_nH_{2n-2}.	(*a*) Acetylene series.	Acetylene, C_2H_2; Allylene, $C_3H_4=C\begin{cases}CH\\CH_3\end{cases}$.	Acetylene may be formed by direct combination of carbon and hydrogen. Higher members by appropriate synthetical methods. Produced by distillation of coal, &c.
		(*b*) Allene series.	Allene, $C_3H_4=C\begin{cases}CH_2\\CH_2\end{cases}$.	Synthesis.
IV.	C_nH_{2n-4}.	(*a*) Valylene series. (*b*) Terpenes.	Valylene, C_5H_6. Turpentine oil, $C_{10}H_{16}$; lemon oil, $C_{10}H_{16}$.	Found largely in the vegetable kingdom, constituting turpentines and essential oils. Also producible synthetically. See page 45.
V.	C_nH_{2n-6}.	1. Dipropargyl series. 2. Benzene series.	Dipropargyl, C_6H_6. Benzene, C_6H_6; toluene, C_7H_8; cymene, $C_{10}H_{14}$; mesitylene, C_9H_{12}.	Synthesis. Found in petroleum. Produced largely in dry distillation of coal, &c., a high temperature being essential to formation. Coal-tar naphtha is almost wholly benzene hydrocarbons. See page 75.
VI.	C_nH_{2n-8}.	Cinnamene or styrolene series.	Cinnamene, C_8H_8.	Cinnamene occurs in liquid storax. Produced by distilling cinnamic acid alone or with baryta.
VII.	C_nH_{2n-10}.	Phenyl-acetylene series.	Phenyl-acetylene, C_8H_6.	Synthesis.
VIII.	C_nH_{2n-12}.	Naphthalene series.	Naphthalene, $C_{10}H_8$.	By dry distillation of coal, &c., a high temperature being essential. Present largely in heavy coal-tar oil. See page 92.
IX.	C_nH_{2n-14}.	Diphenyl series.	Diphenyl, $C_{12}H_{10}$; acet-naphthene $C_{12}H_{10}$.	By dry distillation of coal, &c. Synthesis.
X.	C_nH_{2n-16}.	Stilbene series.	Fluorene, $C_{13}H_{10}$; stilbene, $C_{14}H_{12}$.	By dry distillation of coal, &c., and synthetical methods.
XI.	C_nH_{2n-18}.	Anthracene series.	Anthracene, $C_{14}H_{10}$; phenanthrene, $C_{14}H_{10}$; methyl-anthracene, $C_{15}H_{12}$; retene, $C_{18}H_{18}$.	By dry distillation of coal, &c. Present in coal-tar pitch. See page 95.
XII.	C_nH_{2n-20}.	Benzyl-naphthalene series.	Fluoranthrene, $C_{15}H_{10}$.	By synthesis; and in coal-tar pitch.
XIII.	C_nH_{2n-22}.	Pyrene series.	Pyrene, $C_{16}H_{10}$.	By synthesis; and in coal-tar pitch.
XIV.	C_nH_{2n-24}.	Chrysene series.	Chrysene, $C_{18}H_{12}$.	Present in coal-tar pitch, and shale oil.
XV.	C_nH_{2n-26}.	Dinaphthyl series.	Dinaphthyl, $C_{20}H_{14}$.	By synthesis; and in coal-tar pitch.

to the useful hypothesis of the "benzene chain." Thus while the olefins, acetylene, valylene, and dipropargyl combine with bromine in the dark readily, and in some cases even violently, benzene enters into direct combination with chlorine or bromine with some difficulty, and only under the influence of light. Indeed, in many of their reactions the benzene hydrocarbons simulate the paraffins, though differing from that series in other important respects. Thus the series V., VI., and VII., stand to each other in much the same relationship as subsists between the paraffins, olefins, and acetylenes, and a similar analogy may be traced between some of the members of the series IX., X., and XI. The assumption that the hydrocarbons in question are formed from the members of series I., II., and III., by the introduction in place of hydrogen of monad radicals derived from benzene or its homologues at once furnishes an explanation of their behaviour.

Certain hydrocarbons, such as naphthalene, diphenyl, anthracene, phenanthrene, pyrene, chrysene, and dinaphthyl, exhibit properties which show that they have little resemblance to the paraffins, but are closely related to benzene, the carbon atoms forming one or more closed chains. Benzene, naphthalene, anthracene, phenanthrene, and chrysene, appear to form a series, the terms of which differ by C_4H_2. These hydrocarbons combine with fewer atoms of bromine or chlorine than benzene does, though the compounds are produced far more readily, and do not require light for their formation; but the power of forming these additive compounds becomes less with each member of the series, until chrysene forms no additive compound with bromine.*

The hydrocarbons of series I. strongly resist the action of concentrated sulphuric or nitric acid (see page 14), and do not under any circumstances form substitution-products or additive

* It is remarkable that all the hydrocarbons in which the carbon atoms are united so as to form a closed chain containing two or more loops joined together at *two* points (such as naphthalene, fluorene, acetnaphthene, anthracene, phenanthrene, pyrene, and chrysene), combine with picric acid (see page 9), and that no such compound is produced from hydrocarbons such as diphenyl, in which there are two loops, but united only at one point. Similar compounds are also wanting in the case of the paraffins and other open-chain hydrocarbons.

compounds with them. The olefins and acetylenes, on the other hand, combine directly with sulphuric acid, and also often suffer polymerisation, but they do not yield characteristic products by the action of nitric acid. The terpenes appear to combine with sulphuric acid, but the resulting compounds are extremely unstable, and therefore the treatment usually ends in their being polymerised; by nitric acid they are violently attacked, but do not yield characteristic products. Benzene and its homologues, as also most of the hydrocarbons of the remaining isologous series, yield substitution-products by treatment with strong sulphuric or nitric acid, one or more atoms of hydrogen being replaced by the corresponding number of SO_3H or NO_2 groups; the replaced hydrogen atoms being always attached to carbon and atoms which form part of the closed chain.

Any further consideration of the theoretical relationships of the hydrocarbons would be out of place here. On the other hand, a description of the generic properties and behaviour with reagents of the more important series is of interest from an analytical standpoint.

This general description will be limited to the paraffins, terpenes, and hydrocarbons of the benzene series; but the very detailed descriptions given of the properties and reactions of naphthalene and anthracene, and the hydrocarbons associated with the latter, practically cover all the more important series, at least as far as the principal members of such series are concerned.

As by far the larger number of hydrocarbons of commercial importance are or can be obtained by processes of destructive distillation, it may be desirable to consider this subject somewhat in detail before proceeding to describe the generic and specific properties of the hydrocarbons.

DESTRUCTIVE DISTILLATION.

When non-volatile organic substances are subjected to heat in a close vessel they undergo destructive distillation.

Many substances which can be distilled without decomposition when cautiously heated undergo destructive distillation

when heated rapidly, or in admixture with inorganic matters, such as sand or clay.

The presence of oxygen, sulphur, nitrogen, &c., in the substance heated gives rise to products containing these elements. When the heat is applied gradually, the products first obtained usually contain the largest proportion of oxygen, the distillates becoming more highly hydrogenated and carbonated as the temperature rises.

The nature of the decomposition which takes place on heating is indicated by the term cumulative resolution. A familiar instance of this action occurs in inorganic chemistry, when manganese dioxide is heated to full redness. Three units of the substance then decompose in partnership, thus—

$$3MnO_2 = Mn_3O_4 + O_2 .$$

Another example is furnished by the action of heat on ordinary phosphate of sodium (hydrogen-disodium phosphate).

$$2Na_2HPO_4 = Na_4P_2O_7 + H_2O .$$

In a similar manner when glycerin (glycerol) is heated, polyglycerins are formed by the loss of the elements of water.

A parallel mode of decomposition is common to all polyalcohols. Thus, in the case of woody fibre (cellulose) we may have the following series of changes:—

$$\begin{aligned} C_6H_{10}O_5 - H_2O &= C_6H_8O_4 \\ C_6H_8O_4 - H_2O &= C_6H_6O_3 \\ C_6H_6O_3 - H_2O &= C_6H_4O_2 \\ C_6H_4O_2 - H_2O &= C_6H_2O \\ C_6H_2O - H_2O &= C_6 . \end{aligned}$$

In practice, the bodies formed are not those indicated by the above formulæ, but polymers of these.

The above changes, complicated by other reactions, occur in the natural formation of coal from cellulose, as also in the artificial distillation of wood.

By analogous reactions occurring simultaneously with the above, oxides and hydrides of carbon are formed, and are condensed in the receiver or pass away as permanent gases. The nature and proportions of these bodies obtained will be largely

dependent on the character of the substance distilled, the temperature of the retort, and other conditions. When the heat is very moderate the hydrocarbons produced are chiefly of the series known as the paraffins, having the general formula, C_nH_{2n+2}, of which marsh gas is the first member; but as the higher members of the series readily split up into lower members and hydrocarbons of the formula C_nH_{2n}, the latter bodies are always simultaneously obtained. By further degradation, hydrocarbons allied to acetylene are formed, whilst benzene and its homologues contain a still smaller proportion of hydrogen.

When the temperature is very high, hydrogen, acetylene, benzene, and naphthalene are the chief unoxygenated products. Thus, coal being distilled at a high temperature for the manufacture of coal gas, the liquid hydrocarbons consist chiefly of benzene and its homologues, and naphthalene.

At a dull red heat, such as is employed for the distillation of bituminous shale, the liquid products are wholly free from benzene and naphthalene, whilst little or no hydrogen or acetylene is present in the gases. On the other hand, the liquid products are rich in paraffins and olefins, with some anthracene and chrysene; and it is a remarkable fact that the oxygenised and nitrogenised products consist chiefly of phenols of the formula $C_nH_{2n-7}OH$, and bases of the formula $C_nH_{2n-5}H$ (pyridine bases), although the corresponding hydrides, $C_nH_{2n-7}H$, *i.e.*, benzene and its homologues, are wholly absent.

As a rule, when the temperature of the distillation is low, a large yield of liquid products is obtained, together with a low yield of gas of high illuminating power. At a high temperature, a maximum production of gas of low illuminating power results, while the proportion of liquid products is small. The higher the temperature of the retort, the larger the percentage of solid carbonaceous residue (coke or charcoal) left in it.

The following table indicates the general nature of the more prominent organic products of the dry distillation of coal, bituminous shale, peat, and wood, *as the processes are carried on in practice.* To facilitate comparison the leading organic constituents of natural petroleum are shown in juxtaposition

with the products of the various artificial destructive distillations:—

Organic Products.	Coal.	Bituminous Shale.	Peat.	Wood.	Petroleum.
Hydrogen	large	traces	large	large	present
Gaseous Hydrocarbons.					
Marsh Gas and Homologues	large	large	large	considerable	present
Olefins	large	large	...	...	present
Acetylene	present	none			
Liquid and Solid Hydrocarbons.					
Liquid Paraffins	small	large	considerable	absent	very large
Solid Paraffins	traces	considerable	present	present	moderate
Liquid Olefins	small	very large	moderate	...	considerable
Liquid Acetylenes	present	present	...	...	...
Benzene and Homologues	large	none	present	moderate	present
Benzene Hydrides or Paraffenes	(?)	(?)	(?)	(?)	considerable
Naphthalene	large	none	...	moderate	none
Anthracene	moderate	trace	...	...	present
Chrysene	moderate	considerable	...	present	present
Oxygenated Bodies.					
Acetic Acid	present	present	large	large	
Methyl Alcohol	none	...	considerable	considerable	
Phenols	large	considerable	...	moderate	
Oxyphenols (Creosote)	none	none	...	considerable	
Nitrogenised Bodies.					
Anfline bases	present	none			
Pyridine bases	considerable	considerable			
Acridine	present				
Carbazol	present				

It will be seen from this table that the products of the distillation of each of the raw materials contain certain characteristic bodies. Thus, oxygenated products are found most largely in the products of the distillation of wood; paraffins are *especially* characteristic of petroleum; olefins, and, to a lesser extent paraffins, of the distillation of shale; whilst coal-tar is remarkable for the large proportions of benzene and naphthalene contained in it.

The consideration of the gaseous products of destructive distillation lies outside the scope of this volume. The liquid and solid hydrocarbons of coal-tar are described under the heads of benzene and its homologues, naphthalene, and anthracene. The hydrocarbons from petroleum and the distillation of shale are considered in the series of sections commencing on page 14. The chief oxygenated bodies produced by destructive distillation were described in Volume I.

SEPARATION OF HYDROCARBONS.

The separation of individual hydrocarbons from complex mixtures is often effected by processes of fractional distillation, fusion, &c. (see pages 44 and 87). Fractions of perfectly constant boiling and melting point often contain, however, several isomeric hydrocarbons of the same series, as well as members of several isologous series.

The analysis of mixtures of hydrocarbons of different series is, in many cases, exceedingly difficult, especially when their fusing and boiling points are approximately the same, in which case the methods of fractional fusion and distillation are not available. The following principles may in many cases be successfully applied to the analysis of complicated mixtures of hydrocarbons:—

(*a*) The hydrocarbons of the paraffin series are not acted on by bromine in the dark or diffused daylight; whereas the olefins and the hydrocarbons of most other series form compounds having higher boiling points than the original bodies. Hence the paraffins may be separated from the resultant bromo-compounds by fractional distillation. The olefins, or hydrocarbons of the general formula C_nH_{2n}, are remarkable for the facility with which they combine with bromine to form dibromides, $C_nH_{2n}Br_2$. The fact may be utilised for the determination of olefins in coal-gas, or for the comparative assay of shale and petroleum products (see page 27).

(*b*) By treatment with bromine and water in sunlight, the paraffins are converted into monobromo-substitution products, the aqueous liquid containing an amount of bromine in the form of hydrobromic acid, equal to that which has entered into the hydrocarbon ($C_nH_{2n+2}+Br_2=C_nH_{2n+1}Br+HBr$). By separating the aqueous liquid, removing free bromine by agitating with shale naphtha (see page 31), and estimating the hydrobromic acid formed, a determination can be made of the amount which has combined with the paraffins contained in the sample of oil.

(*c*) All the hydrocarbons except those of the paraffin series are readily attacked by warm nitric acid of 1·45 specific gravity. In some cases nitro-compounds are formed, in others products of oxidation result.

(*d*) By treatment in the cold, or at any rate at 100° C., with concentrated sulphuric acid, specific gravity 1·85, all liquid hydrocarbons except paraffins are either polymerised or converted into sulpho-acids, which are usually soluble in water or alkaline liquids.

(*e*) Acetylene and other hydrocarbons of that and the next series form metallic derivatives on treatment with an ammoniacal solution of argentic or cuprous chloride, or of argentic nitrate. These metallic derivatives are solid bodies, insoluble in water, but decomposed by hydrochloric acid with liberation of the original acetylene or similar hydrocarbon.

(*f*) The hydrocarbons of the eighth and many of the subsequent series form characteristic crystalline compounds with picric acid (see page 3).

Various instances of the application of these and similar principles will be found in the succeeding pages.

PARAFFINS. $C_nH_{2n+2}=(C_nH_{2n+1}),H.$

The hydrocarbons having the above formula are known by the generic name of paraffins, and may be regarded as the hydrides of the monatomic alcohol radicals.

The lower members of the paraffin series are permanent gases, the intermediate liquids, their viscidity, density, and the temperature of ebullition* rising with each increase in the number of carbon atoms, till the paraffin $C_{20}H_{42}$, and the still higher homologues are crystalline solids. All the members of

* Normal butane, C_4H_{10}, boils at 0 to 1° C., and normal pentane, C_5H_{12}, at 37 to 39° C., but the difference between the boiling points of each successive pair of the series decreases by about 4° C., till it reaches the normal difference of 19° C. for each addition of CH_2. According to Goldstein, the above expression is not strictly correct. As the difference between each successive pair of boiling points continually decreases, some other factor must be involved besides increase of molecular weight. Goldstein finds this in the decrease in the ratio of the number of hydrogen atoms to the number of carbon atoms. Thus in

CH_4	C : H = 1 : 4
C_2H_6	C : H = 1 : 3
C_3H_8	C : H = 1 : $2\frac{2}{3}$
C_4H_{10}	C : H = 1 : $2\frac{1}{2}$

Hence the ratio is continually decreasing.

Any paraffin boils at $19+a°$ higher than the homologue immediately below it. a is a smaller difference as the number of carbon atoms increases.

the series above propane, C_3H_8, are capable of isomeric modification, the iso-varieties having somewhat different boiling points and densities from the normal paraffins; they also yield different products on oxidation. Above nonane, the normal and iso-varieties have not been satisfactorily differentiated. The percentage of carbon in pentane is 83·33 per cent., and the proportion rises very gradually with the number of carbon atoms, candle-paraffin of the composition $C_{25}H_{52}$ containing 85·23 per cent. of carbon.

The hydrocarbons of the paraffin series are especially characteristic of petroleum, in which every known normal member of the series has been found, as well as some iso-paraffins.

Paraffins are also contained more or less largely in the oils obtained by the distillation of Boghead and Cannel coal, bituminous shale, &c., wood, peat, and in Menhaden oil. Normal heptane has been obtained by Thorpe from the turpentine of *Pinus Sabiniata.** By the solution of the variety of white cast-iron known as spiegeleisen in hydrochloric or sulphuric acid,† Cloez obtained various hydrocarbons of the ethylene series, absorbable by bromine and combining easily with hydrochloric acid; and in addition to these the following paraffins, which were isolated by treatment with sulphuric acid, decantation, drying first with caustic potash and then with metallic sodium, the purified oils being then fractionally distilled. The following are the boiling points and densities of the products obtained by Cloez :‡—

Formula.	Boiling Point.	Sp. Gravity.
$C_{10}H_{22}$	155°–160°	·760
$C_{11}H_{24}$	178°–180°	·769
$C_{12}H_{26}$	195°–198°	·782
$C_{13}H_{28}$	215°–220°	·793
$C_{14}H_{30}$	234°–238°	·812
$C_{15}H_{32}$	258°	·830
$C_{16}H_{34}$	276°–280°	·850

* It has been suggested by Mendelyeff that petroleum has its origin in the action of water or steam on heated carbide of iron in the interior of the earth.

† *Compt. Rend.* lxxxv. 1003, and *Journ. Chem. Soc.* xxxiv. 481.

‡ *Journ. Chem. Soc.* xxxv. 296.

METHANE, $CH_4=CH_3.H$, is the first member of the paraffin series, and constitutes the greater part of the gas evolved by the decomposition of vegetable matter in presence of moisture, whence its name of "marsh gas." Fire-damp also consists essentially of methane, though smaller quantities of ethane and other gases are also present. Methane also constitutes the greater portion of ordinary illuminating gas, and is a constant product of the destructive distillation of organic matter.

ETHANE, $C_2H_6=C_2H_5.H$ or $CH_3.CH_3$. This gas may be regarded either as ethyl hydride or di-methyl. It occurs in admixture with methane in coal-gas, fire-damp, and the permanent gases which escape from petroleum wells (see page 15).

PROPANE, C_3H_8, and BUTANE, C_4H_{10}, are met with to a considerable extent in petroleum gas. The latter paraffin forms the greater part of the petroleum product known as "cymogene" (see page 19).

PENTANE, or Amyl Hydride, $C_5H_{12}=C_5H_{11}.H$. This paraffin has a density of ·645 at 0° C., and boils at 37 to 39° C. It occurs, together with isopentane, boiling at 30°, in the most volatile portions of petroleum spirit, and in the products of the distillation of cannel coal and bituminous shale.

HEXANE, C_6H_{14}; HEPTANE, C_7H_{16}; OCTANE, C_8H_{18}; and certain of their isomers constitute the greater part of the liquid known in commerce as petroleum naphtha or "benzoline" (see page 30). Normal hexane boils at 69 to 70°, heptane at 97 to 98°, and octane at 123 to 125° C.; their respective isomers boiling in each case from 6 to 8° below the normal paraffins.

Normal heptane has also been met with in a state of approximate purity in the liquid obtained by distilling the terebinthinous exudation of the *Pinus sabiniata*.*

The higher paraffins require no separate description. The chemical and analytical characters of the paraffins as a class are discussed below. The properties and modes of assaying the various liquids consisting essentially of paraffins, and of commercial importance, are described on page 14, *et seq.*,

* *Journ. Chem. Soc.* xxxi. 296.

under the heads of petroleum, petroleum products, and paraffin wax.

The following reactions, amongst others, result in the formation of paraffins :—

1. The destructive distillation of wood, coal, or other organic matter (see page 6).

2. The action of water and metallic zinc on the iodides of the corresponding alcohol radicals; thus—

$$2C_2H_5I + Zn_2 + 2H_2O = ZnH_2O_2 + ZnI_2 + 2C_2H_5H.$$

3. The action of zinc alone on the iodides of the corresponding alcohol radicals. In this case a portion of the product suffers decomposition with formation of a lower paraffin and olefin.

$$2C_2H_5I + Zn = ZnI_2 + \underset{\text{Butane.}}{C_4H_{10}}.$$

and

$$\underset{\text{Butane.}}{C_4H_{10}} = \underset{\text{Ethylene.}}{C_2H_4} + \underset{\text{Ethane.}}{C_2H_6}.$$

4. The electrolysis of the fatty acids; as

$$2C_2H_4O_2 = C_2H_6 + H_2 + CO_2.$$

5. The action of lime or baryta on the salts of the fatty acids at a high temperature—

$$2KC_2H_3O_2 + CaH_2O_2 = CaCO_3 + K_2CO_3 + CH_4.$$

The paraffins are saturated hydrocarbons incapable of entering into direct combination. This fact, and their resistance to the action of reagents originated the name paraffin (*parum affinis*).

The paraffins are unaffected by chlorine or bromine in the dark—a character which distinguishes them from hydrocarbons of the ethylene and acetylene series. In sunlight, the paraffins are acted on by chlorine or bromine with production of hydrochloric or hydrobromic acids and of chloro- or bromo-substitution products. The paraffins are, however, more readily acted on by chlorine at their boiling points than in the cold. Cold heptane readily absorbs chlorine in diffused daylight, becoming yellow. The liquid suddenly becomes very hot, and evolves torrents of hydrochloric acid. From this

point it remains colourless, absorbs the chlorine quietly, and evolves hydrochloric acid continuously. In presence of a little iodine the action continues in the dark, but secondary products are readily formed.

The substitution-products obtained by the action of chlorine or bromine on the paraffins reproduce the original bodies under the influence of nascent hydrogen, and are converted into the corresponding alcohols on treatment with alkalies. Iodine has no direct action on paraffins, but substitution-products containing iodine can be obtained by indirect means. (Thus, tri-iodo-methane, or iodoform, $CHCl_3$, is a product of the simultaneous action of iodine and an alkali on various organic bodies, such as alcohol, sugar, &c.)

The lower homologues of the paraffin series are unaffected by nitric acid, though nitro-substitution compounds may be obtained indirectly. The higher members of the series are but little affected by *cold* nitric acid, even when fuming and mixed with concentrated sulphuric acid, but paraffin wax is attacked by *hot* nitric acid, even if dilute.*

When the higher paraffins are heated in a sealed tube, or otherwise subjected to a high temperature, they suffer more or less complete decomposition, with formation of a lower paraffin and olefin, thus—

$$C_{20}H_{32}=C_5H_{12}+C_{15}H_{30}=C_7H_{16}+C_{13}H_{26}=\text{ &c.}$$

Hence, the actual product is a mixture of several paraffins and olefins.†

L. Prunier ‡ finds that bromine absorbs nothing from the gas obtained during the first part of the process of distilling crude petroleum, but large quantities of unsaturated hydro-

* Schorlemmer obtained succinic acid and other products by the action of boiling fuming nitric acid on octane from petroleum.

† This reaction has an industrial application in the "cracking" of the heavier and denser of the petroleum oils. By this means Mr J. Merrill found it possible to obtain "a continuous production of light distillates having a specific gravity of ·818, was effected from hydrocarbon oils of specific gravity ·880, in an apparatus holding 1000 gallons, by properly regulating the heat applied; the other products being only uncondensed gases, and deposited carbon left in the apparatus at the end of the distillation."—*American Chemist*, ii. 11, 444.

‡ *Ann. Chim. Phys.* [5] xvii. 5, and *Journ. Chem. Soc.* xxxvi. 1025.

carbons are disengaged when the bottom of the retort is nearly or quite red hot. Among the bodies recognised were the ethylenes from C_2H_4 to C_5H_{10}, several members of the acetylene series, and crotonylene ($C_2H.C_2H_5$). Among the solid hydrocarbons recognised were anthracene, pyrene, chrysene, fluoranthene, acetnaphthene, petrocene, and carbopetrocene.

Paraffins in the vaporous or gaseous state can be separated from hydrocarbons of the ethylene and acetylene series by treatment in the dark with excess of bromine. The paraffins remain unaffected, while the admixtures are converted into liquid bromine compounds. This plan is sometimes employed for determining the proportion of olefins in illuminating gas, and is also applicable to the determination of olefins in mixtures of liquid hydrocarbons such as shale oil and petroleum (see page 27).

When paraffins are heated with bromine and water for some time in sunlight, they are converted into bromo-substitution compounds, half the bromine which enters into reaction being afterwards found as hydrobromic acid. This reaction is peculiar to paraffins, and may, under favourable circumstances, be employed for their recognition and quantitative determination.

Liquid paraffins may be separated from hydrocarbons of other series by treating the mixture first with fuming nitric acid, and afterwards with sulphuric acid, avoiding rise of temperature. Other bodies are oxidised or converted into nitro-compounds which remains dissolved by the acids or are much less volatile than the unaltered paraffins. After washing with water, drying over caustic potash, and rectification over sodium, a distillate of pure paraffins is obtained. A practical use of this principle is sometimes made in analysis.

Petroleum; Rock Oil; Mineral Oil; Liquid Bitumin.

French—Pétrole; Huile de Pierre; Bitume Liquide.
German—Erdöl; Steinöl.

Petroleum is a natural product occurring in the earth at very varied depths, and in a great many localities. It consists of a mixture of a considerable number of hydrocarbons, not unmixed with small quantities of sulphuretted, nitrogenised,

and oxygenised bodies. All varieties of petroleum are combustible liquids, burning with a luminous, more or less smoky flame.

Petroleum has an exceedingly variable composition, and is more or less volatile and mobile according to its content of bitumin and solid bodies. In general, it contains about 85 per cent. of carbon and 15 of hydrogen, but its elementary composition gives no idea of the variety of hydrocarbons contained in it. In short, the constituents of petroleum present the following varieties of character :—

(*a*) Their volatility is very different, for they extend from permanent or nearly permanent gases, to solids which do not boil except at very elevated temperatures (370° and 420° C).

(*b*) The volatility of these hydrocarbons is usually inversely as their density, the lightest oils being the most volatile.

(*c*) The inflammability is of course a function of the volatility, the more volatile constituents taking fire on approach of a flame at any temperature, while the denser and less volatile oils require to be considerably heated before they can be inflamed or made to give off inflammable vapours. The hydrocarbons of petroleum belong to several series, the paraffins largely predominating. A complete series of paraffins from CH_4 to $C_{16}H_{34}$ have been isolated from American petroleum, and the solid members $C_{25}H_{52}$, $C_{27}H_{56}$, and $C_{30}H_{62}$ are also present. Isoparaffins are present as well as the normal hydrocarbons.* Schorlemmer considers that petroleum consists chiefly of an inextricable mixture of isomeric and homologous paraffins, in which, however, the normal paraffins predominate.

The paraffins from CH_4 to C_4H_{10} are gaseous at ordinary temperatures, and hence escape in admixture with hydrogen from petroleum wells, or when the petroleum is stored or gently heated.† The hydrocarbons of the paraffin series from C_5H_{12} to $C_{15}H_{32}$ constitute the greater part of the liquid

* With the exception of certain isomeric varieties producible by synthetical means, all the known members of the paraffin series of hydrocarbons have been recognised in American petroleum. (See note on page 16.)

† Petroleum gas contains from 60 to 90 per cent. of methane, CH_4, with smaller proportions of hydrogen and ethane, C_2H_6, and traces of higher homologues. Olefins are present only in insignificant quantity. On the other hand, the liquid obtained by J. J. Coleman, by the action of cold and pressure on the

portion of American petroleum, while still higher members of the series, solid at ordinary temperatures, are also met with.* †

One of the most characteristic constituents of American petroleum is the paraffin hexane, C_6H_{14}, a hydrocarbon which is closely allied to cellulose, $C_6H_{10}O_5$.

Hydrocarbons of the ethylene and benzene series are also found in petroleum, and especially in the naphthas from the Caspian Sea. Distinct traces of benzene and its homologues have also been recognised in Canadian petroleum, and Warren also found the olefins from $C_{10}H_{20}$ to $C_{13}H_{26}$.

According to very recent researches, Caucasian petroleum contains a large proportion of additive hydrogen compounds of hydrocarbons of the benzene series, $C_nH_{2n-6}H_6$.† These hydrocarbons are isomeric with the olefins, C_nH_n, but do not form compounds with bromine, and are not acted on by cold fuming nitric or sulphuric acid. American petroleum is also stated to contain this series of hydrocarbons, a belief to which some experiments of the author likewise lend support.

Although the origin of petroleum cannot be very distinctly traced, there can be no doubt that in many cases it is a product of the action of long-continued moderate heat on coal or analogous matters of vegetable origin. Were the temperature required for its production a high one, gaseous emanations would probably be more frequent and abundant than is actually the case.

By the distillation of the Torbanehill mineral, Boghead

gases produced in the distillation of bituminous shales, consisted chiefly of butylene, C_4H_8; amylene, C_5H_{10}; and hexylene, C_6H_{12}; that is, members of the olefin series.

* The method pursued by Schorlemmer for the detection of the hydrocarbons of the benzene series was as follows :—The portion of oil distilling below 150° C. was treated with concentrated nitric acid. The acid liquid was diluted, and the water separated from the heavy nitro-products which possessed the odour of bitter almonds. These nitro-compounds were treated with tin and hydrochloric acid, and the solution thus obtained was distilled with caustic potash. The aqueous distillate, in which some drops of an oily liquid were suspended, had the odour of aniline, and gave with a solution of bleaching power a most distinct violet coloration. The rosaniline reaction could be obtained by heating one of the oily drops with mercuric chloride.

† *Ber.* xiii. 1818 and 2028; and *Journ. Chem. Soc.* xl. 159, and 705. Beilstein and Kurbatow question even the presence of paraffins in Caucasian petroleum.

cannel coal, or bituminous shale, products closely allied to natural petroleum are obtained. Their manufacture is largely conducted in the south of Scotland. Besides homologous paraffins, and olefins and other unsaturated hydrocarbons, the crude shale oil contains phenols, nitrogenised bodies, and other products met with in coal-tar. When freed from those by successive treatment with acids and alkalies the residual oil presents a close analogy to native petroleum.*

Petroleum is found in many parts of the world, and in various geological formations. By far the largest quantity is now obtained from the palæozoic rocks of the United States and Canada.† These sources so completely overshadow all others from a commercial point of view, that the following description applies chiefly to the American product:—

CRUDE NATURAL PETROLEUM is an oily liquid varying in density from ·74 to ·92. It has a characteristic odour, which is sometimes, but by no means invariably, disagreeable, and its colour varies from straw-yellow to brownish black. Its coefficient of expansion varies according to the proportion of naphtha present.‡ This is shown by the following table:—

Sp. Gravity at 15° C.	Expansion Coefficient for 1° C.
Under ·700	·00090
·700 to ·750	·00085
·750 to ·800	·00080
·800 to ·815	·00070
over ·815	·00065

Crude petroleum was formerly frequently adulterated with petroleum spirit. As this was less valuable than the heavier and less volatile kerosene oil it not unfrequently found its way back to the wells, to be re-pumped as crude petroleum, or was even directly added to the latter in the tanks. The

* The proportion of olefins in purified burning oil from bituminous shale is very much larger than in that obtained from American petroleum. Shale burning oil contains about 36% by measure of paraffins, and 64 of olefins and other hydrocarbons acted on by fuming nitric acid, whilst in American kerosene these proportions are reversed.

† For an interesting description of the petroleum district of Baku on the Caspian Sea, see the *Journal of the Society of Arts*, August 29, 1879.

‡ On a stock of 1,000,000 barrels of petroleum the shrinkage in winter amounts to 7000 to 10,000 barrels.

difference in the commercial value of the products is not now sufficiently great to afford much inducement to continue this practice. Excess of the lighter oils reduces the density of the petroleum, and causes it to give off inflammable vapour at a lower temperature. Of course the percentage of naphtha yielded on distillation is increased. Hence the best petroleums give only a moderate percentage of naphtha.

Crude petroleum is always distilled before being imported to this country. The character and proportion of the various products obtained depend largely on the nature and source of the oil and the details of the mode of treatment, which is capable of considerable variation in detail.* As a rule, the lighter and more volatile portions are fractionated into a number of products, known commercially as cymogene, rhigolene, gasolene, naphtha, and benzine or benzolene; but in many cases the proximate separation of the products of the distillation of crude petroleum is less complete, only three principal products being made, namely, naphtha, kerosene, and lubricating oil. By the present system of manufacture, with some "cracking" of the heavier oils (see page 13), about 75 per cent. of burning oil flashing at 68° F. by Abel's test may be obtained. The yield of higher class oils (such as would pass English inspection) is proportionately smaller, and of "water-white oil" as little as 30 per cent. is obtained. The proportion of naphtha varies from 9 to 18 per cent., according to the age of the oil-producing territory.

* The following is an outline of the usual process of petroleum distillation: The oil is heated in large stills of wrought iron. The more volatile portions soon come over; they are either burnt, or condensed by artificial cold and pressure. The liquids thus obtained are known as "cymogene" and "rhigolene." After these, products condensible by cold water are obtained, the first portions having a density of ·630, the product becoming heavier as the distillation proceeds. (The distillate obtained in this part of the operation is usually again distilled, when it yields "gasoline," "naphtha," and "benzine.") When the liquid passing over acquires a density of ·725 to ·750, —according to the works' custom—the stream is diverted from the "naphtha" tank to the "kerosene" receiver, where it is collected till its gravity reaches about ·840, when it is run into the "paraffin oil" tank till there is nothing further to be obtained. The residue in the still is only conbustible with difficulty, but is used as fuel. In some cases the operation is arrested before actual coking occurs, in which case the residue has the consistency and characters of thick tar.

"CYMOGENE," from petroleum, consists chiefly of butane, C_4H_{10}. It has a density of ·590, boils at 0° C. and is condensed by artificial pressure when not used under the stills or allowed to burn to waste. It is employed in refrigerating machines.

"RHIGOLENE" has a density of ·625, boils at 18°, and is now largely used for producing local anæsthesia.

"GASOLENE" has a density of ·650 to ·665. It is the lightest and most volatile portion of petroleum "naphtha." It is employed for naphthalising air and gas.

"NAPHTHA" has a density of ·695 to ·705, and is employed in the manufacture of oil-cloths, for cleaning, and for adulterating kerosene. (See also below.)

BENZOLENE, KEROSENE or BURNING OIL, LUBRICATING OIL, VASELENE, and PARAFFIN WAX, are obtained from successive fractions of the products of the distillation of petroleum, or from the undistilled residuum. They consist chiefly of mixtures of hydrocarbons of the paraffin and olefin series, and are described on page 24, *et seq.*

PETROLEUM RESIDUES, produced in the distillation of petroleum, are largely imported to England. They usually yield about 5 or 6 per cent. of burning oil, 50 per cent. of lubricating oil, and 5 to 7 per cent. of crude paraffin scale. Petroleum residues contain a notable quantity of water, which is very obstinately retained. The proportion may be determined by diluting the sample with petroleum spirit, when the water will gradually settle out. Smaller quantities may be determined as in the case of paraffin scale (see page 44).

EXAMINATION OF COMMERCIAL PETROLEUMS.—The ordinary characters relied on as commercial tests of the quality of petroleum are—its specific gravity, its odour and colour, its feel when rubbed between the fingers, and the percentage of naphtha of ·700 sp. gravity yielded on fractional distillation. This should not exceed 17 per cent. of the sample.*

* The New York Produce Exchange has decided that by the term "crude petroleum" is to be understood pure natural oil, neither steamed nor treated, and free from water, sediment, or any adulteration, and of specific gravity 44° to 48° Beaumé (= ·792 to ·810 sp. gravity). In general, the New York crude oil has a density varying from ·790 to ·800.

The temperature at which a sample of petroleum oil commences to give off sensible quantities of inflammable vapour is technically called its "flashing point." Clearly the lower the temperature at which an oil "flashes" the more dangerous its transportation, storage, and use must become.

According to the Petroleum Act of 1871 (34 and 35 Vict. cap. 105), "the term 'petroleum' includes any rock oil, Rangoon oil, Burmah oil, oil made from petroleum, coal, schist, shale, peat, or other bituminous substance, and any products of petroleum or any of the above-mentioned oils; and the term 'petroleum to which this Act applies' means such of the petroleum so defined, as when tested in manner set forth in Schedule I. to this Act, gives off an inflammable vapour at a temperature of less than one hundred degrees of Fahrenheit's thermometer."

This definition is expressly intended to exclude the better class of kerosene oil, which does not give off sensible quantities of inflammable vapour (under the conditions prescribed in the schedule) till heated above 100° F.* The apparatus to be employed and the mode of conducting the test were set forth in the schedule of the Act; but as they are happily now merely of historical interest, it is not necessary to detail them. It is sufficient to say that, owing to an insufficient description of the mode of performing the operation, and inherent sources of

The density of the first ninety fractions obtained by distilling the average petroleum oil of the New York market has been determined by Bourgongnon. The following table shows the density of every tenth fraction obtained, the original oil having a specific gravity of ·7982 at 15° C.:—

	Sp. Gr.		Sp. Gr.
1st Fraction . .	·679	50th Fraction . .	·777
10th ,, . .	·705	60th ,, . .	·790
20th ,, . .	·728	70th ,, . .	·815
30th ,, . .	·750	80th ,, . .	·829
40th ,, . .	·765	90th ,, . .	·825

The composition of the crude oil furnished by the distillation was—naphtha at ·700, 17 %; benzine at ·730, 9 %; burning oil at ·783, 64 %; residue and loss, 10 %; and the residue contains about ¼th of its weight of solid paraffin.

* Some time since the Midland Railway Company attempted to enforce the provisions of the Petroleum Act on the carriage of wood-naphtha—a product which, both in spirit and letter, is excluded from the operation of the law.

error in the process itself, the results obtained were extremely unsatisfactory. One of the great faults of the apparatus was that the vapour rising from the warm liquid was in no way prevented from diffusing into the surrounding air, and hence the operation of ascertaining the flashing-point by this apparatus was known as the "open test." A close test, or process in which the vapour was confined, was proposed by Mr Keates in 1872,* and its advantages were discussed in evidence before a Parliamentary Committee in the same year. In 1876 the whole question was very carefully inquired into by Professor Abel, who recommended a close test to be made by an improved form of apparatus. This was definitely adopted in the Petroleum Amendment Act of 1879, and since the end of that year has become the legal form of the test. The construction of the apparatus, and the mode of performing the test are minutely described in a schedule to the Act, and a model apparatus is deposited at the Weights and Measures Department of the Board of Trade. The method of employing the apparatus is sufficiently indicated in the following description, abridged from Schedule I. of the Petroleum Act, 1879:—

The test apparatus is to be placed for use in a position where it is not exposed to currents of air or draughts.

The heating apparatus is filled by pouring water into the funnel until it begins to flow out at the spout of the vessel. The temperature of the water at the commencement of the test is to be 130° F. (neither more nor less).

The test-lamp is prepared for use by fitting it with a piece of flat-plaited candle-wick, and filling it with colza or rape oil up to the lower edge of the opening of the spout or wick tube. The lamp is trimmed so that when lighted it gives a flame of about 0·15 of an inch diameter, and this size of flame, which is represented by the projecting white bead on the cover of the oil cup, is readily maintained by simple manipulation from time to time with a small wire trimmer. When gas is available it may be conveniently used instead of the little oil

* A close test has also been devised by Tagliabue, of New York, and employed to some extent in America and France. Mr B. Redwood's experience of it is unfavourable.

lamp, and for this purpose a test-flame arrangement for use with gas may be substituted for the lamp.

The bath having been raised to the proper temperature (130° F.), the oil to be tested is introduced into the petroleum cup, being poured in slowly until the level of the liquid just reaches the point of the gauge which is fixed in the cup. (In pouring in the oil to be tested great care should be taken not to splash it against the sides of the cup. In warm weather the temperature of the room in which the samples to be tested have been kept should be observed in the first instance, and if it exceeds 65° the samples to be tested should be cooled down to about 60° F.). The lid of the cup, with the slide closed, is then put on, and the cup is placed in the bath or heating vessel. The thermometer in the lid of the cup has been adjusted so as to have its bulb just immersed in the liquid, and its position is not under any circumstances to be altered. When the cup has been placed in the proper position, the scale of the thermometer faces the operator.

The test-lamp is then placed in position upon the lid of the cup, the lead line or pendulum, which has been fixed in a convenient position in front of the operator, is set in motion, and the rise of the thermometer in the petroleum cup is watched. When the temperature has reached about 66° the operation of testing is to be commenced, the test flame being applied once for every rise of one degree in the following manner:—The slide is slowly drawn open while a pendulum performs three oscillations,* and is closed during the fourth oscillation. In moving the slide so as to uncover the holes, the oscillating lamp is caught by a pin fixed in the slide, and tilted in such a way as to bring the end of the spout just below the surface of the lid. Upon the slide being pushed back so as to cover the holes, the lamp returns to its original position. The temperature at which the vapour of the oil gives a blue flash on applying the test-flame is noted as the flashing-point of the sample.

* By an oversight, the Act contains no description of the pendulum to be used; but from a letter from Mr Abel to Mr B. Redwood it appears that the pattern pendulum or lead line deposited in the Standards' office is 24 inches in length from the point of suspension to the centre of gravity of the weight. A properly adjusted metronome is a convenient substitute for the pendulum.

To determine the flashing-points of oils of very low volatility (*e.g.* lubricating oils), the air-chamber which surrounds the lamp is filled with cold water to a depth of 1½ inches, and the heating vessel or water-bath is filled as usual, but with cold water instead of water at 130°. The heating lamp is then placed under the apparatus, and kept there during the entire operation. If a very heavy oil is being dealt with, the operation may be commenced with water previously heated to 120°, instead of with cold water.

The results by the close test now legalised are very satisfactory, and the process has been freed as much as possible from sources of error due to "personal equation." The disadvantage of the new test is that the flashing of the vapour occurs at a temperature much lower than was the case with the old apparatus for the open test.* As the result of the

* Professor Abel found that, on comparing the results given by 29 samples of oil when tried by the close and open tests, that the flashing-point was 23 degrees lower in one case, and from 25 to 29 degrees lower in the remaining 28 cases, by the close test than by the open. At the suggestion of Professor Abel, Mr Boverton Redwood, the chemist to the Petroleum Association, examined as many as 1000 samples of commercial kerosene (representing 97,766 barrels of oil), and obtained the following comparative results by the old and new methods :—

Of 968 samples, all of which consisted of the ordinary petroleum oil of commerce, 92 samples showed a difference between the two tests of 25° F.

208	,,	,,	,,	26° ,,
225	,,	,,	,,	27° ,,
281	,,	,,	,,	28° ,,
162	,,	,,	,,	29° ,,

Hence, so far, Mr Redwood's results fully corroborated those obtained by Professor Abel.

The remaining 32 samples were all specimens of the special product known in the trade as "water-white oil." This brand shows a flashing-point by the open test as high as 116° F., and even up to 140° and over, and this slight volatility is accompanied by comparatively low specific gravity. These characters, somewhat unusual in the same oil, are due to the mode of manufacture adopted, by which a considerable portion of the first and last portions which distil are rejected. Hence the water-white oil is doubtless a mixture of a smaller number of hydrocarbons than is the case with other varieties of kerosene. When tried by the close and open tests, the 32 samples of water-white oil showed a difference between the two tests of from 20° to 25° F. As the lowest flashing-point by the open test was 118° F., a deduction of the mean difference of 27° would still leave water-white oil with a flashing-point far above the ordinary kinds. Hence the smaller difference in the results of the tests, when applied to water-white oil, is of no practical importance.

experiments of Professor Abel, supplemented by those of Mr Redwood, the flashing-point by the close test of the Act of 1879 has been fixed at 73° F., which is equal to 22·7° C.*

Besides those already mentioned, other methods of assaying petroleum and products therefrom have been based on the boiling point of the liquid, the tension of the vapour, the temperature of inflammation of the liquid ("American burning test"), and other characters; but none of these are thoroughly satisfactory, and are likely to become very quickly obsolete, now that the method of testing the flashing-point of the vapour has been rendered more exact.

Petroleum, within the meaning of the Act, is only allowed to be kept and sold under certain restrictions, which vary to a certain extent, according to a discretionary power exercised by the local authorities, any breach of the provisions of the Act being punishable by heavy fines.

Petroleum and Shale Products.—The parallel products obtained by the fractional distillation of petroleum and bituminous shale present a marked similarity in general character, though differing notably in certain respects. As a rule, the treatment of petroleum is a much simpler operation than the manufacture of marketable products from crude shale oil, but, broadly speaking, the same method of treatment is applied to both of the raw materials. The process employed consists essentially in fractional distillation, and treatment of the separate fractions successively with sulphuric acid and caustic soda, to remove bodies of acid and basic character, and to destroy the less stable hydrocarbons. The less volatile portions deposit paraffin wax on cooling.†

The following table shows in parallel columns the character and quantities of the products obtainable from average Pennsylvanian petroleum of about ·807 specific gravity, and crude Scotch shale-oil of ·860 to ·890 specific gravity.

* The same apparatus and limit has been adopted by the inspectors of the New York Produce Exchange in testing oils for exportation to England.

† Outlines of the methods of treating petroleum and of manufacturing paraffin wax from shale will be found on pages 18 and 39 respectively.

	Petroleum Products.		Shale Oil Products.	
	Sp. gravity.	Percentage.	Sp. gravity.	Percentage.
Cymogene and Rhigolene .	·590 to ·625	very small.	...	...
Gasolene)	·650 to ·665	1½)		
Naphtha } "Naphtha" . }	·695 to ·705	10 }	·740	5
Benzine)	·725 to ·737	4)		
Photogene, or Burning Oil .	·802	55	·815	40
Lubricating, or "Paraffin" Oil	·875	17½	·885	15
Paraffin Wax . . .	...	2	...	8
Coke, Gas, and Loss. . .	...	10	...	32

The number of products into which the more volatile portions of shale oil and petroleum are fractionated vary considerably according to the practice of the works, but gasolene and the more volatile products are obtainable from shale oil equally with shale. The only commercial product producible from petroleum, and having no analogue amongst the products from shale oil, is the gelatinous substance known as vaselene (page 37).

The more volatile products from petroleum are shortly described on page 19. The similar fractions from shale oil closely resemble the petroleum products in their physical characters, but they contain a much larger proportion of olefins, or hydrocarbons of ethylene series. This chemical distinction has been traced by the author in each of the parallel products from petroleum and shale oil, and is the cause of some curious differences in the behaviour of these substances as solvents and with chemical reagents.

The following table gives a general idea of the chemical composition of the leading commercial hydrocarbon products derived from bituminous shale and petroleum. Of course the quantitative composition is liable to considerable variation, and hence must not be interpreted too strictly.

The general and analytical characters of the products named in the following table are described in the succeeding sections * (page 30 to page 45).

* The hydrocarbon products of the distillation of coal do not admit of strictly parallel comparison with those from petroleum and shale. Coal-tar naphtha consists chiefly of benzene, C_6H_6, and its homologues; of the less volatile liquid oils ("dead oils") naphthalene, $C_{10}H_8$, is the most characteristic hydrocarbon (see page 94), while the solid hydrocarbons are naphthalene, anthracene, $C_{14}H_{10}$, and the bodies found associated with the latter (see page 97).

Product.	Bituminous Shale.	Petroleum.
Naphtha.	At least 60 to 70 per cent. of heptylene, C_7H_{14}, and other hydrocarbons of the olefin series, C_nH_{2n}. The remainder paraffins, C_nH_{2n+2}. No trace of benzene or its homologues.*	At least 70 per cent. of heptane, C_7H_{16}, and other hydrocarbons of the paraffin series, C_nH_{2n+2}. The remainder apparently olefins, with distinct traces of benzene, C_6H_6, and its homologues.*
Photogene or Burning Oil.	50 to 80 per cent. or more of the higher members of the olefin series, C_nH_{2n}. The remainder paraffins, C_nH_{2n+2}.	50 to 80 per cent. of higher members of the paraffin series, C_nH_{2n+2}. The remainder, chiefly olefins, C_nH_{2n}.
Lubricating Oil.	Chiefly olefins, C_nH_{2n}, with some polymerised members of acetylene series, C_nH_{2n-2}.	A large proportion of higher olefins, C_nH_{2n}, but less than in corresponding shale-product.
Vaselene, or Mineral Jelly.	No such product.	Higher paraffins of low melting point.
Wax.	Solid paraffins, C_nH_{2n+2}.	Solid paraffins, C_nH_{2n+2}.

From this table it will be seen that while hydrocarbons of the paraffin series are conspicuous in the petroleum products, the shale hydrocarbons are remarkable for their richness in olefins.* In consequence of this peculiarity of constitution concentrated nitric and concentrated sulphuric acid act far more vigorously on shale products than on the parallel hydrocarbons from petroleum, and the proportion of paraffins stated in the above table to exist in the various products really represent the percentage by measure of hydrocarbons which withstand a consecutive treatment with nitric acid of 1·45 of gravity, concentrated sulphuric acid, fuming sulphuric acid, and caustic soda.

A much more satisfactory method, and one which gives very constant results, is based on the fact that paraffins are not acted on when treated with bromine, whilst the hydrocarbons of the olefin and most other series greedily assimilate bromine with formation of additive or substitution products.

* For a notice of very recent researches, see page 16.

The estimation of the bromine-absorbing power of shale and petroleum products is best effected by the following plan, the mode of conducting which is due to the author:—

A solution of hypobromite of sodium is prepared by measuring out 40 c.c. of bromine, gradually adding solution of caustic soda (avoiding any rise of temperature), till the liquid is slightly alkaline and of a light yellow colour, and then diluting the liquid with water to one litre. The strength of this solution is then ascertained by measuring out 20 c.c., diluting with about 150 c.c. of water in a porcelain dish, adding a strong solution of pure iodide of potassium, and then acidulating the mixture with hydrochloric acid. If any black precipitate of iodine occur, more potassium iodide solution is added till the liquid has a clear brown colour. The iodine set free is then titrated with decinormal solution of sodium thiosulphate (hyposulphite, 24·8 grammes of crystallised $Na_2S_2O_3$ per litre), each 1 c.c. of which, if of accurate strength, corresponds to ·0080 grammes of bromine in the 20 c.c. employed for the experiment. The end of the reaction is indicated by the disappearance of the brown colour, and may be rendered still more sharp by adding a few drops of starch solution towards the end of the titration.*

Five grms. or five c.c. of the sample of mixed hydrocarbons to be tested is next placed in a small tapped separator, or Mohr's burette with a glass tap, five c.c. of the bromine solution added, the mixture acidulated with dilute hydrochloric acid and well agitated. The liberated bromine will be dissolved by the hydrocarbon, and in most cases will combine with it to form a bromide, or be acted on with production of a bromo-substitution product. In either case, the red colour of the free bromine will disappear partially or completely. If on standing a minute or two the layer of hydrocarbon is found to have a marked red or yellow colour, the bromine treatment is at an end, but otherwise a further addition of a known measure of hypobromite solution is made and the agitation repeated.†

* It is desirable to ascertain the strength of the hypobromite solution every few days.

† In the analysis of shale-naphtha, 5 c.c. of the sample often requires an addition of 25 c.c. of bromine solution to effect complete bromination.

Excess of bromine solution having been added, as indicated by the permanent red or yellow colour of the hydrocarbon layer, the mixture is allowed to rest a few minutes to permit the aqueous liquid to separate. In some cases this occurs readily, but in others the brominated oil adhers to the sides of the vessel, and, if of about the same density as the aqueous liquid, only separates with great difficulty. In such cases it is desirable to add sufficient petroleum spirit to cause the hydrocarbon to rise readily to the surface.*

Complete separation of the two layers having been effected, the aqueous liquid is run off through the tap into a porcelain basin, and the brominated oil is shaken with sufficient solution of caustic soda to render it colourless. The soda solution is run off into the porcelain basin, the oil washed by agitation with a little water, and the washings run off in their turn. Iodide of potassium is then added to the liquid in the basin, and sufficient hydrochloric acid to render it distinctly acid. The mixture is then titrated with thiosulphate in the same manner as the bromine solution. The quantity of bromine thus found is the excess employed, and if deducted from the total quantity present in the volume of hypobromite solution added to the oil, the weight of bromine will be found which is required to combine with the quantity of hydrocarbon taken for the experiment.†

* This plan never fails. The petroleum spirit employed may be ordinary commercial "benzoline," but it must be previously agitated with enough bromine water to render it permanently coloured, and then with sufficient caustic soda to decolorise it. Treated in this manner it is rendered indifferent to bromine.

† The mode of calculation will be made clear by the quotation of the following results obtained in the assay of a sample of shale burning oil of ·806 sp. gravity:—5 c.c. of the sample were treated with 15 c.c. of hypobromite solution containing ·1416 grammes of bromine in each 1 c.c. The excess of bromine, when removed by soda and treated with iodide of potassium in an acid solution, required 8·2 c.c. of decinormal thiosulphate.

Bromine in 15 c.c. of hypobromite taken . 2·1240 grammes.

Bromine corresponding to 8·2 c.c. of $\frac{N}{10}$ $Na_2S_2O_3$ ·6560 ,,

Bromine assimilated by the oil . 1·4680 ,,

$1{\cdot}468 \times 20 = 29{\cdot}36$ grammes Br. taken up by 100 c.c. of oil.

$\frac{29{\cdot}36}{{\cdot}806} = 36{\cdot}42$ grammes Br. taken up by 100 grammes of oil.

136·42 : 100 = 36·42 : 26·70 per cent. of Br. in brominated oil.

When a solid hydrocarbon, such as vaselene or paraffin wax, is to be examined, two grammes of it should be dissolved in the smallest necessary quantity of petroleum spirit (previously brominated, see footnote, p. 28), and the solution so obtained treated in the usual manner.

Operating in the manner above described the method gives very constant results. The following figures show the proportion of bromine which the author found to react with samples of representative commercial products consisting wholly or chiefly of hydrocarbons:—

Substance.	Sp. Gravity at 15·5° C.	Grammes of Bromine combining with 100 grms. of Sample.	Percentage of Bromine in Product.
Naphthas—			
1. Gasolene from Shale. .	·665	67·1	41·6
2. Gasolene from Petroleum,	·652	5·1	4·8
3. Shale Naphtha. . .	·718	94·9	48·7
4. Petroleum Spirit . .	·690	10 0	8·8
5. Benzol	·876	86·2	26·6
Burning Oils—			
6. From Shale . . .	·801	38·7	27·9
7. From Shale . . .	·806	36·4	26·7
8. From Petroleum . .	·800	17·2	14·7
Lubricating Oils—			
9. From Shale . . .	·889	56·4	36·0
10. From Shale (Bloomless) .	·875	45·3	31·2
11. From Petroleum (Spindle Valvoline) . .	·862	21·6	17·7
12. From Petroleum (Oleonaphtha) . .	·905	31·8	24·1
13. Rosin Oil . . .	·973	45·3	31·2
14. Refined Rosin Oil . .	·978	42·7	29·9
Solid Products—			
15. Vaselene	...	19·7	16·5
16. Paraffin Wax . . .	...	5·2	5·0

From these results it will be seen that there is in each case a striking difference between the proportion of bromine assimilated by any of the shale products, and the quantity which combines with the parallel product from petroleum. Thus, while the shale naphtha took up nearly its own weight of bromine, the petroleum naphtha combined with only 10 per

cent., and the gasolenes, burning oils, and lubricating oils exhibit similar but somewhat less striking differences. Benzol does not give a satisfactory result, the reaction with bromine occurring slowly instead of instantaneously, as is the case with the shale and petroleum products.

Owing to the complex character of commercial hydrocarbon-products, a determination of the amount of bromine combining with them does not give the means of calculating the percentage of olefins contained in them. If, however, a fraction of constant boiling point were prepared, and its vapour-density ascertained, its mean combining weight could thence be deduced, and then a determination of its power of assimilating bromine would give a means of obtaining a close approximation to the proportion of olefins contained in the fraction. This suggested method assumes that the fraction consists essentially of paraffins and olefins. Any admixture of hydrocarbons of other series would further complicate the problem.

Mineral Naphtha. Petroleum Spirit; Petroleum Naphtha; Shale Naphtha; "Benzoline;" "Benzine."

The employment of the terms "benzoline" and "benzine" to indicate the lighter fractions of the distillation of petroleum and shale oil has caused great confusion between these liquids and benzene or benzol, C_6H_6, the leading constituent of coal-tar naphtha. This confusion has been increased by the intentional substitution, partial or complete, of one liquid for the other. Methods for distinguishing petroleum spirit from coal-tar naphtha, and for analysing mixtures of the two, are given on pages 32 and 74.

COMMERCIAL PETROLEUM SPIRIT consists of a mixture of several of the lower members of the paraffin series from pentane to octane (see page 11), and even higher homologues. Traces of benzene and its homologues and certain olefins are also present. The most abundant constituent of petroleum spirit is heptane, C_7H_{16}, but considerable quantities of hexane, C_6H_{14}, are also present. From some experiments of the author the proportion of heptane in petroleum spirit is probably about 50 per cent. (see page 16).

Petroleum spirit is a thin colourless liquid of ·69 to ·74 sp.

gravity. It gives off inflammable vapour at ordinary temperatures, and rapidly evaporates. It should leave no permanent stain when dropped on paper. Petroleum spirit dissolves gutta-percha, naphthalene, paraffin wax, and many similar bodies, and is miscible in all proportions with amyl alcohol, ether, chloroform, benzene, oil of turpentine, creasote, and cresylic acid (but not with carbolic acid. See page 32).

Petroleum spirit is employed as "turpentine substitute" in paints and varnishes. For this purpose it is well-fitted if free from sulphur compounds, the presence of which renders it liable to discolour light paints. It is also used as an illuminating agent in sponge-lamps.

SHALE NAPHTHA.—A product very similar to petroleum spirit in most of its properties and uses is the lighter and more volatile portion of the oils obtained by the distillation of bituminous shale (see pages 24 and 26). The author has found, however, that the shale-naphtha presents certain differences, which are due to the much larger proportion of olefins, C_nH_{2n}, than exist in petroleum naphtha. The following table exhibits these differences in a condensed form, and compares in juxtaposition the characters of a sample of coal-tar naphtha, with specimens of similar products from shale and petroleum. Of course variation in minor details will be met with in different samples from similar sources:—

	Petroleum Naphtha.	Shale Naphtha.	Coal-Tar Naphtha.
Chemical Composition	Contains at least 75 per cent. of heptane, C_7H_{16}, and other hydrocarbons of the marsh gas or paraffin series, the remainder apparently olefins, C_nH_{2n}; with distinct traces of benzene, C_6H_6, and its homologues.*	Contains at least 60 to 70 per cent. of heptylene, C_7H_{14}, and other hydrocarbons of the olefin series. The remainder paraffins, C_nH_{2n+2}. No trace of benzene or its homologues.*	Consists almost wholly of benzene, C_6H_6, and other homologous hydrocarbons. A small percentage of light hydrocarbons in some samples.

* For note on most recent researches, see page 16.

	Petroleum Naphtha.	Shale Naphtha.	Coal-Tar Naphtha.
Specific gravity at 15° C.	·690	·718	·876
Chiefly distils between	65° and 100° C.	65° and 100° C.	80° and 120° C.
Solvent action on coal-tar pitch.	Very slight action; liquid but slightly coloured even after prolonged contact.	Behaves similarly to petroleum spirit.	Readily dissolves pitch, forming a deep brown solution.
Behaviour on shaking three measures of sample with one measure of fused crystals of absolute carbolic acid.	No apparent solution; the liquids are not miscible. (For real nature of reaction see Vol. I. p. 317.)	The liquids form a homogeneous mixture.	The liquids form a homogeneous mixture.
Reaction with bromine in the cold.	Combines with about 10 per cent. of its weight of bromine.	Combines with upwards of 90 per cent. of its weight of bromine.	Combines slowly with 30 to 40 per cent. of its weight of bromine.

Mineral Burning Oil. Kerosene; Photogene; Paraffin Oil.

Kerosene, or "refined petroleum," is the principal product of the distillation of petroleum, the crude American oil yielding from 50 to 70 per cent. of its weight. A similar product is obtained from bituminous shale.

Kerosene imparts its taste and smell to water, but is practically insoluble in that liquid. It is only moderately soluble in alcohol, but is miscible in all proportions with ether, chloroform, benzene, petroleum spirit, fixed and volatile oils.* It dissolves phosphorus, sulphur, iodine, camphor, many resins, wax, fats, and softens indiarubber to a glairy varnish.

Most specimens of photogene present a well-marked blue fluorescence, a character which sometimes serves for the detection of petroleum products in admixture with animal and vegetable oils.

Kerosene usually has a specific gravity varying from ·78 to

* Except castor oil.

·82, but special qualities often exhibit a considerable departure from these figures.*

Good lamp oil should have a tolerably high boiling point, and should neither be too viscous nor too volatile. In addition to the density, the temperature at which kerosene oil commences to give off inflammable vapour is an important character. Cold kerosene oil of good quality will not take fire when a light is applied, nor will the supernatant vapour inflame. The "flashing point," or temperature of ignition of the vapour is greatly reduced by a small admixture of naphtha.† The burning point is not a reliable test of the safety of an oil, since oils, when spilled, will ignite instantly on approach of a flame, when heated only a degree or two above their flashing point, even although the burning point is 10° or 20° F. higher. Experiment shows that an oil flashing at 86° by the open test, and burning at 107° F., can be made to flash at 100° F., by removing 6 or 7 per cent. by distillation.

The method of applying the "flashing point" test to kerosene and other petroleum and shale-distillation products is fully described on page 21.

"Liquid gas," "safety gas," "aurora oil," "petroline," "puroline," "septoline," and other fanciful names have been given to various petroleum and shale products employed for illuminating purposes. In many cases purification is pretended to have been practised with the result of removing the dangerously inflammable constituents. All such products come under the legal definition of "petroleum" (see page 20), and the "flashing point" is a perfectly satisfactory test of their nature.

The petroleum kerosene oil recently imported to England has a distinctly greater density than was formerly the case. This is in a great measure due to the partial exhaustion of the United States' supply, and the larger use of the heavier

* For a description of the variety of photogene known as "water-white oil," see note or page 23.

† Dr B. W. White found that when a kerosene oil having a flashing point of 113° F. (= 45° C.) by the open test was mixed with 1 per cent. of naphtha, it flashed at 103° F., with 2 per cent. at 92°, with 5 at 83°, with 10 at 59°, and with 20 at 40° F. On addition of 20 per cent. of naphtha, the oil itself burned at a temperature of 50° F. The specific gravity of the naphtha added greatly affects the reduction in the flashing point occasioned.

Canadian oil. The density is an important character, for the heavier and more viscous oils require a more loosely-woven wick for their satisfactory consumption.

The photogene oil from shale resembles refined petroleum in all essential physical respects, but, when examined by the bromine process described on page 27, the shale product is found to contain a much smaller percentage of paraffins than is the case with petroleum. Some samples of shale photogene contain only 5 or 6 per cent. of paraffins. The author has repeatedly found that when three measures of petroleum photogene were shaken with one of fused crystals of absolute carbolic acid, the phenol gradually assumed a dark purple, and ultimately a black colour. No such reaction was observed to occur with burning oil from shale.

Mineral Lubricating Oil.—The products known in commerce by the above title are obtained chiefly from two sources, namely, the less volatile fluid portions of petroleum, and the less volatile fluid portions of the oil produced by the distillation of bituminous shale. In the case of petroleum, the lubricating oil has not always undergone distillation, but is obtained from the residues by treatment with charcoal and other purifying agents.

Whether obtained from petroleum or from shale, mineral lubricating oil has essentially the same chemical composition. It consists chiefly of the higher members of the olefin series of hydrocarbons, C_nH_{2n}, with, in the case of the shale product, smaller amounts of polymerised acetylenes, and possibly also terpenes. Small proportions of solid paraffins are often present in solution, but liquid paraffins exist in much smaller proportion than in the lighter fractions. A considerably larger proportion of paraffins is usually found in lubricating oil from petroleum than in that derived from shale.

Mineral lubricating oil is called by various fancy names, such as "oleo-naphtha," "valvoline," "vulcan oil," "globe oil," &c. Its colour ranges from pale yellow through all shades of red, brown, green and blue, to black. The better qualities have very little taste and no marked smell either at the ordinary temperature or when heated. Some samples develop

a peculiar and characteristic smell on gently heating, and have a disagreeable, burning taste.

Mineral lubricating oils have a density ranging from ·850 to ·915, the most usual gravities falling between ·880 and ·905.

Mineral lubricating oils boil at a very high temperature, the "flashing point" (see page 20) of the pale Scotch oils from shale range from 130° to 180° C.; and of the darker oils and greases from 180° to 230° C. These oils usually become viscous about 0° C. The viscosity at 15° C. is very variable, being from two to seven times that of water. The denser samples are the more viscous.

Mineral lubricating oils are not optically active, but they usually exhibit a strongly marked blue or green fluorescence, a character which plays an important part in their detection when mixed with fat oils. The method of applying the test will be described in a subsequent article.

The fluorescence or "bloom" of mineral lubricating oil may be destroyed by subjecting it to a process of limited oxidation by treatment with nitric acid. Turmeric and picric acid also obscure the fluorescence. Oil thus treated regains its fluorescence by treatment with an equal measure of strong sulphuric acid. There are, however, varieties of mineral lubricating oil wholly non-fluorescent, and in which the character cannot be developed by any known treatment. These oils usually deposit solid paraffin on cooling to about − 8° C. They distil without decomposition, are unaffected by alkalies, and behave in the ordinary manner with sulphuric acid.

Mineral lubricating oil is not acted on by alkali, a fact on which is founded the process of detecting and estimating it when mixed with fat oils.

When treated with bromine, mineral lubricating oils form bromides in which the bromine varies from 24 to 36 per cent. of the weight of the oil. The method is of some value in forming an opinion as to the origin and constitution of an oil.

Examination of Mineral Lubricating Oils.—In determining the general character of hydrocarbon lubricating oils, as also their suitability for special purposes, the properties to be taken into account are the same as those which are important in the case of fixed lubricating oils. These are fully

detailed in the section on the lubricating properties of oils. In addition to these characters the following are of service in judging of the quality of hydrocarbon oils, but are not generally applicable to the fixed oils:—

1. Agitate a small quantity of the oil in a test tube with an equal measure of boiling water, and then keep the tube in the water-oven till separation occurs. The formation of a granular white layer at the junction of the two liquids indicates the presence of resin. If the liquid assume a milky-white appearance, the oil has been insufficiently washed after the final treatment with soda. Alkali is often purposely left in the oil* with the view of increasing the "body" or viscosity of the product. Such oil is very prone to oxidise, and becomes turbid on exposure to air from absorption of moisture. It is also liable to change in colour.

2. Boil the oil with a large excess of water for three or four hours. If of first-rate quality the oil will be practically unaltered in colour.

3. Agitate the oil with an equal measure of caustic soda solution of 1·36 specific gravity, and keep the tube at about 55° C. till the liquids have separated. A precipitation of tarry matter indicates that the oil has previously been insufficiently treated with soda, and hence is liable to deteriorate in colour. A first-rate oil gives no trace of tarry matter when submitted to this test. The formation of white emulsion with the alkali is due to an admixture of some fat oil or fatty acid or resin, the quantity of which may be determined in the manner subsequently described. A diminution in the bulk of the oil indicates the presence of carbolic acid or its homologues. By employing the alkali in the manner described in Volume I. page 310, as for the assay of crude carbolic acid, any phenoloid bodies may be separated and approximately determined.

4. If the oil be not perfectly free from suspended matter, the amount and nature of the impurity should be ascertained by diluting the oil with ether or volatile petroleum

* This is effected by blowing air through the imperfectly washed oil. As the moisture is got rid of, the oil takes up the soda whilst remaining perfectly transparent.

spirit, filtering, washing the residue with ether, drying it gently, and weighing.

5. Agitate the oil with an equal measure of sulphuric acid of 1·53 specific gravity. Good oil will remain unchanged, but if the sample be imperfectly refined, or if coal-tar oil be present, more or less browning or blackening will ensue. On treatment with *concentrated* sulphuric acid in the proportion and manner described in the division on fixed oils, lubricating oils from shale and petroleum give only three or four degrees increase of temperature; while with rosin oil the rise is from 18° to 20° C., and with coal-tar oil still higher. Fat oils are also sharply distinguished from mineral oils by this test, none of the former giving much less rise than 40° C.

6. Agitate 10 c.c. of the oil with an equal measure of fuming nitric acid of 1·45 specific gravity. But little rise of temperature will occur with good mineral or shale oil; much heating indicates the presence of coal-tar oil. Rosin oil mixes quietly with the acid, and then suddenly evolves great heat.

Vaselene.* Cosmolene; Saxolene; Petroleum Jelly. Vaselene consists of those portions of petroleum which are soft or pasty at ordinary temperatures. It is obtained from the last distillate or from the undistilled portion by treatment with superheated steam, followed by filtration through animal charcoal. Vaselene is a colourless or pale yellow, translucent, slightly fluorescent semi-solid. Under the microscope distinct crystals are visible, which become more numerous on application of cold. It melts at 35 to 40° C., and has a density of ·840 to ·866 in the melted state. It is odourless, fixed at ordinary temperatures, but commences to fume at 160° C., and distils under pressure with slight decomposition It usually contains about ½ per cent. of moisture and a trace of ash.

Vaselene is insoluble in water, and nearly so in alcohol. In ether it dissolves freely, the solution exhibiting a strong blue fluorescence. It is also readily soluble in chloroform, benzene, carbon disulphide, and turpentine. From these and its ethereal solution alcohol precipitates it, it is said, as a

* I have ventured to alter the popular spelling of the word "vaseline" an other petroleum products, so as to render the termination more scientific.

crystalline mass. Vaselene is miscible in all proportions with fixed and volatile oils. With glycerin it forms an intimate mixture which separates into its constituents when warmed, the melted vaselene floating on the glycerin. Treatment with water also removes the glycerin.

Vaselene is a mixture of hydrocarbons, consisting chiefly of hydrides between $C_{16}H_{34}$ and $C_{20}H_{42}$, but its behaviour with bromine shows that olefins are also present (see page 29). As a true paraffin it is neutral in reaction, and but little affected by chemical reagents. It is not saponified or otherwise acted on by alkalies, and is unaffected by hydrochloric or dilute nitric acid. Some samples blacken on treatment with cold concentrated sulphuric acid, a reaction which indicates the presence of bodies other than paraffins.

Vaselene does not oxidise or turn rancid on exposure to air, and this property, together with its indifference to reagents, renders it a valuable substitute for lard in the preparation of ointments liable to change, such as those containing sulphur, iodides, and compounds of lead, zinc, and mercury. For these and similar purposes it is well suited, especially as it appears to possess decided curative powers of its own. On the other hand, considerable local irritation has been observed to be caused by vaselene in certain cases, a fact which is not improbably due to imperfect removal of the agents used in its purification.

Good vaselene should be completely volatile when heated in platinum, without giving any smell of burning fat (acrolein) or rosin. When agitated with twice its measure of strong alcohol it should remain practically undissolved. The spirit should not acquire an acid or alkaline reaction, and should not give any notable precipitate on dilution with water. When agitated with cold concentrated sulphuric acid, diluted with $\frac{1}{5}$th of its weight of water, vaselene gives no marked increase of temperature, and ought not to become very strongly coloured. When subjected to the saponification process employed for the determination of hydrocarbons in fixed oils, vaselene should yield to the ether an amount of unsaponifiable matter almost equal to the original weight of vaselene used for the experiment; while, on the other hand,

the aqueous liquid separated from the ethereal layer should yield no notable precipitate on being acidulated.

Paraffin Wax. Mineral Wax. This substance consists of mixture of such of the higher hydrocarbons of the paraffin or marsh gas series as are solid at ordinary temperatures. Its chemical constitution is established more by its indifference to reagents (see page 12) than by the results of elementary analysis, which is incompetent to show whether its constituents belong to the series expressed by the general formula C_nH_{2n+2}, or to the olefin series, C_2H_{2n}.

Paraffin wax is found native in the coal measures and other bituminous strata, constituting the minerals known as fossil wax, hatchettin, ozokerite, &c. It exists also in solution in many kinds of petroleum, and is obtainable therefrom by distilling off the more volatile portions, and exposing the remainder to a low temperature. In a similar manner solid paraffin may be obtained from the tar of wood, coal, or bituminous shale, and is now manufactured on an enormous scale from the last source.*

Paraffin wax, or more shortly, paraffin, is a white or bluish-white waxy solid, without taste or smell. Its density and melting point vary with its composition (see page 40), and the same is true of its boiling point, which is very high. A

* The following is an outline of the process of manufacturing paraffin from the bituminous shale of the South of Scotland :—The mineral is heated in vertical iron retorts, a low red heat being employed and a jet of steam introduced. Coke, crude oil, ammoniacal liquor, and permanent gas holding volatile hydrocarbons are produced, as in the manufacture of illuminating gas from coal. The crude paraffin oil is then purified in a manner similar to that employed for petroleum (see page 18). The process consists essentially in a fractional distillation, by which several varieties of naphtha are obtained, a heavier burning oil corresponding to kerosene, and a still heavier oil holding solid paraffin in solution. The last product is treated with sulphuric acid to remove substances of a basic nature, and to oxidise certain unstable compounds, and then with caustic soda of 1·30 sp. gravity, to remove phenols and allied bodies. On exposure to cold, the purified oil usually deposits more or less paraffin, but in some cases another distillation is resorted to. The crude paraffin scale is melted and dissolved in naphtha, allowed to crystallise out, and then submitted to hydraulic pressure. This process is repeated three times. The paraffin is then again melted and steam forced through it to rid it of the last traces of naphtha. Finally, when perfectly free from moisture, it is melted and filtered through animal charcoal.

continued heat, aided by pressure, resolves it into liquid hydrocarbons (see page 13), and the same result is partially obtained by distillation. By merely raising the temperature to 370° C. the paraffin undergoes decomposition, with separation of carbon, and formation of permanent gas, liquid products, and a paraffin of lower melting point. Paraffin is an exceedingly bad conductor of electricity. The specific gravity of paraffin wax increases with its boiling point, as is shown by the following results attained by Galletly from Boghead coal products:—

Sp. Gravities.	Melting Points.	
·8236	32·0° C.	89·6° F.
·8480	39·0 „	102·2 „
·8520	40·5 „	104·9 „
·9090	*53·3 „	128·0 „
·9110	*53·3 „	128·0 „
·9243	58·0 „	136·4 „
·9248	59·0 „	138·2 „
·9400	80·0 „	176 „

Paraffin melting from 32° to 43° C., exhibits a well-defined crystalline fracture, from 43° to 50° C. the crystals become much smaller and less marked, and from 50° C. upwards the fracture is very close and fine in the grain. On the other hand, paraffin melting at 65° C. presents, on fracture, brilliant, white, acicular crystals having a silky lustre. Paraffin melting at 77° C. closely resembles bleached bees'-wax, but the fracture is not conchoidal.

When paraffin is kept for some time under gentle pressure, the temperature being somewhat below its melting point, a molecular change occurs and the substance becomes transparent. A sudden change of temperature or a sharp blow or knock causes this vitreous paraffin to return to its original state, but it may be annealed by slow cooling.

Paraffin becomes plastic at a temperature considerably below its melting point, a fact which is disadvantageous when it is employed for making candles, but which is to a

* These temperatures are correctly quoted.

great extent obviated by a small admixture of stearic acid, wax, or other foreign body.

Mixtures of paraffins of different fusing points melt at a temperature which is the mean of the melting points of the constituent hydrocarbons; but the products obtained by melting together paraffin wax and stearic or palmitic acid, bees'-wax, &c., always have a melting point *lower* than the mean of those of their constituents.*

When two pieces of paraffin are sharply struck together a metallic ring is heard, the sound being sharper the higher the melting point of the paraffin.

Paraffin wax is completely insoluble both in hot and cold water. It is insoluble in rectified spirit, and but sparingly soluble in boiling absolute alcohol, the dissolved portion separating again on cooling. It dissolves readily in ether, and is very soluble in petroleum spirit, shale-naphtha, kerosene, and benzene.

Paraffin dissolves readily in essential oils in the cold, and in warm fixed oils, and does not again separate from the latter on cooling. Hence it is miscible with all kinds of vegetable and animal oils and fats. It differs from these in its indifference to alkalies, and hence cannot be saponified. If, however, the soap be made from a mixture containing carnaüba wax as well as paraffin, the latter is completely dissolved by the

* This is well shown by the following table from Vincent's *Manufacturing Chemistry*, the results recorded being obtained from mixture of the Musselburgh Company's stearic acid, melting at 130° F., with various proportions of three varieties of Young's paraffin.

Percentage of Stearic Acid.	Percentage of Paraffin.	Melting point of mixture. Paraffin melting at		
		120° F.	126° F.	127° F.
55	45	114	113½	115½
60	40	119	116	118
65	35	121	118	120
70	30	122½	122½	122
75	25	124½	124	124
80	20	125½	125½	125½
85	15	126	127	127
90	10	127½	128	129½
95	5	128½	129	130

alkali, a fact which is said to be attributable to its solubility in the myricyl alcohol, $C_{30}H_{61}.OH$, which is a constituent of the carnaüba wax. Paraffin wax burns when kindled with a very bright but not smoky flame, and hence is much employed for making candles and tapers.

When paraffin wax is boiled with concentrated nitric acid it is oxidised with formation of various products, of which the most characteristic are succinic acid $C_4H_6O_5$, and cerotic acid, $C_{27}H_{54}O_2$, the production of the latter of which points to the presence of the hydrocarbon $C_{27}H_{56}$, in the original paraffin. Pouchet has described a yellowish, combustible, light solid, which he obtained by similar means. He found it to melt between 45 and 47° C., to be crystalline, and slightly soluble in alcohol. It has been named paraffinic acid, and from the analysis of its lead, silver, and barium salts the formula $C_{24}H_{48}O_2$ has been assigned to it. The action of nitric acid on paraffin occurs the more readily the higher the melting point of the sample, the variety obtainable from ozokerite melting at 80° C. being very easily acted on.

Paraffin is also violently oxidised by permanganate of potassium mixed with sulphuric acid and heated. Concentrated sulphuric acid will attack paraffin at high temperatures, and the more readily the higher the melting point of the hydrocarbon.

When heated with sulphur paraffin is decomposed, with evolution of nearly pure sulphuretted hydrogen and separation of carbon.

Other chemical characteristics of paraffin, and methods for separating it from hydrocarbons of other series are given on page 12, *et seq.*

Paraffin candles usually contain from 5 to 15 per cent. of stearic acid. The presence of the admixture may be detected by adding a little powdered fuchsine to the sample and keeping it at 100° C. for some time. If pure, the melted paraffin will remain uncoloured, but with 2 per cent. of stearic acid a pink colour is produced, and if as much as 5 per cent. be present the whole mass becomes crimson.*

* Coloured candles are made by dissolving the fuchsine or other colouring matter in stearic acid or bees'-wax, and adding the product to the paraffin till the desired tint is obtained.

For the quantitative analysis of mixtures of paraffin wax with stearic acid or fats, the process described in the section on "Foreign Matters in Fat Oils" is suitable.

The detection of paraffin in bees'-wax is described in section on Bees'-wax.

OZOKERITE; CERITE; CERESIN; MINERAL WAX.—Native solid paraffin occurs in many parts of the globe, the most remarkable and best known deposit being that in Galicia. It occurs in the neighbourhood of petroleum springs, and in association with bituminous sandstone, clay-schist, gypsum, and common salt.

Native ozokerite is as hard as bees'-wax, and is often transparent and of a bright yellow colour. The best earth-wax is pure yellow or greenish, and easily kneaded between the fingers. When melted, this variety constitutes ceresin.

Poorer kinds of ozokerite are black and soft, or hard, with a fibrous structure and conchoidal fracture, varying in colour from yellow ("butter stone") to black. Some pieces are as hard as gypsum, fusible at about 100° C., and are dichroic, the transmitted light being a pure yellow, and the reflected dark green.

Ozokerite is separated from the gangue by being melted, and, after being pressed, is treated with alkali and filtered through fine animal charcoal.*

Inferior ozokerite is largely distilled for paraffin.†

Ceresin or ozokerite may be distinguished from bees'-wax by the following characters:—

1. It is not so easily kneaded as bees'-wax, being apt to become brittle. The character is uncertain.

* Frequently both acid and alkali are used in the purification of ozokerite. The charcoal used is preferably the fine carbonaceous residue produced in the manufacture of potassium ferrocyanide.

† The following are the average products:—

2 to 8	per cent. of	Benzine } see page 30.
15 to 20	,,	Naphtha }
15 to 20	,,	Heavy Oils.
36 to 50	,,	Solid Paraffin.
10 to 20	,,	Coke.

Sometimes the products are less carefully differentiated, the chief being—

30 to 40 per cent. of Benzine of 0·73 specific gravity, and
50 to 70 ,, Ceresin melting at from 60° to 70° C.

2. Ozokerite is scarcely attacked by warm concentrated sulphuric acid, whereas bees'-wax is completely destroyed by the same treatment. This reaction may be made quantitative.

Further information respecting the detection of ceresin in bees'-wax will be found under "Bees'-wax."

In all its chemical relationships ozokerite resembles paraffin wax, of which indeed it is simply a variety.

PARAFFIN SCALE is the technical name for the crude paraffin wax deposited by cooling the oils holding it in solution to a low temperature. The lower the temperature employed for refrigeration, the lower the melting point of the paraffin deposited.

The assay of crude paraffin scale is limited to determinations of the water, insoluble matter, and oil, and to observations of the melting point of the scale before and after expression of the oil.

The water cannot be expelled from paraffin scale by mere heating. To determine the amount present, 10 grammes of the sample should be melted rapidly and treated with 50 c.c. of light petroleum spirit. The solution obtained is kept warm until the water has thoroughly settled. If the water be present in quantity, it may be tapped off into a graduated tube and estimated by measure. The insoluble matter may be separated by filtration or simple decantation. If the water be present in proportion too small to admit of its being readily measured, it may be determined by agitating the solution of the scale in petroleum spirit with a known weight of gently ignited plaster of Paris. This may be filtered off, washed with petroleum spirit, dried at a gentle heat, and again weighed. The increase of weight gives the water taken up. Of course, in employing this method the petroleum spirit used for the solution and washing must be previously dehydrated by agitation with plaster. The water in crude paraffin scale usually amounts to about 2 per cent. of the weight.

The oil in paraffin scale is determined by folding up 30 grammes of the finely-powdered sample in a piece of closely-woven cloth about 12 inches square, so that the scale may form a cake about 3 inches square. The parcel is placed between forty folds of blotting-paper, twenty on each side, and

the whole put between iron plates and subjected to a moderate pressure in a vice for one or two hours, when the pressure should be increased to 10 or 12 cwt. per square inch, and maintained at this for twelve hours. The parcel is then removed, the pressed scale detached from the cloth and weighed. The loss from the original weight taken is the oil, soft paraffin, and a portion of the water. The residual water and insoluble matter are determined in an aliquot part of the pressed cake in the same way as in the original sample, and the sum of their weights deducted from that of the pressed cake gives the corrected weight of the latter.

TERPENES. C_nH_{2n-4}.

The hydrocarbons of the series expressed by the above generic formula are capable of sub-division into two distinct groups.

GROUP A. comprises at present only the two hydrocarbons valylene, C_5H_6, and carpene, C_9H_{14}, both of which are produced by synthetical means, and have no practical interest.

GROUP B. contains the terpenes proper and their polymers, having the common formula $C_{10}H_{16}$, $C_{15}H_{24}$, or $C_{20}H_{32}$ (see page 46). A very considerable number of hydrocarbons of this composition are known. The isomeric modifications are very numerous, and even those which are apparently chemically identical often present marked differences in certain of their physical characters. There is little doubt, however, that many of the terpenes which have been assumed to be distinct have been far from pure, and it is probable that further research will prove that many which have been hitherto regarded as isomeric are really identical.

Artificial Terpenes, $C_{10}H_{16}$, have been prepared by polymerising isoprene, C_5H_8, and by the de-hydrolysis of the oxygenated bodies of the composition $C_{10}H_{18}O$ contained in various essential oils. A hydrocarbon of the formula $C_{10}H_{16}$, having no action on polarised light, but possessing

most of the characteristic properties of the natural terpenes, has been obtained by the action of alcoholic potash on dibrom-rutylene, $C_{10}H_{18}Br_2$.

Natural Terpenes, $C_{10}H_{16}$.—Hydrocarbons of the above formula have been obtained from plants of very different kinds, but those which are of the greatest commercial importance are the turpentines, which are derived from the coniferæ. The hydrocarbons which constitute the larger portion of a great number of the essential oils also are isomeric terpenes (see page 54).

With the exception of the different varieties of oil of turpentine, the terpenes have been very incompletely studied. As a class they are colourless or yellowish liquids, having a marked power of rotating the plane of vibration of a ray of polarised light, the rotation being in some cases to the right and in others to the left. The terpenes are usually volatile without decomposition, and may all be distilled unchanged in a vacuum, or with the vapour of water.

The terpenes are practically insoluble in water, but readily soluble in alcohol, ether, chloroform, benzene, petroleum spirit, and the fixed and volatile oils.

The natural terpenes may be divided into three well-defined classes as follows:—

(*a*) The true terpenes, having the formula $C_{10}H_{16}$; the hydrocarbons constituting the major parts of the essential oils of turpentine, orange-peel, caraway, nutmeg, anise, thyme, myrtle, &c., belong to this class.

(*b*) The cedrenes, having the formula $C_{15}H_{24}$; the essential oils of cloves, rosewood, cubebs, calamus, cascarilla and patchouli contain hydrocarbons of this class.

(*c*) The colophene hydrocarbons, having the formula $C_{20}H_{32}$; represented only by colophene itself, and perhaps by para-cajuputene.

Class *a*, containing the true terpenes, may be subdivided into two well-distinguished groups, which are represented by the oils of turpentine and orange-peel respectively.

The following table exhibits the leading physical and chemical differences between the hydrocarbons of the above classes:—

	$C_{10}H_{16}$; Terpenes.		$C_{15}H_{24}$; Cedrenes.	$C_{20}H_{32}$; Colophene.
	Turpentine Oil Group.	Orange Oil Group.		
Vapour density (H=1)	136		204	...
Character of liquid	Limpid.		Viscous.	Very viscous.
Specific gravity at 20° C.	·855 to ·880	·846 to 853	·904 to ·929	·939
Boiling point, ° C.	156 to 163°	174 to 178°	249 to 260	315
Action of strong Sulphuric Acid	Polymerises and gives SO_2, cymene, &c.		Doubtful.	None.
Combination with Water	Forms a crystalline hydrate, $C_{10}H_{20}O_2,H_2O$.		Forms no crystalline hydrate.	...
Combination with Hydrochloric Acid	$C_{10}H_{16}$,HCl and $C_{10}H_{16}$,2HCl (see page 51).		$C_{15}H_{24}$, HCl and smaller proportions	Very small proportion.
Derivative with Nitrosyl	Forms crystalline $C_{10}H_{15}(NO)$		Forms no nitrosyl derivative.	...
Products of the action of warm water and air	Forms camphoric acid and hydrogen peroxide		Forms no hydrogen peroxide.	...

Proof of polymerisation of an oil by sulphuric acid is obtained by washing the product with water and distilling it. As the polymers boil at a much higher temperature than the original oils, the observation of a thermometer immersed in the vapour affords proof of the change. As the polymerising action of the acid may be incomplete, it is desirable to observe the boiling points of the less volatile fractions of the altered oil.

The nitroso-derivatives are prepared by passing nitrosyl chloride gas (NOCl) into the oil, either pure or diluted with chloroform or alcohol, and cooled in a mixture of ice and salt. A white crystalline body is deposited, of the formula $C_{10}H_{16}NOCl$. From this compound, by treatment with alcoholic potash, or by cautious heating, the elements of hydrochloric acid may be removed, and the substitution-product $C_{10}H_{15}(NO)$ obtained.

The production of peroxide of hydrogen may be observed by treating the oil with an equal bulk of warm water, agitating in a capacious bottle with air, allowing the oil and water to separate, and testing the latter liquid for the characteristic product of the reaction. The most delicate test is the formation of brown manganese dioxide on immersing in the

acid is filtered off, and purified by solution in ammonia boiling liquid a paper soaked in solution of manganous sulphate mixed with acetate of sodium; the bleaching of a paper previously blackened by moistening with a weak solution of lead acetate and exposing it to sulphuretted hydrogen; and the blue coloration imparted to ether when a few c.c. of that liquid and a minute trace of chromic acid are added to the liquid supposed to contain peroxide of hydrogen, and the whole agitated.

It is not certain that the characters specified in the table belong to all the members of the respective groups. Also it is not to be supposed that all the terpenes can be arranged under one of the above heads. The subject is very incompletely investigated at present. Pure terebenthene, the hydrocarbon of turpentine oil, boils at 156° C.; myristicene, the terpene of nutmeg oil, at 163 to 164° C.; hesperidene, from oil of orange-peel, at 178°; and the hydrocarbon of oil of cloves at 254° C.*

Wright has shown that a great number, if not all, of the terpenes may be regarded as cymene dihydrides, $C_{10}H_{14}H_2$, and when, as by treatment with bromine or iodine and distillation, they are converted into cymene, they all yield the *same* cymene, not isomeric varieties of that hydrocarbon.

Cymene, $C_{10}H_{14}$, is a member of the benzene series of hydrocarbons, C_nH_{2n-6}. It occurs ready formed in many natural essential oils, and is apparently the nucleus of all the isomeric hydrocarbons known as terpenes, $C_{10}H_{16}$.

Cymene is a colourless strongly-refracting liquid, having an agreeable odour, recalling that of oil of lemons. It boils at 176 to 177° C., and has a density of ·86 at 15° C. When boiled in a flask for thirty or forty hours with a large excess of strong chromic acid mixture (see Vol. I. p. 93), or until the liquid dropping from the inverted condenser no longer appears oily, cymene is oxidised with formation of acetic, paratoluic and terephthalic acids. To detect the last characteristic product, the contents of the flask are diluted with water and thoroughly cooled. The insoluble terephthalic acid is filtered off, and purified by solution in ammonia boiling

* The cedrenes, or hydrocarbons of the formula $C_{15}H_{24}$, are not improbably tri-propyl derivatives of benzene, $C_6H_3(C_3H_7)_3$.

with animal charcoal, and reprecipitation by hydrochloric acid. It is insoluble in water, alcohol, ether, chloroform, or acetic acid. It sublimes without fusing. Heated with excess of soda-lime it yields benzene, C_6H_6, and a carbonate.

According to Wright, the presence of cymene in an essential oil may be detected by mixing it very gradually with twice its volume of strong sulphuric acid so as to avoid all heating. After standing twenty-four hours, the acid is diluted with water, and the oily liquid separated and distilled in a current of steam. If the oily portion of the distillate blackens when shaken with sulphuric acid the above treatment should be repeated. The product is then oxidised by chromic acid mixture, when terephthalic acid will be obtained if cymene were present.

Oil of Turpentine.. Spirit of Turpentine. $C_{10}H_{16}$.

French—Essence de Térébenthine. *German*—Terpentinöl.

Oil of turpentine is obtained by distilling the turpentine or oleo-resinous juice exuding from various kinds of pine (see page 65). The non-volatile portion constitutes rosin, and the distillate, varying in yield from 10 to 25 per cent., is the oil or spirit of turpentine, vulgarly known as "turps." Rectified oil of turpentine is obtained by treating the first product with alkali, to saturate any rosin acids, and redistilling. The product so prepared from French turpentine oil consists chiefly of the terpene terebenthene, which when obtained pure by a long series of fractional distillations exhibits the following properties :—

Terebenthene is a colourless, mobile liquid of marked and characteristic odour. It is highly refractive, and exerts a *lævo*-rotatory action on polarised light. Its specific rotatory power is $-40{\cdot}3°$ for the sodium ray. On the other hand, the terpene which constitutes the essential part of English or American oil of turpentine is called austra-terebenthene. It has the same boiling point and specific gravity as that from the French oil, but is *dextro*-rotatory, the value of S_D being $+21{\cdot}5°$. Though apparently chemically identical, a marked difference in optical properties is recognisable in the various compounds and polymers of the two turpentine oils.

Oil of turpentine has a density of ·864. Pure terebenthene boils at 156°, but the boiling point of the commercial oil varies from 156 to 160° C. Oil of turpentine is readily combustible, burning with a very smoky flame.

Oil of turpentine is almost wholly insoluble in water, glycerin, and dilute alkaline and acid solutions. It is very soluble in absolute alcohol, but its solubility is greatly lessened by the presence of water, spirit of ·85 specific gravity dissolving only 10 per cent. of its weight of oil of turpentine.

Oil of turpentine is very soluble in (probably miscible in all proportions with) ether, carbon disulphide, chloroform, benzene, petroleum spirit, and fixed and essential oils.

Oil of turpentine is itself a solvent for iodine,* sulphur, phosphorus, resins, fats, waxes, caoutchouc, &c.

On heating oil of turpentine to about 300° C. in a sealed tube for several hours, it is converted into a polymer called iso-terebenthene, $C_{20}H_{32}$, which is so oxidisable that it is converted into a viscid mass on exposure to the air for a few hours. Iso-terebenthene has a marked odour resembling that of oil of lemons; it boils at 176 to 177°, and has a rotatory power of −10 to −11°.†

On treatment with a *small* proportion of sulphuric acid, oil of turpentine yields an optically inactive liquid, which boils at 160° C. This is a mixture resolvable by repeated fractional distillations into terebene, $C_{10}H_{16}$, boiling at 150°; cymene $C_{10}H_{14}$, boiling at 175°‡; a small quantity of a camphoroid body boiling about 200°; colophene, $C_{20}H_{32}$, boiling at 318°; and a mixture of semi-solid products of high boiling points. Terebene has a faint thyme-like odour, and is optically inactive; in density and other respects it much resembles terebenthene. Colophene or di-terebene has a density of 0·94, and is optically inactive; it exhibits a strong blue fluor-

* When iodine and turpentine oil are mixed in any considerable quantity a violent explosion results.

† The properties of iso-terebenthene given in the text apply equally to the polymers of French and of English turpentine oils. It is doubtful whether the two products are really identical.

‡ Wright considers that a small percentage of cymene is a normal constituent of turpentine oil.

escence. Colophene is also produced by treating turpentine oil with a very small proportion of boron fluoride.

Still more complicated polymers can be obtained by acting on turpentine oil with antimonious chloride.

Turpentine oil, and all the terpenes, combine with a single molecule, and some with two molecules of hydrochloric, hydrobromic, and hydriodic acids, to form definite compounds. On passing a slow current of hydrochloric acid into cooled terebenthene, a mixture of two isomeric monohydrochlorides, $C_{10}H_{16},HCl$, is formed, of which one is solid and the other liquid. These products may be separated by pressure, and the solid compound purified by crystallisation from alcohol or ether. It crystallises in white needles, and closely resembles common camphor in appearance, odour, and the property of subliming readily at ordinary temperatures. Its specific rotatory power is $-32{\cdot}2°$. The liquid monohydrochloride is not readily obtained pure,* and is rapidly decomposed by boiling water with formation of hydrochloric acid. The solid isomer, on the other hand, is stable at the ordinary temperature, and but slowly decomposed at 100°, but at 200° C. it is resolved into hydrochloric acid and the isomer of turpentine oil called terebene. Terebenthene dihydrochloride, $C_{10}H_{18}Cl_2=C_{10}H_{16},2HCl$, is formed when turpentine oil is left in contact with concentrated hydrochloric acid. It forms rhombic plates, insoluble in water and decomposed by boiling with alcoholic potash with formation of terpinol $(C_{10}H_{17})_2O$. When pure, the dihydrochloride melts at 49·5. Mixed with a drop of a concentrated solution of ferric chloride and very gently heated, a rose coloration is produced, changing to an intense violet-red, and ultimately to blue.

This reaction, which was first observed by Riban, is apparently common to the dihydrochlorides of all the terpenes. To obtain it, it is not necessary to prepare the hydrochloride, but a few drops of the oil itself may be stirred in a porcelain capsule with a drop of concentrated hydrochloric acid and another of a strong solution of ferric chloride. As the

* Tilden doubts the existence of the liquid monohydrochloride, but agrees with Berthelot that the mono- and di-hydrochlorides combine to form a liquid compound.

cedrenes, $C_{15}H_{24}$, do not form dihydrochlorides, the test may be used to detect oil of turpentine and other terpenes in presence of those oils.

When solid terebenthene monohydrochloride is heated under pressure with alcoholic potash or dry soap, and the product rectified, separated from liquid bodies by pressure, and fractionally distilled, an isomer called camphene, $C_{10}H_{16}$, is obtained. Camphene boils at the same temperature as the terebenthene itself, but is solid at ordinary temperatures. It melts at about 46° C., and is lævo-rotatory. Several optically inactive camphenes are known.

Chlorine and bromine are so rapidly absorbed by turpentine oil that inflammation frequently occurs, with separation of carbon. An unstable additive-compound with bromine is however obtainable. When distilled with bleaching powder and water, turpentine oil yields chloroform, $CHCl_3$.

Moderately strong nitric acid oxidises turpentine oil to resinous bodies, which ultimately yield terebic acid, $C_7H_{10}O_4$, together with terephthalic and paratoluic acids.* Fuming nitric acid acts very violently, often setting the turpentine on fire.

A well-defined compound of the formula $C_{10}H_{16}NOCl$ has been obtained † by passing nitrosyl chloride, NOCl, into very cold English turpentine oil. The snow-white crystalline powder is filtered off rapidly and washed with alcohol. By treatment with alcoholic soda it yields an optically inactive crystalline body, of the formula $C_{10}H_{15}NO$ (see page 47). All true terpenes appear to form similar nitrosyl-derivatives.

On leaving turpentine oil in contact with water, crystals are gradually deposited, the formation of which is favoured by the presence of nitric acid. Recrystallised from boiling water, these crystals have the formula $C_{10}H_{20}O_2,H_2O$. When heated to 100°, the water is driven off, and anhydrous terpin, $C_{10}H_{20}O_2=C_{10}H_{18}(OH)_2$, melting at 103°, is formed. Together with terpin, a liquid monohydrate of the formula

* The two latter appear to be produced by the oxidation of the small percentage of cymene present in ordinary turpentine oil.

† Tilden. *Journ. Chem. Soc.* xxviii. 514; also *Year Book of Pharmacy*, 1877, p. 489.

$C_{10}H_{18}=C_{10}H_{17}OH$, is often formed. It boils at 200–210°, whereas turpin sublimes at 150°, in slender needles.

Turpentine oil and other terpenes absorb oxygen on exposure to air, gradually becoming thick, and ultimately resinous. Kingzett has shown that the oxidation is accompanied with the formation of a body of the formula $C_{10}H_{14}O_4$, which he regards as camphoric peroxide. This substance by the action of water is converted into hydrogen peroxide and camphoric acid. The disinfectant known as "sanitas" is produced by passing air through oil of turpentine in contact with warm water.

According to Barbet, oil of turpentine is liable to adulteration with light rosin oil, crude undistilled turpentine, and rosin itself. These admixtures can be recognised by the alteration in the gravity of the oil and by the reaction produced on adding 8 drops of strong ammonia to 90 c.c. of the sample. The following are the results:—

	Sp. Gravity.	Reaction with Ammonia.
Pure Oil of Turpentine, recently distilled	·8678	No effect. The mixture separates rapidly.
Pure Oil of Turpentine, old	·8693	Solidifies in a few seconds, forming a white crystalline mass of the consistence of butter.
Oil of Turpentine, with 10 per cent. of Rosin Spirit	·8784	An emulsion, which rapidly becomes clear; the ammonia which separates has a pale yellow colour.
Oil of Turpentine, with 10 per cent. undistilled turpentine	·8784	An emulsion, which becomes clear on standing, giving a semi-transparent gelatinous magma of a bluish colour; the liquid above being colourless.
Oil of Turpentine, with 10 per cent. of Rosin	·8831	Each drop of ammonia appears to solidify as it falls into the oil. On agitation, the whole solidifies into a consistent semi-transparent mass.

It is evident that for the detection of resinous impurities,

whether purposely introduced or due to the spontaneous oxidation of the oil, evaporation of a weighed quantity of the sample furnishes the most certain means, and allows of the foreign matter being quantitatively determined. Old oil of turpentine may contain from 1 to 2½ per cent. of non-volatile matter.

Volatile or Essential Oils.—A great number of the volatile oils of plants consist mainly of terpenes or hydrocarbons of the formula $C_{10}H_{16}$; and others of polymeric derivatives of the terpenes having the formula $C_{15}H_{24}$ (see page 46). The volatile oils of plants probably originally consist of hydrocarbons (terpenes) only; but these hydrocarbons are prone to change in contact with air or moisture, and hence the oils, even when freshly obtained, and still more so as usually met with, are generally mixtures of the unchanged hydrocarbons or oleoptenes, with solid oxygenated camphoroid bodies termed stearoptenes. The hydrocarbons are also frequently associated with more highly oxidised bodies called resins. On cooling such a crude complex volatile oil, the stearoptene often crystallises out; on distilling the oil the more volatile hydrocarbon first passes over, and on raising the temperature the stearoptene may also be obtained in some cases, the non-volatile matter consisting of resin (see page 65). The more volatile portion of the distillate may be wholly freed from oxygenised bodies by distillation over sodium, and thus the hydrocarbons obtained pure. Even then, however, these are not always wholly terpenes, some volatile oils containing considerable proportions of cymene, $C_{10}H_{14}$.

Some essential oils consist chiefly or largely of certain ethers (see Vol. I. pp. 56, 144), and aromatic aldehydes (Vol. I. pp. 338 and 339) are not unfrequently met with. In some cases the constituents of an essential oil are highly characteristic of its origin, as in the case of the oils of mustard, winter-green, and bitter-almonds, but the opposite is the fact in the majority of cases.

The volatile oils of plants are obtained—

(*a*) By *pressure*, as the oils of laurel, lemon, bergamot.

(*b*) By *distillation with water*, or by passing a current of

steam over the matter to be extracted. This is the most common and generally applicable method.

(*c*) By *fermentation and distillation;* as, for instance, with the essential oils of mustard and bitter-almonds, the seeds containing no ready-formed oil, but the latter being produced when the crushed seeds are left in contact with water, owing to the influence of peculiar nitrogenised ferments; the oil formed being then separated by distillation with water.

(*d*) By *solution in a fixed oil* devoid of smell, such as poppy oil, or oil of ben. The scents of various flowers are extracted in this manner.

Most of the oxygenated and sulphuretted essential oils have been obtained by synthetical means.

The essential oils of plants are usually liquid at ordinary temperatures, but deposit stearoptenes or camphors by severe cooling. They have marked, and in many cases highly characteristic odours, though their boiling points are mostly somewhat high, and the oils are usually lighter than water. Essential oils are usually colourless or yellow when freshly prepared, but rapidly darken and ultimately become resinoid. The oils of bitter-almonds, cloves, cinnamon, and spiræa, which contain aromatic aldehydes, deposit crystals of acids on exposure to air. Most of the essential oils are optically active.

The essential oils are all readily combustible. They are insoluble, or nearly so, in water, but distinct traces of some of them pass into solution, the water acquiring the characteristic taste and smell of the oil.* In alcohol they are freely soluble, and are reprecipitated from their solutions by dilution with water. The separation, however, is rarely, if ever, complete. The essential oils are miscible in all proportions with fixed oils, turpentine, petroleum spirit, and carbon disulphide, and may be separated from aqueous liquids by agitation with these solvents; they are destroyed by treatment with strong nitric or sulphuric acid, but as a rule are unsaponified or otherwise acted on by alkalies.

* Dragendorff states that 1 litre of water holds in solution the following quantities of essential oils :—Oil of cloves, 1·5 gramme; oil of rosemary, 0·9; oil of lavender, 0·5; oil of peppermint, 0·2; oil of savin, 0·4; oil of copaiba, 0·12, and oil of bitter-almonds, 2·2 grammes.

The accurate determination of the essential oils is difficult and often impossible, in consequence of their volatility and limited tendency to form stable and definite chemical compounds. A useful approximation to the truth may be obtained in some cases by extracting the oil with carbon disulphide, or petroleum spirit boiling below 40° C. (gasolene). In either case the solvent should be recently redistilled from lard, to keep back traces of odorous bodies. The solution is evaporated at the ordinary temperature in a porcelain capsule, by the aid of a current of air dried by passing it through a tube containing pumice-stone moistened with sulphuric acid. The process is continued till hardly any odour of the solvent is perceptible. The operation is completed by allowing the last traces of the solvent to evaporate spontaneously, weighing the capsules at intervals of one minute. When the loss of weight per minute becomes constant, the weight of the residual oil is taken, and corrected by adding to it the product of the loss of weight per minute multiplied by the number of minutes occupied in the evaporation.

ASSAY OF ESSENTIAL OR VOLATILE OILS.—Essential oils are extremely liable to adulteration, the usual sophistications being by addition of alcohol, chloroform, oil of turpentine, fixed oils, and by mixing the cheaper essential oils with the more expensive. In addition to the above intentional adulterants, volatile oils are apt to contain water, and resinous and other oxygenated bodies produced by their exposure to air.

The proportion of water in essential oils is never very large. The hydrocarbons in some cases dissolve about $\frac{1}{1000}$, but in the oxygenated oils it is more soluble. The presence of water may be detected by mixing 10 c.c., the sample of oil, previously filtered if not perfectly clear, with 40 c.c. of petroleum spirit. Any water will be separated in the form of minute globules, which, if in sufficient quantity, will ultimately coalesce and sink to the bottom of the liquid. On adding a small quantity of plaster of Paris, previously gently ignited and weighed, and agitating thoroughly, the water will be absorbed; on filtering the liquid through dry paper, washing the plaster with a little anhydrous ether or very volatile

petroleum spirit and drying it at a gentle heat, the increase in its weight will represent the water in the 10 c.c. of the sample of oil employed. The petroleum spirit employed for the above test must be previously dehydrated by agitation with plaster of Paris.

Alcohol in essential oils may be detected by gradually adding some dry powdered calcium chloride, agitating well, and heating in a water-bath between each addition. Mere traces of alcohol render the first portions of the calcium chloride pasty, but if present in larger proportions the salt dissolves and forms a heavy liquid layer. If the experiment be performed in a graduated tube and a known measure of the oil employed, the diminution in its volume will give that of the alcohol mixed with it. The calcium chloride should be added until it no longer dissolves in the heavier liquid. In testing for small quantities of alcohol by this test, the oil should be previously dehydrated by agitating it with recently ignited plaster of Paris. When the proportion of alcohol is considerable, fair quantitative results may be obtained by agitating the oil in a graduated tube with an equal measure of glycerin. The increase in the bulk of the latter liquid, measured after separation is complete, gives that of the alcohol (and water) in the sample examined.

Chloroform may be detected by dissolving the oil in alcohol, and warming the liquid with zinc and dilute sulphuric acid. After some time several volumes of water are added, the aqueous liquid separated from the oil by passing it through a wet filter, and the filtrate is tested for chloride by adding nitrate of silver and nitric acid. An affirmative reaction proves the presence of chloroform in the oil. Chloroform may also be detected by method 3, Vol. I. page 175.

The detection and determination of alcohol and chloroform in essential oils is rendered more delicate and accurate by previously distilling the sample, and applying the tests to the portion which passes over below 100° C. A still better method is to pass a current of steam through the sample of oil contained in a small retort or tubulated flask. Any alcohol or chloroform will be found in the first portions of the distillate. On continuing the operation the essential oils

distil over, though their boiling points are considerably above 100°, and, after a time, little or nothing but resinous matters, or fixed oils added as adulterants, will remain in the retort. These may be weighed in the retort after heating it moderately, and passing a current of coal-gas or air (previously filtered through cotton-wool) to separate any condensed steam and unvolatilised essential oils. The nature of the residue can then be ascertained by treating it with alcohol of ·85 specific gravity. If wholly resinous it will dissolve, but fixed oils remain insoluble, with the exception of castor oil. To detect this, the alcoholic solution should be treated with an equal measure of carbonate of sodium solution, and then boiled till the alcohol is driven off. Any castor oil will remain as an oily layer, but the resin will have dissolved in the alkaline liquid, and may be detected by separating any undissolved oil and acidulating with hydrochloric acid, when a turbid liquid will be formed from which resinous flocks or globules will gradually separate.

The adulterant of essential oils most difficult to detect is oil of turpentine. Perhaps the best test is that founded on the solubility of the sample in alcohol, but as this is only a question of degree, and some of the oils closely simulate the behaviour of oil of turpentine itself, it is impossible to prescribe any definite mode of examining all specimens. The test has been exhaustively reported on by Dragendorff,* whose original paper must be consulted for details of the solubility of the various essential oils. Dragendorff found that old samples of oils exhibited marked differences of solubilities as compared with recently distilled specimens, a fact which materially diminishes the practical utility of the test as a means of detecting adulteration. In fact, a reliable test for the detection of oil of turpentine in other essential oils is still a desideratum.

Dragendorff has also described in great detail the reactions produced by a number of essential oils with various reagents. A recapitulation of his results would occupy more space than can be spared, especially as the testing of essential oils is not

* "Studies on Essential Oils," *Pharm. Journ.* [3], vi. pp. 541, 581, 641, 681, and 721.

of importance to the great majority of chemists. For this reason, it appears unnecessary to describe the character of the individual essential oils employed in pharmacy, &c.

Camphors.—Many natural essential oils contain oxidised principles which are solid at ordinary temperatures, and are deposited from the oils on cooling or standing. Some of these camphors or stearoptenes are phenols (*e.g.* thymol), whilst others are apparently oxidised terpenes. But few are of any importance or interest except to the pharmacist.

COMMON CAMPHOR, $C_{10}H_{16}O$, is obtained from the wood of the camphor-laurel (*Camphora officinarum*) by a rough process of distillation with water, and is purified by resublimation.*

Commercial camphor forms a white, translucent, tough, fibrous mass, but may be obtained crystallised in white prisms. It has a peculiar, fragrant odour and burning taste. The density of common camphor varies from ·986 to ·996. It melts at 175° C., and boils at 205°, but vaporises rapidly even at the ordinary temperature. Camphor is optically active, the apparent specific rotation varying with the nature of the solvent and the concentration of the solution. For a 10 per cent. solution in alcohol it is about +42·8 for the sodium ray. Oil of feverfew yields a camphor which is lævo-rotatory to the same extent, but in all other respects is undistinguishable from ordinary camphor.

Camphor is nearly insoluble in water, only one part per 1000 being taken up; but it is readily soluble in alcohol, ether, acetone, acetic acid, carbon disulphide, chloroform, and oils. The "spirit of camphor" of the Pharmacopœia is a solution of one part by weight of camphor in nine measures of rectified spirit. The author found that such a solution occupied the exact bulk of the spirit used, *plus* that of the camphor before solution, there being no contraction in the act of solution. Rubini's "essence of camphor" is a solution of the solution in an equal weight of rectified spirit.†

* During the process an oil distils over called liquid camphor or oil of camphor, $(C_{10}H_{16})_2O$, which deposits camphor on exposure to the air.

† "Compound Tincture of Camphor, B.P." may be analysed as described in Vol. I. p. 114.

On diluting an alcoholic solution of camphor with water, the solid is precipitated in white flocks. If the proportion of alcohol exceed a certain limit, no amount of dilution will cause precipitation.

The chemical relationships of camphor are somewhat uncertain. It has some analogy to the aldehydes, but is not oxidised by chromic acid mixture, and forms no compound with acid sulphite of sodium. It absorbs hydrochloric acid, sulphur dioxide, and nitric peroxide gases, forming colourless liquids decomposed on addition of water. Camphor is not affected by the ordinary reducing agents, but if dissolved in an inert liquid, such as toluene, and heated to 90° with sodium, it forms sodium camphor, $C_{10}H_{15}NaO$, and borneol, $C_{10}H_{18}O$. By distillation with zinc chloride or phosphoric anhydride camphor yields cymene, $C_{10}H_{14}$, and other products.

With alcoholic potash camphor yields borneol and camphic acid, $C_{10}H_{16}O_2$, a behaviour which appears to establish its analogy to benzoic aldehyde.* Heated to 400° with soda-lime it yields campholic acid, $C_{10}H_{18}O_2$. By prolonged treatment with nitric acid of 1·37 sp. gravity, camphor is converted into camphoric acid, $C_{10}H_{16}O_4$, which on further boiling is oxidised to camphoronic acid.

Camphor unites with bromine to form a crystalline, very unstable dibromide, which on distillation splits up into hydrobromic acid and monobrom-camphor, $C_{10}H_{15}BrO$. This substance is of some therapeutic interest. It crystallises in prisms fusible at 76° C., is readily soluble in alcohol, and is not decomposed by alcoholic potash.

Camphor is said to be liable to be adulterated with the solid terebenthene hydrochloride. Such a sophistication would be readily detected by the formation of hydrochloric acid on burning the substance.

Camphor can be readily separated from most substances with which it is liable to occur. From alcohol it may be partially separated by addition of water, the solution being afterwards fractionally distilled. The camphor may also be determined

* Benzoic aldehyde, on treatment with alcoholic potash, yields benzyl alcohol, $C_7H_7.OH$, and benzoic acid, $C_7H_6O_2$.

by treating the tincture with excess of chromic acid mixture, when the alcohol will be oxidised to acetic acid. After neutralising the liquid the camphor may be filtered off, pressed, and weighed; or the acetic acid may be determined, calculated to its equivalent of alcohol, and the camphor estimated by difference. If this plan be adopted, any water should be previously separated by agitating the tincture with dry potassium carbonate.

BORNEOL. $C_{10}H_{18}O = C_{10}H_{17}.OH$. This body is imported under the name of "Borneo camphor," which contains 2 to $3\frac{1}{2}$ per cent of resin and other impurities, from which the borneol can be obtained pure by sublimation. It crystallises in prisms, melts at 197·5 to 198° C., solidifies at 195°, and boils at 212° C. The apparent specific rotatory power is +32·7° for the sodium ray. Artificial borneol resembles the natural product in every respect, except in its optical activity, the portions obtained at the beginning and end of the process being dextro-gyrate, while the intermediate fractions are lævo-rotatory.

On treatment with nitric acid borneol is converted into common camphor, $C_{10}H_{16}O$.

A terpene called borneene, $C_{10}H_{16}$, is found in association with borneol. It occurs in commerce under the name of camphor oil, but differs from the similar product obtained with laurel-camphor by not yielding crystals on exposure to air.

CANTHARIDIN, $C_{10}H_{12}O_4$, the active principle of *Cantharides* or Spanish fly, and of other vesicating insects, has most of the properties of a stearoptene or camphor. When pure it forms four-sided prisms, but is often deposited from its solutions in needles or brilliant micaceous plates. It melts at 200° C., and volatilises in white fumes, which strongly irritate the eyes, nose, and throat, and condense in lustrous rectangular prisms.

Cantharidin has feebly-marked acid properties. It is insoluble in pure water, but dissolves in caustic alkalies, being reprecipitated on acidulating the liquid with acetic acid. It may be crystallised from hot nitric or hydrochloric acid, and is soluble in strong sulphuric acid, being reprecipitated on dilution.

Cantharidin dissolves readily in rectified spirit, and is also

soluble in ether, acetic ether, and chloroform ; but is nearly insoluble in petroleum spirit or carbon disulphide. It is extracted from acidulated aqueous liquids by agitation with chloroform.

Cantharidin has well-marked poisonous properties, and the beetles containing it have not uncommonly been administered with criminal intent, on account of their powerful aphrodisiac character. In toxicological inquiries, the coats of the stomach and intestines should be carefully examined with a lens, with a view of detecting particles of the characteristic iridescent, green wing-cases of the beetles. In the event of a tincture having been administered, the only available test is the isolation of the cantharidin in the form of an extract or tincture, and the application of a small portion of the product to a sensitive part of the skin (*e.g.* the lobe of the ear, or the inside of the fore-arm). If cantharidin be present, even in small quantity, a well-marked blistering will occur. A mixture of 1 part of cantharidin in 500 of lard produces very strong vesiculation.

In examining for cantharides the viscera should be cut small, and digested with rectified spirit slightly acidulated with acetic acid. The filtered liquid is then concentrated by evaporation till the alcohol is driven off, and then agitated with chloroform. The chloroform is separated from the aqueous liquid, evaporated, and the residue applied to the skin. If desired, the cantharidin may be further purified by treatment with carbon disulphide to remove fat, and then recrystallised from chloroform. 0·001 gramme of cantharidin dissolved in a drop of alcohol will produce marked vesiculation.

Cantharides may be assayed for cantharidin by the following process:*—25 grammes of the powdered flies are exhausted by treatment with gasolene in a percolator or Xoxheth's tube. The solvent should be limited to 100 c.c. measure and a correction of 0·0108 gramme of cantharidin made for the slight solubility of the principle in the liquid. The flies thus freed from fat are now thoroughly moistened with solution of soda, and the mixture dried at 100° C. Much ammonia is evolved, and a soluble cantharidate of sodium

* H. G. Greenish, *Pharm. Journ.* [3], x. 729.

formed.. The dried mass is finely powdered and transferred to a separator, where it is treated with excess of dilute hydrochloric acid, and the liberated cantharidin extracted from the aqueous liquid by agitation with a mixture of equal measures of ether and chloroform; the ether-chloroform is separated, and the agitation repeated with a fresh quantity till the extraction is complete. The ether-chloroform is evaporated to dryness at a gentle heat, and the residue weighed. The crude cantharidin thus obtained may be transferred to a small tared filter and washed with a little *absolute* alcohol, and then with 2 or 3 c.c. of water. Any remaining traces of oil may be removed by a little gasolene. If the washing with alcohol and water be employed, the volumes used must be noted and a correction made of ·00077 gramme for each 1 c.c. of alcohol, and ·00050 for each 1 c.c. of water.

Resins.—Resins occur as natural or induced exudations from plants, in admixture with the essential oil peculiar to the plant. In chemical constitution they are usually oxidised terpenes, and are produced in the plant and during collection by the oxidation of the essential oil.

In some cases resins are prepared by simple exudation (*e.g.* copal); in other cases by distilling off the essential oil mixed with the resin (as common rosin or colophony); and in some instances by destructive distillation (*e.g.* pitch and guaiacum).

As a class the resins are solid, transparent bodies, sometimes crystallisable. They have no well-marked odour or taste. They are easily fusible, but not volatile, and are decomposed when heated in close vessels. They are readily combustible. Resins are very bad conductors of electricity, and when excited by friction become negatively electrified.

The resins are insoluble in water, but they dissolve in alcohol and many other organic liquids. The solutions of many of them are acid to litmus, and yield a lather on treatment with a solution of caustic alkali. Their solutions in alkaline liquids differ from ordinary soaps in being incapable of precipitation by addition of common salt.

The resins are rarely even approximately pure definite bodies, but are usually mixtures of several analogous oxy-

genated bodies in various proportions. Their chemical relations are at present but very imperfectly understood.

The resins are employed in medicine, in the manufacture of varnishes and soap, for making sealing-wax, and for stiffening purposes.

Resins may be separated from the essential oils and camphors with which they so frequently occur by distilling the substance, first in a current of steam, and then, if necessary, immersing the flask or retort in a chloride of calcium bath, still continuing the current of steam.

From the neutral fixed oils resins may be separated by treating the mixture with alcohol of about 0·85 sp. gr. The alcohol is subsequently separated, and the dissolved resin recovered by evaporating it to dryness. The results are only approximately correct. Acid resins, such as common colophony, may be separated from the neutral fats by boiling the substance with a strong solution of bicarbonate of sodium or borax. After cooling, the aqueous liquid is separated from the oil, and the resin precipitated from its solution in the sodium salt by adding hydrochloric acid. (For other and detailed methods of separating resins from fixed oils and fatty acids, see the section on "Foreign Matters in Fat-Oils.")

Water and general impurities may be separated from the resins by dissolving the substance in oil of turpentine or petroleum spirit. If the operation be conducted in a graduated tube the separated water may be measured; while the insoluble matters may be filtered off, washed with petroleum spirit, dried, weighed, and further examined.

When separated by the above-described means from the bodies with which they are apt to be associated, the resins may usually be identified by their physical characters. The identification of the various individual resins is a matter of considerable difficulty even when only one is present, and in admixture the task is usually insuperable. As such identification or separation of the resins is rarely required by others than wholesale druggists, it is unnecessary to detail such analytical characters as have been observed.*

* A systematic scheme for the recognition of resins, gum-resins, and balsams has been devised by Hirschsohn (*Pharm. Journ.* [3], vii. 369; viii. 389).

Turpentines and Balsams.—The first of these names ought, strictly speaking, to be limited in its application to the oleo-resins obtained as exudations from various species of *Pinus*, *Abies*, *Juniperus*, and other allied genera. The name "turpentine" is, however, often applied to the spirit or essential oil obtained by distilling the crude turpentines above mentioned.

TURPENTINES.—Although differing considerably in their physical characters, the various turpentines of commerce resemble each other in being indefinite mixtures of an essential oil or terpene, of the empirical formula $C_{10}H_{16}$ (see page 49), and an oxygenated non-volatile body called a "resin," which is obtained as a residual product when the terpene is separated from the crude turpentine by distillation. The characters of the terpenes are described on page 46, and those of the resins on page 63.

As a class, the turpentines of commerce are viscous, honey-like liquids or soft or brittle solids, varying in colour from light yellow to dark brown or black. In odour they are usually terebinthinate, but sometimes agreeably aromatic, and their taste varies from bitter, nauseous and acid, to a pleasant aromatic flavour. They usually possess more or less rotatory power on a ray of polarised light, but as the extent of the rotation depends on their composition, and this is very variable, the character is not of much value as a means of discriminating one turpentine from another.

The turpentines are not sensibly soluble in water, though some yield traces of formic and probably succinic acid to that solvent.

In absolute alcohol the turpentines are mostly soluble, though some leave distinct residues, and this fact may be employed for their discrimination. In weaker alcohol their solubility is much diminished, some varieties leaving a very decided residue. The alcoholic solutions usually have a distinctly acid reaction.

Glacial acetic acid and acetone closely resemble alcohol in their solvent power for the turpentines, while ether, chloroform, petroleum spirit, carbon disulphide, and oil of turpentine dissolve all the varieties with great facility.

The turpentines vary considerably in their siccative powers. Some varieties, such as common turpentine, if exposed to the air as a thin layer on paper, become converted into a dry brittle resin in twenty-four hours, while other kinds, such as Venice turpentine, harden but very gradually. When mixed with calcined magnesia, the drying properties of the turpentines become more strongly marked, and they may thus be to some extent differentiated.

BALSAMS are, correctly speaking, such of the oleo-resinous exudations of plants as contain benzoic or cinnamic acid, and yield cinnamate or benzoate of methyl or ethyl by dry distillation. They are liquid, more or less viscous, and yield essential oils on distillation with water. The term balsam is misapplied to "Canada balsam," which is a true turpentine not containing or yielding benzoic or cinnamic acid; whilst gum benzoin and dragon's-blood would be more properly classed among the resins.

The description of the minute and often inappreciable differences between the various oleo-resins known in commerce as turpentines and balsams, belongs rather to a work on pharmacy and materia medica than to one on chemical analysis,* and as their recognition and examination are rarely required by others than pharmacists, it is unnecessary to describe them individually or in detail.

Resin Oil or Rosin Oil.—By the distillation of common rosin, either with or without steam, products are obtained of which the chief are:—an aqueous liquid containing acetic acid; a light and readily volatile oil or spirit, containing sundry hydrocarbons and oxygenated bodies; and a heavy oil, volatile only at a very high temperature, and known in commerce as rosin oil.

Rosin oil has been very imperfectly examined. It appears to consist in large part of polymerised terpenes, but oxygenated bodies are also present. It is not capable of saponification,

* Much information on the botanical origin, methods of obtaining, characters and composition of the turpentines and balsams will be found in Watt's *Dictionary of Chemistry*, vol. i. p. 491, *et seq.*; and a most exhaustive series of articles by Dr Julius Morel, published in the *Pharmaceutical Journal* [3], vol. viii. pp 21, 81, 281, 342, 542, 725, 886, 981, 1024; and vol. ix. pp. 673 and 714. See also footnote on page 64.

but some varieties at least appear capable of forming unstable compounds with slaked lime and other bases, which compounds are resolved again on distillation, and are of importance in the preparation of commercial "rosin grease."* Phenol-like bodies are sometimes present. Superior rosin oil free from such substances is often made by distilling the lime compound.

Rosin oil has a large legitimate employment as a lubricant for machinery and waggon wheels. It is used in the condition of rosin grease, and in admixture with olive, rape, and other oils.† Mixed with rape oil it is employed for adulterating olive oil.

Rosin oil has a specific gravity carrying from ·96 to ·99; and hence is heavier than any of the vegetable or animal oils, and much heavier than mineral lubricating oils (see page 35). It is usually of a brownish yellow colour, and generally presents a strong bluish or violet fluorescence, which is apparent even in its dilute etherial solutions. Rosin oil is often strongly dextro-rotatory; but the rotation is variable, being sometimes very slight, and occasionally left-handed. Armstrong and other chemists contend that samples free from rosin and similar impurities are optically inactive.

Refined rosin oil has but little smell at ordinary temperatures, but when strongly heated it gives fumes having a marked odour of resin, neutral or nearly so in reaction, and which burn when inflamed with a large and very smoky flame. When rosin oil is distilled, a portion usually passes over below 250°, a considerable quantity below 300, and nearly the whole below 360° C. The taste of rosin oil is peculiar, and the after-taste strong and highly characteristic.

* Rosin grease is made by stirring rosin oil with slaked lime made into a cream with water. Combination takes place, probably according to the formula $C_{10}H_{16},2CaH_2O_2$, and the superfluous water separates and is run off. The solid product is diluted with more rosin oil, and the solution obtained stirred into a further quantity, till the proportions of the constituents are about $13C_{10}H_{16},CaH_2O_2$. The resultant rosin grease is used as a lubricant for iron bearings, and especially for the axles of pit-waggons, which are much exposed to moisture. It rapidly acetifies by heat and friction, and hence is not adapted for brass bearings. Rosin grease is often mixed with neutral coal-tar oils (naphthalene oils).

† Information respecting the mode of manufacture of rosin oil, and the composition of various lubricants containing it, will be found in the *Journal of the Chemical Society*, vol. xxvi. pp. 304, 305, and 1175.

Rosin oil is insoluble in water, and but slightly soluble in alcohol, but it is miscible in all proportions with fat-oils, mineral oils, ether, chloroform, carbon disulphide, and petroleum spirit.

Chlorine and bromine act somewhat violently on rosin oil. Nitric acid is sometimes without immediate action in the cold, but if warmed a violent reaction often suddenly ensues.

Rosin oil shows a rise of 18 to 20° C. in temperature when treated with concentrated sulphuric acid as described under "Fixed Oils," and forms a reddish brown liquid which separates into two strata on standing.

When rosin oil is shaken with anhydrous stannic chloride, a characteristic violet coloration is produced, often requiring some time for its development. The reaction is liable to be masked by the presence of a large proportion of fat oil, but the test may be successfully applied to such mixtures by distilling them in a small flask or retort, and adding stannic chloride to the first fractions which pass over.

When agitated with about $\frac{1}{3}$ of fuming hydrochloric acid, most samples of rosin oil gradually acquire a dark and ultimately a black colour.

Rosin oil is quite unsaponifiable, and hence may be estimated in fatty oils by agitating the solution of the soap with ether. When thus isolated, it may be identified as rosin oil by its taste, smell on heating, specific gravity, and reaction with stannic chloride. In the original substance rosin oil may sometimes be recognised by its action on polarised light.

The presence of fat oils or fatty acids in rosin oil may be detected and their proportion determined as indicated in the last paragraph. The reduction in the density of the sample will furnish an approximate indication of the amount of admixture present. Samples containing fat oils or fatty acids give, on heating strongly, an odour of acrolein and fumes of marked acid reaction.

The presence of mineral oil in rosin oil is indicated by the diminished density of the sample. Mineral lubricating oil having an average density of about ·900 and rosin oil of about ·987, an approximate estimate of the proportion present may be arrived at. Neither the density nor any other

property known to the author will suffice for the positive recognition of a small proportion of mineral oil in rosin oil, though the contrary problem admits of easy solution, owing to the strongly-marked physical characters of rosin oil and its reaction with stannic chloride.

BENZENE AND ITS HOMOLOGUES. C_nH_{2n-6}.

Benzene is the lowest and most important member of a series of homologous hydrocarbons occurring in coal-tar and some analogous products.

The benzene series of hydrocarbons *diminish* in volatility but *increase* in density with the number of carbon atoms present. As a rule they behave as saturated molecules, or the hydrides of alcohol radicals, but they are not incapable of forming additive compounds (see pages 3 and 16).

The members of the benzene series present very close resemblances both in their physical and chemical characters, and hence, with the exceptions specified below, the description given of benzene on page 72, *et seq.*, may be regarded as of general applicability to the other hydrocarbons of the series.

The homologues of benzene may be regarded as being produced by the substitution of the group methyl, CH_3, or one of its homologues, for one or more of the six hydrogen atoms of benzene. At present, however, no more than four atoms of hydrogen have been thus displaced, and hexyl, C_6H_{13}, is the highest alcohol radical which has been introduced.

The following table shows the hydrocarbons of the benzene series the presence of which has been observed in coal-tar and other products of destructive distillation.

It will be seen that all the homologues of benzene, the presence of which in coal-tar has been certainly recognised, are bodies in which one or more of the atoms of hydrogen of benzene are replaced by methyl, CH_3. Hydrocarbons, in which the homologues of methyl occur, are producible by synthetical means, but do not appear to occur in coal-tar. It is also doubtful whether coal-tar oils contain any higher homologues of the benzene series than those shown in the table. Cymene, $C_{10}H_{14}$, however, is not improbably present in

HYDROCARBONS OF THE BENZENE SERIES FOUND IN COAL-TAR.

Empirical Formula.	Name of Hydrocarbon.	Dissected Formula.	Sp. Gr. at 15° C.	Boiling Point.	Product of the action of	
					Chromic Acid.	Dilute Nitric Acid.
C_6H_6	Phenyl Hydride. Benzene. . . .	$C_6H_5.H$	·885	81	...	Not affected.
C_7H_8	Methyl-benzene. Toluene. . . .	$C_6H_5.CH_3$	·871	111	Benzoic Acid, $C_6H_5.COOH$	Benzoic Acid, C_6H_5COOH
C_8H_{10}	Dimethyl-benzene { Para-xylene (1 : 4) .	$C_6H_4.(CH_3)_2$	·868	136	Tere-phthalic Acid, $C_6H_4(CO.OH)_2$	Paratoluic Acid, $C_6H_4(CH_3).COOH$ melting at 176°.
	Dimethyl-benzene { Meta-xylene (1 : 3) .	$C_6H_4.(CH_3)_2$	·868	137 to 138	Iso-phthalic Acid, $C_6H_4(CO.OH)_2$	Not attacked.
C_9H_{12}	Trimethyl-benzene { Mesitylene (1 : 3 : 5) .	$C_6H_3.(CH_3)_3$	...	163	Acetic Acid, $C_2H_4O_2$, only.	Mesitylenic Acid, $C_9H_{10}O_2$, melting at 166°, &c.
	Trimethyl-benzene { Pseudo-cumene (1 : 3 : 4)	$C_6H_3.(CH_3)_3$	...	166 to 167	...	Xylic Acid, $C_9H_{10}O_2$ melting at 120. Paraxylic Acid melting at 163 ; and Xylidic Acid, $C_9H_8O_4$.

coal-tar, and is the leading constituent of some essential oils (see page 48), as is also the higher homologue cedrene, $C_{15}H_{24}$.

The light oil of coal-tar known as commercial "benzol" consists chiefly of a mixture of benzene and its homologues in very variable proportions. Its mode of assay is described on page 80. The characters and tests for benzene itself are detailed in the section commencing on page 73.

Benzene. Benzol. Phenyl Hydride. $C_6H_6=C_6H_5.H$. The term benzol is one frequently applied to the hydrocarbon benzene, but when used at all it should be strictly limited in its signification to the mixture of homologous hydrocarbons obtained from light coal-tar oil, of which benzene, C_6H_6, is the most important constituent.

Benzene is produced by a great number of reactions, among which are the following:—

1. Action of a red heat on acetylene: $3C_2H_2=C_6H_6$.
2. Distillation of benzoic acid with slaked lime: $C_7H_6O_2+CaH_2O_2=CaCO_3+H_2O+C_6H_6$.*
3. Distillation of phthalic acid with excess of lime: $C_8H_6O_4+2CaO=2CaCO_3+C_6H_6$.
4. Action of highly heated zinc dust on phenol: $C_6H_6O+Zn=ZnO+C_6H_6$.

Benzene also results from the heating of various hydrocarbons and other organic bodies, and is produced by the destructive distillation of turf, wood, resin, coal, &c. It occurs naturally in certain petroleums.

In practice, benzene is obtained from the portion of coal-tar which distils below 100° C., which is technically known as "light oils." This is agitated successively with dilute sulphuric acid, water, and milk of lime or caustic soda solution. It is next digested at 100° C., with 5 per cent. by measure of concentrated sulphuric acid, in order to separate hydrocarbons of the olefin and acetylene series, and this treatment is repeated as long as fresh quantities of acid continue to blacken it. The purified product is then separated and fractionally distilled, the portion which passes over below

* Benzene is obtained by heating any of the benzene-carboxyl acids with excess of a strong base.

90° C. being collected separately. This is cooled by a freezing mixture, when the benzene crystallises out, and is separated from the more fusible hydrocarbons by draining on a vacuum filter. If a pure product be required the benzene is melted and recrystallised several times, the mother liquor being separated as before.

Pure benzene is a colourless, very limpid, highly refractive liquid, of a peculiar and somewhat agreeable odour. Its specific gravity at 0° C. is ·8995, and at 15° C. ·885. When subjected to a freezing mixture it solidifies to a brilliant white mass of fern-like tufts, which melt at 5·5° C. Benzene boils at 80·5° C., emitting a highly inflammable vapour, which burns with a luminous and very smoky flame.

Benzene is practically insoluble in water, but is miscible (apparently in all proportions) with alcohol, amyl alcohol, ether, chloroform, petroleum spirit, turpentine, anhydrous carbolic acid (see page 32), and fixed and volatile oils.

Hot benzene dissolves sulphur, phosphorus, and iodine. It is an excellent solvent for gutta-percha and india-rubber, and leaves them unaltered on evaporation. It dissolves waxes, fats, and fatty acids, with facility.

Benzene distils without decomposition, but when passed through a tube heated to bright redness it yields hydrogen, and diphenyl, $C_{12}H_{10}$, and other hydrocarbons.

Benzene is not acted on by distilling it with metallic sodium, and caustic alkalies have no effect on it.

Benzene dissolves entirely when heated to 100° C. for some hours with four or five times its bulk of concentrated sulphuric acid. The resulting liquid contains benzene-sulphonic acid, $C_6H_5HSO_3$, and is colourless if pure benzene be employed.

Under the influence of oxidising agents benzene yields a number of interesting products, according to the treatment to which it is subjected; thus—

1. By the action of chromic oxychloride on a solution of benzene in glacial acetic acid, trichloroquinone, $C_6HCl_3O_2$, is formed.

2. By the action of manganese dioxide and concentrated sulphuric acid benzene yields carbon dioxide, formic acid, and

water, together with small quantities of benzoic, phthalic, and terephthalic acids.

3. By the action of concentrated nitric acid benzene is readily converted into nitro benzene, $C_6H_5NO_2$; and by the continued action of the acid dinitro-benzene, $C_6H_4(NO_2)_2$, is produced.

4. By the action of chlorine or bromine in the dark or diffused light benzene is converted into chlorinated or brominated derivatives, in some cases five out of the six atoms of hydrogen being replaced. In direct sunlight, chlorine and bromine form additive compounds with benzene, of which benzene hexachloride, $C_6H_6Cl_6$, is a type.

Separation and Recognition of Benzene. When in a pure state and in tolerable quantity, benzene is readily recognisable by its smell, specific gravity, and boiling point. The chemical tests for benzene capable of ready application are very few, the most satisfactory being that based upon the formation of nitro-benzene by treatment with nitric acid, followed by recognition of the aniline resulting from the action of reducing agents on the nitro-compound.

This test is only applicable when the benzene is in a state of approximate purity, or at least free from certain kinds of admixture. Hence in the case of complex mixtures one or all of the following means must be adopted to separate the benzene from interfering bodies:—

1. The liquid should be agitated with solution of caustic soda, and separated from the aqueous layer. This treatment removes phenols and other bodies of an acid character.

2. The purified oily liquid should be separated from non-volatile matters by distillation in a small retort or flask furnished with a thermometer and good condensing arrangement.

3. The portion passing over between 65° and 100° C. will contain any benzene which may be present, and should be collected separately and treated as follows:

4. The fraction passing over between 65° and 100° C. is shaken with cold concentrated sulphuric acid, and the treatment repeated, if necessary, till no further blackening ensues.

This process removes hydrocarbons of the ethylene and acetylene series.

5. The purified oil is separated from the acid and washed by agitation with dilute caustic soda solution. The purified benzene thus obtained is then treated as follows :—

6. The oily layer separated from the alkaline liquid is treated with about four times its measure of fuming nitric acid of 1·45 specific gravity. The operation is conducted in a small flask or retort furnished with an inverted condenser. If a vigorous action occur no extraneous heat need be applied, but if the reaction be sluggish the liquid should be well agitated and moderately heated for a few minutes. The flask is then cooled and the contents transferred to a tapped separator. If separation into distinct strata occur, *all except the top one* * are run off while still warm through the tap into a quantity of cold water. If this liquid remain clear no nitrobenzene can have been formed, and consequently no benzene can have been present. In presence of a considerable quantity, a distinct separation of yellow oily nitro-benzene will occur at the bottom of the water and a marked odour of bitter-almonds will be perceived. With smaller quantities, the nitrobenzene will form a finely-divided precipitate, which will collect after some hours at the bottom of the vessel. The liquid is passed through a wet filter, washed with cold water, and the nitrobenzene collected is dissolved by dropping alcohol on the filter. The alcoholic solution thus obtained is then mixed with hydrochloric acid and boiled for some time with metallic zinc, whereby the nitrobenzene is reduced to aniline, C_6H_7N. The liquid is next diluted, neutralised with caustic soda, and a clear solution of bleaching powder cautiously added. A blue or purple coloration, often appearing somewhat slowly and gradually changing to brown, will be produced if aniline be present, thus indicating the presence of benzene in the sample examined.

* In the case of mixtures of petroleum spirit and benzene, three layers are formed, the uppermost consisting of unaltered paraffins, the middle one of nitrobenzene, and the lowest of a solution of nitrobenzene in nitric acid. If the proportion of benzene in the mixture be moderate the nitro-compound produced remains wholly in solution in the nitric acid until the latter is diluted.

For the determination of benzene in complex mixtures the only available method is to separate fixed matters, purify by treating with acid and alkali, as already described, then to remove any carbon disulphide by alcoholic potash (see page 80), and subsequently to carefully fractionate the purified hydrocarbons in a bulb-apparatus, as directed on page 87.

Commercial Benzols and Coal-tar Naphthas.—In the first rough distillation of coal-tar, two fractions are obtained which are known respectively as "first light oils," and "second light oils." These together constitute "crude naphtha," the composition of which is exceedingly complex, many or all of the following bodies being sometimes present simultaneously:—

	Boiling points. °C.
1. Ammonia, ammonium sulphide, and other ammoniacal compounds	...
2. Carbon disulphide, and probably other sulphur compounds	...
3. Aceto-nitrile (C_2H_3N), and probably homologous bodies	...
4. Acetylene, and probably other homologous hydrocarbons	...
5. Hydrocarbons of the paraffin or marsh-gas series, especially hexane (C_6H_{14})	68 to 160
6. Hydrocarbons of the olefin or ethylene series, especially pentylene, hexylene, and heptylene (C_5H_{10}, C_6H_{10}, and C_7H_{14})	40 to 100
7. Benzene (C_6H_6)	80
Toluene (C_7H_8)	111
Higher Homologues of the Benzene series	137 to 180
8. Naphthalene ($C_{10}H_8$)	218
9. Nitrogenised bases, especially pyridine and picoline	117 to 135
10. Aniline (C_6H_7N); traces	182
11. Phenols, especially carbolic acid (C_6H_6O)	182 to 213

On the large scale, the crude naphtha is purified by treatment with concentrated sulphuric acid, which removes the bases and the hydrocarbons of the ethylene series. A subsequent treatment with milk of lime or caustic soda eliminates the phenols and any other bodies of acid character. The oil is then washed with water and again distilled, the temperature and mode of operating being varied somewhat according to the class of "benzol" desired.

The products obtained from the crude naphtha by purification and fractional distillation are known technically as once-

run naphtha; 90 per cent. benzol; 50 and 90 per cent. benzol (called "50/90 benzol"); 30 per cent. benzol; solvent naphtha; and last runnings. Each of these qualities has distinctive characters by which it is known and recognised both in England and on the continent. In addition, benzene, toluene and xylene are now manufactured on a commercial scale in a condition of almost absolute purity.

CRUDE NAPHTHA, as obtained by the first distillation of coal-tar, is an extremely complex liquid (see page 75), of a disagreeable smell; it has usually a dark coffee colour, and is more or less fluorescent. Crude naphtha has a density of ·935 to ·940, or even more, and evolves ammonia abundantly on distillation.

The assay of crude coal-tar naphtha is usually limited to a determination of the volume percentage of distillate obtained at a temperature not exceeding 120° C. The details of the operation are fully described on page 84. The proportion of distillate obtained varies from 15 to 35 per cent., according to the quality of the naphtha.

ONCE-RUN NAPHTHA is the product obtained by distilling crude naphtha, pushing the process as far as practicable. The residual portion constitutes last runnings. It is highly charged with naphthalene, and is used as a common burning oil in street vapour-lamps.

Once-run naphtha is a more or less amber-coloured fluid, of a specific gravity varying from ·886 to ·892. It usually yields from 40 to 50 per cent. of distillate at a temperature not exceeding 120° C. (see page 87). In most cases the indication thus obtained is sufficient, but occasionally once-run naphtha is further examined by noting the quantity distilling below 160° also. The total distillate thus obtained is then re-distilled, and the process arrested at 100° C. An ordinary sample will yield about 50 to 56 per cent. over at 120°, and an additional 32 to 36 at 160°. These products mixed and redistilled will yield from 19 to 26 per cent. at 100° C.

For technical purposes the results thus obtained are generally sufficient, and their interpretation is well understood. By distilling the sample into 10 per cent. fractions

and noting the temperature at each point, the complex character of the naphtha is readily seen. The results of fractional distillation of a very fair sample of once-run naphtha are given on page 87. Once-run naphtha is the starting-point from which the manufacturer derives, by fractional distillation, the following more definite products:—(*a*) 90 per cent. benzol; (*b*) 50/90 benzol; (*c*) 30 per cent. benzol; (*d*) solvent naphtha; (*e*) a further produce of last runnings.

COMMERCIAL BENZOLS. In commerce, the term "benzol" is applied generically to the more volatile portions of redistilled coal-tar naphtha. It is a convenient name to indicate this more or less complex liquid consisting chiefly of benzene and its homologues; while the use of the term benzene should be restricted to the definite hydrocarbon of the formula C_6H_6.

Commercial benzols consist essentially of mixtures of very variable proportions of benzene and its homologues, together with smaller percentages of carbon disulphide; certain light hydrocarbons technically known as "petroleum" and which are incapable of nitrification;* traces of water; very frequently acetylene, and probably homologous hydrocarbons;† and traces of other impurities of an indefinite nature.

The light hydrocarbons are not of much importance, except in so far as they diminish the yield of colouring matter from the aniline made from the benzols containing them. Carbon disulphide is a somewhat troublesome impurity, and is difficult to get rid of by ordinary means. The details of the method of effecting the assay of benzols are given on page 84. According to the behaviour of the sample when distilled, it is classed as 90 per cent. benzol, 50/90 benzol, or 30 per cent. benzol.

90 per cent. Benzol is a product of which 90 per cent. by volume distils before the thermometer rises above 100° C. A good sample should not begin to distil under 80° C.,

* See footnote on next page.

† By boiling such benzol rapidly, and passing the vapours into ammonio-nitrate of silver or ammoniacal cuprous chloride, an abundant precipitate of the corresponding metallic acetylide is obtained.

and should not yield more than 20 to 30 per cent. at 85°, or much more than 90 per cent. at 100° C. An excessive distillate, *e.g.* 35 to 40 per cent. at 85°, indicates a larger proportion of carbon disulphide or light hydrocarbons than is desirable. The actual percentage composition of a 90 per cent. benzol of good quality is about 70 of benzene, 24 of toluene, a trace of xylene, and 4 to 6 of carbon disulphide and light hydrocarbons. It should be colourless ("water-white"), and free from opalescence.

The specific gravity of English 90 per cent. benzols ranges from ·880 to ·888 at 15·5° C. (= 60° F.), but the density is a fallacious guide as to the quality of a sample, owing to the presence of carbon disulphide and light hydrocarbons, which impurities, from their high volatility, become concentrated in this class of benzol. Carbon disulphide has the high density of 1·27, while the light hydrocarbons ("petroleum") average 0·860.* Hence, when present together in certain proportions, these impurities do not sensibly affect the density of the benzol.

Scotch 90 per cent. benzols contain but little carbon disulphide, but a considerable proportion of light hydrocarbons; hence the specific gravity is often as low as ·871. The first 20 per cent. distilled from such a sample may have a density of ·866; while the residual 80 per cent. will be as dense as ·872. The low density of the first fraction here distinctly indicates "petroleum," and not carbon disulphide, as the predominant impurity. By eliminating the carbon disulphide from 90 per cent. benzol in the manner described on page 80, the anomalies in the density and distillation results almost disappear, and the interpretation of their indications becomes much simpler.

Until recently, 90 per cent. benzol was the highest quality in the market; but, by improved methods of fractionating, products are now obtained at one operation, which distil com-

* The nature of these light hydrocarbons is not fully made out, but Vincent has shown that they are almost wholly absorbable by bromine, and consist largely of amylene, C_5H_{10}. They are sometimes present to the extent of 8 or 10 per cent., being most abundant in the products from gas works in which cannel coal is extensively used. See also Watson Smith, *Chem. News*, Sept. 16, 1881, page 138.

pletely within a few degrees of the true boiling points of benzene, toluene, and xylene respectively.

50 and 90 per cent. Benzol, or more shortly, "50/90 benzol," is a product of which 50 per cent. by volume distils over at a temperature not exceeding 100° C., and 40 per cent. more (making 90 in all) below 120° C. The density is about ·880. This class of benzol is nearly free from carbon disulphide and "petroleum" hydrocarbons; whilst the proportion of toluene and xylene is of course larger than in 90 per cent. benzol. 50/90 benzol is employed for producing the heavy aniline used for preparing rosaniline or magenta.

30 per cent. Benzol is a product of which 30 per cent. distils below 100°, about 60 per cent. more passing over between 100 and 120. It consists chiefly of toluene and xylene, with smaller proportions of benzene, cumene, &c.

Solvent Naphtha is so called from its wide application as a solvent for india-rubber in the manufacture of waterproof articles. It gives from 8 to 30 per cent. of distillate below 130°, and about 90 below 160°. Solvent naphtha is of extremely complex composition, but consists chiefly of toluene and xylene, with notable quantities of cumene and still higher homologues, and several units per cent. of naphthalene.

For the manufacture of aniline red or fuchsine, a benzol is required which will yield (by nitration and subsequent reduction) an aniline oil (see "Aniline"), of which three-fourths distil between 180 and 190°, and the remainder between 190 and 215°. Such an aniline oil is producible from a benzol of which three-fourths pass over between 80 and 100°, and the rest between 100 and 130°. For the manufacture of methyl-violet, on the contrary, an aniline as free as possible from higher homologues is required, and this must be made from a benzol which almost wholly distils below 83 or 84° C. For xylidine-red an aniline oil derived from benzols boiling above 115 or 120° is required, but it is often found preferable to prepare this by fractionating an ordinary aniline oil rather than to employ a benzol of specially high boiling point for the purpose.

Assay of Commercial Benzols and Naphthas.

The observations of importance in judging of the quality of a commercial benzol or naphtha are, in addition to the appearance and smell of the sample, its specific gravity; the results of its fractional distillation; the proportion of carbon disulphide; and the proportion of the light hydrocarbons technically known as "petroleum."

Water, if present in such quantity as to render the sample turbid, must be got rid of previous to any process of assay. This may be done sufficiently perfectly by passing the liquid through a dry filter. A complete elimination of the water may be easily effected by agitating the sample with a little recently gently ignited plaster of Paris, and filtering. The dehydration is almost instantaneous. If a known weight of plaster be employed, and it be afterwards washed with a little gazolene (page 19), dried at a gentle heat, and reweighed, a quantitative estimation of the water may be readily effected.

Carbon disulphide often exists in very sensible quantity in crude and once-run naphtha and in 90 per cent. benzol. From the less volatile classes of benzol it is usually absent. Its presence is only important in 90 per cent. benzol. Carbon disulphide may be eliminated from benzol, and its amount determined with a near approach to accuracy by the following method devised by B. Nickels:*—100 cc. measure of the sample of benzol (preferably dehydrated with plaster of Paris, as above described) is treated with a solution of 1 grm. of caustic potash in the smallest possible quantity (about 20 c.c.) of hot absolute alcohol,† and the mixture agitated thoroughly. If carbon disulphide be present a yellow colour is usually developed, and the mixture becomes pasty from the formation and separation of potassium xanthate (Vol. I. p. 150) in crystals of a characteristic silky appearance. The mixture is shaken at intervals during half an hour, and is then passed through a dry filter. To complete the extraction of the sulphur compound the filtrate should be treated a second time with half the original quantity of

* *Chem. News*, xliii. 148 and 250.

† The alcohol used may be methylated. It may be rendered anhydrous by agitating with a large excess of dry potassium carbonate, and decanting.

alcoholic potash, as before. The filtered benzol is then agitated in a cylindrical separator with its own volume of warm water, which removes the excess of alcohol and a little dissolved xanthate. The aqueous liquid is run off, and the benzol again agitated with its own measure of cold water, after the removal of which it may be dehydrated with plaster, and then further examined by fractional distillation (see page 84). The potassium xanthate collected on the filter is washed with a little ether, dissolved in alcohol, and the solution obtained rendered slightly acid with acetic acid. On adding a solution of cupric sulphate, a brownish precipitate of cupric xanthate is formed, which rapidly changes to bright yellow cuprous xanthate, $CuC_2H_5(CO)S_2$, insoluble in water and dilute acids (Vol. I. p. 151).

The cuprous xanthate may be collected on a filter, washed, ignited in the air, and weighed as CuO, or the cupric oxide may be ignited with sulphur in hydrogen, and thus converted into cuprous sulphide. The weight of CuO or Cu_2S obtained, divided by ·523, gives that of the carbon disulphide in the sample operated upon.

Instead of weighing the cuprous xanthate, H. Macagno* titrates the acidulated solution of potassium xanthate with a solution of cupric sulphate containing 12·47 grammes of the crystallised salt per litre, the end of the reaction being indicated by the brown colour produced when a drop of the liquid taken out with a glass rod is added to a drop of potassium ferrocyanide solution on a porcelain plate. 1 c.c. of the above cupric sulphate solution corresponds to ·0076 gramme of carbon disulphide. The foregoing process is convenient and fairly accurate. If conducted on 300 c.c. of the sample, sufficient of the purified benzol is obtained to allow of a very perfect fractional distillation; but in such cases the potassium xanthate should be dried by pressure between blotting-paper, weighed, and 1 gramme of the dry substance dissolved in alcohol and titrated with copper solution.

The result of eliminating the carbon disulphide from a benzol is very noticeable. Thus, in the case of a sample which would be conveniently classified as a "light 90 per cent.,"

* *Chem. News*, xliii. 138.

there will be an entire removal of the previous alliaceous odour; a diminution of density from ·885 to ·882 or ·880, according to the amount of carbon disulphide which has been removed; and a disappearance of the abnormally large proportion of liquid distilling below 85° C., the reduction in this respect being from 30 per cent. or more, down to 12 per cent.

The proportion of carbon disulphide eliminated by treatment with alcoholic potash is approximately indicated by the reduction in the density of the sample, thus:—

1	per cent.	by volume of	carbon disulphide	raises the density by ·0033
2	,,	,,	,,	·0065
3	,,	,,	,,	·0093

Till recently the assay of benzols for carbon disulphide has usually been neglected, but of late there has been some demand for products containing only a limited amount of this impurity.

The specific gravity of benzols and naphthas is often a valuable indication of their character, but is apt to be fallacious, especially in the case of 90 per cent. benzols (see page 88). If carbon disulphide be previously eliminated in the manner already described, a determination of the specific gravity affords a much more reliable indication. The specific gravity of benzols is not readily determined by the bottle, owing to their high coefficient of expansion. Somewhat better results are obtainable by the use of a Sprengel's tube, but the easiest and most satisfactory plan is to employ a delicate hydrometer, care being taken to bring the liquid exactly to the standard temperature of 15·5° C. (=60° F.).* As the hydrocarbons of the benzene series decrease in density with each increase in the number of carbon atoms and rise in the boiling point, low volatility of a benzol corresponds with a low density, though such samples are technically called "heavy benzols."

Fractional distillation is the method now almost universally employed for the commercial assay of benzols and naphthas; and if carefully conducted, and the results inter-

* A set of three instruments specially adapted for benzol-testing, but very useful for other purposes, is made by L. Casella, of Holborn Bars, at a very moderate price. They are adapted for reading from the bottom of the meniscus of the liquid.

preted in connection with the specific gravity and the test for carbon disulphide, it affords very satisfactory indications. These indications, however, are of a purely arbitrary character, and, unless the prescribed conditions of manipulation be rigidly adhered to, great discrepancies result. Thus, the barometric pressure, the rapidity of the distillation, the size and shape of the retort, the position of the thermometer-bulb, and even its shape and length are all important factors in the result obtained. On this account it is usual in contract-notes to specify minutely the mode in which the test is to be made, and the slightest departure from the prescribed directions may invalidate the contract.

The following "mode of test" is taken *verbatim* from a form of contract-note largely employed in commercial benzol transactions:—"A quantity of 2000 grains, or 4 fluid ounces, to be distilled in a glass retort of a capacity of 8 fluid ounces; bulb of thermometer to be placed $\frac{3}{8}$ths of an inch from bottom of retort; distillation to be made over a naked flame, and at such a speed that the distillate shall not pass over in a stream, but as quickly as it can drop in separate particles. Any deficiency in quantity arising from evaporation or other natural causes, during the operation, to be added to the product at each point."

The proportion by volume of the sample which passes over below and at a given temperature is called the "strength" of the sample at that temperature. For crude naphtha it is usually sufficient to note the volume distilling below 120° C. (=248° F.); in the examination of once-run naphtha, an observation of the volume distilling below 160° C. is also made; in the case of 90 per cent. benzols the volumes distilled are noted at 84° or 85° C., and again at 100° C.; whilst with 50/90 and 30 per cent. benzols the temperatures noted are 100° and 120° C.

The very great majority of parcels of benzol and naphtha sold in this country are bought, or are supposed to be bought, on the above test; and contrary to the statements which have been recently published,* the results obtained by different

* See the correspondence in the *Chemical News*, vol. xliii. pp. 46, 69, 93, 115, 128, 164, and 185.

operators understanding the test agree exceedingly closely, the variations rarely exceeding 1 or 1½ per cent.

The following is the best mode of conducting the test so as to ensure results which are constant, and which can be trusted to be as accurate as the process will admit of. The instructions given apply to the assay of a 90 per cent. benzol. The temperature to be observed must, of course, be modified according to the contract-note, or to the nature of the product under treatment:—

100 c.c. of the benzol to be tested is measured in an accurately graduated cylinder, and poured thence into a tubulated retort, of such a size as to be capable of retaining 8 fluid ounces when placed in the ordinary position for distillation.* A delicate thermometer is fitted in the tubulure of the retort by a cork, so that it may be vertical and the lower end of the bulb be ⅜ inch distance from the bottom of the retort.† The neck of the retort is then inserted into the inner tube of a Liebig's condenser, and pushed down as far as it will go. The condenser should be from 15 to 18 inches in length, and well supplied with cold water. The neck of the retort should not project too far into the condenser; if necessary it should be

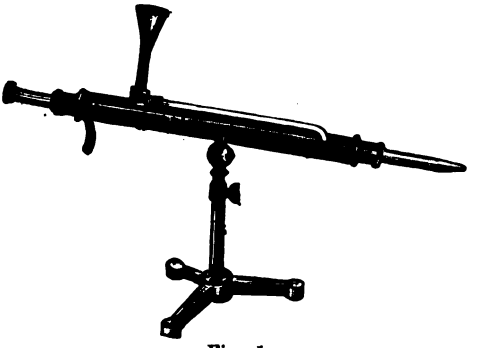

Fig. 1.

* The retort should be previously rinsed with some of the sample to be tested, or a little may be distilled in it, and the residue carefully drained out.

† The thermometer used for benzol testing should be 14 inches long; the bulb sufficiently small to ensure its remaining well immersed in the boiling liquid, the first marking or division at 70° C., which point should be well out of the tubulure of the retort; the graduation should be continued up to 130° C., with divisions at each ½, or (better) ½ of a degree Centigrade. It is a curious but undeniable fact that thermometers, otherwise similar, but differing some 6 inches in the height of the 100° C. mark, give distinctly different percentages in benzol testing. Instruments guaranteed to ⅒ degree, and constructed in the manner above detailed, are obtainable of L. Casella, 147 Holborn Bars, E.C.

cut short. No cork or other connection is necessary between the retort-neck and condenser-tube. Before use, the tube of the condenser should be rinsed with a little of the sample, and allowed to drain, or some of the benzol may be sprayed through it. The graduated cylinder employed for measuring out the sample is next placed under the further end of the condenser-tube in such a manner as to catch all the distillate, while allowing it to drop freely. The retort is then heated by the naked flame of a bunsen burner.* The flame should be small, about the size and shape of a filbert, and when the distillation of the benzol commences, must be so regulated that the condensed liquid shall fall rapidly in distinct drops, not in a trickle or a continuous stream.

When the distillation commences the flame is regulated, if necessary, and the rise of the thermometer carefully watched. The moment it registers a temperature of 85° C.† the flame is extinguished. Four or five minutes are allowed for the liquid in the condenser to drain into the measuring cylinder, and then the volume of the distillate is carefully read off and recorded. The lamp is then re-lighted and the distillation continued till the thermometer rises to 100° C.,† when the gas is turned off as before, and the volume of the distillate read off, after allowing time for drainage. The residual liquid in the retort is allowed to cool, and is then poured, to the last drop, into the measuring cylinder. A deficiency from the 100 c.c. originally taken will generally be observed. This is

* The bunsen should be furnished with an air-regulator working automatically with each movement of the tap, and should be surrounded with a cylinder to exclude currents of air. The lamp should be placed in a deep tin basin containing sand or sawdust, in order to absorb the benzol in the event of the retort cracking.

† It is found in practice that if the light be turned out exactly when the thermometer registers the required temperature, that the mercury subsequently rises to an extent varying from ½ to fully 1 degree. With a little experience of a thermometer the range of this "after-rise" will become known, and in subsequent operations the lamp should be turned out when the mercury is as much below the critical temperature as it is expected afterwards to rise about it. Thus if the after-rise of a thermometer has been found to be 1° C., the gas should be turned out when the instrument registers 84·5 instead of 85°, as it will subsequently rise to 85·5, and hence 85·0° may be considered to be the mean reading.

the loss arising "from evaporation or other natural causes," referred to in the contract-note (page 83).

The difference between the collective volume after distillation and that of the original sample is to be added to the measure of the distillate collected at each temperature, and the corrected volumes reported as the "strength" of the benzol examined.*

In benzol testing it is very desirable to observe the barometric pressure before making an experiment, and to modify the manipulation accordingly. A difference of 1 inch in the height of the barometer makes a difference of about 1° C. in the boiling point of a benzol. Hence if the barometer register 29·5 inches instead of 30 inches, the gas should be extinguished so that the thermometer may show a mean temperature of 90·5° instead of 100°.

The foregoing method of testing benzols is admittedly crude and unscientific, but its indications are well understood; and, till recently, it has sufficed for the technical examinations required. Now, however, that a demand has arisen for practically pure benzene, toluene and xylene, the value of the crude products will depend on their content of these hydrocarbons, and hence the test will probably be eventually replaced by others giving absolute analytical results, though such a change will very likely be strongly opposed.

A preferable plan to observing the volume of distillate obtained at one or two temperatures only, is to note the height of the thermometer at every 5 or 10 c.c. of liquid which passes over. The following table shows the thermometric indications at each succeeding fraction obtained by the distillation of representative samples of different classes of benzol and naphtha. It is of interest to observe the characters of Scotch 90 per cent. benzol, which exhibits an abnormally low density owing to the presence of a notable proportion of

* Thus, if by distilling 100 c.c. of a benzol there were obtained 20 c.c. at 85° and 90 c.c. at 100°, and the total liquid mixed after distillation measured 99 c.c., the difference between that and 100 c.c., *i.e.* 1 c.c., must be added to the yields at 85° and 100° respectively, making the corrected figures 21 per cent. at 85°, and 91 at 100° C. As a matter of fact the loss of volume by distillation is due far more to expulsion of acetylene and other gases than to actual loss of benzol.

light hydrocarbons. On the other hand, the synthetical mixture of pure benzene and toluene gives remarkable figures owing to the total absence of these hydrocarbons and carbon disulphide (see page 77).

	Very good Once-run Naphtha	Good 90 per cent. Benzol	Scotch 90 per cent. Benzol	50/90 per cent. Benzol	30 per cent. Benzol	Solvent Naphtha	Pure Benzene 70 per cent.; Toluene 30 per cent.
Sp. Gravity .	...	·882	·873	·880	·875	·877	·880
1st drop collected at	...	82°	...	...	...	...	85·4°
10 p. cent. ,,	96°	83¼°	84½°	94°	97°	128½°	86·6
20 ,, ,,	99½	84½	85	95	98	130	87·2
30 ,, ,,	102	85	85¾	96½	99½	132½	87·8
40 ,, ,,	107	85¾	86½	98	101	135	88·8
50 ,, ,,	111	86¾	87¾	100	104	137	89·8
60 ,, ,,	119	88	89	102½	106	140	91·4
70 ,, ,,	128	89¾	91¼	106	109½	143½	93·2
80 ,, ,,	145	92½	94¾	110½	113½	148½	96·2
90 ,, ,,	170	...	...	120	120	156	102·6
92 ,, ,,	...	100	100	...	...	...	...
95 ,, ,,	...	...	...	...	...	...	107·0

When there is no contract-note to prescribe the mode of conducting the distillation, it is very much better to substitute for the 8 oz. retort a flask fitted with a three-bulbed apparatus for fractional distillation. This ingenious device* consists of a number of bulbs, varying from two to six, blown upon a tube, which is fitted by means of a cork into an 8 oz. flask containing the liquid to be distilled. The upper end of the tube is furnished with a tubulure, which can be fitted by a cork to a Liebig's condenser, and with an orifice into which a thermometer can be fitted so as to observe the temperature of the vapour which passes over. Each of the bulbs is connected with the one below by a small side-tube. In the constriction of each bulb is placed a little cup of platinum- or copper-gauze, of the size and shape of a small thimble. These cups are made by folding the gauze over the end

Fig. 2.

* Obtainable from Messrs Townson & Mercer, Bishopsgate Street, E.C.

of a stout glass rod. The ascending vapour condenses in the cups, and thus serves to wash the vapour subsequently formed, as it bubbles through. When the liquid rises to a certain height in each bulb it runs off by the side tube, and ultimately finds its way back to the distilling flask, the flame under which is so regulated as to keep all the cups full and cause the distillate to fall in separate drops.

By employing this apparatus, greatly improved results are obtainable, and a complex liquid may be fractionated at one operation into approximately pure constituents.* Hence it is probable that the present empirical method of testing will be superseded by the more rational process. Almost absolutely pure benzene, toluene and xylene are now articles of

* The following figures are due to the kindness of Mr B. Nickels, to whom I am also indebted for numerous other data respecting coal-tar products. Column A. represents the temperatures recorded by the thermometer when the *original* benzol was distilled in an 8 oz. retort in the ordinary way; B. shows the alteration produced *by removing the carbon disulphide* in the manner described on page 80; and C. shows the results obtained when the *purified* benzol was distilled in a three-bulbed apparatus, instead of in an 8 oz. retort:—

	A. Commercial 90 per cent. Benzol in 8 oz. retort.	B. A. after being purified from CS_2, in 8 oz. retort.	C. B. distilled in flask with three-bulb apparatus.
Specific Gravity, water at 15·5 being 1·000 . .	·884	·881	·881
First drop distilled at . .	79·5° C.	83·4° C.	...
5 per cent. over at . . .	...	84·2	81·25° C.
10 ,, ,, . . .	...	84·3	82·0
20 ,, ,, . . .	...	85·0	82·8
25 ,, ,, . . .	84·0	...	...
30 ,, ,, . . .	85·0	85·8	83·0
40 ,, ,, . . .	85·4	86·4	83·5
50 ,, ,, . . .	86·4	87·1	84·7
60 ,, ,, . . .	88·0	88·3	85·3
70 ,, ,, . . .	90·0	90·0	86·5
80 ,, ,, . . .	93·0	93·0	89·3
90 ,, ,, . . .	100·0	100·0	100·0
95 ,, ,, . . .	...	112·4	111·8

When the original sample A. was fractionated in the three-bulb apparatus at 45° it gave oily drops indicative of carbon disulphide; and these become more abundant at 60°. At 70° 5½ per cent. had distilled, and the thermometer rose

commerce;* and it will be necessary to ascertain the percentage composition of the benzols used in their production. This is approximately possible by operating with the bulb apparatus, but it is wholly beyond the powers of the ordinary retort.

Nitrobenzene; Nitrobenzol, $C_6H_5NO_2$. Nitrobenzene is a product of the action of nitric acid on benzene, $C_6H_6 + HNO_3 = C_6H_5NO_2 + H_2O$. The nitric acid should not be of lower gravity than 1·45, and on the large scale is employed in admixture with sulphuric acid. Great heat is evolved, and more or less red fumes are produced. When the action is over, the product may be poured into waters, when the nitrobenzene sinks to the bottom as a yellow oil.

at once to 80°. The process being stopped at this point, the contents of the flask were found to have decreased in density from ·884 to ·882, showing the removal of a substance heavier than benzene. That this was largely carbon disulphide is proved by the figures in column B.; the complete removal of the impurity reducing the gravity and raising the boiling point. When the purified sample B. was fractioned by the three-bulb apparatus into 20, 70, and 10 per cent. portions, they showed a density of ·883, ·885, and ·8715 respectively. Had carbon disulphide been present, the first fraction would have been denser instead of lighter than benzol (sp. gr. ·885). Hence the first portion of the distillate must have contained light hydrocarbons ("petroleum"). By operating originally on 300 c.c. of the same sample, removing the carbon disulphide by alcoholic potash, and several times repeating the process of fractioning with the three-bulb apparatus, Mr Nickels obtained the following results as indicative of the proximate analysis of the benzol tested:—

Carbon disulphide, removed by alcoholic potash .	1·5	per cent.
Light hydrocarbons, specific gravity ·872 (not nitrifiable; probably chiefly amylene and acetonitrile)	3·5	,,
Benzene, specific gravity 885, and distilling wholly within a range of 2 degrees	78·4	,,
Toluene, specific gravity ·8715, and distilling within 2 degrees	16·6	,,
	100·0	,,

* Not only are these hydrocarbons obtainable in commerce in a state approaching to purity, but they are produced by *a single distillation* in an apparatus based on the principle of the three-bulbed tube. These products are almost wholly of foreign manufacture, only one English firm having adopted the necessary plant up to the present time (August 1881).

Pure nitrobenzene is a pale yellow liquid, having an odour closely resembling that of the essential oil of bitter-almonds * or benzoic aldehyde, C_7H_6O, but differs from that body in many respects besides chemical composition (see Vol. I. p. 342). Nitrobenzene has a density of 1·186, and boils at a temperature of 212 to 213° C. When cooled below 3° it crystallises in prisms.

Nitrobenzene is nearly insoluble in water, but dissolves in nitric acid, being reprecipitated on dilution. It is readily soluble in alcohol, and is miscible in all proportions with ether, benzene, and oils.

Nitrobenzene is a body of great stability, being unattacked by chlorine or bromine even at its boiling point, unless iodine or antimonic chloride be simultaneously present.

By treatment with sulphuric and the strongest nitric acid, nitrobenzene is converted into a mixture of three isomeric dinitrobenzenes, $C_6H_4(NO_2)_2$.

Nitrobenzene is scarcely affected by aqueous alkalies even when boiling, but is converted by alcoholic potash into a mixture of azobenzene, $(C_6H_5)_2N_2$, and azoxybenzene, $(C_6H_5N)_2O$.

Under the influence of reducing agents, *e.g.*, sulphuretted hydrogen, zinc and hydrochloric acid, or acetic acid and iron filings, nitrobenzene is converted into aniline, $C_6H_5.H_2N$. This reaction affords one of the most delicate and characteristic tests for nitrobenzene. The mode of operating is detailed on page 74.

The following methods of detecting small quantities of nitrobenzene are due to Jacquemin.† A single drop of nitrobenzene dissolved in 20 c.c. of alcohol is stated to suffice for all three tests:—

(*a*) The liquid is treated with zinc and sulphuric acid to reduce the nitrobenzene to aniline. The liquid is treated with excess of sodium carbonate and filtered; to the filtrate one drop of carbolic acid is added, and then some sodium hypochlorite, when a brown coloration, rapidly changing to

* Nitrobenzene is employed extensively as a scenting and flavouring agent under the name of "Essence de Mirbane."

† *Journ. Pharm. Chim.* [4], xxii. 375 and 455; *Journ. Chem. Soc.* xxix. 776.

blue, due to formation of sodium erythrophenate, indicates the presence of nitrobenzene.

(*b*) The liquid is treated with some dioxide of lead. If excess of the oxide be used, a rose tint, changing to brown, is developed, but otherwise the rose colour changes to blue. The reaction is said to be very delicate.

(*c*) A crystal of potassium chlorate is added to the liquid, and a drop of concentrated sulphuric acid allowed to run down the side of the tube, when a violet coloration is produced.

TOXICOLOGICAL DETECTION OF NITROBENZENE.—The symptoms produced by nitrobenzene, when taken either in the liquid or the gaseous state, show that it is an active poison of a peculiarly insidious nature. For the most part its action is that of a powerful narcotic, and as a rule it produces but little local irritation of the stomach or bowels. Its vapour may prove injurious even when largely diluted with air.

The first symptoms are usually headache and drowsiness, followed by flushing of the face, difficult breathing, irregular pulse, dilation of the pupils, more or less loss of voluntary power, and sometimes convulsions. On attempting to walk, the poisoned person will sometimes reel as if drunk, and the breath will smell of nitrobenzene. These symptoms are followed by coma, which may come on slowly, but is more frequently sudden, increasing in intensity till death ensues in five or six hours from the commencement of the symptoms. When the stage of coma is reached there is but little chance of preventing a fatal termination of the case. On the whole, the symptoms of poisoning by nitrobenzene simulate those of apoplexy; but the strong and persistent odour and the intense salivation it is apt to produce sufficiently distinguish it from the latter affection.

The *post-mortem* appearance of the stomach is normal, but the smell of the poison will usually be perceptible, unless death has ensued by inhalation of the vapour. The brain is always congested, and the blood everywhere black and thick, but fluid, the heart being full of dark treacly blood. There is usually well-marked and long-continued rigidity. In cases of delayed death, nitrobenzene may be smelt or found on analysis, owing to its reduction to aniline, which will be met with in

the brain and urine. In many cases a distinct colour will be observed on the skin, at least in some parts.

The poisonous effects of nitrobenzene are identical with those of aniline, and are most probably due to the reduction of the nitrobenzene to that substance in the body.

For the detection of nitrobenzene, the portions of the body to be examined should be reduced to fragments and acidulated with dilute sulphuric acid. The liquid is distilled, and the distillate examined from time to time, with the view of detecting the presence of any unchanged nitrobenzene. Then treat the contents of the retort with rectified spirits and filter. Precipitate the filtrate with excess of basic lead acetate, and again filter. Remove any lead from the liquid by adding a slight excess of sodium sulphate. Evaporate the filtered liquid nearly to dryness, and render the solution alkaline with sodium carbonate. Then agitate with ether to dissolve the aniline, run off the aqueous liquid, and agitate the etherial solution with a little very dilute sulphuric acid. Separate this, which will contain any aniline as sulphate, concentrate by evaporation at a low temperature, and test for aniline by the tests described under "Aniline."

COMMERCIAL NITROBENZOL.—The products obtained on a large scale by the action of nitric acid on commercial benzols (page 77) vary in composition with the character of the benzols employed in their manufacture, but are often exceeding complex, containing simultaneously several isomeric varieties of the different mono- and di-nitro-derivatives of the benzene series of hydrocarbons, which diminish in volatility and fusibility with the number of atoms of carbon or nitryl, NO_2, contained in them. By the action of reducing agents the various nitro-compounds yield aniline and other bases, the constitution of which depends on that of the nitro-compounds from which they are derived. Some of these yield colouring matters materially differing in shade or brilliancy from those given by purer products.

NAPHTHALENE.

Naphthalin. $C_{10}H_8 = C_{10}H_7.H$. Naphthalene is a frequent product of the dry distillation of organic substances. It is

produced largely when various organic vapours are passed through a red-hot tube, and is present most abundantly in products resulting from the employment of an excessive temperature. Thus naphthalene occurs very largely in the tar produced in the distillation of coal for the manufacture of illuminating gas, but is said to be wholly absent from the products of the distillation of bituminous shale, in which it is replaced by paraffin.*

Naphthalene is obtained by sublimation or by the cooling of its boiling saturated solutions, in large white crystalline rhombic plates of silvery lustre, and having a characteristic odour.† Its taste is biting and somewhat aromatic.

Naphthalene melts at 79° C. to a liquid as clear as water, and on cooling forms a brilliant white radiated mass, often filled with cavities. Naphthalene boils at 216 to 220° C., but evaporates copiously with the vapour of boiling water, and volatilises very sensibly even at ordinary temperatures, When inflamed, naphthalene burns with a luminous and very smoky flame.

Naphthalene has a density of 1·15. In a molten state it dissolves sulphur, phosphorus, iodine, indigo, &c.

Naphthalene is insoluble in water, and in alkaline or dilute acid liquids. It dissolves readily in alcohol, wood-spirit, ether, chloroform, carbon disulphide, benzene, petroleum spirit, and fixed and volatile oils. It is also slightly soluble in concentrated acetic acid.

Nitric acid converts naphthalene into nitro-naphthalene, $C_{10}H_7NO_2$, or dinitro-naphthalene, $C_{10}H_6(NO_2)_2$, according to the strength of the acid employed.

Chromic acid and certain other oxidising agents convert

* Berthelot has shown that naphthalene is a constant product of the mutual reaction of benzene, ethylene, and acetylene at a high temperature, the two first reacting to form styrolene, and this product with another molecule of ethylene to generate naphthalene.

$C_6H_6 + C_2H_4 = C_8H_8 + H_2$; and $C_8H_8 + C_2H_4 = C_{10}H_8 + 2H_2$.

Again, by the reaction of benzene and acetylene, $C_6H_6 + 2C_2H_2 = C_{10}H_8 + H_2$; or of styrolene and acetylene, $C_8H_8 + C_2H_2 = C_{10}H_8 + H_2$. As benzene and its homologues are wholly absent from shale products, the simultaneous absence of naphthalene becomes intelligible.

† It is said that absolutely pure naphthalene is free from smell.

naphthalene into naphthal-quinone, $C_{10}H_8O_2$, which by further treatment is converted into phthalic acid (Vol. I. p. 350).

Concentrated sulphuric acid converts naphthalene into sulpho-naphthalic acids, the exact nature of which varies the temperature and proportions of materials employed.

Chlorine and bromine act on naphthalene with formation of various chloro- and bromo-substitution products.

Commercial Naphthalene.—Naphthalene is contained largely in the less volatile portions of coal-tar naphtha, in the crude carbolic acid and "creosote oils" which subsequently distil, and in the semi-fluid "anthracene oils" obtained at a still higher temperature. It is said to be wholly absent from the products of the distillation of bituminous shale. By cooling the portion of the coal-tar distillate which passes over about 200° C., naphthalene is frequently deposited in such quantities as to render the product semi-solid. It may be separated by pressure from the liquid oils, and purified by heating strongly with a *small* proportion of sulphuric acid, washing thoroughly, and subliming the product.

Naphthalene is now prepared commercially in beautiful colourless crystals which wholly distil within a very few degrees of the boiling point of pure naphthalene. Besides this nearly pure product, naphthalene occurs in commerce as an impure coarsely crystalline substance of peculiarly rank odour, technically known as crude naphthalene or "naphthalene salts."

The methods of testing naphthalene salts are of a very simple character, the following being those most commonly employed:—25 grammes weight of the sample is wrapped up in several layers of coarse filter paper, so as to form a flat thin cake. This is placed between two iron plates and strongly pressed in a vice, as long as any oil is expressed. The usual proportion of oil eliminated varies from 6 to 16 and occasionally 20 per cent. of the sample, 13 per cent. is the maximum proportion which should be present.

The "salts" freed from oil in the above-described manner may then be further examined by distilling 10 grammes in a small retort in the manner described on page 84. A good sample of pressed salts should yield 90 per cent. of distillate

before the temperature of the contents of the retort rises above 225° C.

The sublimed naphthalene of commerce contains from 70 to 99 per cent. of the pure substance. The finer qualities form colourless crystals, but the inferior grades have a fawn or brown colour. A useful and reliable test for the purity of sublimed naphthalene consists in warming the substance in a test tube with a little pure concentrated sulphuric acid. With pure naphthalene the solution remains colourless, but a decided pinkish tint is observed if the sample contains 1 per cent. of impurity, and the coloration becomes deeper pink, or even brown, the greater the proportion of foreign matters in the naphthalene.

ANTHRACENE.

Paranaphthalene. $C_{14}H_{10}=C_6H_4''\begin{Bmatrix}CH\\|\\CH\end{Bmatrix}C_6H_4''$. Pure anthracene crystallises in colourless rhomboidal plates, which exhibit a fine violet fluorescence. It melts at 213° C., and distils unchanged at about 360°.*

Anthracene is insoluble in water, and but slightly soluble in alcohol. The following results by Versmann show the solubility of anthracene in various liquids at a temperature of 15° C. :—

Solvent.	Percentage of Anthracene at 15° C.	
	Per 100 c.c. of solution.	Per 100 grammes of solution.
Alcohol, sp. gr. ·800 . . .	·472	·591
,, ,, ·825 . . .	·424	·574
,, ,, ·830 . . .	·408	·491
,, ,, ·835 . . .	·397	·475
,, ,, ·840 . . .	·387	·460
,, ,, ·850 . . .	·360	·423
Ether	·858	1·175
Chloroform	2·587	1·736
Carbon disulphide	1·180	1·478
Glacial acetic acid	·472	·444
Benzene	1·470	1·661
Petroleum spirit	·291	·394

* Nearly pure anthracene may be obtained by melting a partially purified sample in a retort, and passing a strong current of air through it, when the anthracene is carried off and is deposited in brilliant flakes.

Anthracene in admixture with caustic potash may be distilled without change. Perkins states this is the only method by which crude anthracene can be obtained pure on a large scale. If to a solution of anthracence in boiling benzene picric acid be added, ruby-red crystals of picrate of anthracene, $C_{14}H_{10},C_6H_3(NO_2)_3O$, are formed. The compound is decomposed by alcohol or water (see page 105).

By the action of oxidising agents, anthracene is converted into anthraquinone, $C_{14}H_8O_2$ (see page 101). Chromic acid is the best oxidiser for the purpose, as with nitric acid nitro-anthraquinone is apt to be produced. Anthraquinone is a very stable body of considerable importance, as the best method of assaying commercial anthracene is based on its formation, and it is also produced as an intermediate product in one of the processes of manufacturing artificial alizarin.

By the action of bromine or chlorine, anthracene is converted into various bromo- and chloro-derivatives. By treating dibromanthracene, $C_{14}H_8Br_2$, with oxidising agents it is converted into dibromanthraquinone, $C_{14}H_6Br_2O_2$, and this when heated with caustic potash yields dioxyanthraquinone or alizarin, $C_{14}H_6(OH)_2O_2$. Similarly, by treatment with chlorine anthracene is converted into the theoretical weight of dichloranthracene, $C_{14}H_8Cl_2$, a reaction which forms an important step in the manufacture of artificial alizarin.

When a cold saturated solution of anthracene in benzene is exposed to sunlight, an allotropic modification of anthracene crystallises out in microscopic plates. Par-anthracene is but very sparingly soluble. It melts at 244° C., and is reconverted into anthracene. It does not combine with picric acid, and is not attacked by bromine or by concentrated (ordinary) nitric acid, but yields anthraquinone by the action of chromic acid or warm fuming nitric acid. Other analytical reactions of anthracene are described on page 104, *et seq.*

Commercial Anthracene.—Anthracene is now manufactured on a large scale from the last portions which pass over in the distillation of coal-tar. It is contained in notable quantity in coal-tar pitch, and hence the distillation of this product is frequently carried as far as actual coking, in order

to obtain the greatest yield of anthracene. In preparing anthracene the well-known process of tar distilling is carried out as usual, and the last 10 or 15 per cent. of the products of the distillation are set aside, and allowed to stand for some time, when a crystalline deposit of solid hydrocarbons separates. This is freed as much as possible from the adherent oil by filtration, pressure, or other mechanical means, when the residue, more or less dried and more or less impure, is ready for sale. To obtain a superior product, it is desirable to use powerful hydraulic pressure, and to press the crude anthracene, first cold and then hot. It may be further purified by treatment with petroleum spirit boiling between 70° and 90° C., and, after sufficient washing, should then be again submitted to strong pressure. The crude anthracene thus obtained is still extremely impure, containing more or less of the following hydrocarbons:—

Empirical Formula.	Name of Hydrocarbon.	Dissected Formula.	Melting Point ° C.	Boiling Point. ° C.
$C_{10}H_8$	Naphthalene, ...	...	79	218 to 220
$C_{12}H_{10}$	Diphenyl, or Phenyl-benzene .	$C_6H_5.C_6H_5$	70.5	254
	Acetnaphthene	$C_{10}H_6 \begin{cases} CH_2 \\ \vert \\ CH_2 \end{cases}$	95	268
$C_{13}H_{10}$	Fluorene, or Diphenylene-methane	$CH_2 \begin{cases} C_6H_4 \\ \vert \\ C_6H_4 \end{cases}$	113	300 to 305
$C_{14}H_{10}$	Phenanthrene, or Di-ortho-diphenylene-acetylene .	$\begin{cases} C_6H_4.CH \\ \Vert \\ C_6H_4.CH \end{cases}$	96 to 100	340
	Anthracene, or Paranaphthalene	$C_6H_4 \begin{cases} CH \\ \vert \\ CH \end{cases} C_6H_4$	213	360
$C_{15}H_{10}$	Fluoranthene	...	109	...
$C_{16}H_{10}$	Pyrene, or Phenylene-naphthalene	$C_{10}H_6.C_6H_4$	140 to 142	...
$C_{18}H_{18}$	Retene	...	95 to 99	400
$C_{18}H_{12}$	Chrysene	$\begin{cases} C_{10}H_6.CH \\ \Vert \\ C_6H_4.CH \end{cases}$	248 to 250	...

Besides the bodies classified in the foregoing table, others called benzerythrene, synanthrene, pseudo-phenanthrene, and chrysogene are said to be present. In the anthracene derived from cannel coal and bituminous shale, a paraffin is present in considerable quantity, and is one of the most objectionable of impurities (see page 99). Crude commercial anthracene also contains

liquid hydrocarbons of high boiling point, and various nitrogenised bodies, especially acridine, $nC_{12}H_9N$; carbazol, $C_{12}H_9N$; and a body of the formula $C_{16}H_{11}N$ (see page 100).

The recognition and separation of the various constituents of commercial anthracene are attended with great difficulties. Fractional fusion and distillation are processes indicated in the above table, and, in addition to these, other methods have been based on the different action of solvents on the various hydrocarbons, on the properties of their compounds with picric acid, on the oxidation-products yielded on treating them with chromic acid, and on their reaction with the fused chlorides of bismuth and antimony.

The following table, due to G. von Bechi,* shows the behaviour of anthracene and various analogous bodies with solvents. The sign ∞ signifies that the substance dissolves in all proportions:—

	100 parts of Toluene dissolve		100 parts of Absolute Alcohol dissolve	
	At 15° C.	At 100° C.	At 15° C.	At 78° C.
Naphthalene	31·94	∞	5·29	∞
Phenanthrene	33·02	∞	2·62	10·08
Anthracene	·92	12·94	·076	·83
Pyrene	16·54	Very soluble.	1·37	3·08
Chrysene	·24	5·39	·097	·17
Anthraquinone	·19	2·56	·05	2·25
Carbazol	·55	5·46	·92	3·88
Phenylene-naphthylene-imide	Scarcely soluble.	·39 – ·57	Scarcely soluble.	·25

The following data are due to Perkin:†—

	100 parts of Petroleum Spirit boiling between 70° and 100°C. dissolve	100 parts of Coal-tar Naphtha (toluene) boiling between 80° and 100°C. dissolve
Phenanthrene	3·207	21·94
Anthracene	·115	·976
Dichloranthracene	·137	·52
Anthraquinone	·013	·166
Carbazol	·016	·51

* *Ber.* xii. 1976, and *Journ. Chem. Soc.* xxxviii. 258.

† *Journ. Soc. Arts*, xxvii. 598.

A table by Versmann showing the action of various solvents on anthracene itself is given on page 95.

The paraffin referred to as existing in Scotch and north-country anthracenes, greatly reduces the value of the product and even renders some batches wholly unmarketable, has a high melting point, and very limited solubility in either petroleum or coal-tar naphtha. It dissolves in the hot liquids, but is almost entirely deposited on cooling. A small percentage of this paraffin greatly impedes the subsequent treatment of the anthracene, and, being a very stable substance, it passes through most of the processes unchanged. Experience has proved that in the operation of oxidising anthracene on a large scale by treatment with potassium bichromate and dilute sulphuric acid, all other admixtures may be dealt with, and to a great extent removed; but paraffin resists the oxidising action, melts, and retards the operations to a hopeless extent.

This objectionable impurity may be detected and determined in crude anthracene in the following manner:—10 grammes weight of the sample is treated with 200 grammes (=108 c.c.) of strong sulphuric acid. The mixture is heated on a water bath for about ten minutes, or until the anthracene is completely dissolved. Any considerable quantity of paraffin will rise to the surface in the form of oily globules. The solution obtained is cautiously poured into 500 c.c. of water contained in a tall beaker. After being thoroughly stirred the liquid is allowed to cool, when any paraffin will rise to the surface, and having solidified, can be removed, washed with a little cold water, dried between blotting paper, and weighed. From 2 to 5 per cent. is the quantity commonly present in Scotch anthracenes.

NAPHTHALENE may be separated pretty easily, as all the solvents take it up more readily than they do other hydrocarbons. The low melting and boiling point of naphthalene are very marked, and it distils even with vapour of water,*—a fact which may be used for its purification.

Of BENZERYTHRENE very little is known. It is the very

* This circumstance accounts for the occurrence of naphthalene in the pipes used for conveying illuminating gas, in which it sometimes occurs in such considerable quantities as to cause no little inconvenience.

last product obtained in the distillation of pitch, and may thus be separated without difficulty. After nearly all the other bodies have passed over, the benzerythrene appears as a bright-red powdery vapour. It has a resinous character, and assumes a dull brown colour on exposure to light.

ACRIDINE, $nC_{12}H_9N$, is a peculiar organic base of great stability. It crystallises in brownish yellow, four-sided, rectangular prisms, and is remarkable for its intensely irritating effect on the skin and mucous membrane. Violent sneezing and coughing are produced on inhaling the smallest particle of the dust or vapour.

CARBAZOL, $C_{12}H_9N$, forms beautiful crystals which resemble anthracene. It often exists in crude washed anthracene to the extent of 10 or 12 per cent. It may be separated by fusing the substance with caustic potash (not soda), when a compound of potash and carbazol is formed which separates from the lighter anthracene. When heated with mercuric chloride, or other oxidising agents, carbazol yields a blue colouring matter.

A derivative of carbazol, containing $C_{16}H_{11}N$, has been isolated from crude anthracene. It crystallises in greenish or golden-yellow metallic-looking plates, which melt when pure at 330° C. It is soluble with difficulty in naphtha of high boiling point. Both in the solid state and when dissolved in benzene it is remarkable for its superb greenish fluorescence and banded fluorescent spectrum, and for its broad and well-defined absorption-bands, two situated between the F and G lines, and another slightly more refrangible than G.* This substance, which has the constitution of phenylene-naphthylene-imide is not improbably identical with chrysogene, and appears to be that to which the yellow colour of impure chrysene is due.

A very valuable mode of differentiating the solid hydrocarbons of coal-tar, and of determining the proportion of real anthracene in the commercial product, is based on the reaction

* This description of the position of the absorption-bands applies to the solution in benzene. When the substance is examined in the solid state the bands are nearer to the red end of the spectrum. (See *Chem. News*, xxvi. 199, and xxxi. 35, 45.)

which occurs when the sample is heated with a solution of chromic acid in glacial acetic acid. The mode of applying the reaction to the assay of commercial anthracene is described on page 109, but the following is an epitomised account of the products obtained from the different hydrocarbons on treatment with the chromic acid mixture.

Naphthalene is converted into naphthaquinone, $C_{10}H_8O_2$, and ultimately into phthalic acid, $C_8H_6O_2$, which is readily soluble in alkali.

Acetnaphthene is oxidised to naphthalic acid, $C_{12}H_8O_4$, while diphenyl yields benzoic acid, $C_7H_6O_2$.

Fluorene is oxidised to diphenylene-ketone, $C_{13}H_8O$, volatile in a current of steam, and deposited in crystals from its solution in alcohol.

Phenanthrene is transformed by the chromic acid mixture into phenanthraquinone, $C_{14}H_8O_2$, and this is ultimately converted into diphenic acid, which is susceptible of still further oxidation and is also soluble in alkaline liquids. Phenanthraquinone crystallises in dark orange-yellow prisms, melting at 198° C. It is sparingly soluble in hot water, but dissolves freely in benzene or acetic acid. Ignited with soda-lime it yields diphenyl $(C_6H_5)_2$, in almost the theoretical proportion, whereas anthraquinone gives benzene when similarly treated. The two bodies also differ in their behaviour with the acid sulphites of the alkali-metals, with which anthraquinone does not combine. Phenanthraquinone, when warmed with sodium-hydrogen sulphite is dissolved, and may be re-precipitated by mixing the filtered solution with hydrochloric acid. This reaction may be used for the detection of phenanthrene. The hydrocarbon is oxidised by warm chromic acid mixture, the oxidation-product treated with alkali, and then warmed with the sulphite solution. Pyrene-quinone gives a similar reaction.

ANTHRAQUINONE, $C_{14}H_8O_2$, is the product obtained by acting on anthracene by the chromic acid mixture. It is an exceedingly stable body, resisting further action to a remarkable degree. Anthraquinone melts when pure at 277°, and sublimes in yellow needles or prisms. Its boiling point is above that of mercury but below that of sulphur.

Anthraquinone is neutral in reaction, insoluble in water and in dilute acid and alkaline liquids. It is sparingly soluble in alcohol and ether; more soluble in hot benzene. Anthraquinone is not affected by hot hydrochloric acid or by boiling with solution of caustic potash or milk of lime. It dissolves in hot nitric acid of 1·4 specific gravity, and is deposited in crystals on cooling, a more complete separation occurring when the acid is diluted. In concentrated sulphuric acid anthraquinone dissolves unchanged, and on exposing the solution to a moist atmosphere is gradually re-deposited in crystals, or may be obtained in a more finely-divided state by pouring the acid into water. Solution in sulphuric acid is employed for purifying commercial anthraquinone. When strongly heated with concentrated sulphuric acid, or more easily if fuming acid be used, anthraquinone is converted into a mixture of mono- and di-sulphanthraquinonic acids. These bodies are also obtained by the action of sulphuric acid on dichloranthracene, $C_{14}H_8Cl_2$, and play an important part in the manufacture of artificial alizarin. The proportion of the two sulpho-acids formed depends on that of the sulphuric acid employed. On nearly neutralising the product with caustic soda, sparingly soluble sodium monosulphoanthraquinonate separates, and may be obtained in brilliant pearly scales by pressure and recrystallisation. Heated with caustic soda and potassium chlorate it yields pure alizarin. When fused with caustic potash, anthraquinone yields potassium benzoate ($C_{14}H_8O_2+2KHO=2KC_7H_5O_2$), and when ignited with or distilled over soda-lime benzene, C_6H_6, results. By the action of certain reducing agents, such as sodium amalgam, or caustic soda solution and zinc dust, anthraquinone is reduced to hydro-anthraquinone, $C_{14}H_{10}O_2$. This reaction affords an extremely delicate means of detecting anthraquinone, and hence anthracene. A few particles should be placed in a test tube with some sodium amalgam, covered with ether free from water and alcohol, and the whole well shaken together. On adding a drop of water a splendid red colour appears, but is destroyed by shaking on contact with air, reappearing on standing. If absolute al-

cohol be substituted for the ether, the colour is dark green, turned to red by a trace of water, and destroyed by shaking with air.*

Fluoranthene is converted by the chromic acid mixture into fluoranthene-quinone, $C_{15}H_8O_2$, and an acid soluble in alkaline liquids.

Pyrene yields pyrene-quinone, $C_{16}H_8O_2$, and finally, with some difficulty, products soluble in alkali.

Retene forms dioxyretistene, $C_{16}H_{14}O_2$, and other products. Dioxyretistene is a brick-red powder, crystallising from alcohol in orange-yellow needles. It is insoluble in soda, and can be further oxidised only with great difficulty.

Chrysene yields chrysoquinone, $C_{18}H_{10}O_2$, and is afterwards converted, with some difficulty, into phthalic acid, which is readily soluble in alkali.

Benzerythrene yields soluble products under the chromic acid treatment.

Chrysogene, said to exist in considerable quantity in certain kinds of anthracene (see page 100), is alleged to be completely and readily converted into soluble products by the chromic acid mixture. This is doubtful, for,—

The phenylene-naphthylene-imide described on page 100, yields a quinone of the formula, $C_{16}H_9N_2O_2$, which forms reddish yellow needles and obstinately resists further oxidation. It appears always to be produced by the oxidation of anthracenes which give banded absorption spectra of the nature described on page 100, and leads to excessive estimates of the yield of real anthracene. The quinone, $C_{16}H_9N_2O_2$, is destroyed by prolonged treatment with sulphuric acid at 100° C.

A dark green hydrocarbon, fusing at 271° C., is occasionally present in anthracene. It is soluble with difficulty in glacial acetic acid, and should, if present, be separated as far as possible by this solvent before employing the chromic acid mixture, as its oxidation is very difficult to effect.

The paraffin, the presence of which is referred to on page 99, is practically unaltered by treatment with the chromic acid mixture.

* *A. Claus. Deut. Chem. Ges. Ber.* x. 925.

Watson Smith* has recently proposed to employ the fused chlorides of antimony and bismuth for the discrimination of solid hydrocarbons. The test is made in the following manner:—A small quantity of the crystallised choride is placed in a small porcelain crucible and melted, and then further heated over a small flame. A small particle of the hydrocarbon to be tested is next placed on the side of the crucible, which is then so inclined that the melted chloride comes in contact with it. Fusion follows, accompanied in many cases by a coloration. On restoring the crucible to a vertical position, the coloured spot elongates and forms a coloured streak. Tested in this way the hydrocarbons give the following reactions:—

	With Antimony trichloride.	With Bismuth trichloride.
Naphthalene, pure .	No coloration. During cooling, characteristic rhombic tables form in the fused chloride.	No coloration. During cooling, yellow, transparent needles separate.
Naphthalene, impure	More or less carmine coloration.	More or less orange coloration.
Diphenyl . .	No coloration.	No reaction.
Phenanthrene . .	Difficulty soluble Faint greenish coloration.	Brown or greenish brown.
Anthracene . .	Traces even give a yellowish green colour. Colourless needles formed during cooling.	Purple-black coloration; very characteristic.
Dinaphthyls . .	No coloration.	No reaction.
Pyrene . . .	Same as phenanthrene.	. .
Chrysene . . .	Traces even produce golden yellow colour.	...
Stilbene, $C_{14}H_{12}$.	At 40° C., smallest trace gives orange colour, destroyed at higher temperature.	...
β Phenyl-naphthalene	No reaction.	...
Triphenyl-methane .	No reaction. Greenish colour with excess.	...

Anthracene and many other hydrocarbons form characteristic crystalline compounds with picric acid, having the general formula, $X,C_6H_3(NO_2)_3O$, in which X represents an atom of the hydrocarbon. In some cases the reaction with

* *Chem. News*, xl. 26.

picric acid affords a valuable means of recognising the hydrocarbon. The "picrates" of the hydrocarbons are usually decomposed by water or alkaline solutions, and in some cases even by alcohol. To produce them, a saturated solution of the hydrocarbon in hot benzene should be mixed with an approximately equivalent quantity of picric acid also dissolved to saturation in hot benzene, and the mixed solution then allowed to cool. In other cases alcohol may be substituted for the benzene, and for the detection of naphthalene cold alcoholic solutions should be employed. The following is a description of the compounds of picric acid with the more important solid hydrocarbons:—

Naphthalene. The only solid hydrocarbon (except pyrene) giving a precipitate when its cold alcoholic solution is mixed with a cold alcoholic solution of picric acid. Picrate forms stellate groups of yellow needles, melting at 149° C.

Diphenyl. Forms no definite crystalline picrate.

Acetnaphthene. Picrate forms orange-yellow needles on cooling the boiling alcoholic solution.

Fluorene. Compound crystallises from benzene in slender red needles, melting at 81°.

Phenanthrene. Compound crystallises from benzene in yellow needles, melting at 145°, and not decomposed by alcohol.

Anthracene. Picrate deposited from solution in hot benzene in ruby-red crystals, very soluble with red colour in a little alcohol, the solution being decolorised and compound decomposed on adding more alcohol.

Fluoranthene. Compound forms reddish yellow needles, melting at 182°, difficultly soluble in cold alcohol, and decomposed by boiling with water.

Pyrene. Compound deposited from hot alcohol as a red crystalline precipitate or long dark red needles, nearly insoluble in cold alcohol, but very soluble in benzene.

Retene. Orange-yellow needles, readily soluble in alcohol.

Chrysene. Compound crystallises from benzene in orange needles, decomposed by cold alcohol.

Benzerythrene. Deposited from very concentrated hot alcoholic solutions in brownish yellow flocks.

It will be seen that the identification and separation of the various constituents of anthracene are attended with great difficulty. The difference in the action of alcohol, ether, carbon disulphide, benzene, petroleum spirit, and other solvents on the hydrocarbons of anthracene is only a question of degree.* Nitric acid and sulphuric acid, chlorine and bromine, produce similar compounds of addition or substitution. The compounds with picric acid are in some cases characteristic, but they are so little stable that even an excess of solvent—alcohol, for instance—causes the decomposition of some of them. On oxidation, the hydrocarbons form similar or identical products, though that from anthracene is remarkable for its stability and resistance to solvents (see page 102).

Assay of Commercial Anthracene.† The valuation of crude anthracene has now become an important laboratory operation. Crude anthracene contains from about 15 to 36 per cent. of real anthracene, and in other respects varies extremely in composition and character. It cannot be too strongly insisted on that the true value of a sample of commercial anthracene is dependent not merely on the proportion

* The liquid oil itself is the best solvent for all the hydrocarbons, including anthracene; and hence, when a sample containing much liquid oil is treated with a solvent, the combined action of the oil and the solvent removes considerably more anthracene than the solvent alone. This is one of the causes of the discrepancies in anthracene assays made by alcohol or carbon disulphide, a soft sample containing much oil always showing a lower percentage of anthracene than the same sample previously pressed and separated from the oil.

† The literature of anthracene assaying has reached very considerable dimensions. The following contributions to English journals have been consulted in the compilation of the text, besides certain foreign memoirs:—E. Lück, *Journ. Chem. Soc.* xxvii. 291; Paul and Cownley, *Chem. News*, xxviii. 175; T. H. Davis, *Chem. News*, xxix. 169; R. Lucas, *Chem. News*, xxx. 190; F. Versmann, *Journ. Soc. Arts*, xxii. 414; H. Morton, *Chem. News*, xxvi. 199, xxxi. 35, 46; G. E. and T. H. Davis, *Chem. News*, xxxi. 177, 190, 209; J. T. Brown, *Chem. News*, xxxiv. 136; Meister, Lucius, and Brüning, *Chem. News*, xxxiv. 167; F. Versmann, *Chem. News*, xxxiv. 177, 191, 201, 227; C. Caspers, *Chem. News*, xxxiv. 211; R. Lucas, *Chem. News*, xxxiv. 267; J. Bennett Bros, *Chem. News*, xxxiv. 279; B. Nickels, *Chem. News*, xl. 270, xli. 52, 95, 117.

of real anthracene contained in it, but also on its comparative freedom from objectionable impurities.

An examination for paraffin in the manner described on page 99 should never be omitted, unless it is known to a certainty that bituminous shale or cannel coal has had no share in the production of the sample.

According to Nickels, samples of crude anthracene, containing the body, $C_{16}H_{11}N$ (see page 100), give a highly characteristic absorption spectrum, showing two broad and well-defined black bands between the F and G lines, and another slightly more refrangible than G. Samples showing these bands are purified with some difficulty, and yield by oxidation an impure anthraquinone containing many amorphous particles. For observing the spectrum of the sample, a few grains should be dissolved in 6 c.c. of warm benzene, the liquid passed through a dry filter, and observed with a spectroscope. A micro-spectroscope may be employed, or, in its absence, a direct-vision pocket spectroscope will suffice.* The intensity of the absorption-bands is a measure of the objectionable impurities of the sample.

For the *quantitative* assay of commercial anthracene three processes based upon the behaviour of real anthracene and the associated impurities with solvents have been employed. In one of these alcohol was employed; in the second, carbon disulphide; and in the third the sample was subjected to successive treatment with petroleum spirit and carbon disulphide. The method of performing the first two of the above tests need not be given in detail, as both processes are now almost entirely obsolete. The following tabulated statement, by G. E. and F. H. Davis, gives a fair indication of the extent and direction of the errors of the alcohol and disulphide processes, as applied to commercial anthracenes of various degrees of purity. The figures in the column showing the results by the anthraquinone test may be regarded as being practically the *true* percentages of anthracene in the samples operated upon.

* Specimens of hydrocarbons for comparison can be obtained from J. Browning, Strand, W.C.

No.	Percentage of Anthracene.		
	By Alcohol Test.	By CS_2 Test.	By Anthraquinone Test.
1.	37·78	26·37	27·81
2.	56·12	42·20	34·88
3.	43·00	33·46	28·20
4.	36·45	22·00	23·30
5.	37·34	23·50	24·00
6.	36·73	23·30	23·95
7.	35·62	19·90	22·50
8.	38·74	25·90	24·95
9.	39·15	29·40	26·20
10.	52·80	40·50	32·94
11.	73·00	56·60	39·44
12.	71·45	56·40	39·02

The principle of the alcohol and disulphide tests is so far the same that advantage is taken of the greater solubility of the impurities than of anthracene itself. On treating the same sample by both methods alcohol always yields a higher percentage of residue with a low melting point, while carbon disulphide gives a lower percentage of residue of high melting point. There was no fixed relation between the two results, while the residues themselves varied greatly in composition; hence the tests are now seldom, if ever, used.

A far better solution-test is Perkin's "Petroleum and Bisulphide test." 50 grammes of the ground and carefully-mixed sample are further reduced in a capacious mortar, and treated therein with 8 fluid ounces of light petroleum spirit at the ordinary temperature. The whole is thoroughly blended by rapid grinding, and any fragments of wood, cork, &c. removed. The liquid is then filtered through a piece of fine cotton-sheeting about ten inches square, and the residue washed with 4 ounces more of light petroleum spirit. When drained the filter is removed, opened out perfectly flat, and the contents carefully wrapped up in it. The cloth is then placed between two iron plates and subjected to *heavy pressure* in a vice, till the residual oil is wholly expressed. The cloth is then removed, and its contents transferred to a dry mortar, finely pulverised, and transferred to a 6-ounce stoppered

bottle with a square shoulder. 5 fluid ounces of carbon disulphide, at a temperature of 15° C., are then added, the stopper inserted, and the mixture frequently shaken during ten minutes. The contents of the bottle are then carefully transferred to a tared filter, any grit, sand, or similar foreign matter being retained in the shoulder of the test-bottle. The filtration of the disulphide solution must be effected as rapidly as possible, and the funnel must be covered by a ground glass-plate. When drained remove the filter quickly, and fold in the upper sides and top so as to secure its contents; wrap in an outer paper, and this again in a cotton cloth. Then rapidly press the whole in a vice as before, until the fluid contents are completely expressed. Finally, dry the residue at 100° C. till constant in weight, and weigh. The product so obtained should melt between 195° and 212° C.

ANTHRAQUINONE TEST.—The most satisfactory mode of assaying crude anthracene is based on the fact that, while anthracene itself is converted by the action of chromic acid into a characteristic insoluble body not liable to further change, nearly all the associated hydrocarbons are completely oxidised, or else are converted into products readily removed by treatment with water or dilute alkali. This method of assay was first proposed by E. Lück, and affords a very satisfactory solution of a most difficult problem.

The details of the mode of performing Lück's anthraquinone test for anthracene have undergone several modifications, as experience of the sources of error has become greater. The following process is essentially that of Meister, Lucius, and Brüning, with some precautions and modifications recommended by Messrs G. E. & T. H. Davis, who verified the accuracy of the method by operating on pure anthracene and impure samples of known composition :*—

1 gramme of the carefully sampled specimen is placed in a flask holding 400 to 500 c.c. 45 c.c. of the very strongest glacial acetic acid is then added, and an inverted condenser or long glass tube adapted to the flask. The liquid is then

* This test is commercially known as "Meister, Lucius, and Brüning's Anthraquinone test, with Appendix."

brought to the boiling point, and, while boiling, the chromic acid is added to it gradually, drop by drop, by means of a tapped pipette passing through the india-rubber stopper of the flask, or adapted to the top of the vertical condenser. The chromic acid mixture is prepared by dissolving 15 grammes of crystallised chromic anhydride (perfectly free from lead salts, and insoluble matter generally) in 10 c.c. of water and 10 of glacial acetic acid. The addition of the oxidising agent should occupy two hours, and the contents of the flask should be kept in continued ebullition for two hours longer, four hours in all being necessary to ensure complete conversion of the impurities. The flask is then left at rest for twelve hours, when the contents should be diluted with 400 c.c. of cold water,* and allowed to rest another three hours. The precipitated anthraquinone is then filtered and well washed with water. It is next washed on the filter with hot dilute caustic soda of 1·04 specific gravity, and again thoroughly washed with water. The anthraquinone is then rinsed through the pierced filter into a small dish by means of a jet of water, and the water is evaporated off and the residue dried at 100° C. An alternative method is to dry the anthraquinone on the filter, and then carefully remove it with a knife. This plan is apt to involve a loss, varying from 4 to 8 milligrammes, through incomplete removal of the substance.

Fig. 3.

* The use of this large proportion of water ensures the complete precipitation of the anthraquinone, and renders it necessary to make a correction of 10 milligrammes for its solubility in the acetic solution, as was formerly done. Versmann contends, however (*Chem. News*, xxxiv. 188), that the use of so large a quantity of water merely causes the precipitation of impurities, and that there is no evidence of anthraquinone being soluble in the more concentrated liquid. He prefers to filter the undiluted liquid to the last drop, wash the anthraquinone with boiling water, and make up the filtrate and washings to 600 c.c., when a pulverulent precipitate is obtained, which is treated separately from the crystallised anthraquinone deposited by the undiluted liquid. After purification by alkali and permanganate the crystals and powder are dried at 100° and weighed separately, and the melting and solidifying points of the latter observed. It is considered as consisting of valueless impurities or of real anthraquinone, according to the result of these observations. Versmann's modified test gives lower results than that usually employed, and has been severely criticised by R. Lucas (*Chem. News*, xxxiv. 267).

To avoid this the stained portion of the filter should be cut small and heated in a test tube with about 1 c.c. of benzene. The resultant solution is poured off into a small dish, and the residue obtained by its evaporation added to the main quantity of anthraquinone. Either of the foregoing methods of treatment is preferable to weighing the anthraquinone on the filter, which is apt to be altered in weight by the reagents employed, though this source of error may be to a great extent avoided by using a double filter, the apex of the outer one being cut off. The weights of the two filters are accurately adjusted before use by trimming with a pair of scissors, and on weighing the anthraquinone the outer filter is used as a counterpoise to the inner.

The weight of anthraquinone thus obtained ought not to be regarded as representing that of the pure product, as it usually contains extraneous matters, such as sand, and very frequently more or less oxide of chromium. Some anthracenes yield anthraquinones which carry down much Cr_2O_3 in combination. Hence the anthraquinone obtained should be ignited in platinum and the resultant ash deducted from the weight previously found. This corrected weight multiplied by the factor 0·856 gives the real anthracene in the 1 gramme of the sample employed.

Several methods have been proposed for the further purification of the anthraquinone obtained, the details of which are as follows:—

Meister, Lucius, and Brüning * mix the product, in the dish in which it was weighed, with ten times its weight of fuming sulphuric acid of 1·88 specific gravity, and heat the whole to 100° C. for ten minutes. The solution obtained is poured into a flat dish and left in a damp place for twelve hours to absorb water. 200 c.c. of cold water are then added, the precipitated anthraquinone collected on a filter, and washed first with pure water, then with dilute soda solution, and finally again with water, after which it is dried at 100°, and weighed. After weighing, the anthraquinone is volatilised by

* *Chem. News*, xxxiv. 167. The authors ultimately adopted the treatment with sulphuric acid, described in the text, in preference to one with potassium permanganate formerly recommended by them (see note to page 110).

gradually heating the dish on a sand-bath, and any residue is deducted from the weight found before calculating it to anthracene.

R. Lucas proposes to supplement the sulphuric acid treatment, of which he expresses a high opinion, by re-treating the product with the chromic acid mixture exactly like the original sample of anthracene, subsequently adding water, and washing with water and dilute alkali, as already described. After drying and weighing the purified product, he ignites it and deducts any ash from the gross weight.*

The anthraquinone obtained should be crystallised, and of a uniform pale-yellow colour. Certain strange quinones are apt to be present in some cases, and are recognisable by the modified form of the crystals and the colour of the product. Phenanthraquinone is orange, and chrysene-quinone deep red. Complete treatment with the chromic acid mixture removes all these bodies, but does not affect the quinone, $C_{16}H_9NO_2$, produced by the oxidation of the body of the formula $C_{16}H_{11}N$, referred to on pages 100 and 107 as giving a characteristic absorption-spectrum. This quinone, unlike those from phenanthrene, chrysene, &c., tends to prevent the crystallisation of the anthraquinone, and is the source of the so-called "amorphous particles," which are frequently present in sufficient quantity to obliterate all trace of crystallisation in the oxidised product. This troublesome impurity may, however, be destroyed by heating with sulphuric acid in the manner recommended by Meister, Lucius, and Brüning (see page 111), and hence this supplementary treatment should never be omitted in the case of samples which originally yielded absorption-bands, or which have produced crude anthraquinones of unhealthy appearance.

In the anthraquinone test described in the foregoing pages, which is the one commonly employed for assaying anthracene, a very large excess of the chromic acid mixture is employed, the object being to convert all the hydrocarbons except anthracene itself into oxidation-products soluble in water or in alkaline solutions. In some alizarin works a modified process is employed, in which the aim is to work as closely as possible

* *Chem. News*, xxxiv. 267.

by the method of oxidation pursued on a manufacturing scale. With this view, the oxidation is carried out in very dilute liquids, under which conditions the anthracene is converted into anthraquinone, while the foreign hydrocarbons suffer but little change. On subsequently treating the product with sulphuric acid, the unoxidised hydrocarbons are converted into soluble substances, and a nearly pure anthraquinone results, which may be obtained perfectly pure by a second treatment with acid. In experienced hands and with careful manipulation, this miniature factory-operation gives constant and very accurate results. The chief source of error is incomplete conversion of the anthracene itself, and its consequent solution and loss on treating the crude anthraquinone with sulphuric acid, but this can be guarded against by a microscopic examination of the oxidation-product. The following are the details of the process:*—10 grammes of the sample of anthracene are ground to an impalpable powder in a mortar; 20 grammes of potassium bichromate are added, and the whole thoroughly mixed by grinding. The mixture is transferred to a large porcelain dish, 1 litre of water added, and the liquid brought to the boil. 30 grammes of sulphuric acid are diluted with about an equal measure of water, and added in successive small portions during about one hour, the liquid being kept constantly boiling and frequently stirred. The boiling is continued for three hours after the whole of the acid has been added, care being taken to replace the loss by evaporation by adding boiling water, as it is only in such dilute solutions that the anthracene can be converted into anthraquinone without simultaneously oxidising the accompanying substances. The liquid is next filtered, and the filter washed with hot water till all traces of chromium salts have been removed. The contents of the filter are then dried at 100° and weighed. The weight obtained represents the yield of "crude factory anthraquinone," and may contain from 40 to 50 per cent. of the pure substance. Before purifying this crude product a minute quantity of it should be dissolved in hot benzene, and a drop of the solution placed on a glass slide. After allowing the dissolved matters to crystallise, a glass cover is applied,

* Communicated by Mr B. Nickels.

and the slide observed under the microscope. Unoxidised anthracene, if present, assumes the form of sharp, tabular, overlaying plates; while the anthraquinone will be in the form of distinct needles and stellated groups. Naphthalene is the only associated hydrocarbon which at all simulates anthracene, but with a little care it is readily distinguished. The other bodies liable to be present assume more or less characteristic forms, which cannot be confounded with anthracene. Examined with the polariscope, the appearances of anthracene and anthraquinone are extremely characteristic. If no unoxidised anthracene be detected under the microscope, the purification of the crude anthraquinone is proceeded with as follows:*—

The crude anthraquinone is next treated in a small, shallow dish with four times its weight of strong sulphuric acid, and the mixture is heated in the water-oven for about one and a half hours, being frequently stirred during that time. The capsule is then placed in a box or under a bell-jar, side by side with a larger dish of boiling water, so as to maintain a damp atmosphere, which causes the gradual dilution of the acid and facilitates the crystallisation of the anthraquinone. After twelve hours the capsule is removed and immersed in about 500 c.c. of water, which is then boiled. After cooling, the liquid is filtered, the residue washed till free from acid, and then treated on the filter with a dilute boiling solution of caustic soda (sp. gr. 1·04) till the filtrate runs through colourless. The alkali is then washed out with warm water, and the substance on the filter dried at 100° C., and weighed. The product has a greenish grey or slate-grey colour, is highly crystalline, and contains from 80 to 95 per cent. of real anthraquinone. A known weight of it (about 1 gramme) is further purified by heating it in the water-oven for ten minutes with ten times its weight of strong sulphuric acid. The product is exposed to a damp atmosphere, dissolved in water, filtered, treated with alkali, &c., and weighed in a manner exactly similar to that previously adopted. The precautions

* If any notable quantity of the anthraquinone has been dissolved in benzene for microscopic examination, it must either be recovered by evaporating off the solvent, or due allowance must be made in the subsequent calculations.

on page 110 respecting the treatment of the anthraquinone on the filter should be observed here. The weight of pure anthraquinone obtained is calculated first on the grey product and this on the original sample, or intermediately on the crude anthraquinone, if some of the latter was not recovered from the benzene solution used for its microscopic examination. The pure anthraquinone found, multiplied by ·856, gives the real anthracene in the sample.

For the determination of anthracene in coal-tar, Carl Nicol* distils 20 grammes in a small luted retort, and the vapours are received in a U-tube, kept at 200° C. by being immersed in a bath of hot paraffin. The more volatile products are not condensed, but the anthracene and other hydrocarbons of high boiling point collect in the U-tube. Care must be taken to prevent bumping, and the condensation of the distillate on the neck and sides of the retort. When the contents of the retort become coked, the process is stopped and the neck is cut off, pounded, and the powder added to the distillate. The whole is then dissolved in glacial acetic acid, and subjected to oxidation with the chromic acid mixture, in the manner already described.

* *Zeitschr. Anal. Chem.* xiv. 318, and *Jour. Chem. Soc.* xxx. 553.

FIXED OILS AND FATS.

UNDER the names of fixed oils, fatty oils, fats, and waxes, are classed a number of analogous bodies occurring naturally in animals and vegetables. When of definite chemical composition, they are also producible by synthetical methods.

The term fixed or fatty oil is generally used for such members of the group as remain liquid at ordinary temperatures, but beyond the physical character of ready fusibility there is no absolute distinction between the liquid and the solid fixed oils or fats. The liquid fats, however, contain a relatively large proportion of olein or other glycerides of readily-fusible fatty acids.

The waxes possess certain well-defined physical characters and exhibit differences in chemical composition which distinguish them pretty sharply from the true solid fats. They are, however, in many respects closely related to the fats, and hence are conveniently described in the same division.

The following are the general properties characterising the true fats and fixed oils:—

1. The specific gravity is less than that of water, varying between the limits of ·875 and ·964, at 15° C.

2. The fusing or melting points of the fixed oils vary within wide limits, and are liable to modification in an obscure manner by certain treatment.

3. The fixed oils and fats are practically insoluble in water, but they dissolve somewhat in absolute alcohol or strong spirit, especially when hot, and are readily soluble in ether, chloroform, carbon disulphide, benzene, petroleum spirit (see "Castor Oil"), turpentine and other volatile oils. The various fixed oils and fats are also readily miscible with each other.

4. The fixed oils and fats are not fluorescent, and have no rotatory action on a ray of polarised light.

5. When pure, the fixed oils are usually colourless or of a pale yellow colour. Impure and commercial oils vary in colour from light yellow to red, and even brown and black. Many vegetable oils have a distinct shade of green from the presence of chlorophyll, and show banded absorption-spectra, which is never the case with oils of animal origin.

6. The smell and taste of the fixed oils are often peculiar and characteristic of their origin. As these characters become less perceptible the more completely the oil is purified, they are probably due to the presence of certain associated and difficultly removeable foreign matters, rather than to the constituents of the true oil.

7. The fixed oils and fats are composed of carbon, hydrogen, and oxygen; any nitrogen or sulphur existing in particular specimens is due to the presence of albuminous or other foreign matters. The chemical constitution of the fatty oils is discussed in a separate section (see page 118).

8. The fixed oils and fats, as their name denotes, are not capable of being distilled without decomposition. When heated alone they darken and evolve acrid and offensive vapours; and when further heated to about 315° C. (= 600° F.) carbonic acid is evolved, together with peculiarly irritating vapours of acrolein, C_3H_4O, various volatile organic acids, and gaseous, liquid, and solid hydrocarbons. The temperature at which these decompositions occur has been improperly called the "boiling point" of the oil, the phenomenon of apparent ebullition being really due to the escape of the gases formed by the decomposition. When caused to pass slowly through a red-hot tube the fixed oils are almost wholly decomposed into volatile products, consisting of carbonic oxide, hydrocarbons, &c.

9. On distillation with superheated steam, fatty oils suffer a simpler decomposition, with formation of glycerol and fatty acids. This change may also be effected by acting on the oil with sulphuric acid or a strong base. The reaction is known as "saponification" (see page 119).

10. If air be excluded the fixed oils may be preserved un-

changed for a lengthened period, but, on exposure to air many of them thicken with absorption of oxygen, and are ultimately converted (if exposed in sufficiently thin layers) into a yellowish, transparent membrane or varnish.* Such oils (*e.g.*, linseed, walnut, hemp-seed, and poppy-seed oils) are called drying oils (see page 131).

11. The non-drying oils behave in a different manner on exposure to air. When absolutely free from foreign matter most of them remain unchanged, but commercial specimens gradually turn *rancid*, that is, they gradually lose their colour (and to a certain extent their fluidity), and acquire an acrid disagreeable taste and acid reaction to litmus paper. This alteration is due to the presence of certain foreign matters, such as the cellular substance of the animal or plant from which the oil was extracted. These bodies act as ferments, and set free fatty acids, besides producing small quantities of certain volatile acids (*e.g.* butyric, valeric, caproic) of strong odour. By agitating such rancid oil with hot water, and subsequently treating it with a cold and dilute solution of sodium carbonate, the products of decomposition may be removed and the fat restored to its original state.

CONSTITUTION OF FATTY OILS AND WAXES.

In chemical constitution all fixed oils and waxes of animal and vegetable origin consist of ethers of the higher fatty acids. (See table on pages 218 and 219.) The alcohol-radical with which the fatty-acid-radical is associated to form the natural fixed oils is the triad radical glycyl, C_3H_5. Thus the fixed oils are the glycyl ethers or glycerides, and have a constitution expressed by the formula:—

$$\left.\begin{matrix}(C_3H_5)''' \\ \overline{F}_3\end{matrix}\right\} O_3.$$

In this formula $\overline{F}$ represents the radical of one of the fatty acids, and may have the general formula, $C_nH_{2n-1}O$, as the radical of stearic acid, $C_{18}H_{35}O.OH$; $C_nH_{2n-3}O$, as the

* Under certain conditions, as when cotton-waste, shoddy, or hemp is moistened with oil and exposed to the air, the oxidation of the oil becomes so energetic as to lead to considerable elevation of temperature, and even actual inflammation.

radical of oleic acid; $C_nH_{2n-5}O$, as the radical of linoleic acid; or $C_nH_{2n-3}O_2$, as the radical of ricinoleic acid. Thus, glycyl tristearate, which has the composition—

$$\left.\begin{matrix}(C_3H_5)'''\\(C_{18}H_{35}O)_3\end{matrix}\right\}O_3=C_{57}H_{110}O_3;$$

is also called tristearin, or simply stearin, and is the chief constituent of mutton-fat. Similarly, triolein is the principal component of almond and olive oils, and tripalmitin of palm oil; while the glycerides or glycyl ethers of linoleic and ricinoleic acids respectively constitute the chief parts of linseed and castor oils. Olein and linolein being liquid fats are found most largely in the fluid oils, while stearin and palmitin constitute the major portion of solid fats.

As far as is at present known, all natural glycerides contain three atoms of acid-radical, but glycyl monostearate or monostearin, glycyl distearate or distearin, and similar ethers, can be obtained artificially by heating glycerol under pressure with the requisite proportion of the fatty acid. Although these bodies do not appear to exist naturally, experiments by Mr J. Bell render it probable that in butter-fat the same molecule of glyceride contains the radicals of several different fatty acids. (See "Fatty Acids of Butter.")

While the various vegetable and animal fixed *oils* and *fats* appear to consist, almost without exception, of glycerides or glycyl ethers, the *waxes* are the ethers of higher alcohols of the ethylic series. Thus, spermaceti consists chiefly of cetyl palmitate, $C_{16}H_{33}.O.C_{16}H_{31}O.$, whilst Chinese wax, carnaüba wax, and bees'-wax contain still higher monatomic alcohols. The experiments of the author show that sperm oil has a constitution similar to that of the waxes (see page 199).

Saponification.—When fatty oils are distilled with superheated steam they react with the elements of water, and are decomposed into fatty acids and glycyl alcohol, glycerol, or glycerin, according to the equation—

$$\left.\begin{matrix}(C_3H_5)'''\\F_3\end{matrix}\right\}O_3+\left.\begin{matrix}H_3\\H_3\end{matrix}\right\}O_3=\left.\begin{matrix}(C_3H_5)'''\\H_3\end{matrix}\right\}O_2+\left.\begin{matrix}H_3\\F_3\end{matrix}\right\}O_3.$$

This method of decomposing fats has met with an enormous

application in the industrial production of fatty acids and glycerin.

A similar reaction occurs when a fatty oil is heated to 110° C. with about seven or eight per cent. of concentrated sulphuric acid. On washing the product with hot water, the sulphuric acid and glycerin are removed, and the fatty acids separate in the form of an oily layer.

A parallel reaction takes place when a fatty oil is treated with caustic potash or soda. The change occurs much more readily with some oils than with others, and is greatly promoted by employing heat and using an alcoholic instead of an aqueous solution of the alkali. A potassium or sodium salt, or "soap," of the fatty acid is produced, glycerol being likewise formed—$C_3H_5'''(O\overline{F})_3 + 3NaOH = C_3H_5'''(OH)_3 + 3NaO\overline{F}$.

By boiling fatty oils with milk of lime or oxide of lead and water similar reactions occur, and insoluble soaps are formed, together with glycerol.

When a wax is similarly treated with a base it yields a soap of the fatty acid, together with a higher monatomic alcohol, instead of glycerol. The decomposition is usually effected with difficulty, and alcoholic potash or soda should always be the agent employed.

Whenever an ether is split up into an acid and an alcohol, the change is called "saponification," no matter whether the agent effecting the change be steam, an acid, or a base. The term is even extended to the decomposition of ethers which do not yield fatty acids at all.

For the purposes of chemical analysis, an alcoholic solution of caustic potash or soda is by far the most convenient reagent for effecting saponification of fatty oils and waxes. As the process is frequently employed it is desirable to describe it once for all.

A solution is prepared by dissolving 80 grammes of good caustic potash, or 60 of caustic soda in 1 litre of redistilled methylated spirit. In some cases it is desirable to dehydrate the spirit by keeping it over a large excess of dry potassium carbonate. About 5 grammes of the clarified fatty oil is placed in a hemispherical porcelain basin of about 5 inches diameter, and 25 c.c. of the solution of alkali in spirit poured

over it. The mixture is well stirred with a glass rod, and the liquid kept gently boiling until the alcohol is nearly driven off and the residual liquid froths strongly.* By this time the whole of the oil should have disappeared, but, if incomplete saponification be suspected, 10 c.c. of alcohol may be added and the evaporation repeated. To ensure the saponification of butter-fat, cod-liver oil, the waxes, and other substances difficult to decompose, it is better to place the sample and alcoholic solution in a strong 6-ounce bottle, closed by an india-rubber stopper firmly fastened by wire. The bottle is then kept at 100° C. for half an hour, or until no globules of oil can be seen, when it is opened, and the contents rinsed into a basin, and evaporated till the alcohol is expelled.

The solution of soap, freed from alcohol, should then be diluted with warm water till it measures 70 to 80 c.c., when a perfectly clear solution will usually be obtained if a pure fatty oil has been saponified, but waxes and mixtures containing hydrocarbon oils give a solution containing solid matter or oily globules in suspension. These admixtures may be removed and determined by agitating the soap solution with ether. which treatment also extracts traces of cholesterin and other unsaponifiable matter present in small quantity in some of the purest fatty oils.

On treating the soap solution with almost any acid, (*e.g.* sulphuric, hydrochloric, tartaric, oxalic, acetic) a milky precipitate is produced, which, either at once or else on warming the liquid, will collect into globules which rapidly rise to the surface and form an oily layer. This layer is not due to a re-formation of the original oil, but consists of the fatty acids produced from the oil. These fatty acids differ from the original glycerides in being readily soluble in alcohol, the solution having a more or less marked acid reaction. They also readily decompose the alkaline carbonates, liberating carbon dioxide and forming soaps.

In consequence of the approximately equal molecular weights of the glycerides constituting most fatty oils, the proportions of total fatty acids yielded on saponification are

* This frothing is an important character, and is never absent unless the sample consists almost wholly of hydrocarbon oil.

nearly the same, being between 95 and 96 per cent., except in the case of sperm oil and the waxes, which give a widely different amount. In most cases, the fatty acids are almost wholly insoluble in water and not sensibly volatile at 100° C., but by the saponification of butter-fat and cocoa-nut and palm-nut oils products are obtained, consisting to a notable extent of the lower fatty acids, and hence the mixed fatty acids are partially soluble in water and capable of distillation with low-pressure steam.

Saturation-equivalents of fatty oils.—In order to ensure complete saponification, the proportion of alkali prescribed in the foregoing process is largely in excess of that required by theory. The proportion of base theoretically necessary for the saponification of fatty oils in some cases affords a valuable means of differentiating them.

The proportion of alkali required for saponification will depend on the nature of the fat under treatment, but if the waxes be excluded the remaining oils and fats give, with but few exceptions, remarkably constant proportions of fatty acids, which require very similar amounts of alkali for their neutralisation. The most important exceptional fats are cocoa-nut oil, palm-nut oil, butter-fat, and sperm oil, all of which present certain peculiarities of composition.

The neutralising power of fats may be expressed either in parts of caustic potash required for the complete saponification of 1000 parts of the fat, or the "saturation-equivalent" may be found by dividing the former number into 56100. The saturation-equivalent is, for most fats, obtainable by dividing the molecular weight by 3, and represents the number of grammes of the fat saponifiable by one equivalent in grammes of any alkali, or, in other words, the number of grammes of fat which would be decomposed by 1 litre of a normal solution of any alkali. The expression in saturation-equivalents has the advantage of being applicable to the results of saponification by any alkali, whilst the parts of caustic potash required for complete saponification are not directly comparable with the figures obtained if soda be the alkali employed.

The table on next page shows both modes of expression. The parts of caustic potash required are stated from the published

results of Koettstorfer (K.), and from a private communication made to the author by Messrs F. W. and A. F. Stoddart (S.S.). The neutralising powers of the pure glycerides are calculated (C.).

From the figures in the table, it will be seen that the majority of oils have saturation-equivalents such as would correspond to mixtures of palmitin, stearin, and olein. Butter-fat shows a different equivalent owing to the presence of butyrin, while the behaviour of sperm oil is quite unique (see page 199). It is worthy of notice that rape and castor oils have higher equivalents than most others, a circumstance which is undoubtedly due to their containing acids of high combining weight.*

Fat.	Grammes of KHO required per 1000 grammes of fat.		Average saturation-equivalent of fat.
Tributyrin	557·3 C.		100·67
Tripalmitin	208·8 C.		268·67
Tristearin	189·1 C.		296·67
Triolein	190·4 C.		294·67
Sperm Oil	130–134 S.S.		425·0
Butter-fat	233·4–221·5 K.		247·1
Coco-nut and Palm-nut Oils	270–275		205·0
Dripping	197–196·5 K.		285·1
Lard	195·8–195·4 K.		286·8
Tallow	196·8 K.		285·1
Olive Oil	191·8 K.	189–196	296·8–286·7
	191–196 S.S.		
Niger Seed Oil	189–191 S.S.		
Cotton Seed Oil	191–196·5 S.S.		
Linseed Oil	189–195 S.S.		
Whale Oil	190–191 S.S.		
Seal Oil	191–196 S.S.		
Lard Oil	191–196 S.S.		
Colza Oil	178·7 K.	175–189	320·6–296·8
Rape Oil	175–179 S.S.		
Castor Oil	176–178 S.S.		
Cod-fish Oil	182–187 S.S.		
Pilchard Oil	186–187·5 S.S.		

* The calculated equivalent of the glyceride of erucic or brassic acid, which is said to be present in rape oil and oil from other cruciferous seeds, is 322·67. That of ricinolein, contained in castor oil, is 310·67.

It is evident that the determination of the saturation-equivalent of a fatty oil will serve, in certain cases, to detect its admixture with other oils, or to effect the indirect estimation of different glycerides in a mixture. As hydrocarbon oils do not react with alkalies, a sample containing such an admixture will have its saturating power proportionately reduced, a fact which may be utilised for the determination of the hydrocarbon oil (see page 164).

The method of accurately determining the saturating power of fats is due to Koettstorfer,* who applied it originally to the analysis of butter. The following are the details of the operation:—About 1½ to 2½ grammes' weight of the fat is treated with 25 c.c. of ½-normal caustic potash in alcohol, or a solution of about that strength. The mixture is heated in a closed bottle till perfect solution of the fat has taken place, and the saponification is judged to be complete. 1 c.c. of an alcoholic solution of phenol-phthaleïn is then added, and the liquid titrated with ½-normal hydrochloric acid. 25 c.c. of the alcoholic potash should then be similarly treated without addition of fat, and titrated with hydrochloric acid in the same way as before. The difference between the volumes of acid used in the two testings gives the number of cubic centimetres corresponding to the alkali neutralised by the fat. Each cubic centimetre of ½-normal hydrochloric acid (18·25 grammes HCl per litre) thus employed represents 0·02805 gramme of KHO; or the saturation-equivalent of the fat can be ascertained by the following formula, in which W is the weight of fat taken, N the number of cubic centimetres of ½-normal acid corresponding to the alkali neutralised by the fat:—

$$\frac{2\,W}{N} = \text{Saturation-equivalent.}$$

In employing this simple and ingenious method of examining fat, it is necessary to use alcoholic alkali as free as possible from colour, as any yellow or brownish tint materially affects the delicacy of the end-reaction with phenol-phthaleïn; while under favourable conditions the change from pink to yellow is very sharply marked. Carbonic acid, however, seriously influ-

* *Zeitschr. f. Anal. Chem.* 1879, p. 199; *Analyst*, iv. 106.

ences the reaction; and hence the saponification and titration should be conducted with as little access of air as possible. It is absolutely necessary to ascertain the strength of the alkali from day to day, as solutions in alcohol rapidly alter, and the mere heating causes a slight change in the neutralising power. The alcohol employed in making the solution must not be methylated. According to Wigner, it is advisable to employ a larger volume of the alkaline solution than that already prescribed. Standard sulphuric acid cannot be substituted for the hydrochloric acid recommended for the titration, as its employment causes a precipitation of sulphate, which masks the end of the reaction.

In employing Koettstorfer's method for the examination of butter, it is necessary to remember that the addition of sodium carbonate or any similar substance to the sample is liable to wholly vitiate the results. In the examination of oils it is necessary to estimate the free fatty acid, if any be present (see page 156), and to deduct the alkali employed for its neutralisation from the total amount required for reacting with the sample of oil.

DETERMINATION OF FIXED OILS.

The ordinary commercial method of extracting fats from animal tissues is by simple heating, either with or without water. The separated melted fat rises to the surface, and is skimmed off. From seeds the oil is usually extracted by pressure, though this method effects a very imperfect separation.

For laboratory purposes solvents are employed, the liquids most generally used being ether, chloroform, carbon disulphide, and petroleum spirit. The two last of these are also employed for extracting grease from seeds, wool-refuse, bones, &c., on a large scale.

Traces of oil suspended in aqueous liquids may be extracted by agitation with one of the foregoing liquids. When the solvent has formed a separate layer it is removed, evaporated at 100° C., and the residual fixed oil weighed.

THE DETERMINATION OF THE OIL IN SEEDS, SHODDY, &c., is effected by treating the finely-divided and previously-dried

substance with the solvent under such conditions as to ensure complete extraction. This may be effected by simply digesting the substance with the solvent at the ordinary temperature, with frequent agitation, in a closed flask. After some hours, the flask should be opened, placed in hot water, and the solvent thus raised to the boiling point, the liquid filtered into a weighed flask, and the residue washed with the solvent. The latter is subsequently evaporated or distilled off at a steam heat, the last portions being removed by a current of air filtered through cotton-wool. The residual oil is then weighed.

The foregoing method is unsatisfactory, as it requires a considerable quantity of the solvent, a notable proportion of which is likely to be lost. A better mode of operating is that of Church, in which the substance to be extracted is placed in a wide tube, drawn out at the lower end and plugged with cotton- or glass-wool. This is fitted by means of a cork into a flask containing the solvent, while the upper end of the extraction tube is fitted with a tube bent twice at right angles, dipping into an empty flask immersed in cold water. On heating the flask containing the solvent by surrounding it with hot water, the liquid distils through the extraction-tube, in which it partially condenses and effects solution of the oil. The remainder is condensed in the further flask. On removing the source of heat a partial vacuum is produced in the distilling flask, and the condensed solvent is forced back through the extraction-tube, carrying the dissolved oil with it. On again applying heat the solvent is redistilled, and may be condensed, and so on until the extraction is judged to be complete. The solvent is then finally distilled off, and the extracted oil subjected to a current of air, and weighed in the manner already described.

The last method is equally applicable whether ether, chloroform, carbon disulphide, or petroleum spirit be employed. The following plan, from the arrangement of the apparatus, is more suitable for use with ether or petroleum spirit than with a liquid heavier than the oil, but with this unimportant restriction it is decidedly the most satisfactory mode of extraction :—5 or 10 grammes' weight of the substance from which the oil is to be extracted is placed in a large test-tube,

having an aperture at the bottom closed by a loose plug of glass-wool. The tube with its contents is then placed in a Xoxheth's tube (fig. 4), having a little glass-wool at the bottom and adapted by means of a cork to a small tared flask containing about 100 c.c. of the solvent (ether, or petroleum spirit redistilled below 80° C.). A small vertical condenser is fitted to the top of the Xoxheth's tube, and the solvent kept boiling by immersion in a vessel of water heated by a gas flame. At first the liquid which periodically syphons off from the extractor will usually be more or less coloured, but this appearance diminishes as the extraction becomes more complete. As the operation requires but little attention, full time (*e.g.* two hours) should be allowed for the extraction. When the exhaustion is judged to be complete, the flame under the water-bath is extinguished, and the flask detached from the extractor. A cork and condenser are fitted to the flask and the solvent distilled off at a steam heat, the last portions removed by a current of filtered air, and the residual fixed oil weighed.

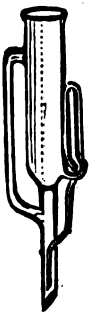

Fig. 4.

According to Vohl, the average percentage of oil extracted by solvents from linseed is 27; from hempseed, 26; from poppyseed, 49; from walnuts, 50; and from almonds, 52 per cent. According to Vœlcker, the proportion of oil in linseed varies from 31 to 38 per cent., the linseed cake containing from a little under 10 up to nearly 16 per cent.; while the oil in cotton-seed cake varies from 6 per cent in the undecorticated to 16 per cent. in the decorticated. Cacao-nibs average about 50 per cent. of fat.

THE DETERMINATION OF THE FAT IN MILK is sometimes very important, and requires to be accurately effected. Many of the methods which have been devised for the purpose are quite untrustworthy. They may be classified in three groups as follows:—

(*a*) Methods based on the opacity of the milk. These are of very little value in practical work.

(*b*) Methods in which the milk is agitated with ether, either with or without alcohol and a little alkali, the

solvent being subsequently separated and evaporated, or its density observed.

(*c*) Methods in which the milk is dried up, either alone or in admixture with sand, gypsum, or similar inert matter, and the fat extracted from the residue by treatment with ether or petroleum spirit, the solution thus obtained being subsequently evaporated and the residual fat weighed.

The various modifications in detail to which the above broadly-described methods have been subjected are very numerous. Of processes on the (*b*) principle the author found a modification of Marchand's method to give satisfactory results with fresh milk. The most generally applicable methods are those on the (*c*) plan, the following being the method of operating which the author has found preferable:— 20 grammes' weight of the milk is evaporated to complete dryness at 100° C. in a small porcelain dish, and the solid residue weighed. The solids are moistened with a few drops of alcohol, and removed from the dish by means of a flexible spatula. The residue is then placed on a glass-wool plug at the bottom of the inner tube of a small Xoxheth's extractor, and thoroughly exhausted by treatment with ether or gasolene in the manner described on page 127. The fat is subsequently recovered by evaporating the solvent at 100° C., and, if desired, the extracted solids also can be weighed.

Some operators prefer to add sand or other inert matter before evaporating the milk to dryness, so as to render the residue more porous.

CLASSIFICATION OF FIXED OILS, &c.

The following tabular scheme shows the name, origin, and leading properties and uses of the principal fixed oils, fats, and waxes of commerce. The classification is founded partly on the origin of the oils and partly on their density, fusibility, drying properties, and chemical constitution. The properties characteristic of each group are given under the several heads, as well as the leading properties and uses of the more important individual members of each group. The numbers given in the column headed "Fluidity" are compared with water at the same temperature, which is taken as 100:—

I.—OLIVE OIL GROUP. VEGETABLE NON-DRYING OILS.—The oils of this group solidify on treatment with nitrous acid or nitrate of mercury, but do not lose their power of producing a greasy stain on paper, however long they may be exposed to the air. Their density varies from ·912 to about ·924, and hence is less than that of the oils of Groups II., III., and IV. Their "fluidity" is notably less than that of the drying oils.

Kind of Oil.	Source of Oil.	Sp. Gravity at 15° to 15·5° C. (=59° to 60° F.)	Solidifying Point, °C.	Fluidity.		Other Characters, Composition, &c.	Chief Applications.
				At 15° C.	At 7·5°C.		
Almond Oil.	*Amygdalis communis.*	·917 to ·920	−10 to −20°	...	...	Straw yellow; limpid; mild nutty taste. Soon becomes rancid. Consists almost entirely of triolein, *i.e.*, the glyceride of oleic acid. Often adulterated with olive, lard, and sesamé oils, &c. See page 182.	In pharmacy, for making emulsions, liniments, ointments, &c.
Oil of Ben.	*Moringa oleifera.*	·912 to ·915	About 0°	...	...	Colourless or slightly yellow; separates into two portions on standing. Contains glyceride of "moringic acid" (*q. v.*). Often adulterated with olive oil.	Extraction of perfumes from flowers; preparation of "Macassar oil."
Colza Oil.	*Brassica campestris oleifera.*	·9136 to ·916	−6°	55·3	40·5	See Rape Oil, and page 189.	Same as Rape Oil.
Earth-nut Oil (Arachis Oil).	*Arachis hypogæa.*	·916 to ·920	−3°	...	...	Pale greenish yellow; smell and taste resemble peas.	Adultering olive and other oils.
Oil of Black Mustard.	*Sinapis nigra.*	·916 to ·920	−18°	63·8	51·4	Reddish or brownish yellow. Does not turn rancid. Contains glyceride of erucic acid.	Same uses as Rape Oil.
Oil of White do.	*Sinapis alba.*	·9145 to ·916	Very low.	57·3	41·7		
Olive Oil.	*Olea Europæa.*	·9144 to ·9176	+4 to −6°	46·1	31·1	Greenish or yellowish; mild and agreeable taste, almost odourless. Largely adulterated with cotton-seed, poppy, and other oils. See page 183.	Cooking of food. Soap; lubricating delicate machinery; woollen manufacture. Turkey-red dyeing.
Rape-seed Oil (winter).	*Brassica campestris; B. napus.*	·9136 to ·916	−6°	56·6	44·1	Yellow, limpid; before refining, brown. Faint disagreeable odour and taste. Very slightly soluble in alcohol. Contains glycerides of brassic and oleic acids. See page 189.	Burning; lubricating; wool spinning; soap making, &c.
Rape-seed Oil (summer).	*Brassica præcox.*	·9155 to ·916	−8 to −10°	60·8	43·9		

II. COTTON-SEED OIL GROUP.—The oils of this group occupy a position intermediate between the vegetable non-drying and the true drying oils (Groups I. and III.). In density they somewhat exceed the oils of Group I., but are lighter than those of Groups III. and IV. They form more or less elaïdin on treatment with nitrous acid or nitrate of mercury, but do not become wholly solidified. On the other hand they undergo more or less drying on exposure to the air, but not so markedly as the oils of Group III.

Kind of Oil.	Source of Oil.	Sp. Gravity at 15° to 15·5° C. (=59° to 60° F).	Solidifying Point, °C.	Fluidity.		Other Characters, Composition, &c.	Chief Applications.
				At 15° C.	At 7½° C.		
Beech-nut Oil.	*Fagus Sylvatica.*	·921 to ·923	−18	...	...	Yellow or yellowish; nearly odourless; mild sweet taste, occasionally acrid.	Culinary purposes, burning, and soap-making.
Cotton-seed Oil.	*Gossypium barbadense*, and other species.	·922 to ·930	+2° to −3°	...	...	Yellow or brownish-yellow to colourless; mild taste; sometimes strong and disagreeable. See page 191.	Used largely for adulterating linseed, rape, and olive oils. Soap-making; lubricating.
Hazel-nut Oil.	*Corylus avellana.*	·920 to ·926	−10 to −19°	54·2	41·2	Light or amber-yellow; viscid; mild sweet taste; no sensible smell; soon turns rancid.	Perfumery; pharmacy, as a substitute for almond oil.
Sesamé or Teel Oil.	*Sesamum orientale.*	·923 to ·924	+3 to −5°	...	...	Pale yellow; taste, mild and agreeable; almost odourless.	Cooking; soap-making; burning; adulterating olive oil.
Sunflower Oil.	*Helianthus annuus; H. perennis.*	·924 to ·926	−15°	78·9	60·8	Colourless or yellowish; limpid; nearly tasteless and odourless.	Wool-dressing, soap-making, burning.
Niger-seed Oil.	*Guizotia oleifera.*	·926 to ·928	below + 9°	...	...	Pale yellow; sweet; more limpid than rape; dries completely on exposure to a temperature of 100° C.	As an adulterant of rape, linseed, and castor oils.

III. LINSEED OIL GROUP. VEGETABLE DRYING OILS.—These oils are not solidified by treatment with nitrous acid or mercuric nitrate, but become gradually converted into solid masses or varnishes by exposure to the air. In density, the oils of this group vary from about ·923 to ·935, and hence are distinctly heavier than the non-drying oils, and than most of the oils of Group II. On the other hand, they are lighter than the oils of Group IV. The numbers representing the fluidity of the drying oils are much higher than those of the non-drying oils.

Kind of Oil.	Source of Oil.	Sp. Gravity at 15° to 15·5° C. (=59° to 60° F.)	Solidifying Point, °C.	Fluidity.		Other Characters, Composition, &c.	Chief Applications.
				At 15° C.	At 7·5° C.		
Camelina Oil.	*Myagrum sativum*, ("Gold of pleasure").	·925 to ·926	−18 to −19°	...	...	Yellowish. Peculiar taste and smell.	Burning, painting, &c.
Cress-seed Oil.	*Lepidium sativum.*	·9240	−15°	87·3	9·2	Brownish-yellow; acrid taste and disagreeable smell; moderately siccative.	
Hemp-seed Oil.	*Cannabis sativa.*	·9252 to ·9307	−15 to −25°	103·4	84·2	Greenish-yellow, becoming less coloured on keeping; disagreeable smell, and insipid taste. Soluble in 30 parts of cold alcohol, and readily in hot.	Painting; soft soap making.
Linseed Oil.	*Linum usitatissimum*; *L. perenne.*	·930 to 935	−20 to −27°	102·2	84·1	Golden-yellow to brownish; strong odour and taste; contains glyceride of linoleic acid. Soluble in 32 parts of alcohol. See page 192.	Painting, varnishes &c.; soft soap; oil-cloth making.
Poppy-seed Oil.	*Papaver somniferum.*	·924 to ·927	−18°	73·1	54·5	Straw-yellow, limpid, odourless; almond flavour (no narcotic properties). Much resembles olive oil. Soluble in 25 parts of cold or 6 of boiling alcohol. Dries rapidly.	Culinary purposes; burning; painting. Adulteration of olive oil.
Scotch-fir-seed Oil.	*Pinus sylvestris.*	·9312	−30°	84·1	59·6	Brownish-yellow. Dries easily.	
Tobacco-seed Oil.	*Nicotiana tabacum.*	·923	−25°	100·0	73·7	Greenish-yellow. Inodorous. Mild taste. Highly siccative.	
Walnut Oil.	*Juglans regia.*	·925 to ·926	−18°	102·2	84·9	Greenish or yellowish; syrupy; agreeable faint smell and nutty taste when fresh, afterwards acrid. Highly siccative.	Paints and varnishes.
Weld-seed Oil.	*Reseda luteola.*	·9358	below −15°	103·7	93·7	Dark green, thin; nauseous odour and taste. Dries rapidly.	

IV. CASTOR OIL GROUP.—The oils of this group are distinguished from those of Groups I., II., and III. by their very high density and viscosity (*i.e.* deficient fluidity). They are also remarkable for their ready solubility in alcohol, and their marked purgative properties. In their drying characters and behaviour with the elaïdin test they resemble the oils of the Cotton-seed Oil Group (II.). Both castor and croton oil are miscible in all proportions with glacial acetic acid.

Kind of Oil.	Source of Oil.	Sp. Gravity at 15 to 15·5° C. (=59 to 60° F.)	Solidifying Point, °C.	Fluidity.		Other Characters, Composition, &c.	Chief Applications.
				At 15° C.	At 7·5° C.		
Castor Oil.	*Ricinus communis.*	·960 to ·964	−18°	4·9	2·3	Colourless or pale yellow; viscid. Taste mild, and then acrid. Gives elaidin with nitrous acid. Dries in thin layers on exposure. Contains glyceride of ricinoleic acid. See page 195.	In medicine. Making toilet-soaps.
Croton Oil.	*Croton tiglium.*	·942 to ·943	...	...	...	Straw to brownish-yellow; viscid. Taste, at first mild, then strong and burning. Intensely purgative. Solubility in alcohol is variable. Produces pustules when applied to the skin. Gives but little elaidin. Thickens somewhat on exposure to air. Contains glycerides of tiglic, crotonic, valeric, and other volatile acids.	In medicine.

V. WHALE OIL GROUP. MARINE ANIMAL OILS.—This group comprises the various fluid oils obtained from fish and cetaceous mammals. They are distinguished as a class by their offensive fishy odour; by the brown colour they assume when subjected to the action of a current of chlorine; and by the reddish colour which is produced on boiling them with a solution of caustic alkali. With sulphuric acid they give colorations varying from light red to purple or brown. Sperm oil is distinguished from the other oils by its peculiar chemical constitution and low specific gravity. The fish oils do not dry up on exposure to air, but mostly yield but little elaïdin on treatment with nitrous acid. The term "train oil" includes whale, seal, shark, cod, and all similar oils.

Kind of Oil.	Source of Oil.	Sp. Gravity at 15° to 15·5° C. (=60° F.)	Other Characters, Composition, &c.	Chief Applications.
Cod Oil. Cod-liver Oil. Tanners' Cod Oil.	*Gadus morrhua*, and allied species. " " Various fish.	·923 to ·929 ·927 to ·930 ·920 to ·926	Three varieties of cod-liver oil are recognised, pale, light brown, and dark brown or black. Cod-liver oil contains iodine. See page 195.	Cod-liver oil is used in medicine. The oil yielded by other parts of the cod and by allied fish (ling, &c.), is used in the manufacture of wash-leather.
Menhaden Oil.	*Alosa menhaden.*	·929 to ·932	Dries rapidly.	For mixing with linseed oil.
Porpoise Oil.	*Delphinus phocæna*, and allied species.	·937	Yellow; much resembles whale oil. Odour fishy, but nearly destroyed by exposure to air and light. Very low solidifying point. Soluble in 5 parts of boiling absolute alcohol.	Illumination; soap-making.
Seal Oil.	*Phoca* of various species.	·924 to ·929	Pale yellow to brown. Smell usually very disagreeable.	Illumination only. Produces very offensive smelling soap.
Shark Oil.	*Squalus maximus* (Basking shark, or sun-fish), and allied species.	about ·870	Light yellow; low solidifying point and specific gravity.	Illumination; tanning; adulteration of cod-liver oil.
Sperm Oil.	Cranial cavities of *Physeter macrocephalus.*	·875 to ·883	Yellow; slightly unpleasant smell. Chemical constitution similar to the waxes. See page 197.	Lubrication; occasionally illumination. Hardening steel weapons.
Whale Oil.	*Balæna mysticetus*, and allied species.	·924 to ·929	Brown; disagreeable, fishy odour, removeable by bleaching powder. Deposits stearin at 0° C. Often adulterated with rosin.	Illumination; soap-making.

VI. LARD OIL GROUP.—This group includes those oils, fluid at ordinary temperatures, which are obtained from terrestrial animals. They resemble the fish oils in their reaction with chlorine, but are not turned red or brown by boiling with caustic soda. On exposure to air, and on treatment with nitrous acid or mercuric nitrate they behave like the non-drying vegetable oils (Group I.).

Kind of Oil.	Specific Gravity at 15·5° C. (=60° F.)	Solidifying Point, ° C.	Other Characters, Composition, &c.	Chief Applications.
Bone Oil.	·914 to ·916	Variable.	Yellowish to dark brown. Often contains lime in notable quantity, which may be detected by the ash left on ignition, and separated by agitating the oil with dilute sulphuric acid.	Soap-making.
Lard Oil.	·915	+4 to −4	Very slightly coloured; clear; slight odour of lard. Soluble in equal weight of boiling alcohol. See page 200.	Greasing wool. Lubricating machinery. Fine soaps.
Tallow Oil.	·916	+6 to 0°	Viscid; much resembles lard oil. Crude oleic acid is often miscalled "tallow oil."	
Neats'-foot Oil.	914 to ·916	below 0°	Yellowish; odourless; bland taste. Not liable to become rancid. Often adulterated with bone oil, lard oil, and fish oils.	Lubricating clocks and machinery exposed to low temperatures. Leather-dressing.

VII. TALLOW GROUP. SOLID FAT OILS.—This group comprises such animal and vegetable fats or oils as are solid at the ordinary temperature. Their melting points vary somewhat, and are capable of permanent alteration. The table shows the density in a solid state at 15° C., and also in a fluid state at 100° C. (=212° F.), compared with water at 15·5° C. (=60° F.). The fats of this division may be arranged in two sub-groups according as they are derived from the vegetable or the animal kingdom.

	Kind of Fat.	Specific Gravity. At 15·5° C. (=60° F.)	Specific Gravity. At 100° C. (=212° F.).	Solidifying Point, °C.	Other Characters, Composition, &c.	Chief Applications.
A. FATS OF VEGETABLE ORIGIN.	Cacao Butter (from *Theobroma cacao*).	·945 to ·952	·857	20° to 30°	Colourless; chocolate-like taste and smell. Not liable to become rancid. Soluble in 20 parts of hot alcohol, deposited on cooling, except 1 per cent.	Pharmacy; manufacture of soap and candles.
	Coco-nut Oil (from *Cocos nucifera*, and *C. butyracea*).	...	·868	16° to 18° (melting point 20° to 28°)	Consistency of butter; slightly coloured; readily turns rancid. Contains glycerides of lauric, myristic, palmitic and stearic acids, and of fatty acids soluble in water.	Making marine soap; candles.
	Japan Wax (from *Rhus succedanea*, and allied species).	·999 to ·1002	·873	42° to 53° *	Freshly-fractured surface nearly white, with a tinge of yellowish green; odour tallow-like and disagreeable. Soluble in boiling alcohol and ether, but almost completely deposited on cooling. Yields a palmitate and glycerin on saponification, and hence not a true wax.	Adulteration of bees'-wax.
	Laurel Oil (from *Laurus nobilis*, or sweet bay tree).	...	...	...	Greenish colour; consistence of butter; peculiar and characteristic smell. Contains glyceride of lauric acid.	Veterinary medicine.
	Palm Oil (from *Avoira elais*, or *Elais guineensis*).	...	·857	26° to 36°	Consistency of lard; orange yellow when fresh, with agreeable odour and sweetish taste. Quickly turns rancid and lighter in colour. Contains tri-palmitin in large proportion, with smaller amount of olein. See page 201.	Making soap; candles; railway grease.
	Palm-nut Oil.	...	·866	25° to 26°	Primrose yellow or pink; resembles coco-nut oil in properties and composition.	Soap-making.
	Shea- or Galam-Butter (from *Bassia Parkii*).	...	...	23° to 35°	White, grey, greenish, or reddish; faint characteristic odour and agreeable flavour. Somewhat resembles tallow.	Soap-making.

* The ordinary melting point is 52° to 53°, but a recently solidified sample melts at exactly 42° C.

VII. Tallow Group. Solid Fat Oils—(*continued*).

	Kind of Fat.	Specific Gravity. At 15·5° C. (=60° F.).	Specific Gravity. At 37·8° C. (=100° F.).	Specific Gravity. At 100° C.* (=212° F.).	Solidifying Point, °C.	Other Characters, Composition, &c.	Chief Applications.
B. Fats of Animal Origin.	Bone-fat.	...	...	...	...	Brownish; unpleasant smell. Usually softer than lard. Often contains lime. See "Bone Oil" (page 134).	Soap making.
	Butter-fat.	·938 to ·940	·911 to ·914	·865 to ·868	27° to 30°	From butter. See page 202.	Food; cooking.
	Butterine; Oleomargarin.	...	·903 to ·906	·859	...	Prepared by purifying animal fat (or palm oil), and incorporating the more fluid portion with milk and salt.	Substitute for butter.
	Hogs' lard, fresh. ,, old.	·931 to ·932 ·940 to ·942	·906 to ·907 ...	·861	28° to 32°	White or yellowish. See page 207.	Cooking; soap making.
	Horse-fat.	...	...	·861	...	Yellow or dirty white to brown. Consistency of lard, or harder. Very variable in quality.	Soap making. Manufacture of fictitious butter.
	Tallow, beef. ,, mutton.	·925 to ·929 ·927 to ·940	·904 to ·906 ·903 to ·905	·860 ·860	36° to 40° 38° to 41°	Consists of stearin, palmitin, and olein in varying proportions. See page 208.	Candles; soap making; lubricating.
	Wool-fat (*Suint*).	...	...	...	...	Tough, dirty, yellowish-brown mass. Contains notable quantity of Cholesterin.	Lubricating. Distilled with steam for oleic and stearic acids.

* The figures in this column are by König. Apparently they are referred to water at 15° or 4° C. taken as unity. Hence, for convenience of comparison, the figures obtained by myself, and given in the similar column on last page, are referred to water at 15° C. as unity.

VIII. SPERMACETI GROUP. WAXES.—Spermaceti and the various waxes differ from the true fixed oils and fats in not forming glycerin when saponified, yielding instead certain of the higher monatomic alcohols, the identity of which varies with the nature of the wax.* These alcohols are quite insoluble in water, and dissolve to but a limited extent in alcohol, but they are soluble in ether, chloroform, carbon disulphide, benzene, and petroleum spirit, and are apt to be mistaken for added paraffin wax when the substance is saponified and the soap extracted with a solvent. (The so-called Japanese wax is not a true wax, but belongs to the Tallow Group (No. VII., page 135.)

Kind of Wax.	Source of Wax.	Sp. Gravity at 15° C.	Melting or Solidifying Point, °C.	Chemical Constitution.	Other Characters.
Bees'-wax.	The honey-comb of various species of bee.	·959 to ·969	62° to 69°	Chiefly a mixture of cerotic acid, $C_{27}H_{54}O_2$, with myricin or melissyl palmitate, $C_{30}H_{61}.C_{16}H_{31}O.O.$ See page 209.	Naturally more or less yellow or brown, but may be bleached by light or nitric acid. See also page 209.
Carnaüba or Brazil wax.	From the leaf-coverings of *Copernicea cerifera*,	·995 to ·999	82° to 84°	Contains a notable percentage of free myricyl or melissyl alcohol, $C_{30}H_{61}.OH$.	Clear yellow colour with greenish tinge. Harder than bees'-wax.
Chinese wax; Pela wax.	Produced by a species of *Coccus* which punctures branches of certain trees.	...	82° to 83°	Consists chiefly of ceryl cerotate, $C_{27}H_{53}.C_{27}H_{53}O.O$, and hence yields on saponification a cerotate and ceryl alcohol, $C_{27}H_{53}.OH$.	Snow-white, crystalline, brittle. Called from its appearance "vegetable spermaceti."
Myrtle wax.	Berries of *Myrica cerifera*.	...	47° to 48°		
Ocuba wax.	From a Brazilian species of myrica (*M. ocuba*).	...	46° to 48°		
Palm wax.	Bark of *Ceroxylon andicola* of the Cordillilas.	...	75° to 86°	... ...	Much resembles Carnaüba wax.
Spermaceti.	Deposited from the oil found in the cranial cavities of the sperm whale, *Physeter macrocephalus*.	·943 to ·946	39° to 49	Consists chiefly of cetin or cetyl palmitate, and hence yields on saponification a palmitate and cetyl alcohol or ethal, $C_{16}H_{33}.OH$.	Crystalline; white or transparent; odourless; turns yellow and rancid on exposure to air. See also page 215.

* A method of differentiating the various kinds of wax has been described by E. Hirschsohn, *Pharm. Journ.* [3], x. 749.

GENERAL METHODS OF EXAMINING FIXED OILS AND FATS.

The chemical composition of the various fixed oils and fats is very similar, and their proximate analysis is attended with such great difficulties that it is rarely attempted.

The adulteration of the more valuable oils and fats with others of a less expensive kind is carried on extensively and in a very systematic manner. In some cases it becomes impossible to ascertain the extent, or even to guess at the nature of the adulteration practised, though the fact of sophistication may be fully established by the properties of the oil.

The following are the general methods employed for the examination of oils. The characters important in judging of the quality of lubricating oils are considered under a separate heading (page 169), and special processes for examining individual oils will be found in the separate sub-sections devoted to the oils in question. The characters and modes of examining such hydrocarbon-oils as are employed as substitutes for and adulterants of the fat-oils are described under the respective heads of "Mineral Lubricating Oil" (page 34), "Rosin Oil" (page 66), and "Paraffin Wax" (page 39).

Specific Gravity of Fixed Oils.—The density of the fixed oils may be taken by means of a specific gravity bottle or hydrometer (see Vol. I. p. 6), but great care is necessary, owing to their high coefficients of expansion. The temperature at which the observation is made must be carefully noted, and it is best always to operate at 15·5° C. (=60° F.). When sufficient of the sample is available, the use of an accurate and delicate hydrometer is perhaps preferable to the determination by weighing, but the liquid should be brought accurately to the standard temperature by immersing the hydrometer glass in water, cooled, if necessary, to 15·5° C., by dissolving in it some sodium thiosulphate (hyposulphite) or oxalic acid. As the various oils have distinctly different coefficients of expansion, it is not desirable to observe the density at a temperature other than 15·5° C. (=60° F.), and then calculate to the standard temperature.

In the case of solid fats, however, it is sometimes convenient

to ascertain the weight of a definite volume of the substance at 100° F. (=37·8° C.) and compare it with the weight of an equal volume of water at the same temperature. The result so obtained is usually called the "actual density of the fat at 100° F." Muter prefers to take the density of all oils and fats at this temperature, while Messrs Stoddart make the observation at 212° F. (=100° C.). As melted fats have a very high coefficient of expansion, it is necessary to exercise great care that the fat is really at the prescribed temperature when the observation is made. This is best ensured by operating in the following manner:—

The clarified fat is brought to a temperature of 35° C., and poured into a specific gravity bottle having a thermometer-stopper. The bulb of the thermometer should be long and the graduations above the stopper. The stopper being pressed in tightly the bottle is placed up to the neck in water at 41° C., contained in a shallow beaker. By operating in this manner the fat slowly rises to 38·0° C., while the water cools to about the same temperature. When the thermometer immersed in the fat registers 38·0, or, more accurately, 37·8° C., the superfluous fat is immediately wiped off the neck of the bottle, the latter removed from the water, and wiped, first with soft paper and then with a dry cloth, after which it is weighed.

The density of melted fatty acids is sometimes observed at 30° C. At that temperature Baudouin states that, except the product from linseed oil, which has a density of ·910, the fatty acids have specific gravities ranging from ·892 to ·900. If the temperature of observation be not exactly 30° C., a correction may be made by multiplying ·00064 by the number of degrees by which the temperature of the experiment differs from 30° C., and adding the product to or subtracting it from the observed density according as the temperature of observation was above or below 30° C. The author has determined the density of certain fats and fatty acids at 100° C. (see page 136).

Hager * has recently described an ingenious method of ascertaining the specific gravity of solid fats at the ordinary temperature. The fat is melted and drawn up into a pipette,

* *Analyst*, iv. 206.

from which it is allowed to drop slowly from the height of an inch into cold alcohol contained in a flat-bottomed dish, care being taken that each drop of fat falls in a different place. An alternative plan is to melt the fat in a small lipped capsule and allow drops of it to fall on a plate of glass which has been previously wiped with a wet cloth. On placing the glass in cold water the drops usually become detached on the slightest touch, but if necessary can be removed with a knife after half an hour. The fat globules obtained by one of the above methods are removed to a beaker containing dilute alcohol. The density of the liquid is then adjusted by addition of alcohol or water, till, after careful stirring, the fat globules remain in equilibrium in any part of the liquid at a temperature of 15·5° C. Ammonia may be substituted for the spirit if preferred. The density of the liquid is then taken, and the result obtained recorded as the specific gravity of the suspended fat. The great objection to this method is that fats and waxes which have undergone sudden cooling have abnormal specific gravities. On this account it is far preferable to employ for the experiment fragments which have been cut off a mass cooled under normal conditions.

The specific gravity of the greater number of vegetable oils lies between ·914 and ·938. As mineral oil is usually lighter than ·914, and rosin oil is nearly as dense as water, the specific gravity of the sample furnishes a valuable indication of their presence, unless, by a judicious admixture of the two adulterants, the density of the sample remains unchanged.

The classification of oils adopted on page 129, *et seq.*, is largely dependent on their specific gravity.

Melting and Solidifying Points of Oils and Fats. The observation of the solidifying point of an oil is often of considerable importance, especially in the case of lubricating oils, in which too high a melting point is a decided disadvantage. Similarly, the suitability of the solid fats for many of the purposes to which they are applied is greatly dependent on their melting points.

Extreme constancy of solidifying or melting points for particular oils and fats is not to be expected, as in most cases the natural fats consist of a mixture of liquid and solid glycerides,

the proportions of which may vary sensibly in different samples of what is nominally the same kind of oil. Moreover, the melting points, like the specific gravity of oils and fats, are liable to obscure alterations by lapse of time. It has also been observed that many of the fats solid at the ordinary temperature have at least two distinct melting points. Thus the ordinary clarified tallow of commerce, if previously melted at a temperature considerably above its fusing point, shows a melting point of 95° to 96° F. If carefully remelted at that temperature, cooled, and the melting point again taken, it will be found to be as high as 115° or 116° F.

In making observations of the melting and solidifying points of fats and oils it is absolutely necessary to get rid of any water or suspended matter. This is best effected by keeping the fat gently melted for an hour or two, and then filtering it through dry paper.

The following are the readiest and most reliable methods of ascertaining the melting points of fats:—

1. The sample is melted at a temperature only slightly above its fusing point, and, while molten, is sucked up into a very narrow glass tube made by drawing out a piece of ordinary quill-tubing. In this it is allowed to become thoroughly solid, and the tube (open at both ends) with the contained fat is placed in cold water contained in a beaker immersed in an outer beaker, which is gradually heated by a small flame. A thermometer is supported in the inner beaker at the same height as the tube containing the fat. The source of heat should be so regulated that the temperature does not rise more than ½ degree centigrade per minute. When the fat in the narrow tube is observed to melt, the temperature is read off on the thermometer. The flame is then removed, and the temperature indicated when the fat re-solidifies also observed. The mean of the two observations may be regarded as the true melting point of the sample.

2. The foregoing method necessitates the use of a transparent bath, and hence renders the use of a freezing mixture very difficult. This practically limits its employment to the observation of the melting points of fats solid at the ordinary temperature.

The following plan, devised by Dr Redwood, is applicable within a greatly extended range of temperature :—

Some clean mercury is placed in a small beaker or wide test-tube, and a delicate thermometer immersed in the metal. A minute drop of the liquid fat or oil is then placed on the mercury. If the fat be easily fusible, the mercury is then cooled down by immersing it in iced water, or in a freezing mixture, until the drop of oil solidifies, the temperature of the change of state being noted. On removing the outer bath containing the cooling agent, the mercury will gradually rise in temperature till the oil liquefies, and the temperature at which this occurs can be observed with great accuracy. In taking the melting points of the more infusible fats, there is no occasion to cool the mercury, which, on the contrary, is immersed in a beaker filled with water to a higher level than the mercury. The water is heated *very* gradually till the fat is observed to become transparent and to spread over the mercury. The temperature at which this occurs is the liquefying point of the sample.

A technical method of determining the solidifying point of the fatty acids from tallow is described under "Stearic Acid." (See page 223).

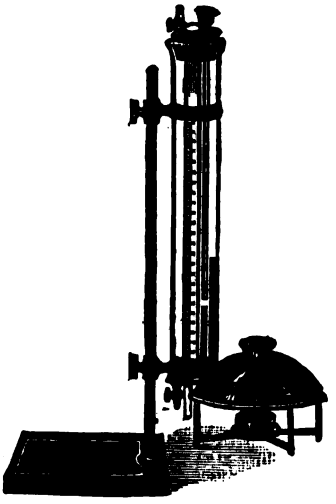

Fig. 5.

Viscosity of Oils.—Another useful physical test for oils is based on their relative viscosity, or body, a property which is the converse of fluidity. The viscosity or fluidity of oils is determined by ascertaining the rate at which they flow through a given aperture. 100 c.c., or some other definite volume of the oil to be tested, should be poured into a wide Mohr's burette furnished with a glass stop-cock. The burette is surrounded with a glass cylinder fitted with an arrangement by which, if desired, hot water can be caused to

circulate through it, thus bringing the liquid in the burette to a definite temperature, as indicated by a thermometer immersed in the upper part of the liquid.*

When the oil has reached the desired temperature the top of the burette is fully opened, and the number of seconds required for the passage of a given volume, or the complete emptying of the burette, noted. The orifice of the burette should be of such a size as to allow German refined rape oil to run completely out in from seven to nine minutes. Some oils which are very fluid at 50° C. and higher temperatures are very viscous when cold, and hence it is desirable to determine the viscosity at two temperatures at least.

It is desirable in all cases to compare a sample of oil with others of known quality and origin, as the figures obtained by the use of one apparatus are not directly comparable with, or even capable of strict conversion into, those yielded by others.

A table is given on page 171 which shows the comparative viscosity of some of the chief lubricating oils at different temperatures.

The following table shows the number of seconds found by Coleman to be required by equal measures of various oils to run out of a burette heated to 50° C.:—

Nature of Oil.	Seconds required.
Olive Oil	495
French refined Colza	660
German „ „	510
Lisbon-seed Oil	395
Earth-nut Oil	480
Sperm Oil	300
Seal Oil	390
Southern Whale Oil	460
Neat's foot Oil	510
Lard Oil	420
Tallow Oil	450

* The woodcut (fig. 5) has been kindly lent me by Messrs Townson and Mercer, and shows the construction of Sacker's viscosity apparatus as sold by them.

The following figures, obtained by the author, are interesting chiefly as showing the variations of viscosity met with in different samples of the same class of oil:—

Nature of Oil.	Density at 15·5° C.	Seconds required.	
		At 15·5° C. (=60° F.)	At 50° C. (=122° F.)
Olive, genuine	·9144	420	135
,, probably genuine	·9156	445	140
Rape, German	·9152	485	200
,, ,, brown	·9171	475	250
,, East Indian, refined	·9157	465	165
,, ,, brown	·9166	520	215
Cotton-seed, crude	·9285	453	180
,, ,,	·9283	450	155
Niger-seed	·9267	316	155
Linseed, East India	·9326	279	124
,, Baltic	·9317	275	130
,, ,,	·9341	318	122
Castor	·9630	16740	...
Sperm	·8826	180	90
Cod-liver	·9270	255	105
Rosin Oil, brown	·9739	585	110
Oleo-naphtha	·9050	925	170

In the tables on page 129, *et seq.*, are given the fluidities attributed to various oils at 15° C. In recording the fluidity of olive oil at 15° as being 46·1, it is to be understood that while a certain measure of water would run out of a given vessel in 100 seconds, the same volume of olive oil would require $\frac{100 \times 100}{46{\cdot}1} = 217$ seconds to pass through the same aperture at the same temperature.

It will be observed that the fluidities of the non-drying oils are less than those of Group II., and these again less than the true drying oils. Castor oil exceeds all others in viscosity.

Cohesion Figures of Oils.—The surface tension of oils is a character which in certain cases is capable of useful application, though its value has been much exaggerated. To obtain the cohesion-figures which depend on the surface tension, it is necessary to allow a drop of the oil to fall gently on the surface of still water contained in a flat

evaporating basin or soup-plate. In order to ensure success, and to obtain bold, well-defined figures, it is necessary that the vessel containing the water should be chemically clean; that the surface of the water should also be clean and free from organic matter; that the temperature should not be below 15° C.; and that the surface of the water should not be too limited. The time required to produce the characteristic figures should be carefully noted.

When a drop of olive oil is placed on the water, it slowly spreads out into the shape of a large disk with slightly re-curved edges. The cohesion of the oil, however, soon causes the disk to contract, the edges first testifying the return of the cohesive force; a number of little spaces begin to appear round the edges, causing them to resemble a chaplet of beads. The spaces between the beads soon open out, and the edges becomes toothed, the detached portions in some parts reuniting themselves to the main sheet of oil, enclosing polygonal spaces bounded by fine beads and covered with an excessively fine dew of oil, which it requires a sharp eye to detect. This succession of changes occurs in about thirty-five seconds.

Oil of Sesamé, treated in the same manner, begins by forming a well-defined sheet. Contraction soon takes place, the final figure being a central spot with distinctly marked rays, between which other smaller rayed spots appear, the whole recalling the aspect of a spider's web loaded with dew. The phenomenon is complete in about sixty seconds.

Mixtures of olive with sesamé oil give figures approaching more or less to the typical, according as one or the other is in excess. Other oils also give more or less characteristic cohesion-figures.

Absorption-spectra of Oils.—The absorption-spectra of the fixed oils often afford valuable indications of their purity. For observing them a micro-spectroscope may be used, but in many cases the light must be caused to pass through several inches of the oil to be examined. Although many vegetable oils give exceedingly striking absorption-bands, the position of these is not capable of employment for their

discrimination in many cases, as the absorption is not a property of the oils themselves, but of the chlorophyll and impurities contained in them. Hence the purification or clarification of an oil tends seriously to reduce the characteristic nature of the absorption-bands, which, indeed, may disappear altogether if the oil be long exposed to sunlight. In one particular, however, the absorption-spectrum furnishes important information. Thus no oils of animal origin give definite absorption-bands, the spectrum being merely obscured at the more refrangible end, whilst in many vegetable oils the absorption bands of chlorophyll are exceedingly well marked, especially a band about the refrangibility of the Fraunhöfer line B. By applying this fact it is easy to detect the presence of rape, olive, or linseed oil in sperm, cod, or lard oil. Castor and almond oil, on the other hand, give no well-defined bands, and the band at B in the case of sesamé oil is but very faint, though there is strongly marked absorption of the whole of the red nearly up to that point. By careful observation of genuine oils, the application of the absorption-spectra as a test for purity might doubtless be considerably extended.

Drying Properties of Oils.—For testing the drying properties of an oil, a definite number of drops of the sample should be placed in a shallow capsule and exposed to a temperature of about 130° C. for twelve hours, side by side with samples of oil of known purity. Or a definite measure of thick filter paper may be soaked in the sample of oil, and then exposed to temperature of 100° C. for some hours, side by side with samples of oil of known purity. In these tests, the drying property of an oil will be indicated by the extent to which it thickens, or in extreme cases, actually dries.

Another useful test for oils is due to Gellatly, and is based on their relative liability to inflame when left in contact with cotton or other waste. The experiment is made by imbuing a handful of cotton waste with the oil to be tested, and placing it tolerably loosely in a paper box in an air-bath kept at a temperature of 80° C. After a certain length of time, characteristic of each oil, the mass enters into active combus-

tion. Mr Gellatly's figures, obtained at about 65° C., are as follow:—

Oil.	Hours.	Minutes.
Boiled Linseed . . .	1	15
Seal	1	40
Raw Linseed	4	0
Lard Oil	4	0
Gallipoli Olive . . .	5	0
Refined Rape . . .	about 9	0

Equal parts of seal and mineral oil refused to ignite, and even 20 per cent. of mineral oil materially delayed the ignition.

The tendency of an oil to ignite under the above conditions bears a close relationship to its drying properties, both characters depending on the oxidisability of the oil. Although commonly grouped as "drying" and "non-drying" oils, the fat oils really exhibit considerable difference in their drying powers. Omitting the fish-oils, which constitute a separate class, and are generally regarded as non-drying, the chief commercial oils possess drying properties in the order of the following list, the most readily oxidisable being placed first:— Linseed oil, cotton-seed and other fancy seed oils, sunflower oil, Lisbon-seed oil, ground-nut oil, rape oil, olive oil, animal oleins.

Elaïdin Test for Oils.—A reaction which is sometimes of very considerable value in discriminating fixed oils is that known as the elaïdin test. It consists in treating the oil with nitrate of mercury, or nitric acid containing nitrous acid, when the non-drying oils are converted into a more or less solid mass of "elaïdin," while the drying oils remain comparatively unaffected.

A very satisfactory mode of applying the test is the following, which is due to Poutet:—12 grms. of mercury are dissolved in 11 c.c. of cold nitric acid of 1·35 specific gravity. 8 grms. of the newly-made solution of nitrate of mercury thus obtained are shaken with 96 grms. of the sample of oil, and the agitation repeated every ten minutes during two hours.

A simpler mode, and one which requires a smaller quantity of oil, is to treat 10 c.c. of the sample with an equal measure of cold nitric acid of 1·2 sp. gravity. A drop of mercury, or a few fragments of copper turnings, should be then added,

and the whole well agitated. The tube is next set aside in a moderately warm place, and observed at frequent intervals.

When treated in the above manner almond oil, olive oil, rape oil, castor oil, bone oil, and lard oil become turbid in one or two hours, and on standing from eight to forty-eight hours set to a more or less solid mass, which is usually of a whitish or yellowish colour. Oils which dry with difficulty (Group II., page 130), such as beech-nut oil, cotton-seed oil, sesamé oil, and sunflower oil, become merely pasty or syrupy under the elaidin test as above applied. The more powerfully drying oils, such as those of Group III., page 131, are scarcely changed during the first hour, and remain liquid and clear, though somewhat coloured, even after two days. Croton oil and cod-liver oil, though possessing no drying properties, behave in a similar manner.

The elaïdin test is valuable for detecting the admixture of a drying oil with a non-drying oil. It is even possible to obtain a rough estimate of the proportion in which they are mixed, by treating the sample as above directed, and, after two days, setting it aside for twelve hours at a temperature of about 25° C. The drying oil will now be found more or less perfectly separated from the elaïdin, and if the liquid be cooled to 8° or 10° C., the fluid portion may be removed by a roll of filter paper of known weight, and thus the proportion of drying oil roughly ascertained.

Colour-Reactions of Oils.—Many fatty oils give, when treated with chemical reagents, products which are often strongly coloured. To a certain extent these colour-reactions are characteristic of the oils by which they are produced, and hence may be employed for their identification. Unfortunately, however, considerable variation is observed in the behaviour of different samples of oil from the same source with the same reagent, and the value of the tests is further reduced by the modifications produced by refining the oils. Still less are the indications to be absolutely trusted when mixed oils are examined. Notwithstanding these drawbacks, colour-tests, when carefully applied, are capable of furnishing very valuable information, and sometimes render the positive

Colza and Rape.	Sesamé.	Walnut	Cod and Live
golden	golden	golden	...
...	...	...	alte
...	white	white	cold d
rape, yellow	...	...	..
colza, green	...	...	green (ho
refined, brown-yellow	yellow	...	.
...	...	red-brown	violet to b
bluish-green green spots	...	...	
...	pale yellow	reddish-yellow	violet
... green	... ...	...	blo
colza	pale yellow	...	
	...	...	
ape, dirty green	...	...	
decolorised	...	white	
...	orange-yellow	...	go red
green	...	...	
... brown-yellow ... blackish	... brown-yellow	... brown-yellow	de g
...	white	no colour	
pe, light yellow	...	...	pa
colza, greenish	...	...	
... greyish or pink	green veins then orange-yellow	... ...	
...	...	various shades of brown effervescence	d
...	...		

identification of an oil, or its detection in a mixture, possible, when no other means are available.

Colour-tests for oils have been devised by Calvert and various other observers; but by far the most complete and systematic series of observations are those published by Chateau in 1861. His mode of operating is to place ten drops of the sample of oil in a small hemispherical porcelain dish or a porcelain crucible, five drops of the reagent are then added, and the mixture thoroughly stirred together with a glass rod, any coloration or other sensible effects being noted. The following are the reagents employed by Chateau. No. 1 was originally polysulphide of calcium, the substitution of barium polysulphide being due to Muter.

1. *Polysulphide of Barium.*—Prepared by dissolving baryta in boiling water, cooling, pouring off the mother-liquor from the residue, boiling it with excess of sulphur, and filtering. Ten drops of the oil are treated with five of the reagent. It should be noted whether the golden-yellow colour remains after twenty strokes of the rod, or bleaches and becomes a very pale yellow or white in the course of a few minutes.

2. *Zinc Chloride,* in a syrupy state of concentration.

3. *Sulphuric Acid* of 1·845 specific gravity, and free from nitrous compounds. The reaction is observed both before and after stirring.

4. *Stannic Chloride.*—The commercial fuming chloride. Both the immediate colour-tint is observed and also the colour of the thickened or solidified mass.

5. *Phosphoric Acid,* evaporated to a syrup of 1·72 specific gravity. The colour of the mixture is observed both before and after heating, as is also the colour of the froth.

6. *Mercuric Nitrate,* prepared by saturating cold nitric acid with mercury, and then boiling for ten minutes with an equal measure of nitric acid. The effect of the reagent on the oil is first observed separately, and then two or three drops of strong sulphuric acid are added and the colour of the liquid covering the precipitate again observed.

The preceding table exhibits Chateau's reactions in a compact form. It contains some additional observations by Muter, but the mode of arrangement in a single table is due to the author.

In employing Chateau's tests, as indeed with all colour tests for oils, it is very desirable to examine specimens of oils of known purity side by side with the sample, instead of trusting too implicitly to the reactions described in the table.

Of the tests employed by Chateau, that with sulphuric acid is one of the most valuable and readily applied. It has also been recommended by various other chemists, some of whom employ several strengths of acid, whilst others modify the proportion, that used by Chateau being in excess of the amount desirable. With care, the violet colour produced by the fish oils is highly characteristic, as also are some of the other reactions.

Oil.	1 or 2 drops of strong Sulphuric Acid to 20 of the Oil.	
	Before Stirring.	After Stirring.
Vegetable Oils—		
Almond Oil	Colourless, or yellow.	Dark yellow, olive, or brown.
Castor Oil	Yellow to pale brown.	Nearly colourless, or pale brown.
Cotton-seed Oil, crude	Very bright red.	Dark red, nearly black.
,, refined	Reddish-brown.	Dark reddish-brown.
Earth-nut Oil	Yellow to orange.	Reddish-brown.
Linseed Oil, raw	Hard brown, or greenish-brown clot.	Mottled, dark brown.
,, boiled	Hard brown clot.	Mottled, dark brown.
Mustard Oil	Dark yellow, with orange streaks.	Reddish-brown.
Niger-seed Oil	Yellow, with brown clot.	Reddish or greenish-brown.
Olive Oil	Yellow, green, or pale brown.	Light brown, or olive green.
Poppy-seed Oil	Yellow spot, with orange streaks or rings.	Olive or reddish-brown.
Rape Oil, crude	Green, with brown rings.	Bright green, turning brownish.
,, refined	Yellow, with red or brown rings.	Brown.
Animal Oils—		
Cod-liver Oil	Dark red spot, with purple streaks.	Purple, changing to dark brown.
Lard Oil	Greenish yellow, or brownish, with brown streaks.	Mottled or dirty brown.
Seal Oil	Orange spot, with purple streaks.	Bright red, changing to mottled brown.
Sperm Oil	Pure brown spot, with faint yellow ring.	Purple, changing to reddish or dark brown.
Tallow Oil	Yellow spot, with pink streaks.	Orange red.
Whale Oil	Red, turning violet.	Brownish-red, turning brown.
Hydrocarbon Oils—		
Petroleum lubricating Oil	Brown.	Dark brown, with blue fluorescence.
Shale lubricating Oil	Dark reddish-brown.	Reddish-brown, with blue fluorescence.
Rosin Oil, brown	Bright mahogany brown.	Dark brown, with purple fluorescence.
,, pale	Mahogany brown.	Red-brown, with purple fluorescence.

The above table shows the effect produced on placing a drop or two of sulphuric acid in the centre of about

twenty drops of the oil, and observing the colour both before and after stirring. The reactions described include those produced by the generality of mineral and rosin oils. As already stated, the colours produced by different samples of the same kind of oil are liable to considerable variation.

A test which has been found of value for the assay of olive oil consists in agitating 15 c.c. of the sample with 5 c.c. of a mixture of nitric acid of 1·42 specific gravity with one-third of its measure of water. After thoroughly shaking, the mixture is left at rest for an hour and a half and the colour then observed. Olive, castor, and lard oils give merely a yellow coloration, but in presence of rape, cotton, or other seed oils, sperm, seal, fish, mineral, or rosin oil, a red or reddish-brown colour is said to be produced, even if the proportion be very small. The nitric acid test was originally due to Hauchcorne, but has been extended in its application by Messrs Stoddart, who have also proposed to employ hydrochloric acid in a similar manner (see "Olive Oil").

Temperature-Reactions of Oils.—The rise of temperature which occurs on mixing a fixed oil with concentrated sulphuric acid (sp. gr. 1·845) is a reaction which has been employed by Maumené, Fehling, and others. Maumené employed 50 grms. of the oil and mixed it with 10 c.c. (or 18·45 grms.) of sulphuric acid, while Fehling used 15 grms. of oil to 5 grms. of acid. In the latter mode of manipulation the temperature obtained is less elevated owing to the greater proportionate loss by conduction and radiation. Whatever weight of the samples be employed, a similar experiment should be made on an oil of known purity side by side with the sample. The oil should be placed in a narrow beaker and vigorously stirred with an accurate and delicate thermometer, while the acid is gradually added from a burette or pipette. The temperature of the oil is observed before the experiment, and the highest degree to which the thermometer rises on adding the acid is also noted. The difference is the rise of temperature. It is desirable to surround the beaker with an outer one stuffed with glass- or cotton-wool, to prevent loss of heat.

The following table shows the rise in temperature in centigrade degrees, observed by Maumené and Fehling, on applying the test to various oils, and working in the manners already mentioned, as also some results of the author obtained by operating in the manner described by Maumené:*—

Nature of Oil.	Rise of Temperature observed, °C.		
	Fehling.	Maumené.	Allen.
1. Olive Oil	37·7	42	42
2. Sweet-Almond Oil	40·3	52½ to 53½	...
3. Bitter-Almond Oil (fixed)	...	52	...
4. Colza Oil	...	58	...
5. Rape Oil (various specimens)	55	57 to 58	51 to 56
6. Beech-nut Oil	...	65	...
7. Arachis (earth-nut) Oil	...	67	...
8. Sesamé Oil	...	68	...
9. Cotton-seed Oil	...	...	57 to 60½
10. Poppy-seed Oil	70½	74½	...
11. Niger-seed Oil	..	...	81
12. Hempseed Oil	..	98	...
13. Walnut Oil	...	101	...
14. Linseed Oil (various specimens)	...	103	108 to 111
15. Castor Oil	...	47	...
16. Lard Oil	...	...	41
17. Tallow Oil	...	41 to 43½	..
18. Horse-foot Oil	...	51½	...
19. Sperm Oil	...	...	45 to 46
20. Skate-liver Oil	...	102	...
21. Cod-liver Oil	...	102 to 103	113
22. Lubricating Oil from Petroleum	...	...	2½ to 3
23. Lubricating Oil from Shale	...	...	4
24. Lubricating Oil from Rosin	...	...	19

The figures in the above table have been confirmed by various observers. MM. Faisst and Knauss, employing Fehling's proportions, observed a rise of 38° C. in the case of pure olive oil, whilst with poppy-seed oil the rise was not less than 70° C. In mixtures of the two oils the *additional* rise of temperature (*i.e.*, the increase above 38°) was regularly 1·6° C. for every 5 per cent. of the adulterant. In certain other cases, as

* These results were published in the *Analyst* for June 1881. In the same paper I showed that there was no foundation for Maumené's statement that *recently heated* sulphuric and *old* sulphuric acid produced different rises of temperature when mixed with linseed and other fixed oils.

when rape oil is added to linseed oil, the rise of temperature is a valuable indication of the adulteration, the heating becoming less marked with an increase in the proportion of rape oil present. The increase of temperature is also a useful test for the purity of sperm oil, which gives much less heat than those oils employed for its sophistication.

In the case of linseed oil and the fish oils giving high temperatures, the reaction with the acid is so violent as to render loss likely unless the experiment be carefully conducted. Whale oil gives the highest temperature of any oil.

Muter has described an improved method of applying Maumené's test, by which more constant results are obtained. He immerses the bottle of acid and 50 grms. of the oil in a vessel of water at a temperature of 28° C. The oil is contained in a wide tube of thin glass mounted on a foot. When the oil and acid are both at a temperature of 27° C., 10 c.c. of the acid is withdrawn by means of a pipette and added to the oil at the rate of 1 c.c. per 5 seconds. The mixture is stirred with the thermometer during the addition of the acid and for 30 seconds afterwards, the highest temperature being noted.

EXAMINATION OF FIXED OILS FOR FOREIGN MATTERS.

By the term foreign matters used in this connection it is not intended to signify the traces of cholesterin, chlorophyll, gummy and albuminous matters, colouring matters, &c., which are *natural* constituents of the animal and vegetable fixed oils and fats; but the term is applied to intentional admixtures of resin, free fatty acids, soap, hydrocarbon oils, water, and mineral matter. These bodies are often added to oils, either as adulterants, or with the view of giving them some special property. When used in small quantity the detection of some of them is attended with considerable difficulty.

In the case of butter, lard, and palm oil, more or less water, curd, salt, &c., are not unfrequently present. The methods of detecting and estimating such of these admixtures as are peculiar to each of these are described in the sections

devoted to the fats in question. A fluid oil, if clear, may be regarded as free from such extraneous matters, and their presence in a solid fat may be at once detected by melting the sample. If an opaque or opalescent oil result, or one containing visible particles of suspended matter or globules of water, it should be purified from these in the manner described under butter, before proceeding to search for resin, fatty acids, soap, or hydrocarbon oils.

A systematic method of detecting and determining foreign matters in fixed oils has been described by Rémont.* In one of its main features, that of the isolation of hydrocarbon oils, it has been improved on by the author, and therefore it is unnecessary to give M. Rémont's instructions in detail, but many of the facts stated in the succeeding pages are culled from his valuable paper.

The table on next page shows the skeleton of a generally applicable method of examining fixed oils for foreign admixtures. The details of the operations are given in the subsequent pages. In practice it is rarely necessary to make an examination for all the admixtures, the nature and origin of the sample usually indicating whether free fatty acid, soap, resin, or hydrocarbon oil is the addition to be sought for. The method in the table will be more or less erroneous if the sample contain butter, sperm oil, spermaceti, or wax (see page 167).

Soap is sometimes directly added to an oil, but its presence is more frequently due to the use of alkali employed to increase the density and viscosity of the article. Soap is readily detected by dissolving the oil in about three times its measure of ether or freshly-distilled carbon disulphide, adding a little water, and agitating the whole thoroughly in a tapped separator. The soap will dissolve in the water, while all other foreign matters will dissolve, together with the oil, in the ether or carbon disulphide employed, and may be recovered therefrom by distilling off the solvent. The soap may be determined by evaporating the aqueous liquid and weighing the residue after drying at 100° C.

* *Bull. Soc. Chim.* [2], xxxiii. 461; and *Journ. Chem. Soc.* xxxviii. 683, and xl. 202.

Outline Method of Analysing Fatty Oils containing Foreign Admixtures.—Agitate 10 grammes of the sample in a tapped separator with about 30 c.c. of ether or recently-distilled carbon disulphide and 50 c.c. of water. Separate.

<table>
<tr><td>Aqueous Liquid.

Evaporate to dryness and weigh the residual soap.</td><td colspan="3">Solution in ether or carbon disulphide. Distil off the solvent, and agitate the residual oil with about 60 c.c. of alcohol, and a few drops of tincture of turmeric or phenol-phthaleïn. Then add standard soda cautiously, agitating the whole between each addition, until a brown or pink colour remains after shaking. Note the volume of soda solution required, as the quantity used is a measure of the free fatty and resin acids, and will determine the necessity of looking further into their nature. Separate any undissolved oil, dilute the alcoholic liquid, evaporate off the alcohol at a gentle heat, agitate with petroleum spirit; separate, evaporate off solvent, and add any separated oil to the main portion.</td></tr>
<tr><td rowspan="2"></td><td>Aqueous Liquid.—Add hydrochloric acid and agitate with ether. Evaporate the ethereal layer at 100°, and weigh residue representing mixed and free fatty and resin acids of original sample. If present in notable quantity, separate as described on page 160.</td><td colspan="2">Oil.—Saponify with alcoholic potash or soda. Boil off alcohol, dissolve soap in about 120 c.c. of warm water, and agitate with about 60 c.c. of ether. Separate, and agitate aqueous liquid a second and third time with ether.</td></tr>
<tr><td>Aqueous Liquid contains the glycerin of the soap formed by saponification of the neutral fixed oil of the sample. If the solution be treated with hydrochloric acid and agitated with ether, the weight of the fatty acids left on evaporating the ethereal layer, multiplied by 1·055, will give, approximately, the weight of the neutral fixed oil.</td><td>Ethereal Liquid distilled at 100°, and the last traces of the solvent removed by a current of air leaves the hydrocarbon oils in a state fit for identification and further examination. (See page 168.)</td></tr>
</table>

Free Fatty Acids may be normally present in small quantity, from natural decomposition of the oil, but any considerable amount of free fatty acid must be due to its intentional addition; except in palm oil, which often contains a large proportion of free acid. Free oleic acid is largely employed as a lubricant in wool-spinning, and free palmitic and stearic acids are employed for making candles and night-lights.

Free fatty acids differ from neutral fats or glycerides by being converted into soaps by treatment with alkaline carbonates or borax, and by being freely soluble in alcohol even if somewhat dilute. On largely diluting the solution of oleic acid in spirit of ·850 specific gravity, the liquid becomes cloudy, but may be clarified by a few drops of hydrochloric acid.

The simple detection of free fatty acid may be effected by shaking the oil with alcohol, and adding an alcoholic solution of lead acetate to the spirituous liquid. If a notable quantity of free fatty acid be present, a white precipitate will result. Resin and soap produce the same reaction. The solubility of free fatty acids in alcohol has been applied by Laugier* to their estimation when in admixture with neutral fixed oils. He agitates 10 grammes of the sample of oil with 50 c.c. of rectified spirit, removes the alcoholic liquid and repeats the operation three times with equal quantities of spirit. The free fatty acids are then estimated by evaporating the whole or an aliquot part of the alcoholic solution, and weighing the residue. The method is quite inapplicable to the assay of castor oil or mixtures containing it, and in other cases an allowance must be made for the solubility of the neutral fat in the spirit used. This allowance varies with the oil assayed, the following being the solubility of a few of the principal oils:—poppy-seed oil, 1 in 25; linseed, 1 in 40; almond, 1 in 60; hempseed, 1 in 30.

A great improvement on the above process consists in titrating the alcoholic solution of the fatty acid with standard alkali, using turmeric or phenol-phthaleïn as an indicator. The following mode of operating is applicable to the assay of oils for free fatty acids, no matter in what proportion these are present. To 10 grammes' weight of the sample of oil is

* *Dingl. polyt. J.* ccxxx. 430.

added about 60 to 70 c.c. of redistilled methylated spirit, and a few drops of a faintly alkaline alcoholic solution of phenolphthaleïn. The whole is then agitated and allowed to settle.* If the alcoholic liquid retain its pink colour no free fatty acid can be present, but if it be decolorised a few drops of decinormal caustic alkali should be added and the whole again shaken. The addition of alkali is repeated until the pink colour remains permanent on agitation. If the proportion of fatty acid be very large, it may be necessary to employ a stronger alkaline solution or to work on less of the sample. The amount of fatty acid present is then deduced from the volume of standard alkali consumed. 1 c.c. of decinormal caustic alkali corresponds to 0·0282 gramme of oleic acid.† If preferred, the alcoholic liquid can be separated from the oil, the alcohol evaporated off and the liquid diluted. This solution is then agitated with a little petroleum spirit (not ether) to separate suspended oil, the aqueous liquid separated and the fatty acid liberated from the soap solution by adding dilute hydrochloric acid. On agitating with ether (page 165), separating, and evaporating the ethereal solution to dryness, the fatty acids can be weighed. This plan should always be adopted in cases in which the presence of resin acids is suspected. The author has obtained very good results by the above method of titration, checked by weighing of the fatty acids. In the case of a sample containing soap, this admixture does not affect the titration, but renders the estimation by weight valueless unless the soap be previously separated as directed on page 154.

Any rosin acids in the sample will behave like free fatty acids. Their separation from fatty acids is described on page 160.

Occasionally, oils contain traces of free sulphuric acid, from imperfect elimination of the acid employed in refining. If present, sulphuric acid will be readily detected

* In applying the foregoing process to palm oil or other solid fats, it is best to dissolve the sample in mineral lubricating oil, so as to facilitate the manipulation.

† It must not be assumed that oleic acid is always the sole or even the chief free fatty acid present.

by agitating the oil with water, separating the aqueous liquid, and testing it with litmus paper and barium chloride. It can, if required, be readily determined by the same means, and if found in sensible quantity its presence must be duly allowed for in estimating the free fatty acids by titration, though it does not affect their gravimetric determination.

The presence of free acid in an oil seriously affects its suitability for lubricating purposes. Burstyn found that the extent of the action of olive oil on brass was regularly and directly proportional to the percentage of free acid present. He has proposed the following areometrical method of estimating the traces of free acid naturally present in olive oil.

The oil is shaken with an equal measure of rectified spirit of ·83 to ·84 specific gravity. After the oil has separated, the density of the spirit is accurately observed by a gravity-bottle or a delicate hydrometer graduated from ·825 to ·850. The density of the original alcohol must also be accurately known. If the density be observed by the hydrometer, there is no occasion to note the temperature, provided the specific gravity of the original spirit be taken side by side with that with which the oil has been agitated. M. Burstyn * finds that an oil 100 c.c. of which contains free acid in quantity sufficient to neutralise 1 c.c. of normal alkali (=·282 per cent. of oleic acid) will raise the density of the oil from ·8300 to ·8325, and that each additional 1 c.c. of alkali neutralised causes an increase of ·0003 in the density of the spirit. Hence it may be taken that the increase due to the solution of a trace of neutral fat in the spirit is ·0022, and that each ·0001 of increase of density beyond this number represents $\frac{\cdot 282}{3} = \cdot 094$ grammes of free acid per 100 c.c. M. Burstyn's method appears very suitable for rapid technical investigations of the quality of oil.

Resin is an addition to fixed oils the detection of which is attended with some difficulty, whilst its determination is very troublesome, and, in some cases, impossible.

Common rosin or colophony is added to oils to increase their density and viscosity, but its employment often wholly unsuits them for their intended purposes. Rosin con-

* *Dingl. polyt. J.* ccxvii. 314; *Journ. Chem. Soc.* xxix. 769.

sists almost wholly of a mixture of several resin-acids which are readily saponified by caustic alkalies, and even by alkaline carbonates or borax. The resultant soap is not completely precipitated by caustic alkalies or common salt, about 20 per cent. remaining in solution, and communicating a dark-brown colour to the liquid. Rosin has the comparatively high density of 1·07, and is of a yellowish brown colour. It is insoluble in water. Rosin dissolves readily in moderately strong alcohol, the solution having a variable dextro-rotatory power, which is usually about +15° for the transition-tint. Rosin resembles the oils in being readily soluble in ether, carbon disulphide, chloroform, benzene, and petroleum spirit.

The presence of resin in fixed oils may be detected by titrating the sample with alcohol aud alkali in the manner employed for the isolation of free fatty acids (see page 156), and in the absence of the latter the amount of alkali required is an indication of the proportion of resin acids present—1 c.c. of decinormal alkali representing ·033 grm. of rosin. The author has successfully employed this method for the analysis of linseed oil which contained less than 2 per cent. of rosin. The rosin extracted, and left on evaporating the ethereal solution to dryness, is readily recognisable by the taste and smell on heating, and in favourable cases has the physical characters of rosin.

Another method of detecting rosin in oils is based on the brown colour it imparts to caustic soda. The original sample is saponified, the alcohol boiled off, and the liquid treated with sufficient caustic soda ley to cause precipitation of the soap. The solution, separated from the soap by decantation or filtration through glass-wool, is found to have a dark brown colour if resin were present. The same reaction serves for the recognition of rosin in soap, any previous saponification being of course superfluous. The above method of treatment with caustic soda solution may also be applied to the mixture of fatty and resin acids separated from the oil in the manner described in the table (page 155). The dissolved resin may be recovered from the alkaline liquid by acidulating with hydrochloric acid, when a precipitate of a resinous odour will be

formed. The resin may be isolated by agitating with ether and evaporating the ethereal layer to dryness. It may then be identified by its physical and sensible characters.

In all methods for the isolation of resin from oils, it is obtained in admixture with any free fatty acids existing in the sample. In the absence of these its determination is comparatively simple, but the separation of mixed fatty and resin acids is difficult and at best only approximate. When a rough determination is sufficient it may often be effected by ascertaining the density of the mixed acids at a temperature of 100° C. The specific gravity of the fatty acids at that temperature varies from ·892 to ·900, while resin acids have a density greater than water, or about 1·07.* The dextro-rotatory power of rosin may occasionally be employed for its recognition, but the optical activity is too variable to allow of a quantitative determination being founded on it.

The following method for the separation of fatty and resin acids is due originally to F. Jean, but has been modified by Rémont, and to a slight extent by the author. It is based on the solubility of a portion of the resin soap in caustic soda and the conversion of the insoluble portion into a barium soap, which, on treatment with ether-alcohol, yields a solution of barium pinate and sylvate, whilst barium oleate, &c., remain undissolved.

The mixed fatty and resin acids from 10 grms. of the oil are first isolated in the manner described in the table on page 155, and after weighing are treated with a strong solution of caustic soda in quantity sufficient first to dissolve them and then to re-precipitate them as soaps. The aqueous solution is separated and the dissolved resin recovered from it by acidifying and agitating with ether in the manner already described. The precipitated soap is treated with warm water till dissolved, and the resultant solution mixed with sodium bicarbonate to get rid of any caustic alkali. The solution is then precipitated with a moderate excess of barium chloride, the liquid being constantly stirred. The precipitated barium soap is drained from the mother-liquor, and thoroughly dried at 100° C. It is then powdered and treated with 30 to 40 c.c.

* See also page 138, and "Resin in Soap."

of alcohol of ·850 specific gravity, kept gently boiling. The soap is well stirred up and mixed with the solvent. The liquid is allowed to settle for a few moments and is then poured off. The residue is treated with 10 to 15 c.c. of fresh alcohol, which is boiled, allowed to settle, and poured off as before. This treatment is repeated till the alcohol extracts scarcely anything more, which should be when a total volume of about 60 c.c. has been employed.

The alcoholic solution is distilled to a small bulk, and the resin precipitated from the solution by hydrochloric acid, isolated by agitation with ether, the ethereal layer separated, evaporated to dryness, and the residual resin weighed.

The insoluble barium soap is treated with hydrochloric acid and ether in a precisely similar manner, and the isolated fatty acids weighed.

Another tolerably simple process for separating resin and fatty acids has been described by Barfoed.* The author has no personal experience of it, but has some reason to doubt its value.

Detection and Determination of Hydrocarbons in Fat Oils and Waxes.—The extensive production of various hydrocarbon oils suitable for lubricating purposes, together with their low price, has resulted in their being largely employed for the adulteration of animal and vegetable oils. The hydrocarbons most commonly employed for such purposes are:—

1. Oils produced from petroleum and by the distillation of bituminous shale. The characters of these oils are described on page 34.

2. Oil produced by the distillation of common rosin, having the nature and properties detailed on page 66.

3. Neutral coal oil; being the portion of the products of the distillation of coal-tar boiling about 200° C., and freed from phenols by treatment with soda.

4. Solid paraffin, employed for the adulteration of bees'-wax and spermaceti, and used in admixture with stearic acid for making candles.

THE DETECTION OF HYDROCARBON OILS in fat oils is based

* *Zeitschr. Anal. Chem.* xiv. 20; and *Journ. Chem. Soc.* xxix. 773.

on the density of the sample, which is decreased by oils of the first class, and increased by rosin and coal-tar oils; by the diminished flashing and boiling point of the sample as compared with genuine oil of the same sort; by the fluorescent characters of the hydrocarbon oils of the first two classes; and by the incomplete saponification of the oil by alkalies. The taste of the oil and its odour on heating are also valuable indications.

Specific gravity is a character of some little value for detecting and approximately estimating hydrocarbon oils in fat oils, but in practice the indications obtained are apt to be rendered valueless by the employment of a *mixture* of mineral and rosin oil of the same density as the oil to be adulterated. The specific gravity of the hydrocarbon oils employed for adulterating fat oils and waxes will be found on pages 35, 40, and 67, while the specific gravities of the various fixed oils and waxes themselves are recorded in the tables commencing on page 155.

The tendency of an admixture of hydrocarbon oil with a fat oil is to reduce the flashing and boiling point of the sample. In some cases a distinct separation may be effected by fractional distillation, especially if the sample be previously saponified; but if this trouble be worth taking, it is better to effect an accurate separation of the hydrocarbon in the manner described on page 165.

Fluorescence is a character of considerable value for detecting the presence of hydrocarbon oils in fat oils. If undoubtedly fluorescent, an oil certainly contains an admixture of some hydrocarbon, but the converse is not strictly true, as the fluorescence of some varieties of mineral oil can be destroyed by chemical treatment, and in other cases fluorescence is wholly wanting (see page 35). Still, by far the larger number of hydrocarbon oils employed for lubricating purposes are strongly fluorescent, and the remainder usually become so on treatment with an equal measure of sulphuric acid.

If strongly marked, the fluorescence of a hydrocarbon oil may be observed in presence of a very large proportion of fixed oil; but if any doubt exist, the hydrocarbon should be

isolated in the manner described in page 165. As a rule, the fluorescence may be seen by holding a test-tube filled with the oil in a vertical position in front of a window, when a bluish "bloom" will be perceived on looking at the sides of the test-tube from above. A better method is to lay a glass rod, previously dipped in the oil, down on a table in front of a window, so that the oily end of the rod shall project over the edge, and be seen against the dark background of the floor. Another excellent plan is to make a thick streak of the oil on a piece of black marble, or glass smoked at the back,* and to place the streaked surface in a horizontal position in front of and at right angles to a well-lighted window. Examined in this manner, very slight fluorescence is readily perceptible. If at all turbid, the oil should be filtered before applying the test, as the reflection of light from minute particles is apt to be mistaken for true fluorescence. In some cases it is desirable to dilute the oil with ether, and examine the resultant liquid for fluorescence. An exceedingly small amount of mineral oil is sufficient to impart a strong blue fluorescence to ether.†

It must be borne in mind that the fluorescence is not perceptible by gas-light, but may be brought out by burning a piece of magnesium ribbon in the proper position.

DETERMINATION OF HYDROCARBON OILS IN FAT OILS.—The quantitative analysis of mixtures of fat oils with hydrocarbon oils has till recently been very uncertain, the published methods professing to solve the problem being for the most part of very limited applicability, and in some cases wholly untrustworthy,

When the hydrocarbon oil in admixture happens to be of

* Either of these is infinitely superior to, the polished tin plate usually recommended. In short, the background should be black, not white.

† This fact is of service for the examination of very dark oils, as by solution in ether the colour becomes proportionately diluted, and so causes less trouble. If the colour of the oil be very dark, as in the case of a dark Gallipoli or brown rape oil, it is necessary to refine it before applying the above test. This may be effected by agitating the sample successively with small proportions of concentrated sulphuric acid, water, and solution of carbonate of sodium, and subsequently filtering the clarified oil. In some cases decolorisation may be effected by warming the oil, and agitating it with freshly-burnt animal charcoal, the liquid being subsequently filtered.

comparatively low boiling point, it may often be driven off from the sample by exposing it to a temperature of 120° C. till it ceases to lose weight. The estimation thus effected is generally too low, and in many cases is quite untrustworthy. By employing a higher temperature (160° C.) more complete volatilisation is secured; and, as the process is simple, the rough determination it is capable of yielding is often useful.

When the nature of the fatty oil is known, and it is merely desired to estimate the proportion of hydrocarbon oil present, and not to ascertain its exact character, a very fair approximation can be obtained by ascertaining the saturating power of the sample, as described on page 124. Hydrocarbon oils having no power of neutralising alkali, their presence in admixture with a fat oil will tend to increase the saturation-equivalent of the sample to an extent dependent on the proportion present. Thus, if a sample which is professedly rape oil neutralises only 8·8 per cent of KHO, instead of 17·6 per cent., it may be safely assumed to contain about 50 per cent. of hydrocarbon oil.* In presence of free fatty acids or resin, the amount of alkali required is so altered as to render the process of little value.

The following method is the only one hitherto published which combines the necessary qualifications of rapidity, certainty, tolerable accuracy, and pretty general applicability, and at the same time enables the hydrocarbon oils to be obtained in a condition fit for further examination. It has been thoroughly studied and largely used by the author, and is based on the following principles:—

The hydrocarbon oils, of which the determination is desired, agree in the general property of being unaffected by alkalies, whereas all animal and vegetable oils and waxes undergo the decomposition known as "saponification" (page 119). If the alkali employed for the saponification be potash or soda, the resultant soap is soluble in water. The hydrocarbon oils, though insoluble in water and unaffected *chemically* by alkalies, dissolve with greater or less facility in concentrated solutions

* As far as I am aware, the proposal to employ Koettstorfer's process for the estimation of hydrocarbon oils in admixture with fat oils is due to Messrs Stoddart, who have determined the saturation-equivalents of a number of oils.

of soap, and are very imperfectly separated even on dilution. They may, however, be dissolved out from the dry soap, mechanically divided by admixture with sand, by the use of suitable solvents, such as ether, chloroform, carbon disulphide, benzene, or petroleum spirit. In some cases, a very perfect separation is obtainable by such means, but in others not only the hydrocarbon oil but a considerable quantity of soap passes into solution, especially if the solvent be employed at a temperature approaching its boiling point. This tendency of the soap to undergo solution may be wholly avoided by treating its *aqueous solution* with the solvent, instead of exhausting the *dry* soap.

The following are the details of the manipulation:— Five grammes' weight of the sample of oil is saponified by alcoholic alkali in the manner directed on page 120. The solution of the resultant soap, freed from alcohol, is brought to a volume of 70 to 80 c.c. and poured into a globular separator of about 200 c.c. capacity, furnished with a tap below and a stopper at the top. The tube below the tap should be drawn out to form a moderately fine jet. The porcelain basin is rinsed out with an additional 10 to 20 c.c. of water, which is poured into the separator. From 50 to 60 c.c. of ether should next be added, the stopper inserted, and the whole thoroughly shaken and allowed to rest for a few minutes. As a rule, the liquid will readily separate into two well-defined layers, the lower one brownish and consisting of the aqueous solution of soap, while the upper layer consists of ether containing any hydrocarbon oil in solution. Sometimes separation into layers does not occur readily, the liquid remaining apparently homogeneous, or assuming a gelatinous consistency. In such cases, separation may be induced by thoroughly cooling the contents of the separator; by adding more ether and re-agitating; or, if both these means fail, a *few* cubic centimetres of alcohol may be added, and a gentle rotatory movement imparted to the liquid, avoiding complete admixture, when a very rapid separation of the ethereal layer almost invariably occurs. Separation being effected, the aqueous liquid is run through the tap into a beaker. About

Fig. 6.

10 c.c. of water is added to the ether which remains in the separator, and the whole agitated. The washings are then run off in their turn, and, after repeating the treatment with water, the ether is tapped off into a tared flask. The aqueous liquid and washings are then returned to the separator, and agitated with a fresh quantity of ether, which is washed and run into the flask as before. The agitation of the soap solution is repeated once more, when the extraction of the hydrocarbon oil may be relied on as being complete. As a rule, the ethereal solution obtained will be strongly fluorescent. The flask containing the ethereal solution of the hydrocarbon oil is then attached to a Liebig's condenser, and the ether distilled off by immersing the flask in water heated nearly to boiling by a flame. When the distillation ceases, a moderate current of air, filtered by passing it through a tube containing cotton- or glass- wool, is blown through the flask for a few minutes by a second tube passing through the cork. In this way the evaporation of the ether is readily perfected. To eliminate the last traces, the flask may be detached from its fittings and placed in a horizontal position in a hot-water oven for about twenty minutes. Prolonged heating should be avoided, as many classes of hydrocarbon oils used for adulterating fixed oils are sensibly volatile at 100° C. This is notably the case with coal-tar oil, and hence, in analysing mixtures containing it, the heating in the water-oven should be wholly dispensed with. With rosin oil, paraffin wax, and the denser mineral oils there is but little danger of loss by volatilisation at 100° C. The flask is then weighed, when the increase in weight over the original tare gives the amount of hydrocarbon oil extracted.*

The foregoing process has been proved to be accurate on numerous mixtures of fat oils with hydrocarbon oils. The results obtained are correct to within about 1 per cent., in all ordinary cases. In cases where extreme accuracy is desired, it is necessary to remember that most, if not all, animal and

* Occasionally, from defective manipulation, the hydrocarbon oil will contain globules of water. These, if very small, may be neglected, but if considerable, six or eight drops of absolute alcohol should be added and thoroughly incorporated with the oil by agitation. On re-heating the flask in a horizontal position, the alcohol will evaporate and carry the water with it. The residual oil may be weighed as soon as it is clear and no longer smells of alcohol.

vegetable oils contain traces of matter wholly unacted on by alkalies. In certain cases, as butter and cod-liver oil, this consists largely of c h o l e s t e r i n, $C_{26}H_{44}O$. The proportion of unsaponifiable matter soluble in ether which is naturally present in fixed oils and fats, rarely exceeds 1½ per cent., and is usually much less. Sperm oil, however, constitutes an exception, yielding about 40 per cent. of matter soluble in ether (see page 199). This peculiarity has no practical effect on the applicability of the process, as sperm oil being the most valuable of commercial fixed oils it is never present without due acknowledgment of the fact. An unknown oil may be recognised as sperm by the characters detailed on page 198. Spermaceti and the other waxes yield after saponification large percentages of matter to ether, and hence the process is not available for the determination of paraffin wax in admixture with these bodies, though it gives accurate results with the mixtures of paraffin and stearic acid so largely employed for making candles.*

The table on next page indicates the behaviour of the constituents of complex mixtures of fats, oils, and waxes when the aqueous solution of the saponified substance is shaken with ether.

* The following figures, obtained in my laboratory by the analysis of substances of known purity and of mixtures of known composition, show the accuracy of which the process is capable. The process was in each case conducted on about 5 grammes of the sample in the manner detailed on page 165. The results are expressed in percentages.

Composition of substance taken in 100 parts.		Unsaponifiable matter found.	Composition of substance taken in 100 parts.		Unsaponifiable matter found.
Fat Oil.	Hydrocarbon Oil.		Fat Oil.	Hydrocarbon Oil.	
Olive . . 40	Shale Oil . 60	58·03	Olive . . 100	0	1·14*
Olive . . 80	Shale Oil . 20	19·37	Rape . . 100	0	1·00*
Olive . . 40	Rosin Oil . 60	59·42	Castor . 100	0	0·71
Olive . . 80	Rosin Oil . 20	19·61	Cod-liver 100	0	1·82
Rape . . 84	Shale Oil . 16	15·95	Palm . . 100	0	0·54
Cotton-seed 60	Rosin Oil . 46	39·74	Butter-fat 100	0	0·46
Linseed . 60	Rosin Oil . 40	39·32	Sperm . . 100	0	41·49
Castor . . 60	Rosin Oil . 40	38·88	Spermaceti 100	0	49·68
Cod-liver . 70	Rosin Oil . 30	30·80	Japan Wax 100	0	1·14
Cotton-seed 48	Coal-tar Oil 52	52·60	Lard . . 100	0	0·23*
Lard . . 60	Paraffin Wax 40	39·54	Cacao Butter . 100	0	0·22
Lard . . 20	Paraffin Wax 80	80·09			

* The experiments marked with an asterisk were not made strictly by the same process as the majority.

Dissolved by the Ether.	Remaining in the Aqueous Liquid.
Hydrocarbon Oils; including Shale and Petroleum Oils, Rosin Oil, Coal-tar Oil, Paraffin Wax and Ozokerite, Vaselene.	Fatty Acids.
Neutral Resins.	Resin Acids.
Unsaponified Fat or Oil.	Carbolic and Cresylic Acids.
Unsaponifiable matter, as Cholesterin.	Glycerol (Glycerin).
Spermyl Alcohol, from Sperm Oil.	
Cetyl Alcohol, from Spermaceti.	
Myricyl Alcohol, from Bees'-wax.	

(In combination with the alkalies used.)

The hydrocarbon oil having been isolated by saponifying the sample and agitating with ether, its nature may be ascertained by observing its density, taste and smell, behaviour with acids, &c. The specific gravity may be determined by means of a very small specific gravity bottle or Sprengel's tube (Vol. I. page 6). If the proportion of hydrocarbon oil be small, it may be necessary to operate on a larger quantity than 5 grammes of the sample. A very fair approximate estimate of the density of the extracted hydrocarbons may be made on Hager's principle (page 139), by adding a drop of the oil to very dilute alcohol, or ammonia, and adjusting the strength of the liquid, so that it may be identical with that of the drop of oil. The specific gravity of the dilute alcohol is then ascertained in the usual way. The fluorescence of hydrocarbon oils is best observed in the manner described on page 163. It often becomes intensified by treating the extracted hydrocarbon with an equal measure of strong sulphuric acid.

The smell and taste of the hydrocarbon oils are often highly characteristic of their origin. The smell of coal-tar oil is readily observed; and the taste, especially the after-taste, of rosin oil is not to be mistaken. The smell produced on strongly heating a drop of the oil in a platinum capsule is also highly characteristic.

The following table may be of service for discriminating the

liquid hydrocarbon oils liable to be employed for the sophistication of fat oils. Paraffin wax is not included.

	Petroleum and Shale Oils.	Rosin Oil.	Coal-tar Oil.
Smell; cold.	None or slight.	None or slight.	Smell of coal-tar.
Smell; on heating strongly.	Variable; rarely characteristic.	Smell of burning rosin.	Smell of coal-tar.
Taste.	Variable.	Slight; after-taste characteristic.	Strong; tarry.
Specific gravity.	·870 to ·915.	·960 to ·990.	·981 to 1·040.
Fluorescence.	Blue or green; rarely absent.	Violet to blue; rarely absent.	Slight; often absent.
Rotatory power.	None.	Variable (page 67.)	None.
Action of sulphuric acid, sp. gr. 1·845.	Very slight heating.	Decided rise of temperature; red-brown colour.	Marked heating; charring.
Action of nitric acid, sp. gr. 1·45.	Slight heating.	Violent action and great heat.	Marked action and heating.

Further details respecting the behaviour of different hydrocarbon oils with tests are given under their respective heads (see pages 35 and 68).

Owing to their extreme similarity in character, it is not possible to ascertain with accuracy the proportions of two hydrocarbon oils of different origin existing together in a mixture. In the case most frequently occurring, which is that of mixed mineral and rosin oils being employed to adulterate fat oils, the proportions in which the adulterants were mixed may be approximately estimated from the density of the oil extracted by agitating the solution of the saponified oil with ether, as directed on page 165.

LUBRICATING PROPERTIES OF OILS.

Lubrication has for its object the reduction of friction between moving surfaces. In order to effect this purpose, it is necessary to employ a lubricant which will form a film of sufficient viscosity to prevent it from being readily squeezed out from between the surfaces. Hence for heavy machinery a highly viscous or even solid lubricant must be employed,*

* For heavy machinery, oils are not unfrequently wholly or partially replaced by graphite, steatite, sulphur, or soft metal. In some cases the viscosity of

while the thinnest oils are suitable for delicate movements, such as exist in clocks and watches. The viscosity of all oils is greatly reduced by an increase of temperature, and hence the temperature to which a lubricant will be subjected by the surrounding atmosphere, or by the heat developed by the friction itself, is an important factor in judging of the suitability of an oil for a particular purpose.

The characters which should be taken into consideration in forming an opinion on the suitability of a lubricating oil for a particular class of work * are—

1. The viscosity or "body" of the oil at certain fixed temperatures (see page 142).

2. The temperature at which the oil thickens or actually solidifies (see page 140).

3. The "flashing point," or temperature at which the

the oil is increased by an admixture of soap, or, what amounts to the same thing, by adding alkali. The following table shows the composition of three mixtures used for lubricating the axles of railway carriages :—

	English.		German.
	Summer.	Winter.	
Tallow	504	420	246
Palm Oil	280	280	98
Rape Oil	...	...	11
Sperm Oil	22	35	...
Caustic Soda	120	126	52
Water	1370	1524	593

* The following propositions descriptive of the characters which should be possessed by lubricating oils are taken, with some verbal modifications, from Spon's *Encyclopædia of the Industrial Arts* :—

(*a*) A mineral oil flashing below 150° C. is unsafe.

(*b*) A mineral oil losing more than 5 per cent. in ten hours at 15° to 20° C. is inadmissible, as the evaporation creates a viscous residue, or leaves the bearing dry.

(*c*) The most fluid oil that will remain in its place, fulfilling other conditions, is the best for all light bearings at high speeds.

(*d*) The best oil is that which has the greatest adhesion to metallic surfaces, and the least cohesion in its own particles; in this respect fine mineral oils stand 1st, sperm oil 2d, neats'-foot oil 3d, and lard oil 4th, consequently the finest mineral oils are best for light bearings and high velocities; the best animal oil to give body to fine mineral oils is sperm oil (?); lard and neats'-foot oils may replace sperm oil when greater tenacity is required.

oil gives off inflammable vapour in notable quantity (see page 23).*

4. The boiling point of the oil.*

5. The "gumming" character, or tendency of the oil to become oxidised (see page 146).

6. The acidity of the oil (see pages 156 and 158.)

7. The tendency of the oil to act on metals (see page 175).

VISCOSITY is a very important character of a lubricating oil. It bears no direct relation to the specific gravity, and

Kind of Oil.	No. of Seconds required.		
	At 60° F. (=15·5° C.)	At 120° F. (=49° C.)	At 180° F. (=82° C.)
Sperm Oil	47	30½	25¾
Olive Oil	92	37¾	28¼
Lard Oil	96	38	28½
Rape Oil	108	41¼	30
Neats'-foot Oil . . .	112	40¼	29¼
Tallow Oil	143	37	25
Engine Tallow . . .	Solid	41	26½

decreases greatly with rise of temperature, the ratio of decrease being notably different for different oils. This is well shown in the above table,† the figures in which represent the

(*e*) The best mineral oil for cylinders is one having a density of ·893, and a flashing point of 360° C.

(*f*) The best mineral oil for heavy machinery has a density of ·880, and a flashing point of 269° C.

(*g*) The best mineral oil for light bearings and high velocities has a density of ·871, and a flashing point of 262.

(*h*) Mineral oils alone are not suited for very heavy machinery, on account of their want of body, but well-purified animal oils are applicable to the heaviest machinery.

(*i*) Olive oil stands first among vegetable oils, as it can be purified without the aid of mineral acids. The other vegetable oils which, though far inferior to olive oil, are admissible as lubricants, are, in their order of merit, sesamé, earth-nut, rape and colza, and cotton-seed oils.

(*j*) No oil is admissible which has been purified by means of mineral acids.

* For convenience these characters are mentioned here, as being important in the case of hydrocarbon lubricating oils; but in the fatty oils the flashing and so-called "boiling" points are so elevated as to be practically unimportant.

† Taken with other valuable and suggestive matter from a pamphlet by Messrs J. Veitch-Wilson, & Co.

number of seconds required by certain typical oils to pass through the same aperture at different temperatures.

From these figures it is evident that the viscosity is always less at a high temperature, the thicker animal oils, containing much stearin, being most sensitive to an increase of heat. Hence, when an oil is to be employed in a situation where it will be exposed to a moderately high temperature, one which is thick or even solid at ordinary temperatures may be advantageously used. But, besides the modification of the viscosity due to rise of temperature, it is necessary to consider the weight of the machinery to be lubricated, and whether it is fast- or slow- running. Thus sperm oil is invaluable for the light and fast-running spindles of cotton-spinning machines, but it would be quite unsuited for oiling heavy machinery. On the whole, it must be remembered that a thick oil takes a greater power to drive and develops a higher temperature than an oil of low viscosity; and, as a rule, the lubricant should be as thin as is consistent with the weight of the machinery and the temperature to which the oil will be subjected. When the driving power is ample, it will be found better and more economical to use a moderately thick oil for heavy machinery, particularly where the temperature is high, but if the driving power be inadequate, it may be necessary to use a thinner oil than would otherwise have been advisable.

THE SOLIDIFYING POINT of a lubricating oil is a character which is so manifestly of importance in judging of its suitability for particular purposes, that nothing further need be said on the subject here; except that lubricating oils as a class ought to remain limpid at 0° C (=32° F.), and, for some purposes, at a much lower temperature.

THE FLASHING POINTS AND BOILING POINTS of the fixed or fatty oils are so high as to be practically unimportant, but as many lubricating oils are now composed largely or entirely of hydrocarbon oils of low volatility, the flashing point becomes a character of importance. A low flashing point is generally due to the presence of naphtha. Some oils, sold for lubricating purposes, have flashing points so low as to bring them under the legal definition of "petroleum" (see pages 20 and 24).

As a rule the flashing points of the pale lubricating oils manufactured in the south of Scotland from bituminous shale, range from 130° to 180° C.; and of the darker oils and greases from 180° to 230° C. In the case of oils employed for engine cylinders, the flashing point should certainly not be lower than 200° C., nor the boiling point below 260° C. (=500° F.). The importance of a high flashing point is two-fold in such cases. Not only is there the chance of inflammation, but any naphtha or oil of high volatility readily destroys the india-rubber packing of the cylinders.

"GUMMING," or tendency to dry, if present to any notable extent, renders an oil unfit for use as a lubricator. The hydrocarbon and animal oils are practically free from drying tendencies; but fish oils are less perfect in this respect, with the exception of sperm oil, which has peculiarities which distinguish it from all others (see page 197). The vegetable oils differ greatly in their drying properties, but even the so-called non-drying oils, like rape and olive (see page 129), are not wholly free from a tendency to thicken. An admixture of hydrocarbon oil notably reduces the tendency of a vegetable oil to thicken, and correspondingly diminishes its liability to generate sufficient heat to cause spontaneous combustion. On the other hand, the presence of resin causes a notable increase in the gumming tendency of an oil.

Besides the methods of examination indicated on page 146, the following furnishes a useful practical means of ascertaining the tendency of an oil to dry or gum:—A plate of smooth iron or glass having parallel grooves on it,* and about six feet in length, is supported so that one end is raised an inch above the other. Equal measures of the oils to be tested are then taken up with a pipette, and placed, as nearly as possible at the same time, at the upper end of the inclined plane. The rate of flow of each oil is then observed from day to day. Some keep ahead at first, but gradually loose speed owing to their tendency to gum or dry. A good lubricating oil will continue to flow for six or eight days, while a drying oil, like

* A piece of corrugated zinc, such as is used for roofing, will serve for an extemporised inclined plane.

linseed, though making rapid progress at first, will soon become stationary.*

ACIDITY of a lubricating oil ought to be conspicuous by its absence. A perfectly neutral oil has no action on metals, and experiment shows that the corrosive action increases in direct proportion with the quantity of free acid present. The method of testing oil for free acid is described on page 156.

Although, *when freshly manufactured*, an oil may be free from any trace of acid, it is not unlikely to acquire a very sensible acidity in time. This is true of many animal and vegetable oils, but the hydrocarbon oils are wholly free from tendency to become acid; hence in this, as in some other respects, they present a decided advantage over the fat oils.

Although, *at the time of using*, an oil may be wholly free from acid reaction, it may, if of animal or vegetable origin, readily *become* acid, and hence corrode the metallic surfaces it is employed to lubricate. This is notably the case when the oil is exposed to the action of high pressure-steam, as under such conditions all the fat oils suffer decomposition more or less readily with formation of free fatty acids and glycerin (see page 119). Hence animal and vegetable oils are wholly unsuited for use in the cylinders of high-pressure engines, and

* The following table shows some actual results obtained in the manner described. The figures give the run of each oil in inches:—

	Best Sperm Oil.	Common Sperm Oil.	Gallipoli (Olive) Oil.	Lard Oil.	Rape Oil.	Linseed Oil.
First day .	32	19	10	10¼	14	17½
Second day .	50	45	14	10½	18	18
Third day .	53½	55	18	10¾	19	18
Fourth day .	54	59	18½	10¾	19	18¼
Fifth day .	54	62	19⅛	11¾	19¼	18⅛
Sixth day .	54	64	21½	still	19½	still
Seventh day .	54	67	21	...	19¾	...
Eighth day .	54	67½	21¼	...	still	..
Ninth day .	...	68	21½	...	...	...

The table is taken from Appleton's *Dictionary of Mechanics*. Certainly the sample described as "common sperm oil" gave better results than the one classified as "best."

should be completely abandoned in favour of hydrocarbon oils of great viscosity and high flashing point.

ACTION ON METALS.—The tendency of an oil to act on metals varies not only with the proportion of free acid and the kind of oil, but also with the nature of the metal in contact. Thus, nearly all fatty oils act more rapidly on copper than on iron, but in the case of mineral oils the rate of action is altered. The following table shows the results obtained with different kinds of oils by Mr W. H. Watson:—

Oils.	Iron dissolved in 24 days.	Copper dissolved in 10 days.
Almond	·0018 grain	·1030 grain
Castor	·1048 ,,	...
Colza	·0800 ,,	·0170 ,,
Lard	·0250 ,,	...
Linseed	·0050 ,,	·3000 ,,
Neats'-foot	·0875 ,,	·1100 ,,
Olive	·0062 ,,	·2200 ,,
Paraffin	·0045 ,,	·0015 ,,
Seal	·0050 ,,	·0485 ,,
Sperm	·0460 ,,	·0030 ,,

In these experiments the amount of metal in the oil was determined at the conclusion of the experiment. An alternative plan is to employ a plate of polished metal of accurately ascertained weight, and after the treatment to clean it thoroughly with ether, and weigh again.

The depth of green tint acquired by an oil in contact with copper is no criterion of the amount of metal dissolved by it.

IDENTIFICATION OF FIXED OILS.

The recognition of an unmixed animal or vegetable oil may usually be effected by a careful application of the methods of examination already described. Various systematic schemes for the purpose have been devised by different chemists, but no such method can be implicitly relied on, owing to the variable nature of the oils themselves. In particular, any positive recognition based on the colour reactions of an oil is

of but little value, unless confirmed by the indications of other tests.

In examining oils for the detection of adulteration, the relative commercial value of the different kinds should never be lost sight of, and it must be remembered that in addition to the adulteration of the more valuable fatty oils with the cheaper, their sophistication by admixture with the hydrocarbon oils obtained by the distillation of petroleum, shale, coal, rosin, &c., is also extensively practised.*

Practically, it is often of less importance to know whether an oil has the origin attributed to it, than to learn whether its characters are such as will allow it to be safely used as a substitute for the genuine oil. This may be ascertained with tolerable certainty, and in some cases the nature of the adulterants definitely detected.

Although it is not possible to lay down any general scheme which shall be available for the identification of any unmixed fatty oil, the recognition is much facilitated by conducting the examination in a systematic manner. By proceeding in the following manner, positive identification of a particular oil may generally be effected, and so much information gained as to the probable constituents of a mixture that special tests for the oils suspected to be present may then be successfully applied:—

Place a drop of the oil on the back of the tongue by means of a glass rod, and taste it carefully, avoiding too hasty a

* The following tabular arrangement by Messrs Stoddart shows the order of commercial value of the principal fluid oils:—

1. Sperm Oil.
2. Seal Oil, Olive Oil, Lard Oil — These three change places in different seasons.
5. Rape Oil.
6. Seed Oils — (*a*) Cotton-seed. (*b*) Linseed. (*c*) Niger-seed.
7. Castor Oil.
8. Fish Oils — (*a*) Cod. (*b*) Pilchard. (*c*) Whale.
9. Mineral Oils.
10. Rosin Oil.

decision. In this manner fish oils, linseed oil, croton oil, mineral oil, rosin oil, and some others may generally be detected. Rosin oil is remarkable for the nauseous after-taste of rosin produced by it. Rancidity of an oil may easily be recognised by the taste.

Heat a portion of the oil in a porcelain or platinum capsule to about 140° or 150° C., and observe the odour carefully. When sufficiently cool pour a little of the oil into one hand, rub with the other, and smell again. A little practice will allow of vegetable oils being readily distinguished from animal oils, and the products of fish and marine mammals from those of terrestrial animals. The odour on heating will also frequently permit the recognition of mineral and rosin oils, and, if the remainder of the oil be strongly heated till it ignites and the flame then blown out, the vapours will often have a highly characteristic odour.

Ascertain the specific gravity of the sample at 15·5° C. (=60° F.) if fluid at that temperature, but at 37·8° C. or 100° C. if solid at the ordinary temperature. This test is a very valuable means of recognising individual oils, but if much free acid be present, or the sample be a mixture of several oils, its indications are less reliable. The following table enables an unmixed oil to be arranged in one of eight groups, according to its specific gravity and physical state at the ordinary temperature. More precise determinations of the densities of the fatty oils are given in the tables commencing on page 129.

The sample having been satisfactorily classified by means of the taste, smell, and density, the subsequent means of identification depend on the results of these tests.

(*a*) Sperm and shark oils are readily distinguished from shale and petroleum products as described on page 198.

(*b*) The distinction of shale and petroleum products from each other may, if required, be effected as described on page 169.

(*c*) The non-drying vegetable oils may be distinguished from each other by a careful determination of the density, viscosity, and heating when mixed with sulphuric acid. The colour-reactions of Chateau may be employed as confirmatory tests. Lard-, tallow-, and neats'-foot-oils may be

Oils Liquid at 15° C.						Oils Solid at 15° C.	
Specific Gravity at 15·5° C. (=60° F.).						Sp. gr. at 37·8° C. (=100° F.).	
a. ·875 to ·883.	*b.* ·883 to 912.	*c.* ·912 to 920.	*d.* ·920 to 937.	*e.* ·937 to ·957.	*f.* ·957 to 1·000.	*g.* ·902 to 909.	*h.* ·909 to 914.
Vegetable Oils. None. *Marine Animal Oils.* Sperm. Shark.	*Vegetable and Animal Oils.* None.	*Vegetable Oils.* Non-drying. Almond. Ben. Rape and Colza. Earth-nut. Mustard. Olive. *Marine Animal Oils.* None. *Terrestrial Animal Oils.* Lard Oil. Tallow Oil. Neats'-foot.	*Vegetable Oils.* More or less drying oils. Beech-nut. Cotton-seed. Hazel-nut. Sesamé. Sunflower. Niger-seed. Camelina. Hempseed. Linseed (raw). Poppy-seed. Walnut. *Marine Animal Oils.* Cod-fish. Cod-liver. Menhaden. Porpoise. Seal. Whale. *Terrestrial Animal Oils.* None. *Mineral Oils.* None.	*Vegetable Oils.* Croton. Boiled linseed. *Animal and Mineral Oils.* None.	*Vegetable Oil.* Castor. *Animal Oils.* None. *Hydrocarbon Oil.* Rosin Oil.	*Vegetable Fats.* Cacao butter. Palm oil. *Terrestrial Animal Fats.* Bone oil. Lard. Tallow. Dripping. Butterine. Oleomargarin.	*Vegetable Fats.* Coco-nut oil. Palm-nut oil. *Terrestrial Animal Fats.* Butter-fat.
						k. Sp. gr. above ·920 in solid or fluid state.	
						Waxes. Bees' wax. Carnaüba wax. Japan wax. Spermaceti.	
Mineral Oils. Shale and Petroleum products.	*Mineral Oils.* Shale and Petroleum products.	*Mineral Oils.* Heavy Shale and Petroleum products.				*l.* Sp. gr. very variable.	
						Paraffin and mineral wax.	

differentiated by the fifth and sixth tests of Chateau, and by their viscosity and heating with sulphuric acid.

(*d*) The vegetable oils possessing more or less well-defined drying characters may be in a great measure differentiated by an exact determination of their densities, viscosities, and heating with sulphuric acid. When cotton-seed oil is saponified, the fatty acids separated on acidifying the solution of the soap are solid at the ordinary temperature, while those from most other oils of the group are liquid. The elaïdin test and colour-reactions will suffice for the positive identification of an unmixed vegetable oil of this group.

The marine animal oils may be distinguished as a class by the brown colour they produce when saponified, and by the darkening that ensues on passing a current of chlorine through the oil. They may be differentiated from each other by Chateau's colour tests. Liver-oils give a fine violet colour changing to brown, when a drop of sulphuric acid is placed in the centre of 10 to 20 drops of the oil. The following table shows the density of the leading "fish-oils" at 37·8° C. (= 100° F.) compared with water at the same temperature taken as unity:—

Oil.	Highest Extreme.	Lowest Extreme.	Usual Density.
Cod-fish . . .	·9220	·9114	·9176
Cod-liver . . .	·9180	·9173	·9179
Seal	·9195	·9136	·9150
Whale	·9066	·9056	·9060

(*e*) and (*f*) Boiled linseed oil is easily distinguished from croton oil by the taste and smell. Croton and castor oils are readily soluble in rectified spirit, but linseed is nearly insoluble. Boiled linseed oil dries very rapidly, but croton and castor very slowly. The viscosity and heating with sulphuric acid also distinguish these oils without difficulty.

Rosin oil is unsaponifiable by alkalies, and is readily identified by its strong after-taste and the terebinthinous odour developed when the sample is heated till it catches fire, and the flame then blown out.

(*g*) and (*h*) The oils of these groups are distinguished by their melting and solidifying points, taste, smell, and by the proportions of soluble and insoluble acids yielded on saponification. Coco-nut oil and palm-nut oil resemble butter-fat in yielding a notable amount of volatile or soluble fatty acids.

In the case of a sample consisting of a complex mixture of wholly unknown oils, the identification of the constituents is often a problem of extreme difficulty, but when the leading component is known or can be recognised, the detection of the others becomes more feasible. It must, however, always be borne in mind that in most cases oils cannot be recognised by distinct and specific tests, such as exist for the different metals, and that in arriving at a conclusion as to the composition of any sample of mixed oils, the analyst must be content to be guided in a great measure by circumstantial evidence, and a careful consideration of probabilities. The foregoing methods of examination are of course employed, and in addition such special tests as will be found described under various heads. The sub-articles descriptive of the more important commercial oils contain a list of the admixtures most commonly found in each oil, and special tests suitable for their detection.

The following facts, which depend on the chemical nature of the oils, are of importance in the examination of complex samples, and to a less extent for the identification of unmixed oils :—

Much information may be obtained by saponifying the oil and determining the products formed by the reaction. Thus most fixed oils are split up into a fatty acid and glycerin, but sperm oil and the waxes yield products differing from glycerin in being insoluble in water but soluble in ether (see page 167). Sperm oil only yields some 63 per cent. of fatty acids, while most other fixed oils (not the waxes) give about 95 per cent. As stated above, butter-fat and the oils from coco-nut and palm-nut yield a notable proportion of acids volatile and soluble in water (see "Soap"), but, in the case of almost all other oils, the whole of the fatty acids are practically insoluble. Resin gives 100 per cent. of resin acids and no glycerin, but mineral and rosin oils do not undergo

saponification at all, and so can be dissolved out of the solution of soap by agitating with ether (see page 165).

The saturation-equivalents and the physical properties of the fatty acids afford important information. The acids from rape and castor oils neutralise sensibly less alkali than those from most oils. Lard- tallow- and neat's-foot-oils yield fatty acids of much higher melting point that the non-drying vegetable oils which they otherwise resemble. Cotton-seed oil yields fatty acids solid at the ordinary temperatures, while most drying and semi-drying oils yield liquid acids. Any admixture of resin acids tends greatly to increase the density of the fatty acids (page 160). When it is intended to examine the characters of the fatty acids, it is highly important that the aqueous and alkaline solution of the soap should be previously agitated with ether until nothing more is removed, as any admixture of wax or hydrocarbon oil would profoundly modify the properties of the fatty acids.

The details of the method of separating these admixtures and of determining the fatty acids will be found on page 163, *et seq.*

It will be observed that the drying oils are heavier but less viscous that the non-drying oils, apparently in proportion to their drying tendency. The non-drying oils give solid elaïdin (page 147), the product becoming less and less firm as it is derived from a more strongly-drying oil. Similarly, the heating produced by mixture with sulphuric acid appears to bear a direct relationship to the drying properties of a vegetable oil. By a careful application of these facts an approximate estimate of the proportions of different oils in a mixture can often be made.

SPECIAL CHARACTERS AND MODES OF EXAMINING FATTY OILS.

The methods of examining oils hitherto described have been mostly general; but the following sections contain more detailed information respecting the specific characters and modes of assaying the more important fatty oils and waxes:—

Almond Oil.

French—Huile d'Amandes. *German*—Mandelöl.

(See also table on page 129.) This oil may be obtained by expression from either bitter or sweet almonds.

The fixed oil of almonds is largely employed in the preparation of ointments and emulsions, for which it is better adapted than olive oil.

Almond oil consists chiefly of triolein. It becomes rancid on exposure to air, but is not siccative. It dissolves in 24 parts of cold alcohol or 6 parts at the boiling point.

Almond oil is not unfrequently adulterated with, and is sometimes completely substituted by, peach-kernel oil. Mustard oil, sesamé oil, arachis oil, olive oil, and lard oil are also employed as adulterants of almond oil. Many of these additions may be detected by observing the absorption-spectrum, almond oil differing from most vegetable oils in not giving either a banded spectrum or producing strong absorption in the red or the violet. The elaïdin test suffices for the detection of poppy-seed oil, the solidification being much retarded by the adulterant. Again, pure oil of almonds gives a homogeneous and very firm mass when shaken with $\frac{1}{5}$th of its bulk of strong ammonia, whilst the product is merely clotted in the case of the sample being adulterated with poppy-oil. The density and the rise of temperature on treatment with sulphuric acid (see page 152) also serve for the detection of poppy-oil.

The same tests, together with the colour-reactions described on page 149, *et seq.*, will suffice for the detection of most other of the adulterants of almond oil, such as olive and lard oil. Many of the additions to almond oil tend to raise the solidifying point of the sample.

Arachis oil may be detected as in olive oil (see page 186).

The detection of mustard oil in almond oil presents some difficulty. It might probably be effected by boiling the sample with an equal measure of a 10 per cent. solution of caustic soda, filtering through a wet filter, and testing the filtrate with lead acetate, when a dark coloration will indicate the probable presence of mustard oil. The test is based on the presence of traces of sulphur compounds in the expressed oils from cruciferous seeds.

The following reactions are recommended by J. D. Bieber for detecting peach-kernel oil and sesamé oil in almond oil:—

Treatment.	Reaction.		
	Almond Oil.	Peach-kernel Oil.	Sesamé Oil.
1. Agitate 5 parts of the oil with 1 part of a cold mixture of equal weights of concentrated sulphuric acid, fuming nitric acid, and water.	White or yellowish-white liniment.	At once assumes a peach-blossom colour, afterwards turning dark orange.	First, pale yellowish-red; afterwards, dirty orange-red.
2. Agitae the oil with nitric acid of 1·4 sp. gr.*	Pale yellowish liniment.	At once a red liniment.	Dirty greenish-yellow; afterwards reddish.

Olive Oil.

French—Huile d'Olives. *German*—Olivenöl.

(See also table on page 129.) Olive oil is extracted from the fruit of the olive by pressure, and of late years by solution in carbon disulphide.

The finest olive oil has a pale yellow colour with a tinge of green. It is almost wholly free from odour, and has a mild and agreeable taste. Occasionally it has a nutty flavour, and produces a slightly acrid sensation in the throat when swallowed.

Olive oil has a density of about ·917 at 15° C. It boils at 315°. At about 10° C. it deposits a white granular fat; and at 0° it solidifies into a product which can be separated by pressure into a solid tallow-like fat, and a fluid oil consisting essentially of triolein. By saponification, olive oil yields glycerin and soaps of oleic, palmitic, and (perhaps) stearic acids.

Olive oil is only slightly soluble in alcohol, but dissolves in about 1½ times its weight of ether.

Olive oil shows well-defined chlorophyll bands when its spectrum is examined. The bands become changed or alto-

* This test is applicable to the detection of a variety of oils (see page 187).

gether destroyed on exposing the oil to sunlight or heating it with caustic alkali.

Of the commercial varieties of olive oil, one of the most esteemed is Provence oil. Florence oil is a fine kind employed for culinary purposes. Lucca and Gallipoli oils are well known brands. Sicily oil is mostly of inferior quality.

The variations in the quality of olive oil are largely dependent on the manner in which the olives are treated, as, *e.g.*, the care with which the fruit is plucked, the length of time it is stored before being crushed, and other conditions which affect the colour, smell, and appearance of the oil expressed. Olive oil varies in colour from clear yellow to a deep olive-green, and in smell from that of salad oil to the powerful odour of the inferior varieties.

In some countries, olive oil is an important article of diet. It is extensively employed in the manufacture of woollen cloth, and in dyeing fabrics turkey-red. The inferior varieties are employed in soap-making. The employment of olive oil for lubricating machinery is decreasing, probably owing to the tendency of the unrefined oil to become acid on account of the fermentation of the contained mucilaginous and albuminous matters.

Owing to its superior value, olive oil is very liable to adulteration. Rape and poppy oils are employed for the purpose, as is also earth-nut oil. A still more common sophistication is by lard oil. "Superfine Lucca Oil" often contains 60 to 70 per cent. of the last-named adulterant, whilst cotton-seed oil is even more extensively employed. Fish oils are also used for adulterating olive oil.

In examining olive oil, the most important indications are the density, the elaidïn test (page 147), the rise of temperature on treatment with sulphuric acid, and the colour-reactions with soda, sulphuric acid, nitric acid, hydrochloric acid, and chlorine. Certain sophistications require the employment of special tests for their detection.

Fish oils will be detected by the smell on warming the sample; by the red colour on heating the oil with solution of soda; by the brown colour developed by sulphuric acid; and

by the darkening produced on agitating with hydrochloric acid, or passing chlorine.

The specific gravity of olive oil is ·917. Any admixture of rape oil will tend to slightly reduce the density, whilst adulteration by the oils of Groups II. and III. will increase it. Hence a judicious admixture of rape and cotton seed-oils will not affect the density of the sample.

The rise of temperature on treating the sample with sulphuric acid, as described on page 152, is a most valuable indication of the purity of olive oil. Almost all oils except oil of ben and tallow and lard oils produce more heat than olive oil, so that an excessive rise of temperature may at once be considered as indicating adulteration, and in some cases (see page 152) it allows of an approximate estimation of the extent of the sophistication.

The elaïdin test is another of great value for detecting sophistication of olive oil. Poutet's method of procedure is best for this particular application. Six grammes of mercury should be dissolved in 7½ grammes of cold nitric acid of about 1·42 sp. gravity. Eight grammes of the freshly-made solution are then shaken with 96 grammes of the sample of oil, and the agitation repeated every ten minutes for two hours. With pure olive oil a perfectly solid mass of pale yellow colour is produced. With adulterated samples, the elaïdin is orange or dark red, and liquid or imperfectly solid. Not unfrequently a distinct liquid layer is formed on the surface of the solid elaïdin. The above test is applicable to the detection of cotton-seed, poppy-seed, linseed, and other oils of Groups II. and III. when in admixture with olive oil. Train oil resembles these in not forming elaïdin. Exposure to air under the conditions prescribed on page 146 is also a test for an admixture of the drying oils.

Sesamé oil, in admixture with olive oil, may be recognised by the cohesion-figure produced when a drop of the sample is placed on clean water as described on page 145. It may also be detected by agitating two parts of the sample with one of hydrochloric acid at 1·17 sp. gravity, in which one decigramme of sugar has been previously dissolved. The acid, on separation from the oil, assumes a rose colour if oil

of sesamé be present, the intensity of the tint increasing with the proportion of the adulterant.

Arachis or earth-nut oil has about the same density as olive oil, but solidifies somewhat less readily. It may be recognised by its well-marked taste of kidney beans. Olive oil containing a mixture of earth-nut oil, when left at a temperature of 8° C., deposits sandy-looking flocks at the bottom of the glass, leaving a perfectly clear supernatant liquid, whilst the matter deposited by pure olive oil remains suspended in the fluid.

Earth-nut or arachis oil may be detected and approximately estimated in olive oil by a process devised by A. Renard,* which is based on the presence of the glyceride of arachidic acid, $C_{20}H_{40}O_2$, (see page 218) in the adulterant. For the purpose of the test, 10 grammes of the sample should be saponified with caustic soda, and the resultant soap decomposed by hydrochloric acid, as described on page 131. The fatty acids obtained are next dissolved in 50 c.c. of hot alcohol of ·817 sp. gravity, and the warm liquid precipitated by an alcoholic solution of acetate of lead.† After cooling, the lead soaps are filtered off and treated on the filter with well-washed ether, which dissolves the oleate of lead, leaving the palmitate and arachidate unchanged. The residue is treated with hot diluted hydrochloric acid, the liberated fatty acids allowed to solidify, and separated from the solution of lead chloride. The cake is next dissolved in 50 c.c. of rectified spirit, to which one drop of hydrochloric acid has been added. On cooling the solution, abundant crystals of arachidic acid will be deposited if the sample contained earth-nut oil. The liquid is filtered, and the crystals washed with a little rectified spirit, and then with spirit of ·89 sp. gr., in which they are completely insoluble. The arachidic acid is next treated on the filter with boiling absolute alcohol, by which it is dissolved, and the resultant solution is evaporated to dryness and the residue weighed. To the amount thus found is added ·0025 grammes

* *Compt. Rend.* lxxiii. 1330.

† Baudrimont recommends direct conversion to lead soaps by boiling the sample with 5 grammes of finely divided litharge and 100 c.c. of water. There is a tendency to the formation of a basic oleate of lead, only with difficulty soluble in ether.

for each 10 c.c. of rectified spirit used in the crystallisation and washing of the acid. The fusion-point of the arachidic acid obtained in the above manner is about 71°, that of the pure substance being 73°. Renard obtained from 4·5 to 5·0 per cent. of arachidic acid from earth-nut oil. Hence twenty times the weight of acid found (duly corrected for solubility as already described) will approximately represent the amount of the adulterant in the 10 grammes of the sample employed for the test. The process requires considerable skill to ensure accurate results. It proved unsuccessful with a mixture containing less than 4 per cent. of earth-nut oil, but with one containing 10 per cent. of the adulterant the result was within one per cent. of the truth.

A sample of so-called "green olive oil, from Malaga," was found by Cailletet to consist solely of arachis oil coloured with acetate of copper.

A very useful test for olive oil is said to consist in agitating three measures of the oil with one of nitric acid of 1·32 sp. gravity, and observing the colour after about one and a half hours. If the oil be pure, or mixed only with lard or castor oil, a transient yellow colour will be obtained; but in presence of seed oils (*e.g.* cotton-seed, linseed, niger-seed, or rape oil); of sperm, seal, or whale oil; or of mineral or rosin oil, a red coloration will be developed, varying in intensity with the proportion of the adulterant. With seal and seed oils the colour is more of a reddish orange, with mineral and fish oils dark red, and with rosin oil reddish brown.

According to F. W. and G. F. Stoddart, marine animal oils and rosin oil are further recognised by the grey or black coloration produced on agitating three measures of the sample with one of hydrochloric acid of 1·16 sp. gravity.*

Mineral and rosin oils may be detected and determined by the methods described on page 161, *et seq.*

Lard oil is the most difficult adulterant to detect in olive oil. Its presence may, however, be deduced from the altered density and viscosity of the sample, and by a very careful

* This test is described in a private communication from Messrs Stoddart, who have also extended the original application of the nitric acid test.

application of Chateau's colour-tests side by side with genuine samples. The diminished intensity of the absorption-bands is also a character of some value.

Oleic acid, due to adulteration with commercial distilled "olein," may be met with in olive oil. It imparts to the sample a rancid taste and a disagreeable smell. The proportion present may be determined by the method described on page 156, based on the solubility of oleic acid in alcohol, and its power of neutralising alkalies.

Intentional adulteration with oleic acid is certain to be practised in considerable proportions. But pure olive oil is apt to acquire slight acidity or "rancidity" by simple keeping, thus becoming unsuited for use as a lubricator. The traces of oleic acid due to this cause may be detected and estimated by the method prescribed on page 158.

TURKEY-RED OIL.—In dyeing cotton turkey-red, a necessary stage consists in treating the cloth with oil. The oil employed for this purpose in England is frequently the variety of olive oil known as "Gallipoli oil." Although it is not essential that *olive* oil should be used, it is important that it should be thoroughly non-drying, and this is ascertained by the elaïdin test in the manner described on page 185. A good sample will give elaïdin not only solid and firm, but nearly white. A yellow, soft, or semi-fluid product indicates undesirable admixtures.

Oil suitable for turkey-red dyeing is prepared from somewhat unripe olives, which are steeped for some time in boiling water before being pressed. This treatment causes the oil to contain a large proportion of extractive matter.

Turkey red oil should form a white emulsion when agitated with a dilute solution of caustic or carbonated alkali. To test its quality, one part of the sample of oil should be beaten up with from thirty to forty parts half-normal caustic soda solution (2 to 2½ parts of caustic soda, NaHO, per litre). If, after standing six hours, the mixture be still found to be homogeneous, without any sign of separation of the oil, the sample is fit for its intended use.

An entirely different preparation, now extensively used as a turkey-red oil, is made by mixing castor oil with sulphuric

acid diluted with about one-third of its bulk of water, and leaving the mixture over night. The acid is then washed away with a solution of common salt, and the fatty acids saponified with ammonia, or a mixture of ammonia with potash or soda. The resultant turkey-red oil consists chiefly of ammonium sulpho-ricinoleate. It may be assayed by heating 10 grammes of the sample with 25 of wax and 75 c.c. of a cold saturated solution of common salt. The wax is allowed to solidify, and the resultant cake weighed, when the excess over the original weight of wax taken is a measure of the strength of the sample. Most samples yield from 61 to 78 per cent. of their weight to the wax when thus treated.

Rape Oil.

French—Huile de Navette. *German*—Rapsöl; Kolsatöl.

(See also table on page 120.) This oil is prepared from the seeds of several species of the genus *Brassica*, belonging to the family *Cruciferæ*. The seed is commonly subjected to steam heat before pressure to coagulate the albuminous matter, and facilitate the extraction of the oil. Freshly expressed rape oil is, however, viscid, owing to the mucus and other foreign and colouring matters invariably present. These lessen the combustibility of the oil, and occasion much smoke during its burning.

Winter rape oil, from *Brassica napus*, has a bright yellow colour; its density is ·9128 at 15° C.,* and it solidifies below 0° C.

Summer rape oil, from *Brassica præcox*, is more viscid than winter rape; its specific gravity is ·9139 at 15° C., it deposits a fat at −8° C., and solidifies at −10°.

Colza oil, from *Brassica campestris oleifera*, or wild navew, is produced in large quantity in France, and employed for the same purposes as rape oil. It is yellow and

* The figures here given are those of Schubler. The gravity is, of course, subject to slight variations. The seed cultivated in France and Belgium gives an oil of about ·912 sp. gravity, while the North German product has a density of ·915. The seed crushed in England, and imported from the East Indies and all parts of the Continent, gives an oil varying in density from ·914 to ·916.

nearly free from odour. The density is ·9136 at 15° C., and it congeals at −6° C. In cold alcohol it is sparingly soluble, but readily so in hot. Chemically, colza oil consists chiefly of a mixture of two glycerides, one of which yields brassic acid, $C_{22}H_{42}O_2$, on saponification, and the other an acid allied to oleic acid. Brassic acid crystallises from alcohol in long needles which melt at 33° C. to 34° C. (see page 219).

Brown rape or sweet rape-oil is the commercial name for the oil as expressed from the seed; the same, after treatment with sulphuric acid, steaming, washing, and filtering, is called refined rape oil.

Rape oils stand on the border-land between drying and non-drying oils. In non-drying characters they are slightly inferior to olive oil, but superior in their smell and appearance. Notwithstanding their slight tendency to gum they are most extensively used for engine and machinery lubrication, as well as for burning in lamps.

Rape oils are subject to numerous adulterations, the more important of which can be detected with tolerable certainty.

1. Pure refined rape oil never shows a higher density than ·916, though the crude oil is sometimes slightly denser. If the specific gravity be above ·916 the presence of some adulterant is nearly certain, as all the ordinary additions are denser than rape oil, with the exception of mineral oil. Foreign seed-oils of a more or less drying character, as sesamé, sunflower, cress, hemp-seed, cotton-seed, or linseed oil, or possibly coco-nut olein, all have a density ranging between ·920 and ·937. Hence, if the sample have a density of ·918, it may possibly contain even 50 per cent. of some of these oils, while the smell and colour will be but little effected. Seed and nut oils deteriorate rape oil by increasing its gumming properties, with the exception of earth-nut oil and coco-nut olein, and these two admixtures are unlikely to be used, as their value is nearly equal to that of rape oil.

2. Fish oils are recognisable in rape oil by the smell and taste, and by the dark coloration they take with soda, chlorine, and sulphuric acid. The colour-test with sulphuric acid

suffices for the detection of a variety of adulterants in rape oil, including mineral and rosin oil, which, however, can be more certainly identified and determined by the methods described on page 161.* Train oil is best detected by agitating 100 drops of the oil with 1 of sulphuric acid, when the depth of the red coloration will follow the proportion of the adulterant.

3. The solidifying point of rape oil is raised by any admixture of cotton-seed oil, which is its most common adulterant. The mixed oil will also be found to require a larger percentage of alkali for its saponification (see page 123), and will yield fatty acids of sensibly higher melting point than pure rape oil.

Cotton-seed Oil.

French—Huile de Coton. *German*—Baumwollensamenöl.

(See also table on page 130.) Crude cotton-seed oil is often very dark and turbid; when refined it takes a bright yellow or sherry colour, and has a pleasant sweetish flavour. It varies considerably in density, the refined being lighter than crude oil.

When raw cotton-seed oil is saponified with alcoholic soda, a violet-blue colouring matter is produced. This reaction is less marked with the refined oil.

When a drop of strong sulphuric acid is added to crude cotton-seed oil, a very bright red coloration results, but with the refined oil the test is less distinctive.

The fatty acids produced by the saponification of cotton-seed oil are remarkable for their high fusing point, being solid at ordinary temperatures.

The means of identifying cotton-seed oil have a special interest and importance, owing to the frequency with which it is employed to adulterate other oils, especially olive, rape, and linseed oils. It may be detected in either of these by a careful determination of the density, aided by the colour-tests given above and by those of Chateau. The results of the

* Refined rape and colza oils are frequently adulterated with purified mineral oil. This addition greatly interferes with the burning qualities of the oil, causing it to smoke and form much deposit on the wick.

elaïdin test, heating with sulphuric acid, and the melting point of the fatty acids enable the proportion in a mixture to be approximately determined.

Linseed Oil.

French—Huile de Lin. *German*—Leinöl.

(See also table on page 131.) This oil is the most important of the so-called "drying oils." Exposed to the air it absorbs oxygen, and is gradually converted into a transparent varnish. The rapidity of the change is much increased by previously raising the oil to a temperature at which it begins to effervesce from evolution of products of decomposition. Such oil is termed "boiled oil." By adding litharge, red-lead, or manganese dioxide during the process, the change is still further facilitated. The applications of linseed oil in the arts, as the manufacture of paint, varnish, oil-cloth, printing ink, &c., are nearly all based on the property of drying.

In consequence of its tendency to combine with oxygen, linseed oil evolves much heat when exposed to the air, in a finely divided condition, the action being sometimes so violent as to cause the inflamation of cotton-waste or similar material saturated with the oil.

Chemically, linseed oil consists chiefly of the glyceride of linoleic acid, $C_{18}H_{32}O_2$ (see page 219).

The varieties of linseed oil recognised in commerce are raw, refined, boiled, and artists' oil.

Flax is commonly grown in India as a mixed crop with mustard and rape, and hence the oil from Indian linseed is never perfectly pure. In the Black Sea ports it is the practice to add 1 measure of hemp to every 19 of linseed, and adulteration is also conducted in much more considerable proportions.

Not only is the seed itself largely sophisticated, but linseed oil also is much adulterated. Of the seed-oils, those of cotton and niger-seeds are most used. Rosin oil, mineral oil, and fish oils may also be present.

1. The density of genuine unboiled linseed oil lies between ·932 and ·937, while that of the boiled oil is usually from ·940 to ·941. Mineral and all seed oils are lighter than lin-

seed oil, whilst rosin oil is much heavier (sp. gr. ·96 to ·99). Some of the fish oils are nearly as dense as linseed oil.

2. The solidifying point of pure linseed oil is as low as −27° C., but samples containing other seed oils freeze at a higher temperature.

3. The siccative characters of the sample should be compared with a genuine specimen, as should also the viscosity.

4. Rapë and other oils of Group I. are also recognisable with certainty by the elaïdin test described on page 147.

5. The sulphuric acid test described on page 151 is a useful indication of the purity of linseed oil. With a genuine sample a dark-brown clot is formed; if rosin oil or fish oil be present, a reddish-brown spot quickly forms, which in the former case retains its red tint for a long time, whilst a peculiar scum forms over it. This test is also applicable to the detection of rosin oil in *boiled* linseed oil, while the reaction is more rapid. The rosin oil employed for adulterating linseed oil is free from smell even when heated, but has a peculiar taste which is not masked by the linseed oil. Other and more elaborate means of detecting and determining rosin oil are described on page 161. The presence of rosin oil causes linseed oil to remain "tacky" for a long time, and prevents it ever becoming hard.

6. Note the rise of temperature on treating the sample by Maumené's test. Admixture of rape, mineral, or rosin oil is readily detected by the diminished heating; and if the nature of the adulterant can be otherwise ascertained, its proportion may be approximately calculated from the reduced increase of temperature.

7. Fish oils may be detected by the brown or black colour produced by passing a rapid stream of chlorine through the oil, and by the red colour produced by boiling the oil with solution of caustic soda.

As a test for cod oil, which is not unfrequently used in the case of linseed oil intended for the preparation of printer's ink, A. Morell recommends the following test:—Ten grammes of the oil are well stirred with 3 grammes of common nitric acid, and the whole left to stand. With pure linseed oil the colour will change during the stirring to a sea-green colour,

afterwards becoming dirty greenish-yellow, whilst the acid assumes a light yellow colour. In presence of cod oil, after standing some time the oil appears of a dark-brown colour, while the acid will be tinged orange or dark-yellow, according to the proportion of the adulterant present. Three per cent. of cod-oil is stated to be thus recognisable.

8. Hydrocarbon oils may be looked for as described on page 161. A. H. Mason has described a case of adulteration with 24 per cent. of mineral oil of ·872 specific gravity. This admixture reduced the density of the sample to ·946, while its flashing point was 330° F.; whereas genuine linseed oil flashes only at 540° F.

BOILED LINSEED OIL has a higher density than the raw oil. It is prepared by heating linseed oil to a high temperature for some time, whereby its tendency to oxidise is much increased. An addition of "driers" is usually made during the operation. The nature, proportion, and mode of adding these substances are usually kept jealously secret. Compounds of manganese and lead are the most frequent additions. They may readily be detected in the ash left on burning 100 grammes of the sample, a little at a time, in a porcelain dish. All but the best qualities of boiled linseed oil are commonly adulterated with rosin and rosin oil. The latter of these additions may be detected and estimated as indicated on last page; but rosin is commonly used in very small proportion, is difficult of detection, and still more so of determination. The method by saponification with alcohol and an alkali, in the manner described on page 159, is the best.

A useful technical method of ascertaining the suitability of linseed oil for the manufacture of linoleum, &c., is the following:—To 100 grammes of the oil add ½ gramme of finely-ground litharge and an equal weight of red lead. Heat the whole in a capacious evaporating basin or small saucepan till an immersed thermometer indicates about 250° C. to 260° C., taking care not to let it exceed the latter limit. Air should be continuously blown into the hot oil by means of a glass tube attached to a foot-bellows. Small samples of oil are taken out from time to time and cooled on an iron plate. As soon as they appear "stringy" when cool, the oil is allowed

to become cold, being constantly stirred during cooling. If the oil be solid when cold, the sample was of good quality. Bad oil remains sticky and semifluid.

Castor Oil.

French—Huile de Ricin. *German*—Ricinusöl.

(See also table on page 132.) Castor oil presents many properties which distinguish it sharply from most other vegetable oils (except croton oil). Thus it has an exceptionally high density and viscosity, and is not soluble in petroleum spirit, though it is itself capable of dissolving its own volume of that liquid.

Castor oil is miscible in all proportions with absolute alcohol or glacial acetic acid.

Castor oil is liable to adulteration with other fat oils, as olive, poppy-seed and lard oils. Such sophistications may be recognised with facility by the following test:—Agitate the sample at 30° C. in a graduated tube with twice its measure of rectified spirit B.P. Pure castor oil forms a perfectly homogeneous solution, but if adulterated, the liquid separates on cooling into three layers, of which the lowest is usually the foreign oil, and its volume will afford an approximate indication of the proportion of the admixture. If the adulterating oil can be identified by its physical or chemical characters, or referred to its proper group, the diminished specific gravity of the sample will also afford a mode of estimating the proportion present.

Oleic acid, if in small proportion, will not be recognised by the alcohol test, but its presence will be detected by the diminished density of the sample, by the acid reaction of its alcoholic solution, and by its property of forming a soap on treatment with sodium carbonate (see page 156).

Refined rosin oil has been extensively employed for the adulteration of castor oil. The experiments of the author show that it be determined with accuracy by the method described on page 165.

Cod-liver Oil.

French—Huile de Foie de Morue. *German*—Leberthran.

(See also table on page 133.) Several qualities of this oil are

known in commerce; pale, light-brown, and dark-brown. The colour depends on the temperature and method of extraction.

Cod-liver oil is supposed to undergo assimilation and digestion very readily. Hence its employment in phthisis and wasting diseases generally.

Cod-liver oil always has a distinctly acid reaction. It contains notable traces of iodine,* and sometimes of bromine. On distilling the oil with caustic alkali and ammonium chloride, a distillate smelling of herrings is obtained, owing to the formation of trimethylamine, $(CH_3)_3N$.

On treating cod-liver oil with strong sulphuric acid a fine violet coloration is developed, which subsequently changes to reddish-brown; this reaction is due to cholic acid, and is common to all liver-oils.

Cod-liver oil is frequently adulterated. Iodine and iodides are commonly introduced to simulate the genuine oil as far as possible. Such additions may be detected by the following reactions. Added iodides are removed on agitating the oil with alcohol, and can be detected in the aqueous liquid by the usual tests. The ash left on igniting genuine cod-liver oil contains no trace of iodine, but if an iodide has been added it will remain in the incombustible residue.†

If the oil be saponified and the soap precipitated by the addition of brine, the aqueous liquid will contain no trace of iodine if the oil were genuine, but if an iodide has been added it will be found in the solution.

Most seed oils can be detected by their peculiar absorption-spectra, the spectrum of cod-liver oil being almost identical with that of almond oil (see page 182). Almond oil itself can be detected by the reduced density of the sample, and by the diminished heating produced by sulphuric acid (see page 152).

For the detection of other fish oils in cod-liver oil M. Boudard employs pure fuming nitric acid. The pure oil

* From 0·2 to 0·3 per cent. is the usual proportion of iodine in genuine cod-liver oil.

† To detect and estimate the iodine naturally present in cod-liver oil the sample should be saponified, and the whole dried and ignited at a low temperature. The residue is then extracted with boiling rectified spirit, and iodides sought for in the solution.

acquires a beautiful rose colour, which is not producible from a mixed oil. M. Cailletet employs a mixture of 12 parts of phosphoric acid of 1·44, 7 of strong sulphuric acid (1·84), and 10 parts of nitric acid of 1·37 sp. gravity; 1 c.c. of this mixture is agitated for some seconds with 5 c.c. of the oil, and then 5 c.c. of petroleum spirit added to dissolve the oil. Pure cod-liver oil shows after twenty-four hours a well-defined yellow colour. All other fish oils give a marked brown tint, except ray-liver oil, which invariably takes a red colour. The last-named adulterant is very common, and is difficult of detection. It has a golden yellow colour, darkens but little under the influence of chlorine, and is said to evolve an odour of valeric acid when heated with a solution of caustic alkali. Shark-liver oil is recognised by its low specific gravity.

Cod-liver oil has always an acid reaction, a character which distinguishes it from most of the oils with which it is sophisticated. On saponification and treatment of the aqueous solution of the soap with ether, cholesterin is dissolved, and may be obtained in crystalline scales on treating the ethereal residue with alcohol.

The density, rise of temperature with sulphuric acid, viscosity, elaïdin test, &c., are other characters which serve for the detection of adulterations of cod-liver oil.

Sperm Oil.

French—Huile de Cachelot. *German*—Wallrathöl.

(See also table on page 133.) Sperm oil not unfrequently holds spermaceti in solution. This admixture may be separated by keeping the oil at a low temperature for some time, or, according to W. Gilmour,* by treating the oil with sulphuric acid.

Sperm oil is one of the most valuable oils in commerce, the amount annually imported being very limited. It has been found preferable to any other oil for lubricating the spindles of cotton and woollen mills.

Adulterants of sperm oil may be detected by a careful application of the following tests :—

* *Pharm. Journ.* [3], vii. 329.

1. Note the specific gravity, which should be from ·875 to ·883. If of less density than the latter figure, the only possible adulterants of the sample are mineral oil, shark-liver oil and African fish-oil. The first may be looked for as described on next page, and the two latter detected by four following tests.

2. Compare the viscosity of the sample with that of a specimen of genuine sperm oil.

3. Note the heat produced on admixture with sulphuric acid, as directed on page 152. African fish oil, which is a common adulterant of sperm oil, but a very bad lubricant, causes a rise of temperature through more than twice the number of degrees observed with pure sperm oil.

4. Note the colour produced by sulphuric acid. Sperm oil is coloured far less intensely than other marine animal oils while shark-liver oil gives a violet coloration.

5. Examine the spectrum of the oil. Vegetable oils may be readily detected by their well-defined absorption-bands, which are absent from sperm and other fish and animal oils.

6. Observe the drying properties of the oil (see page 146).

7. A very valuable means of detecting and determining other fat oils when present in sperm oil is based on the neutralising power of the sample when examined by Koettstorfer's method. As 1000 parts of sperm oil neutralise only 130 to 134 parts of caustic potash (KHO), while other oils require from 176 to 197 parts of potash, the proportion of foreign fatty oil in sperm oil may be very approximately ascertained by the equation

$$F=(P-132)\times 1{\cdot}851;$$

in which P is the number of grammes of caustic potash required for 1000 of the sample, and F is the percentage of foreign fat (see page 122).

8. Owing to the fact that hydrocarbon oils have no neutralising power on alkali, it would be possible to concoct a mixture of mineral oil and rape or lard oil which should be undistinguishable from sperm oil, either by the above test (No. 7), or by that of specific gravity. If any such complex

adulteration be suspected, it is desirable to employ the following method. Saponify 5 grammes of the sample, agitate the solution of the soap with ether, separate and evaporate off the ether, and weigh the residual unsaponifiable matter. The whole operation should be conducted as described on page 165. Pure sperm oil, when thus treated, yields from 39 to 41 per cent. of unsaponifiable matter of a pale yellow colour,* while no other animal or vegetable oil is known to yield more than $1\frac{1}{2}$, or at most 2 per cent. to ether. Hence, if the adulterant be a fatty oil only, the proportion present is readily ascertained from the diminished quantity of this matter obtained. This curious substance, which may be termed "spermyl alcohol," appears to replace the glycerin obtained by the saponification of ordinary oils. Sperm oil yielding no glycerin, the sum of the spermyl alcohols and fatty acids obtained should amount to *more* than 100·00 in a pure sample, and hence the proportions of foreign fat oil and mineral oil in sperm oil can be deduced from a consideration of the analytical data. Thus:—

Oil.	Products of the Saponification of 100 Parts of Oil.		
	Fatty Acids.	Ether Residue.	Glycerin.
Pure Sperm Oil . .	60 to 64	39·5 to 41·5	None.
Other Fat Oils . .	95 to 96	·5 to 1·5	10·4
Mineral Oil . .	None.	100	None.
Rape Oil, 60 Mineral Oil, 40 } .	57·6	40	6

From these figures it will be seen that an admixture of foreign fat oil would increase the percentage of fatty acids in almost the same proportion as the adulterant used, the ether residue being correspondingly reduced. By a judicious mixture of rape and mineral oil, the analytical results of sperm oil might be approximately simulated, but glycerin would be produced, and the sum of the fatty acids and ether residue would be sensibly *less* than 100. Besides, to obtain a mixture

* This substance is solid at the ordinary temperature, but melts very readily and distils, apparently unchanged, at a very high temperature. I am engaged in investigating its exact nature, and shall shortly publish the results.

of the same density as sperm oil, so very light a mineral oil would require to be used that it would necessarily be liquid, even at 0° C., and would have so low a flashing point that it could without difficulty be detected in, and even distilled out of, the original oil or the ether-residue. Sperm oil does not flash below 220° C.

Tallow Oil. Lard Oil.—These oils (see also table on page 134) are obtained by pressure from the corresponding fats. They consist chiefly of triolein, and are valuable from being at the same time of high viscosity and practically free from tendency to become thick and gummy by absorption of oxygen. They vary much in quality, from careless manufacture, and are sometimes slightly rancid. This is especially the case with tallow oil. The chief adulterants of tallow and lard oleins tend to interfere with the non-drying character of the oils.

Lard oil usually thickens at 4° C., and becomes solid at −4°, but some samples remain liquid at a much lower temperature. It flashes at about 346° C.

The specific gravity of tallow or lard oil should not exceed ·915 or ·916. If heavier, the sample is probably adulterated with fish oil, olive oil, coco-nut olein, or cotton or other seed oil. Rape oil has nearly the same density and colour as lard oil. Its detection is attended with some difficulty, but may be effected by a careful application of the following tests:—

1. Heat the sample to about 200 to 205° C., and then allow it to cool to 30°. Tallow and lard oils are deodorised, whilst the peculiarly penetrating smell of rape oil is enhanced.

2. Compare the heat produced on treating the sample with sulphuric acid, as described on page 152, with the rise of temperature obtained with pure tallow or lard oil. These give less heat than any others except olive and ben oils (see page 185).

3. Compare the viscosity of the sample with that of a pure specimen mixed with definite proportions of rape oil.*

4. Observe the spectrum of the sample. Rape and other

* Lard and tallow oils are not identical in viscosity. (See footnote on page 171.)

seed oils give a well-defined absorption-band near the line B, which is not the case with the animal oils.

Mineral oil can be detected and determined in the manner detailed on page 165.

It is important to distinguish true tallow and lard oils prepared from the corresponding fats by pressure, from the commercial oleic acid (miscalled "olein") obtained by decomposing fats by high-pressure steam. This latter product is described on page 226.

Palm Oil.

French—Huile de palme. *German*—Palmfett.

(See also table on page 135.) Water and insoluble matters are often present in palm oil to a considerable extent.* They are best detected by dissolving the sample in warm petroleum spirit which has previously been dehydrated by agitating it with a little dry plaster of Paris and filtering. The insoluble matters settle to the bottom, and can be filtered off and weighed, while any considerable quantity of water will separate in a distinct layer. Water may also be determined by exposing a weighed portion of the sample to a temperature of 120° C. for an hour or two, noting the loss of weight. The free acid of palm oil often reaches a very large proportion. It may be determined as indicated on page 157.

Palm oil is often adulterated with or wholly substituted by wax, tallow, or lard, coloured with turmeric and scented with orris-root, &c. The colouring matter may be detected by the brown tint produced by treating the sample with caustic soda, and the foreign fatty matters may be separated by agitating with acetic ether, which is said to dissolve the palm oil only.

Resin is sometimes employed as an adulterant, and may be detected by solution in alcohol.

Palm oil is a common constituent of railway carriage grease (see footnote on page 170), and is largely used for making soap and factitious butter (Muter).

* The best samples of crude palm oil contain only 1 or 2 per cent. of impurities, but 25 and even 30 per cent. is sometimes met with. The melting point is of no value as an indication of the purity of palm oil.

PALM OLEIN is obtained by subjecting palm oil to hydraulic pressure in the same way that lard oil is made from lard. It usually has a density of about ·914 and solidifies at 10° C. With sulphuric acid it gives a greenish-yellow spot, which changes to a mottled brown on stirring.

Oleic Acid is made by distilling palm oil with steam, and pressing the product. It solidifies at about 4° C., and has the other characters given under "Commercial Oleic Acid."

PALM-NUT OIL is now employed largely instead of cocoa-nut oil for the manufacture of marine soap (see page 135).

Butter.

French—Beurre. *German*—Butter.

The general characters of butter are well known. It consists of a mixture of about 80 to 90 per cent. of butter-fat, with variable proportions of water, curd, and salt. A minute quantity of colouring matter is often added, and carbonate of sodium is sometimes employed to prevent rancidity.

In its ordinary state, butter readily becomes rancid, butyric acid being amongst the most prominent products of the change. Pure butter-fat, on the other hand, is but little liable to change. The composition of butter-fat is peculiar, and is fully considered in the section on the "Fatty Acids of Butter." Its constitution distinguishes it from the fat of the butter-substitutes now so extensively sold under the names of butterine, oleomargarine, &c. The method of estimating the butter-fat contained in milk is described on page 127.

ADULTERATIONS OF BUTTER.—Butter was formerly subject to numerous adulterations, some of which are of a very apocryphal nature. Starch, flour, rags, soluble glass, &c., are among the doubtful sophistications. Lard, tallow, dripping, and other animal and vegetable fats have been extensively employed. Excessive proportions of salt and water are not uncommon, and colouring and flavouring ingredients are also used.

Of late years by far the most extensive sophistication of butter has been by an admixture with, or complete substitution by, the factitious butter now so largely manufactured and

sold under the names of "butterine," "oleomargarine," &c. These products differ from butter in the important particular of being wholly or nearly destitute of butyrin and other glycerides of the lower fatty acids. They are compounded substantially in the manner described on page 203, and the fatty portions consist essentially of olein with more or less palmitin and stearin.*

Numerous methods of examining butter for adulterations have been devised, but many are wholly worthless for their intended purpose, unless the sophistication be of the gross character which is now almost obsolete. Thus the melting or solidifying point of the fat is no longer an indication of value, as butterine fat is carefully adjusted to the same fusibility as butter. The observation of well-defined, double-refracting crystals under the microscope is now well understood to signify nothing but that the fat in question has undergone fusion and subsequent solidification. The detection of stearin as a constituent of the fat is also known to be a very fallacious criterion, and hence all tests based on the limited action of solvents on stearin or metallic stearates have been abandoned. In practice, all methods of detecting butterine or allied products in butter are now based on two characters—1st, The specific gravity of the fat in a molten state; and 2d, The proportion of soluble and insoluble, or volatile and non-volatile, fatty acids produced by saponifying the fat. These determinations, together with estimations of the water, curd, and salt in the sample, and observations of its colour, taste, smell, and general appearance, cover the whole of the experiments which are necessary to ascertain the freedom of a butter from adulteration.

The following is a detailed description of the method of examining butter. The processes given are those which considerable experience has shown the author to be thoroughly reliable.

* A few years since the positive detection, much less the approximate determination, of well-made "butterine" in butter seemed beyond the power of chemistry; but, owing, in the first instance, to the ingenuity of Messrs Angell and Hehner, supplemented by that of Dupré, Muter, Jones, and other public analysts in England, and of Koettstorfer, &c., abroad, it is now possible to analyse such mixtures with considerable accuracy.

WATER is best determined by placing 5 grammes or some other known weight of the butter in a small tared beaker, and exposing it in an air-bath to a temperature of 105° to 110° C. until no more globules of water can be observed on looking at the beaker from below. The loss of weight undergone by the sample shows the amount of water in the quantity taken. Generally the water can be completely expelled in about one hour. The proportion of water normally present in butter is from 8 to 12 per cent. Sixteen per cent. may be regarded as the maximum proportion in good well-made butter. Mr James Bell, however, obtained from 117 samples of butter collected in various parts of the kingdom,* proportions of water varying from 4·15 to 20·75 per cent., the mean of the whole being 14·2 per cent.

CURD and SALT are most conveniently determined in the quantity of butter which has served for the estimation of the water. The fat is re-melted and filtered into a small tared beaker, kept in a warm place. The residual matter is rinsed on to the filter with petroleum spirit, redistilled at a temperature below 80° C., and washed with hot petroleum spirit till free from fat. The filter is then dried at 100 C., and the contents scaped off and weighed. After weighing, the residue, which represents the curd and salt of the butter, may be examined under the microscope for starch, cellular tissue, &c., and then, if desired, treated with cold water, and the solution further examined. Usually, however, it is sufficient to ignite the residue in porcelain at a low temperature, and regard the non-volatile matter as s a l t, the combustible as c u r d. It is evident that if a more minute examination be considered necessary, it will be well to operate on a larger quantity of the sample.

* *Report of the Board of Inland Revenue, May* 31, 1876.—The report states that "the samples may be taken as fairly representing the various qualities of butter as made and brought to market by farmers both in England and Ireland. Every care was exercised by the Board's local officers in procuring them, and there can be no question whatever as to their being genuine." It is evident that this conclusion assumes that no farmer introduces an excess of water into his butter, or makes an addition of foreign fat. There is considerable reason to doubt the accuracy of this assumption; but as the chemists at Somerset House are referees under the Sale of Food and Drugs Act, their views may be regarded as practically fixing the lawful composition of butter in the United Kingdom.

The proportion of salt normally present in butter varies from 0·5 to 5 or 6 per cent. Any higher proportion may be considered excessive, and to some extent suspicious.*

The proportion of curd, except in rare cases, does not exceed 1 or 2 per cent.

FATTY MATTER may be determined indirectly by subtracting the sum of the percentages of water, curd, and salt from 100·00. It may be estimated directly by evaporating off the petroleum spirit from the filtrate from the curd and salt, and adding the weight of the residual fat to that of the main quantity. It is not desirable to mix the filtrate and washings together, as the last traces of the solvent are volatilised with difficulty if the quantity of fat is considerable.

The minimum limit suggested by the Society of Public Analysts for the fat in butter† was 85 per cent., thus allowing 15 per cent. for water, curd, and salt. This limit was probably somewhat too stringent, 80 per cent. being preferable, and amply allowing for all excusable variations in the proportions of the other constituents.

FOREIGN FATS.—For the detection of "butterine" and other foreign fatty matters in butter, it is necessary to examine further the nature of the fat. For this purpose it is desirable to separate the fatty matter from about 100 grammes of the sample. About this quantity should be placed in a dry beaker, and exposed to a moderate temperature (50° to 60° C.), until the whole has melted and the water and curd have settled to the bottom of the vessel. This will be induced more rapidly by careful stirring, so as to cause the curd to adhere to the sides of the beaker. The clear fat is then poured on a dry warm (ribbed) filter, placed in a warm place, and about 50 c.c. of the filtrate collected in a dry beaker. If the filtrate be not perfectly bright and clear, it must be re-filtered after further carefully heating for a time. The fat should be

* One of the 117 samples of "genuine" butter reported on by Mr Bell was found to contain 15·08 per cent. of salt, the next highest amounts being 9·20, 8·56, 8·38, 8·28, and 7·71 per cent.

† Of the 117 samples of "genuine" butter reported on by Mr Bell, only twenty-four contained less than 80 per cent. of fat, and of these only seven contained less than 77 per cent. One of these last contained 15·08 per cent. of salt; another, 19·12 of water and 4·02 of curd; and a third, 20·75 per cent. of water.

kept as short a time as possible in a molten state, and the temperature should certainly not be allowed to exceed 70° C., as otherwise the density may be materially increased.*

The fat having been separated in a pure state in the above manner is next examined as to its density and chemical composition.

The density may be determined in several ways. The method of Hager (page 139) is not satisfactory for this purpose, as the sudden cooling of the melted fats causes a notable change in the density.

Mr C. Estcourt has described a method by which the density can be taken with considerable facility at 100° C., and Mr Wigner has proposed to note the temperature at which the fat acquires a certain density instead of determining its density at a particular temperature. Each of these methods is capable of giving very fair results, but the plan on which it is best to place reliance is that described by Mr James Bell, who ascertains the density of the melted fat at a temperature of 100° F. (=37·8° C.). The method of effecting this is detailed on page 139.

Mr Bell's figures express the specific gravity of the fat at 100° F. compared with water at 60° F. taken as 1000, but it is now more usual to compare the weight of the butter-fat with that of the same volume of water at 100° F taken as unity. When the specific gravity is expressed in the latter way, the density of pure butter-fat is found to range from ·9105 to ·9138, being rarely below ·9110.†

* Inattention to the above essential conditions has led to serious errors. It was not improbably the cause of Mr Bell declaring a sample analysed by Dr Muter to be genuine butter, when the vendor had admitted the said sample to be factitious.

† The gravities (compared with water at 60° F. taken as 1000) given in Mr Bell's report show a range from 909·37 to 913·97. The mode of expression adopted by Mr Bell leads to figures several degrees lower for the same butter than those obtained by comparison with the weight of an equal volume of water at 100° F., a fact which is very difficult to reconcile with the figures of the report. Possibly the gravity bottles employed by Mr Bell were erroneously *assumed* to contain the weights of water marked on them, or more probably the whole of the results were vitiated to an indefinite extent by keeping the fat too long at an elevated temperature. This seems the more likely, as the experiments of Mr Bell, though conducted with great care, were made at a comparatively early date in the history of butter analysis.

The fat from the factitious butters known in commerce by the names of "butterine," "oleomargarine," &c., has a density varying from ·903 to ·906. The gravity of lard is about ·904 to ·905, while that of dripping ranges from ·904 to ·907. A butterine made from palm oil was found by Muter to have a density of ·90294.

It will be seen therefore that the determination of the specific gravity of the molten fat, if conducted under proper conditions, affords a useful indication of the purity of butter, and a means of roughly estimating the proportion of the foreign fat contained in adulterated samples.

By long-keeping, butter becomes so changed that the specific gravity of the fat is worthless as an indication of its purity.

Although the determination of the density of butter fat is a useful mode of sorting samples of butter into good and bad, the indications when taken alone are not sufficiently reliable to justify a positive condemnation of a sample as adulterated. Hence, if the specific gravity be suspiciously low, *certainly* if it be under ·9105, the butter fat should be further examined with a view of determining the proportions of soluble and insoluble acids produced by its saponification. The mode of effecting this is fully detailed in the section on "the fatty acids of butter."

Lard.

French—Axonge; Saindoux. *German*—Schmalz.

Lard is the fat of the pig melted and strained to separate tissue and impurities. The kind known as "bladder-lard" is usually prepared solely from the *omentum* or fat surrounding the kidneys. "Keg-lard" is made from the fat of the entire animal, and melts at about 33° C.; hence at a lower temperature than that from the omentum, which fuses at 42 to 45° C., and alone has the *strict* right to be called lard.

By subjecting lard to a moderate temperature combined with hydraulic pressure, most of the olein is separated, and forms lard oil (page 200), while the stearin and palmitin remain in the form of a solid cake.

Pure lard should contain no foreign matter of any sort. A

little salt is a legitimate addition when the lard is intended for cooking and not for use in pharmacy.

A common practice is to add a little carbonate of sodium to the lard in a melted state, with a view of whitening the product. Milk of lime, used in the proportion of from 2 to 5 per cent., gives a pearly white product, with which a large amount of water can be incorporated by stirring during cooling. Potato-starch and alum have been occasionally mixed with lard.

Pure lard is wholly free from taste or smell, and forms a perfectly clear liquid when melted by immersing the tube containing it in hot water. If either lime, sodium carbonate, water, or any similar addition has been made, the melted fat will be more or less opaque.

The most common adulterant of lard is water, which is introduced in quantities varying from 2 or 3 up to as much as 16 to 18 per cent. of the weight of the lard. By keeping the sample in a molten condition the water gradually settles out, and, if the experiment be conducted in a graduated tube, its volume may be measured. The method is apt to be tedious, and fails wholly with some samples. A better plan is to keep 10 grammes of the sample at a temperature of 110° C. till no more globules of water can be seen, when the loss of weight gives the amount of the adulterant.

Other adulterants of lard will remain on dissolving the sample in petroleum spirit.

Tallow.

French—Suif. *German*—Talg.

Tallow is commercially classed as "beef" and "mutton" tallow, but each of these comprise the fat of other animals besides the ox and sheep. The melting point and density of tallow are given in the table on page 136.

Tallow is not unfrequently adulterated with mineral matters, such as china clay, whiting, and barium sulphate; with starch; and with fats of greater fusibility, especially bone fat. Mineral adulterants are readily detected by melting the sample or dissolving it in petroleum spirit. The residue may be separated, washed with a little ether, dried, and boiled with water. In the solution, starch may be recog-

nised by the blue colour produced on adding iodine. Most mineral adulterants will remain insoluble, and may be determined by igniting or weighing the residue, or by igniting a known quantity of the original sample. Foreign fats can only be recognised by the altered physical characters of the sample.

Pure tallow is white and almost tasteless, but much of that imported has a yellow tint.

Bees'-wax.

French—Cire d'Abeille. *German*—Wachs.

Bees'-wax is the material of which the honey-comb of bees is composed. As it occurs in commerce it is a compact, tough, solid substance, of a yellow or brownish colour. It is almost free from taste, but has a characteristic aromatic odour. It does not feel greasy to the touch. On exposure in thin slices to air and light bees'-wax becomes decolorised. It may also be bleached by nitric acid,* but chlorine cannot be advantageously employed, owing to the formation of substitution-products which give rise to hydrochloric acid when the wax is burnt. The bleached wax has its melting point somewhat altered by the treatment it has received. Thus the yellow wax melts at 64° C., and the bleached at 69 to 70°.

Bees'-wax is insoluble in water, but dissolves readily in fixed oils, oil of turpentine, benzene, ether, and carbon disulphide. In alcohol it is soluble with difficulty and imperfectly.

In chemical composition bees'-wax consists of myricin, cerin, and cerolein. The first of these remains undissolved on treating the wax with boiling alcohol; the second is dissolved, but crystallises out on cooling; and the third is retained in solution in the cold alcohol.

CEROLEIN only constitutes 4 or 5 per cent. of the wax. It has an acid reaction, fuses at about 83°, is of a greasy nature, and is readily soluble in ether. It is the constituent to which the wax owes its colour, odour, and tenacity.

CEROTIC ACID or CERIN, $C_{27}H_{54}O_2$, is described in the table on page 218. It is not a constant constituent of bees'-wax.

MYRICIN, $C_{46}H_{92}O_2$, fuses at 64° C. It forms the chief constituent of the portion of bees'-wax insoluble in alcohol.

* By excessive treatment with nitric acid, the wax is oxidised with formation of succinic acid and other products.

On saponification, myricin yields a palmitate and myricyl alcohol, $C_{30}H_{62}O$, and hence has the constitution of a myricyl palmitate, $C_{30}H_{61},C_{16}H_{31}O_2$.*

MYRICYL ALCOHOL melts at 85° C. It is only with difficulty soluble even in boiling alcohol, but crystallises from hot ether in satiny needles. Benzene is a better solvent for it than ether. In petroleum spirit it is moderately soluble. On fusing it with caustic potash hydrogen is evolved with formation of mellissate of potassium, $KC_{30}H_{59}O_2$.

Bees'-wax is employed in pharmacy for preparing ointments; for moulding and casting; for making candles; and for various other purposes.

Bees'-wax is subject to numerous adulterations, of which the following are the chief:—Water; mineral matters, as kaolin, gypsum, sulphate of barium, yellow ochre; starch and flour; resinous bodies, as galipot and burgundy pitch; fatty bodies, as stearic acid and tallow; paraffin and ozokerite; and vegetable waxes.

Water sometimes exists to the extent of as much as 6 per cent., being in such cases frauduently introduced. It may be detected and estimated as described under "Lard" (page 208).

Mineral matters may be detected and estimated by igniting the wax. They will also remain insoluble on dissolving the sample in turpentine, chloroform, or benzene. As much as 17 per cent. of yellow ochre has been found in unbleached bees'-wax.

Starch and flour will be left undissolved on treating the wax with turpentine. The liquid may be filtered, the residue washed with a little ether, and examined under the microscope with solution of iodine; 60 per cent. of starch has been met with.

Sulphur has been found as an adulterant of unbleached wax. It may be detected by boiling the sample with a weak

* Myricin presents many points of resemblance to spermaceti and Chinese wax. The analogy between the three bodies is as follows:—

Spermaceti.	Myricin.	Chinese wax.
Cetin = $C_{32}H_{64}O_2$	= $C_{46}H_{92}O_2$	= $C_{54}H_{108}O_2$
or, Cetyl Palmitate	or, Myricyl Palmitate	or, Ceryl Cerostate
$C_{16}H_{33},C_{16}H_{31}O,O$	$C_{30}H_{61},C_{16}H_{31}O,O$	$C_{27}H_{55},C_{27}H_{53}O,O$.

solution of soda, and adding lead acetate to the cooled liquid, when the production of a black or brown precipitate indicates the presence of sulphur.

The specific gravity of bees'-wax is a valuable indication of the presence of resinous, fatty, and foreign waxy matters. To a minor extent the melting point is also of value. The physical characters of carnaüba and other vegetable waxes are given on page 137. The densities and melting points of these and other substances soluble in turpentine and liable to be employed as adulterants of bees'-wax, are shown in the following table:—

Substance.	Density.	Melting Point, °C.
Bees'-wax, . .	·959 to ·969*	62 to 69
Carnaüba wax, .	·995 to ·999	83 to 84
Japanese wax, .	·999 to 1·002	42 to 53
Paraffin wax and Mineral wax, .	·868 to ·915	48 to 60
Tallow, . .	·925 to ·940	36 to 50
Stearic acid, . .	·964 to ·969	69
Rosin, . . .	1·07 to 1·09	135

The specific gravity of wax and similar bodies may be conveniently ascertained by the method of Hager described on page 139, but sudden cooling must be avoided. It would be preferable to determine the density of the sample in a molten state. It is evident that only one adulterant having been proved to be present in the wax, and its nature having been ascertained, its amount can be approximately estimated from the known densities of pure bees'-wax and the admixture in question; but too much confidence must not be placed in determinations made in this manner.†

* Hager gives the density of pure white or yellow bees'-wax as ·956 to ·964, being usually between ·958 and ·960. Possibly his results are abnormal owing to sudden cooling.

† According to the figures of C. Mène (*Journ. Chem. Soc.* xxvii. 1027) a mixture of bees'-wax and Japanese wax has a lower density than either body separately. Thus, a mixture of equal parts is said to have a sp. gravity of ·935, and a mixture containing 90 per cent. of Japanese wax a density of only ·851, pure Japanese wax being 1·002. Apparently there is a confusion here between Japanese and paraffin wax.

The following systematic method of examining bees'-wax for admixtures soluble in oil of turpentine is due to E. Donath.* From 1 to 2 grammes of the sample of wax are boiled for one minute in 6 or 8 c.c. of a concentrated solution of sodium carbonate (1 to 6), when one of the following results will be observed:—

(*a*) The wax floats as a distinct layer on a slightly yellowish liquid. In this case the sample is pure, or adulterated with paraffin or mineral wax only, which addition will be indicated by the diminished density of the sample as described on page 211.

(*b*) An emulsion is formed, which persists after the liquid has cooled. In this case the sample is adulterated with rosin, tallow, stearic acid, or vegetable wax. If much froth be noticed, and the milky liquid is thin and often crossed by clear layers, the wax-layer being usually brittle after cooling, stearic acid is probably present. If Japan wax be present the milky layer will become pasty or even stiff on cooling. In presence of pine-resin, if the liquid be allowed to cool gradually it will probably separate into three layers, of which the uppermost is hard and wax-like, the middle one a slightly turbid liquid, while the lowest stratum is a loose or flocculent resinous matter, which can be separated, washed, and weighed.

In the event of the carbonate of sodium test indicating the presence of an adulterant, the sample should be further examined by boiling it with a moderately concentrated solution of caustic potash, and precipitating the soap from the cooled liquid by adding common salt. In presence of Japanese or carnaüba wax a finely-grained magma results, but in their absence a coarsely flocculent soap is precipitated. The presence of vegetable wax is established positively if the density of the sample exceed ·970. The presence of rosin, stearic acid, or tallow, is verified by the following special reactions—

Rosin or colophony may be detected with certainty, even if present only to the extent of 1 per cent., by boiling 5 grammes of the sample of wax for 1 minute with 15 to

* *Dingl. Polyt. Journ.* ccv. 131.

20 c.c. of nitric acid, of 1·33 sp. gravity. When cold, the liquid is diluted with an equal volume of water, and agitated with excess of ammonia. With pure wax a yellow solution is produced, but if resin be present nitro-compounds are formed which impart to the liquid a blood-red or reddish-brown tint.

Cases have been recorded of fictitious bees'-wax composed of 60 per cent. of paraffin and 40 of yellow resin, covered with a thin layer of genuine bees'-wax. The sample, when boiled with 15 times its weight of alcohol of ·87 sp. gravity, left the paraffin in fused, colourless globules, of ·91 sp. gravity, while the solution yielded the resin on evaporation. Such a residue would give a marked terebinthinous odour on being heated, but, if the portion of the wax soluble in alcohol be only small in amount, such a test must not be regarded as absolute proof of the presence of added resin, as many specimens of genuine bees'-wax behave similarly.

Stearic acid is less frequently employed than some of the other adulterants of bees'-wax, as it notably diminishes the malleability of the sample. For its detection the finely-divided wax should be boiled for 40 minutes with 20 parts of alcohol. On cooling, the liquid deposits myricin and cerotic acid, the cerolein and some stearic acid remaining in solution. A portion of the cold liquid is treated with an alcoholic solution of lead acetate; when a flocculent precipitate of lead stearate will be found if the wax contained stearic acid. The rest of the alcoholic extract of the sample is precipitated by addition of water, and the precipitate collected and examined. If the bees'-wax be pure the product is insignificant in amount, of a buttery nature, and non-crystalline; but if stearic acid be present it will be more abundant, harder, and will acquire a distinctly crystalline appearance when slowly cooled. Resin may be recognised by the same test.

The foregoing test is only of qualitative value, owing to the limited solubility of stearic acid in alcohol.

Tallow tends rather to reduce the density of the sample. It may be detected by the same tests as stearic acid. Lead acetate gives merely a light yellowish precipitate in the alcoholic solution, but water renders it distinctly milky. It has also been proposed to consider the presence of oleic acid as a

proof of adulteration of tallow. Oleic acid may be detected by the method described on page 227, but its absence can scarcely be regarded as proof of the freedom of the wax from adulteration by pressed tallow, from which the major part of the olein has been already removed. A better test for tallow is based on the isolation of glycerin, which may be effected by saponifying 25 grammes of the sample by alcoholic potash as described on page 120, decomposing the soap with dilute sulphuric acid, and allowing the precipitated fatty acids to solidify. The filtered liquid is neutralised by chalk, again filtered, evaporated to dryness on a water-bath, and the residue extracted with a mixture of alcohol and ether as described in Volume I. page 127. The glycerin may then be identified by its sweet taste, the production of acrolein, and its power of preventing the precipitation of a solution of cupric sulphate by caustic soda.

Vegetable waxes are now largely employed as adulterants of bees'-wax. Japan wax is described on page 135, and Carnaüba and Chinese wax on page 137. Their detection in bees'-wax is readily effected by the test described on page 212. Japan wax may also be detected by boiling 1 gramme of the sample with 1½ grammes of borax and 20 c.c. of water. If Japan wax be present the aqueous liquid will become milky or gelatinous on cooling, but with pure bees'-wax it remains clear or becomes but slightly turbid. Carnaüba wax and rosin react like bees'-wax.

Paraffin and mineral wax are sufficiently indicated in the absence of other adulterants by the diminished density of the sample, a character which may also be employed for their approximate estimation. As, however, the density of the different varieties of paraffin varies through somewhat wide limits, the process is not capable of giving accurate results.

It has been proposed to determine paraffin in bees'-wax by heating the substance with fuming sulphuric acid till violent action ceases. The liquid is cooled, diluted with water, and the unaltered paraffin melted to a cake, removed and weighed. It is not probable that this method is capable of giving very accurate results. The method of determining mineral oil described on page 165 would be applicable, except for the con-

tamination of the paraffin by myricyl alcohol. Possibly this source of error might be avoided by melting the product with caustic potash, and again dissolving it in ether, when pure paraffin would alone pass into solution.

Spermaceti.

German—Wallrath. *French*—Blanc de Baleine.

(See also table on page 137.) Spermaceti is found in solution in the oil contained in the cranial cavity of the sperm whale. It is deposited spontaneously soon after the oil is drawn from its natural reservoir. To ensure the complete separation of the spermaceti the oil should be exposed for some time to a low temperature.

Spermaceti is white or transparent, smooth to the touch, insipid and inodorous. It fuses at 45° to 49° C., and has a density of ·943. It is insoluble in water and cold alcohol, but is soluble in hot alcohol, ether, and fixed and volatile oils. It separates in a crystalline form from its solution in alcohol or ether. It becomes rancid and acquires a yellow colour on exposure to the air.

Chemically, spermaceti is chiefly composed of cetin. The cetin may be obtained in a pure state by treating the spermaceti with cold alcohol to dissolve the soluble oily portion, and then crystallising the residue from hot alcohol.

CETIN is usually stated to consist of cetyl palmitate, $C_{16}H_{33},C_{16}H_{31}O_2$, but it is doubtful whether its constitution is so simple as is implied by the above formula.*

* Spermaceti, at any rate, yields on saponification a palmitate and cetyl alcohol as principal products, together with smaller quantities of homologous bodies, of which the following have been identified more or less certainly :—

Acids.		Alcohols.	
Lauric	$C_{12}H_{24}O_2$.	Lethal, or Lauryl Alcohol	$C_{12}H_{26}O$.
Myristic	$C_{14}H_{28}O_2$.	Methal, or Myristyl Alcohol	$C_{14}H_{30}O$.
Palmitic	$C_{16}H_{32}O_2$.	Ethal, or Cetyl Alcohol	$C_{16}H_{34}O_2$.
Stearic	$C_{18}H_{36}O_2$.	Stethal, or Stearyl Alcohol	$C_{18}H_{38}O_2$.

The presence of the alcohols, other than cetyl alcohol, is assumed from the fact that on crystallising the crude ethal from alcohol, the substance remaining in solution yields lauric, myristic, and stearic acids (as well as palmitic) on heating with potash-lime to about 280° C.

CETYL ALCOHOL, or ETHAL, $C_{16}H_{31}.OH$, may be obtained in a state of approximate purity by saponifying spermaceti (previously crystallised from hot alcohol) as described on page 165. On evaporation of the ethereal solution the cetyl alcohol remains as a white or yellowish white crystalline mass, melting at 50° C. Ethal has no taste or smell, but when carefully heated distils without decomposition. It is even volatile with the vapour of water. Cetyl alcohol is quite insoluble in water, but is readily soluble in alcohol, ether, and petroleum spirit.

COMMERCIAL SPERMACETI is often adulterated with tallow, stearic, and palmitic acids, and (more rarely with) wax.

Stearic acid may be detected by melting the spermaceti in a test-tube immersed in boiling water, agitating with two measures of ammonia of ·96 sp. gravity, and allowing the whole to cool. If the spermaceti be pure it will rise to the surface and leave the ammonia nearly or entirely clear, but if adulterated with stearic acid a thick white emulsion will be formed, which retains the spermaceti if the proportion of the adulterant be large, but allows it to rise and form a separate layer if the stearic acid is present only in moderate amount. 1 per cent. of the adulterant is said to be recognisable by this test. The stearic acid may be determined as on page 156.

The presence of tallow in spermaceti is recognisable by the change in the fracture, feel, and appearance of the sample, and by the tallowy smell produced on heating. More definite indications and an approximate estimation of the proportion of tallow may be made by isolating and weighing the glycerin produced by saponifying the sample according to the method described on page 120. Pure spermaceti gives no glycerin, and the cetylic alcohol formed from it is insoluble in water, and hence will pass into the soap. The glycerin produced by the saponification of tallow amounts to about 10 to 11 per cent. of its weight. Hence the amount of tallow present may be taken at ten times the weight of glycerin isolated.

Pure cetin, on subjection to saponification and extraction with ether on page 165, yields about 50 per cent. of unsaponifiable matter (ethal), but in commercial spermaceti the

proportion is somewhat variable. Any much smaller yield than this may, however, be regarded as indicating an equivalent admixture of fatty matter or fatty acid, which adulterants may thus be approximately determined in the absence of paraffin wax.

Paraffin wax may be detected in spermaceti in the same manner as in bees'-wax (page 214). Its accurate estimation is attended with similar difficulties.

FATTY ACIDS.

Under the denomination of "fatty acids," used in its widest sense, is included the whole series of acids of which formic acid is the lowest member, together with the various acids of the acrylic or oleic series, the peculiar acids obtained by the saponification of castor and linseed oils, and many others.

The lower acids of the formic, acetic, or stearic series have been fully considered in Volume I. page 184, *et seq.*

The following tables give some particulars respecting such higher fatty acids as are of interest or importance as constituents of the fixed oils or fats. Some information as to the analytical characters of caprylic, pelargonic, and capric acids will be found in Volume I. pages 211 and 219. The other fatty acids of which the assay is of commercial importance are treated in separate sections commencing on page 221.

It will be noted that the acids of the stearic series become less fusible with an increase in the number of carbon atoms. The highest member is melissic acid, with 30 atoms of carbon. According to Kingzett, however, cacao butter contains the glyceride of theobromic acid, to which he attributes the formula $C_{64}H_{130}O_2$.* As the melting point of this acid is only 72° C. it is clearly of anomalous character.

All the fatty acids in the following table are practically insoluble in water, but are mostly soluble in alcohol, ether, and fixed oils. In alcoholic solution they exhibit a more or less marked acid reaction. The salts of the fatty acids are described in the section on "Soap" (page 238).

* *Journ. Chem Soc.* xxxiii. 38

I.—Acids of the Stearic Series. $C_nH_{2n}O_2$.

Name of Acid.	Formula.	Mode of Occurrence.	Fusing Point, °C.	Other Characters.
Caprylic	$C_8H_{16}O_2$ $C_7H_{15}.COOH$.	As a glyceride in coco-nut oil and butter of cow's milk.	14 to 16	Crystallises in needles or plates. Soluble in 400 parts of boiling water, mostly deposited on cooling; readily soluble in alcohol, ether, and benzene. Boils at 236° C. Ba salt moderately soluble.
Pelargonic . . .	$C_9H_{18}O_2$= $C_8H_{17}.COOH$.	In geranium leaves, and as an ether in wine lees. Also obtainable from oil of rue.	18	Boils at 254°. Crystallisable. Ba salt very difficultly soluble in cold water.
Capric or Rutic .	$C_{10}H_{20}O_2$= $C_9H_{19}.COOH$.	As a glyceride in butter and coco-nut oil. As an ether in fusel oil.	30	Boils at 268° to 270° C. Crystallises in brilliant plates. Faint goat-like odour. Slightly soluble in water, readily in alcohol and ether. Ba salt difficultly soluble in boiling water.
Lauric	$C_{12}H_{24}O_2$= $C_{11}H_{23}.COOH$.	As a glyceride in coco-nut oil, spermaceti, fat of bay-tree, pichurum beans, &c.	43·6	Solidifies from fusion in scales. Crystallises from alcohol in white needles. Pb salt insoluble in ether, sparingly in alcohol.
Myristic	$C_{14}H_{28}O_2$= $C_{13}H_{27}.COOH$.	As a glyceride in spermaceti, coco-nut oil, nutmeg butter, &c.	53·8	Crystallises from alcohol in shining laminæ. Exceptional in being insoluble in ether. (?) Pb salt soluble in alcohol, insoluble in ether.
Palmitic	$C_{16}H_{32}O_2$= $C_{15}H_{31}.COOH$.	As a glyceride in many or most natural fats, notably palm oil; as cetyl palmitate in spermaceti; as myricyl palmitate in bees'-wax.	62	Crystallises from fusion in shining scales; from alcohol in shining needles. May be distilled almost unchanged. Pb salt insoluble in ether, soluble in boiling alcohol. Mg salt crystalline, soluble in boiling alcohol, deposited on cooling. See page 221.
Margaric	$C_{17}H_{34}O_2$= $C_{16}H_{33}.COOH$.	Not known to occur naturally.	59·9 (?)	Obtained by action of alkalies on cetyl cyanide.
Stearic	$C_{18}H_{36}O_2$= $C_{17}H_{35}.COOH$.	As a glyceride in admixture with palmitin in many natural fats.	69·2	Crystallises from alcohol in needles or shining scales. Sp. gravity, 1·01 at 0° C. Pb salt insoluble in alcohol or ether. Mg salt insoluble in alcohol. See page 221.
Arachidic . . .	$C_{20}H_{40}O_2$= $C_{19}H_{39}.COOH$.	As a glyceride in arachis or earth-nut oil, and in butter-fat.	73 to 75	Crystallises from hot alcohol in very small shining scales. Insoluble in cold alcohol of ·88 sp. gravity. Lead salt insoluble in ether, but soluble in boiling alcohol. See page 186.
Behenic	$C_{22}H_{44}O_2$= $C_{21}H_{43}.COOH$.	As a glyceride in oil of ben.	76	White crystalline substance.
Hyænic	$C_{25}H_{50}O_2$= $C_{24}H_{49}.COOH$.	As a glyceride in the glandular pouches of the striped hyæna.	77·5	Resembles cerotic acid.
Cerotic	$C_{27}H_{54}O_2$= $C_{26}H_{53}.COOH$.	In the free state in bees'-wax. As ceryl cerotate in Chinese wax and opium wax.	79	Crystallises from fusion in small grains. Soluble in hot alcohol, almost wholly deposited on cooling. Soluble in hot ether, insoluble in chloroform. Lighter than water. When pure may be distilled. Pb salt insoluble in alcohol.
Melissic	$C_{30}H_{60}O_2$= $C_{29}H_{59}.COOH$.	Not known to occur naturally.	89	Obtained by heating myricyl alcohol (from bees'-wax) with caustic potash. Volatilises unchanged.

II.—Acids of the Oleic Series. $C_nH_{2n-2}O_2$.

Name of Acid.	Formula.	Mode of Occurrence.	Fusing Point, °C.	Other Characters.
Hypogœic . . .	$C_{16}H_{30}O_2$= $C_{15}H_{29}.COOH$.	As a glyceride in earth-nut oil (oil of *Arachis hypogœa*).	34 to 35	Forms colourless crystals easily soluble in alcohol or ether. Gradually oxidises by exposure to air. Pb salt soluble in ether. By action of nitrous acid yields the isomer *gaïdic acid*, melting at 39°, and not oxidising by exposure.
Oleic	$C_{18}H_{34}O_2$= $C_{17}H_{33}.COOH$.	As a glyceride in most animal fats and non-drying vegetable oils.	14	Crystallises on cooling in white needles. Oxidises on exposure to air, acquiring a yellow colour and disagreeable taste. Pb salt soluble in ether. By action of nitrous acid yields the isomer *elaïdic acid*, melting at 45°. See page 224.
Brassic, or Erucic .	$C_{22}H_{42}O_2$= $C_{21}H_{41}.COOH$.	As a glyceride in rape, colza, mustard, and other oils from the *Cruciferæ*.	34	Crystallises from alcohol in long, thin, brilliant white needles. Gradually oxidises by exposure to air. Pb salt insoluble in ether. Is not altered by nitrous acid. (These characters render it doubtful if the composition and relationships of brassic acid are rightly understood.)

III.—Acid of the Ricinoleic Series. $C_nH_{2n-2}O_3$.

Ricinoleic . . .	$C_{18}H_{34}O_3$= $C_{17}H_{33}O.COOH$.	As a glyceride in castor oil.	About 0	A yellow or colourless oil. Harsh and persistent taste. The glyceride and all the metallic salts are soluble in alcohol, and the lead salt in ether. Neither acid nor salts oxidise on exposure to air. With nitrous acid gives isomer melting at 50°.

IV.—Acid of the Linoleic Series. $C_nH_{2n-4}O_2$.

Linoleic	$C_{18}H_{28}O_2$= $C_{17}H_{27}.COOH$.	As a glyceride in linseed oil, and probably in other drying oils.	...	Forms a yellowish, limpid liquid of ·921 sp. gravity; oxidising on exposure to air to a thick viscid mass. Not affected by nitrous acid. The salts are also readily oxidisable. They are mostly soluble in alcohol, and the lead salt dissolves in ether also. The formula attributed to linoleic acid is doubtful. If correct, the acid is isomeric with *palmitolic acid*, and homologous with sorbic ($C_6H_8O_2$) and stearolic ($C_{18}H_{32}O_2$) acids.

Determination of Fatty Acids.—The determination of free fatty acids may be effected by titrating the alcoholic solution with caustic alkali, using phenol-phthaleïn as an indicator (see page 156). They may also be determined gravimetrically, being weighed, either in a free state or in the form of a calcium or barium soap; or the weight may be indirectly deduced from the calcium or barium carbonate or sulphate obtained on igniting the soap and weighing the residue at once or after treatment with sulphuric acid (see page 220).

The determination of fatty acids in soaps is fully detailed on page 246, and the same processes are equally applicable to the estimation of insoluble fatty acids in glycerides, if the fat be previously saponified, as described on page 120. The determination of the soluble and insoluble fatty acids produced by the saponification of butter, cocoa-nut oil, and palm-nut oil, is described on pages 232 and 248.

The estimation of free fatty acids in presence of neutral fats is described on page 156.

The separation of fatty acids from resin acids may be approximately effected as described on page 160. A rough estimation of the relative proportions in which they are present may be obtained by taking the specific gravity (see "Soap").

The proximate analysis of mixed fatty acids is a problem of extreme difficulty, and indeed cannot in all cases be satisfactorily solved in the present condition of chemistry. Methods for effecting the recognition and separation of the lower members of the series will be found in Volume I. page 212, *et seq.* The principles which have been applied to the fatty acids enumerated in the tables (pages 218 and 219) include the following:—

1. The mixed free fatty acids are well washed by agitation with hot water, when those containing 10 atoms or fewer of carbon dissolved. This process is applied to the analysis of the fatty acids from butter

2. The acids are converted into barium salts, and the precipitate treated with water or alcohol. The barium salts of lower members up to capric acid can be dissolved out by boiling water.

3. The alcoholic solution of the acids is precipitated by

magnesium acetate. By operating fractionally some useful and difficult separations can be effected.

4. The acids are converted into lead salts, which are then treated with ether or alcohol. An application of this principle enables oleic acid to be separated from stearic and palmitic acids (see page 227).

5. Fractional distillation, fractional fusion and pressure, and fractional solution in or crystallisation from alcohol or other solvents, are other processes employed for the separation of the fatty acids.

Instances of the application of the foregoing principles will be found in the succeeding pages.

The lower fatty acids were fully described in Volume I.; the only other individuals requiring separate consideration are dealt with in the three following subsections.

Palmitic Acid . . $C_{16}H_{32}O_2=C_{15}H_{31}.COOH$.
Stearic Acid . . $C_{18}H_{36}O_2=C_{17}H_{35}.COOH$.

The glycerides of these two important acids constitute the solid portion of natural fats. The properties of the free acids are sufficiently described in the table on page 218. They are colourless crystalline bodies, insoluble in water, but readily soluble in alcohol, ether, carbon disulphide, &c. The alcoholic solutions have an acid reaction. The potassium and sodium salts (soaps) are soluble in water or alcohol, but insoluble in concentrated alkalies or saline solutions (see page 239).

Commercial "stearine" and "palmitine" really consist of mixtures of free stearic and palmitic acids. They often contain a considerable admixture of paraffin wax, which can be detected and accurately determined as described on page 165.

In the analysis of natural oils and fats, the palmitic and stearic acids are usually obtained together, the oleic acid being separated by treating the lead soaps with ether as on page 227. In the mixture of palmitic and stearic acids thus obtained the relative proportions of the two constituents can be *approximately* determined by one of the following methods, but the *accurate* analysis of such mixtures is not at present possible:—

1. Dissolve 2 grammes or some other definite weight of the mixed acids in rectified spirit, add a few drops of phenol

phthaleïn, and titrate the liquid with decinormal soda. The production of a permanent pink tint indicates the point of saturation, and each 1 c.c. of decinormal alkali used corresponds to ·0256 gramme of palmitic or ·0284 of stearic acid. Owing to the difference in their atomic weights, the proportions of the acids present in a mixture not containing too large an excess of one of them can be ascertained indirectly from the volume of alkaline solution used, by means of the following formula, in which N is the number of c.c. of decinormal alkali required for the neutralisation of 1 gramme of the sample, and P the weight of palmitic acid in one gramme of the mixture, the remainder of course being stearic acid.

$$P=\frac{N-14{\cdot}09}{24{\cdot}95}$$

2. Another method by which the composition of a mixture of palmitic acid and stearic acid can be approximately ascertained is by very carefully observing the melting point and solidifying point of the mixed acids. The following table shows the results given by various mixtures of the two acids:—

Mixture melts at °C.	Mixture solidifies at °C.	Percentage Composition.	
		Palmitic Acid.	Stearic Acid.
69·2	...	0	100
67·2	62·5	10	90
65·3	60·3	20	80
62·9	59·3	30	70
60·3	56·5	40	60
56·6	55·0	50	50
56·3	54·5	60	40
55·6	54·3	65	35
55·1	54·0	70	30
60·1	54·5	90	10

The only method of effecting the actual separation of palmitic and stearic acids is by a tedious fractional precipitation of their alcoholic solutions by magnesium acetate.

A useful technical test for fatty acids, extensively used by soap and candle manufacturers for the comparative assay of tallow and similar fats, is based on the determination of their solidifying points. The test, which is due to Dalican, is said

to give very useful and constant results.* The following are the details of the manipulation as applied to the assay of a sample of tallow:—In an enamelled basin of at least a litre capacity 50 grammes' weight of the sample is placed and heated to about 200° C. A mixture of 40 c.c. of caustic soda solution of 1·324 sp. gravity, and 30 c.c. of alcohol of ·815 sp. gravity is made and added gradually to the melted fat, with constant stirring, until a solid mass is formed; one litre of water is then added, and the whole boiled for 50 minutes. The solution is then treated with 60 c.c. of dilute sulphuric acid of 1·205 specific gravity, added gradually, and the whole is boiled till the precipitated fatty acids have formed a perfectly limpid layer free from clots.† The aqueous liquid is then withdrawn as completely as possible by means of a pipette or syphon, and the fatty acids poured into a small beaker. A test-tube about 5 inches in length by $\frac{2}{3}$ inch in diameter is fitted with a ring or collar of cork or india-rubber, by which it is fixed in the mouth of an empty bottle or flask. The melted fatty acid is then poured into the (warmed) tube till it is about two-thirds filled, and a delicate thermometer, previously warmed, is suspended freely in the liquid, so that the bulb may be wholly immersed. When the matter commences to solidify at the bottom of the tube, the thermometer must be attentively observed. The operater then stirs the fatty acid slowly, by giving the thermometer a circular movement, first three times to the right and then thrice to the left. The first effect of the agitation is to cause the thermometer to fall slightly, but subsequently a sensible rise takes place, and the mercury remains stationary for at least two minutes. The temperature thus indicated is regarded as the solidifying point or "titre" of the fatty acids examined.

The following table, constructed synthetically by Dalican, shows the solidifying point of various mixtures of "com-

* Dalican and F. Jean, *Methodes chimiques servant à déterminer la valeur commerciale des Matières Grasses, &c.*

† Dalican's original directions are given in the test, but it is highly improbable that there is any occasion to adhere rigidly to them. The important points are to secure perfect saponification, and to obtain pure fatty acids which have been heated to the boiling point of the liquid. The exact strength of the alkali, acid, and spirit used may evidently be varied at discretion within certain limits.

mercially pure stearic acid" with oleic acid perfectly free from stearic and palmitic acids. In the table the proportion of "stearic acid" only is given. The corresponding oleic acid may be found by subtracting the figure under the head of stearic acid from 95, which is the approximate yield of fatty acids from 100 parts of tallow or other fat:—

Solidifying Point, °C.	"Stearic Acid" per 100 of tallow.	Solidifying Point, °C.	"Stearic Acid" per 100 of tallow.	Solidifying Point, °C.	"Stearic Acid" per 100 of tallow.
40·0	35·15	43·5	44·65	47·0	57·95
40·5	36·10	44·0	47·50	47·5	58·90
41·0	38·00	44·5	49·40	48·0	61·75
41·5	38·95	45·0	51·30	48·5	66·50
42·0	39·90	45·5	52·25	49·0	71·25
42·5	42·75	46·0	53·20	49·5	72·20
43·0	43·70	46·5	55·10	50·0	74·05

As the "commercially pure stearic acid" used for the experiments from which this table was constructed was most probably a mixture of stearic acid with more or less palmitic acid, the figures have but little absolute value, but as a comparative test for different samples the method is convenient and reliable. In Paris, tallow is not unfrequently refused if the fatty acids obtained as above are found to melt below 44° C.

Oleic Acid.

French—Acide Oléique. *German*—Oelsaure.

$$C_{18}H_{34}O_2 = \left.\begin{matrix} C_{18}H_{33}O \\ H \end{matrix}\right\} O = \left\{\begin{matrix} C_{17}H_{33} \\ CO.OH \end{matrix}\right.$$

(See also table on page 219.) Oleic acid is liquid at ordinary temperatures, but is deposited in crystals on cooling. It distils unchanged if heated in a current of steam to about 250° C., but when heated alone is partially decomposed, with formation of sebacic acid, $C_{10}H_{18}O_4$; caprylic, caproic, acetic and carbonic acids; and hydrocarbons.

Sebacic acid is also produced when oleic acid is rapidly heated with excess of caustic alkali. Its formation is a characteristic test for oleic acid. To detect it the alkaline residue should be treated with boiling water, and the liquid acidulated with acetic acid, again boiled, and filtered hot. The

filtered liquid will, on cooling, deposit brilliant needles of sebacic acid, melting at 127° C., and readily soluble in hot water.

When more strongly heated with caustic potash, oleic acid yields palmitate and acetate of potassium and free hydrogen, secondary products being also formed. The temperature necessary for this reaction is about 300° C. The process has been commercially employed for the production of palmitic acid. The following formula expresses the decomposition:—

$$C_{18}H_{34}O_2 + 2KHO = KC_{16}H_{31}O_2 + KC_2H_3O_2 + H_2.$$

When distilled with soda-lime, oleic acid yields "oleone" and other hydrocarbons, a large proportion being olefins.

Oleic acid is insoluble in water, but readily soluble in alcohol, ether, chloroform, and petroleum spirit. It is also miscible with neutral fats and with essential oils. The solution of oleic acid in alcohol turns milky when largely diluted with spirit, but the turbidity disappears on adding a few drops of hydrochloric acid.

Pure oleic acid and its alcoholic solution are stated to have no acid reaction, the power of reddening litmus which is possessed by the ordinary acid being said to be owing to the presence of products of oxidation.

Oleic acid forms two series of salts. Potassium oleate is liquid at ordinary temperatures, the sodium salt solid. Both salts are soluble in water, but insoluble in concentrated alkalies or saline solutions (see "Soap," p. 239).

COMMERCIAL OLEIC ACID is obtained by subjecting to hydraulic pressure the mixture of fatty acids produced by the saponification of tallow, palm oil, and similar products. The oleic acid expressed has a density of ·900 to ·905. If the oil from which the oleic acid is derived be decomposed by lime or treated by other process not involving distillation, the product is fairly pure; but if distillation has been resorted to, the oleic acid is contaminated with a very sensible proportion of hydrocarbons. These can be detected and estimated by the method given on page 165. The isolated hydrocarbons will of course contain any mineral or rosin oil with which the oleic acid may have been adulterated. The practice of adding these products to oleic acid is very

common, although their presence greatly reduces the adaptability of the oleic acid for its most important use, which is the greasing of wool during the process of spinning. Any admixture of hydrocarbon oil reduces the property of ready saponifiability, for which the oleic acid is chiefly valued.

Commercial oleic acid is very commonly, but improperly, called "oleine."

SEPARATION AND DETERMINATION OF OLEIC ACID.—Olein exists in most natural fats, and more especially in liquid fixed oils. To obtain oleic acid in a free and pure state, an oil rich in olein, as almond or olive oil, is saponified by caustic alkali, the soap dissolved in water and decomposed by excess of dilute hydrochloric or sulphuric acid.* The liberated fatty acids are separated from the aqueous liquid, as described on page 247, and heated for some time on the water-bath with about 1 part of finely ground litharge for every 20 parts of oil taken for the operation.†

The product is next treated with about twice its measure of ether, which dissolves the oleate of lead and free oleic acid, and leaves the palmitate and stearate of lead unchanged. The solution is separated from the insoluble salts, and hydrochloric acid added till the aqueous liquid has a strongly acid reaction even after shaking. The lower layer now contains chloride of lead, while the ether retains the oleic acid. It is separated from the acid liquid, washed by agitation with water, and the ethereal layer removed and the ether evaporated off as rapidly and at as low a temperature as possible. The product is oleic acid containing a little colouring matter and products of oxidation, but sufficiently pure for general purposes of estimation of its proportion in oils. If desired, it may be purified by solidification and pressure; or by conversion into a barium salt, and crystallisation of the

* Or, if preferred, white castile soap may be employed as the starting-point, thus saving the trouble of saponifying. Or commercial olein may be saponified, thus obtaining a soap very rich in oleic acid.

† Excess of oxide of lead should be avoided, as it occasions the formation of a basic oleate, which is subsequently treated with difficulty. The proportion of oxide of lead prescribed is insufficient to combine with all the fatty acid, but the result is merely that a portion of the oleic acid remains in the free state, while the more powerful palmitic and stearic acids form lead salts.

latter from boiling alcohol. On decomposing the barium oleate by an acid, the oleic acid will be obtained in a state of purity, if the process and subsequent washing and drying be conducted with exclusion of air.

According to E. C. Saunders, rectified spirit may be advantageously substituted for the ether prescribed in the above process.

An improved method of applying the principles of the foregoing mode of estimating oleic acid in fats has been described by Dr Muter,* who has obtained by its means exceedingly accurate and constant results. About 1·5 grammes of the fat is saponified by an alcoholic solution of caustic potash, and the product well diluted with boiling water. Acetic acid is then cautiously added till precipitation occurs, and then dilute potash solution dropped in with constant stirring till the liquid just clears again. The solution is next transferred to a porcelain basin and precipitated by a slight excess of lead acetate, and stirred till the precipitated lead soap settles thoroughly. The supernatant liquid is then poured off and the lead salts boiled once with a large volume of water and the liquid decanted as completely as possible. By operating in the above manner all tendency to the formation of a basic lead oleate is avoided, and the oleic, palmitic and stearic acids are all obtained as neutral lead salts, and can be readily separated by ether, in which the last two are insoluble. The soap is next transferred to a flask, and treated with 100 c.c. of ether. The mixture is agitated repeatedly during several hours, when it is allowed to subside and subsequently filtered through paper, and the residue washed with ether till the washings are free from lead. The ethereal filtrate and washings, which should together measure not more than 200 c.c., are next transferred to a long graduated tube of 250 c.c. capacity, having a glass tap in the side at 50 c.c. from the bottom.† About 20 c.c. of a mixture of 1 part of hydrochloric acid and 2 of water is then added, the tube closed, well-shaken, and the contents allowed to subside,

* *Analyst*, ii. 73.

† These tubes can be obtained from J. Orme, Barbican, E.C. It is evident that they are not indispensably necessary.

when a clear ethereal solution of oleic acid remains as a layer floating on the acid liquid. The bulk of the ethereal layer is then carefully observed, and a known measure of it run off through the tap into a small tared beaker, in which it is evaporated to dryness on the water-bath as rapidly as possible.* The oleic acid found is calculated to the weight of oil taken, according to the proportion the ethereal liquid evaporated bore to the whole of the layer in the tube.†

If it be desired to estimate the stearic and palmitic acids, the lead soaps insoluble in ether should be detached from the filter and heated for some time with dilute hydrochloric acid, the liberated fatty acids being allowed to solidify, and then removed, and weighed. If it be found impossible to remove the soaps completely from the filter, the latter must be ignited at a low temperature in porcelain, the ash treated with a few drops of nitric and sulphuric acids and again ignited, and 568 parts of stearic acid reckoned for every 303 of lead sulphate thus obtained.‡ In employing any process based on the solubility of lead oleate in ether, it must not be forgotten that the method is intended for the separation of oleic acid from palmitic and stearic acids, and that lead linoleate, ricinoleate, and hypogæate resemble the oleate in being dissolved by ether; while lead arachidate, eruceate, myristate, and laurate remain with the palmitate and stearate. On substituting rectified spirit for ether, more or less arachidate, myristate, and laurate of lead may pass into solution in addition to the lead salts soluble in ether.

The determination of free oleic or other fatty acid in presence of neutral fats (glycerides) can be effected as described on page 156.

* If the fatty acid be derived from a drying oil, the ethereal solution should be evaporated in a tared flask immersed in hot water, a current of hydrogen or carbon dioxide being passed through the apparatus.

† Every 846 parts of oleic acid isolated represent 884 parts of triolein in the oil.

‡ By the above process Muter obtained 34·8 per cent. of oleic and 52·1 per cent. of mixed stearic and palmitic acids (together 86·9) from a butter-fat which gave by direct determination 87·1 per cent. of insoluble acids; and from a sample of lard yielding 95 per cent. of total fatty acids, 47·5 of oleic and 47·4 of mixed stearic and palmitic acids.

A method for the approximate estimation of oleic and stearic acids in tallow, is described on page 223. A process for the separation of oleic and stearic acids has been devised by J. David,* and is based on the solubility of oleic acid in a liquid containing certain proportions of alcohol, water, and acetic acid, and the insolubility of stearic acid in the same mixture. Whether palmitic acid behaves like stearic acid is not stated. The solvent is prepared by adding 22 measures of a mixture of equal volumes of glacial acetic acid and water to 30 measures of alcohol of ·817 specific gravity. The correctness of this mixture is tested by agitating 5·2 c.c. with 1 c.c. of pure oleic acid. Complete solution of the latter should take place, and the fatty acid should wholly separate again on adding 0·1 c.c. more of the mixture of equal volumes of acetic acid and water. If this behaviour does not take place, the proportions of the mixture must be varied till it is sufficiently sensitive. It is kept in a well-closed bottle, in contact with fine shavings of stearic acid.

The analysis is performed by treating 1 gramme of the sample of free fatty acids in a finely divided state with 16 c.c. of the solvent mixture. The tube is closed, agitated several times, and then set aside for 24 hours at a temperature not exceeding 15° C. The liquid is then filtered, air being excluded, and the residue is washed several times with the solvent mixture. The stearic acid can be dissolved off the filter with ether, and the oleic acid recovered from the solution by neutralising it, evaporating to a small bulk, adding hydrochloric acid, agitating with ether, and evaporating the ethereal solution at 100° C.

Fatty Acids of Butter.—Butter-fat is a highly complex mixture of various glycerides, with traces of cholesterin or cholesteric ethers. Wein found in butter-fat more or less of the glycerides of palmitic, oleic, stearic, myristic, arachidic, normal caprylic, capric, normal caproic, and butyric acids. Glycerides of acetic and formic acids were also found, but not those of propionic, valeric, œnanthylic, or pelargonic acids. The greater part consists of the glycerides of oleic and palmitic acids, that of stearic acid being usually present in

* *Comp. Rend.* lxxxvii. 1416; and *Journ. Chem. Soc.* xxxiv. 1011.

smaller quantity. But the characteristic constituent of butter-fat is the glyceride b u t y r i n, which is present together with those of certain of the higher homologues. The following formulæ show the constitution of the three principal glycerides of butter-fat:—

$C_3H_5''' : (C_4H_7O.O)_3$ $C_3H_5''' : (C_{16}H_{31}O.O)_3$ $C_3H_5''' : (C_{18}H_{33}O.O)_3$.
Tributyrin. Tripalmitin. Triolein.

Some experiments of J. Bell indicate that the glycerides contain several acid-radicals in the same molecule, and therefore the butyrin cannot be separated by any process of fractional solution from the less soluble glycerides of palmitic and oleic acids. Hence butter-fat probably contains complex glycerides of the following character:—

$$(C_3H_5)''' : \begin{cases} (C_4H_7O.O) \\ (C_{16}H_{31}O.O) \\ (C_{18}H_{33}O.O). \end{cases}$$

Such a complex glyceride will yield, on saponification, fatty acids and glycerol in the same proportions as would be obtained from a mixture of butyrin, palmitin, and olein in the proportion of their atomic weights. While palmitin, stearin, and olein yield, on saponification, approximately equal proportions of fatty acid, butyrin yields a less percentage. This difference is, of course, a consequence of the comparatively low atomic weight of butyric acid. The following table shows the empirical formula, molecular weight, percentage of fatty acid yielded on saponification, and weight of caustic potash neutralised by 100 grammes of each of the above-named glycerides:—

	Tributyrin.	Tripalmitin.	Tristearin.	Triolein.
Empirical formula . .	$C_{15}H_{26}O_6$	$C_{51}H_{98}O_6$	$C_{57}H_{110}O_6$	$C_{57}H_{104}O_6$
Molecular weight . .	302	806	890	884
Per cent. of Fatty Acid .	87·41	95·28	95·73	95·70
Caustic Potash, KHO,* neutralised by 100 grms. of the glyceride . .	55·73	20·88	18·91	19·04

* The weights of KHO neutralised by 100 grammes of the glyceride are convertible into the equivalent weights of NaHO by multiplying the figures given by $\frac{40}{56 \cdot 1} = \cdot 713$.

From these figures it appears that while butyrin yields a smaller percentage of fatty acids on saponification, it has a higher neutralising power on alkali. The equivalent, or weight of glyceride required to neutralise one atom in grammes of caustic potash or soda, is, for butyrin 100·67; for palmitin 268·67; stearin 296·67; and for olein 294·67. Solid natural fats consisting of olein, palmitin and stearin neutralise, on saponification, proportions of alkali showing that they have experimental equivalents ranging from 285 to 287. On the other hand, butter-fat was found by Koettstorfer to have an equivalent varying from 241·4 to 253·3, the average being about 247.*

The method by which these saturation-equivalents are obtained is due to Koettstorfer, and is fully described on p. 124.

Although the estimation of the saturation-equivalent is a very useful method of examining butter-fat, further and more reliable information is afforded by determinations of the relative proportions of soluble and insoluble fatty acids yielded on saponification. Ordinary fats, consisting of mixtures of palmitin, stearin and olein, yield, on saponification, fully 95 per cent. of fatty acids, of which all but a small fraction will be insoluble in water. Butter, on the other hand, owing to its containing glycerides of butyric and other of the lower fatty acids, yields a product which consists, to a notable extent, of butyric acid and other fatty acids soluble in water. The fatty acids insoluble in water range from 86½ to about 89 parts for every 100 of butter-fat taken, while the soluble fatty acids, as determined by their neutralising power, range from 5 to nearly 7 per cent. Associated with the butyric acid are certain higher homologues, such as caproic acid, having a very limited solubility in water, and therefore only separated with difficulty from the true insoluble acids. If the amount of soluble fatty acids be determined by titrating the aqueous solution with standard alkali, the volume of normal solution required being calculated to its equivalent of butyric acid, the result obtained is below the true amount, owing to the caproic acid, &c., being regarded as butyric acid,

* According to G. W. Wigner, the equivalent of butter-fat is occasionally as high as 263 (*Analyst*, iv. 18).

which has a lower combining weight. This fact may be borne in mind, but has no practical influence on the results.

The examination of butter-fat by the determination of the insoluble fatty acids was first suggested by Messrs Angell and Hehner, but the original process has been greatly improved by Muter, Jones, and other chemists. The following details of operating are those which in the author's experience are most satisfactory. The utmost care is necessary throughout the analysis.

Before commencing the operation, the following standard solutions must be prepared :—

(*a*) Dissolve 14 grammes of good stick-potash in 500 c.c. of rectified spirit (not methylated), and allow the liquid to stand till clear. This solution will be approximately semi-normal.

(*b*) A standard hydrochloric or sulphuric acid of approximately semi-normal strength.

(*c*) Accurately prepared decinormal caustic soda. Each 1·0 c.c. contains ·0040 grammes of NaHO, and neutralises ·0088 grammes of butyric acid, $C_4H_8O_2$.

A quantity of the butter-fat (separated from water, curd, and salt, as described on page 204) is melted in a small beaker, a small glass rod introduced, and the whole allowed to cool and then weighed. It is remelted, stirred thoroughly, and about 5 grammes poured into a strong 6 oz. bottle. The exact weight of fat taken is ascertained by re-weighing the beaker containing the residual fat.

By means of a fast delivering pipette, 50 c.c. of the alcoholic potash (solution *a*) is run into the bottle, and the pipette drained exactly 30 seconds. At the same time two other quantities are measured off in an exactly similar manner into two flasks.

The bottle is fitted with an india-rubber stopper, which is tightly wired down, and is placed in the water-oven, and from time to time removed and agitated, avoiding contact between the liquid and the stopper. In about half an hour the liquid will appear perfectly homogeneous, and when this is the case, the saponification is complete, and the bottle may be removed. When sufficiently cool, the stopper is removed and the contents of the bottle rinsed with boiling water into a weighed

flask of about 250 c.c. capacity, which is placed over a steam-bath, together with the two quantities of alcoholic potash, until the alcohol has evaporated off.

Into each of the three flasks is now run about 1 c.c. more semi-normal acid (solution *b*) than is required to neutralise the potash, and the quantity used accurately noted. The flask containing the butter-fat is nearly filled with boiling water, a cork with a long upright tube fitted to it, and the whole allowed to stand on the water-bath until the separated fatty acids form a clear stratum on the surface of the liquid. When this occurs the flask and contents are allowed to become perfectly cold.

Meanwhile the two blank experiments are completed by carefully titrating the contents of each flask with the decinormal soda, and the results, which should agree closely, noted.

The fatty acids having quite solidified, the resultant cake is detached by gently agitating the flask, so as to allow the liquid to be poured out, but avoiding fracture of the cake. The liquid is passed through a filter to catch any flakes of fatty acid, and is collected in a capacious flask. The flask containing the fatty acids is rinsed with a little cold water and drained.

Boiling water is next poured in till the flask is nearly filled, a cork and long glass tube attached, and the liquid cautiously heated till it begins to boil, when the flask is removed, and strongly agitated till the melted fatty acids form a sort of emulsion with the water. The whole is then thoroughly cooled, and the cake of fatty acids detached, and the liquid filtered as before. This process of alternate washing in the flask by agitation with boiling water, followed by cooling, and filtration of the wash-water, is repeated three times, the washings being added to the first filtrate. It is often difficult or impossible to obtain the wash-water wholly free from acid reaction, but when the operation is judged to be complete, the washings may be collected separately and titrated with decinormal soda. If the measure of this solution required for neutralisation does not exceed 0·2 c.c., further washing of the fatty acids is unnecessary.

The mixed washings and filtrate are next made up to 1000 c.c. or some other definite measure, and an aliquot part

carefully titrated with decinormal soda (solution *c*). The volume required is calculated to the whole liquid. The number so obtained represents the measure of decinormal soda neutralised by the soluble fatty acids of the butter-fat taken, *plus* that corresponding to the excess of standard acid used. This last will have been previously ascertained by the results of the two blank experiments. The mean amount of soda employed in these is deducted from the total amount required by the butter-fat quantity, when the difference is the number of cubic centimetres of standard soda corresponding to the soluble fatty acids. This volume multiplied by the factor 0·0088 gives the butyric acid in the weight of butter-fat employed.*

The cake of washed insoluble fatty acids is allowed to dry by leaving the flask in an inverted position for twelve hours. The flask is then placed on the water bath to melt the contents, and if any globules of water are seen it is kept at 100° C., and frequently agitated till the water is wholly got rid of, when it is weighed. If preferred, the molten fatty acids may be poured into a small tared beaker and weighed, the portion adhering to the flask being removed by a little ether, and the ethereal solution separately evaporated in a small beaker. The piece of cambric must also be treated with ether, the solution obtained evaporated, and the residue weighed.

When it is only required to determine the insoluble acids of butter, the foregoing tedious mode of operating may be avoided by diluting the soap solution obtained by saponifying 5 grammes of the fat till it measures about 300 c.c. The large excess of alkali is thus neutralised by cautious addition of hydrochloric acid, and the hot solution treated with a slight excess of barium chloride or magnesium sulphate. The precipitated barium or magnesium soap is well washed with hot water, and then rinsed off the filter into a separator, where it is decomposed by hydrochloric acid. Ether or carbon disul-

* Thus, suppose an experiment has given the following figures :—Weight of butter-fat taken, 5·120 grammes ; decinormal soda required in each of blank experiments, 3·90 c.c.; decinormal soda required to neutralise one-fifth of the solution of the soluble fatty acids, 6·25 c.c. Then—

$$\frac{\cdot 0088\,(31\cdot 25 - 3\cdot 9) \times 100}{5\cdot 120} = 4\cdot 70 \text{ per cent.}$$

phide is then added, the mixture shaken, and the subsequent manipulation conducted as described on page 247.

Instead of weighing the insoluble fatty acids, W. F. Perkins has proposed to dissolve them in alcohol, and titrate with standard alkali in the manner devised by Koettstorfer (page 124). The objection to this plan is the somewhat variable character of the fatty acids themselves. Calculating their neutralising power on the assumption that they are wholly stearic acid, Perkins found 92·0 and 91·7 per cent. of insoluble acids in pure butter-fat. Calculated to oleic acid, these figures would not be materially modified, but their equivalents in palmitic acid are 83·3 and 83·0 per cent. respectively.*

In the analysis of butter-fat the sum of the insoluble fatty acids by weight and of the soluble fatty acids calculated as butyric acid, should always amount to *fully* 94 per cent. of the fat taken. In the author's own experience the sum is more frequently above 95 per cent. than below, especially if the butter is adulterated.

The soluble fatty acids, calculated as butyric acid, should amount to *at least* 5 per cent., any notably smaller proportion being due to adulteration. The insoluble fatty acids from genuine butter-fat rarely exceed 88½ per cent., occasionally reaching 89 per cent., but a sample ought scarcely to be regarded as certainly adulterated unless the insoluble acids exceed 89½ per cent. As a standard for calculation 88 per cent. of insoluble acids † may be regarded as a fair average, the soluble acids being taken at 5½ per cent.

Tallow, lard, and vegetable oils contain distinct traces of glycerides yielding soluble fatty acids on saponification, the

* Muter obtained from two samples of butter-fat 40·4 and 34·8 per cent. of oleic acid, and 47·5 and 52·1 of mixed stearic and palmitic acids, by applying the process described on page 227 to the insoluble fatty acids. If, after weighing these, and separating the oleic acid as there described, the mixed stearic and palmitic acids were dissolved in alcohol, and titrated with alcoholic potash, the neutralising power of the known weight of mixed acids would give the means of approximately ascertaining the proportions of stearic and palmitic acids present (see page 221).

† The percentage of adulterant in a butter-fat may be calculated from the following formula, in which F is the percentage of foreign fat and I that of the insoluble fatty acids :—$F = (I - 88) \times 13{\cdot}3$.

proportions present corresponding to ·1 to ·5 per cent. of butyric acid;* while coco-nut and palm-nut oils yield notable quantities of soluble or volatile fatty acids (see page 248).

By long keeping, butter becomes so changed that the density is valueless as an indication of its purity, and the proportions of soluble and insoluble fatty acids are perceptibly but not very materially altered.†

SOAP.

French—Savon. *German*—Seife.

By the term soap is commonly understood the various commercial products obtained by the action of caustic alkalies on the fixed oils and fats; but the word is sometimes used in a more extended sense, so as to include all compounds produced by the substitution of metals for the basic hydrogen of the higher fatty acids.

It has already been explained that the great majority of the various fixed oils and fats consist of the glycerides of the fatty acids,‡ and that by treatment with strong bases these yield glycerin and metallic salts of the fatty acids, which last constitute essentially the "soaps."

The fatty acids which play the most important part in the formation of ordinary soaps are—palmitic acid, $C_{16}H_{32}O_2$, a leading source of which is palm oil; stearic acid, $C_{18}H_{36}O_2$, the chief constituent of tallow and other solid animal fats; and oleic acid, $C_{18}H_{34}O_2$, a leading source of which is olive oil. Other acids, homologous with these, are also present in minor proportion, especially in particular cases. Much of the soap now made is prepared partly with colophony or resin, which consists chiefly of pinic, sylvic, and colopholic acids. For soft soaps, the fish oils and vegetable drying oils are also largely used.

Tallow, saponified with soda, yields white curd soap.

* Much valuable information on the determination of the soluble and insoluble fatty acids of butter will be found in the *Analyst*, especially on the following pages: vol. i. pp. 7, 87, 114; vol. ii. pp. 19, 38; vol. iv. pp. 39, 40, 142, 162, 182; vol. v. p. 155.

† *Analyst*, iv. 39.

‡ Sperm oil and the waxes are exceptions to this rule (see page 119).

This is superseded in great part by the superior palm-oil soap. Coco-nut oil and palm-nut oil soaps are much used at sea, on account of their property of dissolving pretty readily in salt water. Of all soaps the most emollient are those of palm oil, castor oil, and spermaceti. Lard soap is very white, solid, inodorous, and very valuable for toilet use. Cotton-seed oil is now employed to an enormous extent for soap-making. Hemp-seed oil, saponified with potash, is also much used for making soft soap. The product is green, pasty, and so soft that the least addition of water renders it liquid. Ordinary "yellow soap" is usually made by saponifying palm oil with soda. More or less resin is always added. The use of too large a proportion renders the soap dark, soft, too readily soluble, and too strongly caustic. Soaps made from the drying oils are usually soft and flabby, and those from fish oils commonly betray their origin by their odour.

Commercial soaps, in addition to what may be regarded as their normal constituents, often contain soluble silicates or borates, insoluble matters, as clay, sand, and steatite, mineral oils, coal-tar products, glycerin, and various other extraneous matters.

The soaps of commerce are divided broadly into two classes —hard and soft. Hard soaps are made with solid animal fats or vegetable fat oils, and soda; for soft soaps, fish oils or vegetable drying oils are used, saponification being effected with potash. Hard soaps may be obtained with potash, provided a solid fat be employed, but a potash soap is always softer than a soda soap produced from the same fat. The hard soaps of commerce usually consist essentially of the soda salts of the fatty and resin acids of the materials, the excess of alkali and the glycerin having been separated; but in the case of soft soaps no such separation is attempted, the whole being boiled down together. Hence soft soaps are more caustic than hard soaps, and contain various impurities. The solid white granulations or "figging," often seen in soft soap, consist of potassium stearate, and to produce them a small quantity of tallow is used in the manufacture. As the figging is commonly but improperly regarded as a proof of quality, it is sometimes imitated by an admixture of starch.

"Marine soap" is made partially or wholly from cocoanut or palm-nut oil, which contains glycerides of the lower fatty acids.

"Cold-water soap" usually contains alkaline carbonates.* Such soap lathers tolerably well with hard water.

The soaps or salts of the higher fatty acids may be produced by the following methods:—

1. By the direct action of the free fatty acid on a metallic oxide, hydrate, or carbonate.

2. By "saponification";—that is, by decomposing the natural glyceride or fixed oil by an appropriate base.

3. By double decomposition of the potassium or sodium salt of the fatty acid by a solution of the metal the soap of which is required.

POTASSIUM AND SODIUM SOAPS.—The only soaps of the higher fatty acids which are soluble in water are those of the alkali metals. Potash soaps are deliquescent, and have a low fusing point; hence they constitute the soft soaps of commerce (see last page). Soda soaps are mostly solid and hard at the ordinary temperature, and in the absence of free alkali are not deliquescent. Both potash and soda soaps are readily soluble in hot water and alcohol; their concentrated solutions solidify to a jelly on cooling. "Opodeldoc" is this jellied soap mixed with alcohol. Copious dilution of a solution of soap with cold water, or the cooling of a hot dilute solution, causes precipitation of acid stearate and palmitate of the metal, while free alkali remains in solution. It is probably to this reaction that the detergent properties of soap are due.

Stearate of sodium forms a typical hard soap. It suffers no marked change in contact with 10 parts of water, while stearate of potassium is converted into a thick paste or viscid solution. The palmitates of sodium and potassium closely resemble the corresponding stearates. Oleate of sodium is soluble in 10 parts of water, and oleate of potassium in 4 parts, forming a jelly with half this proportion. The hardness of soap is not dependent solely on the base present, but is greater in pro-

* Cold-water soap must not be confounded with soap made by the cold process.

portion to the stearin and palmitin pre-existent in the oil, and less in proportion to the olein in it.

Soda soaps are soluble in water, but insoluble in brine and other strong saline solutions. When a moderately strong solution of hard soap is precipitated by addition of common salt, the composition of the separated soap is unchanged, but from very dilute solutions acid soaps are thrown down. Potash soap cannot be separated in a similar manner by adding chloride of potassium to its solution. If common salt be added to the solution of a potash soap, the precipitate consists of a soda soap, an equivalent amount of chloride of potassium being formed in the solution. Concentrated solutions of caustic and carbonated alkalies also separate either potash or soda soap from its solution, but in weak alkaline lyes soap is readily soluble. Coco-nut and palm-nut oil soaps require a much larger proportion of salt to separate them from their solutions than is the case with any other varieties. Hence their use on board ships, as they form a lather with sea-water. These oils require a much stronger alkaline lye for their saponification than is the case with other oils.

The potassium and sodium palmitates, stearates, and oleates are readily soluble in alcohol. When in solution in water they are practically insoluble in ether, benzene, petroleum spirit, or carbon disulphide. Hence these solvents may be employed to separate them from unsaponified oil, free fatty acids, mineral oil, resin, &c. (see page 154.)

Barium Stearate, Palmitate, and Oleate are insoluble in water, or in alkaline or saline solutions. They are also but slightly soluble in ether or alcohol of ·850 sp. gravity, whilst pinate and sylvate ("resinate") of barium dissolve readily in the last two liquids. Barium butyrate, valerate, caproate, œnanthylate, caprylate, pelargonate, and caprate are more or less soluble in water. Hence these acids may be separated from stearic, palmitic, and oleic acids by precipitating the aqueous solution of their sodium or potassium salts with barium chloride, when barium stearate, palmitate, and oleate are precipitated, and the other salts remain in solution. Ricinoleate of barium is soluble in alcohol.

CALCIUM SOAPS closely resemble the corresponding barium compounds.

MAGNESIUM SOAPS are best produced by precipitating potassium or sodium soaps with sulphate of magnesium. Magnesium oleate is soluble in petroleum spirit.

LEAD SOAPS of all fatty acids containing more than 9 atoms of carbon (pelargonic acid, $C_9H_{18}O_2$) are insoluble in water. Palmitate of lead is insoluble in alcohol or cold ether. The stearate resembles it; it is not wetted by water, and melts at 125° C. Neutral oleate of lead is readily soluble in ether, as also are the linoleate and ricinoleate (basic oleate of lead dissolves only with difficulty in ether). The solubility of lead oleate in ether is employed to separate oleic acid from palmitic, stearic, myristic, lauric, and erucic acids, the lead soaps of which are not dissolved by ether (see page 228).

CUPRIC OLEATE is but slightly soluble in alcohol, but dissolves in ether or oil.

Analysis and Assay of Soaps.—A useful and simple comparative test of different soaps consists in ascertaining how much of a standard solution of the sample must be added to a known measure of calcium chloride solution in order to obtain a persistent lather on shaking. The test is made exactly as in determining the hardness of waters. The soap must be dissolved in proof-spirit, and the solution diluted with spirit of the same strength.

A gravimetric modification of this test is that of Greger. Ten grammes of the soap are dissolved in methylated spirit, and the solution diluted with spirit to 100 c.c. It is allowed to deposit, and 10 c.c. of the clear liquid are precipitated with calcic chloride. The precipitate is collected on a weighed filter, dried at 100° C., and weighed. Its weight multiplied by the factor ·977 gives the average weight of anhydrous soda soap in the 10 c.c. of solution operated on.* Barium chloride might probably be advantageously substituted by the calcium chloride employed in this process, the precipitate being ignited, moistened with sulphuric acid, reignited, and weighed.

* These figures are calculated from the mean of the atomic weights of sodium stearate, palmitate, and oleate.

237 parts of $BaSO_4$ represent 592 of anhydrous soda soap. If the soap contain potash instead of soda, or a mixture of the two alkalies, the foregoing figures become erroneous, and the process is wholly useless for soaps made with resin or palm-nut or coco-nut oil, owing to the very different combining equivalents of the acids from these substances.

The technical analysis of a soap is frequently limited to the determination of the fatty acids *plus* resin, the total alkali, and the water. It is sometimes necessary to make a more elaborate examination, distinguishing the different conditions in which the alkali exists, the nature of the fatty acids, the presence in them of mineral oil, resin, carbolic acid, &c. Insoluble earthy matters (silica, boric acid, phosphates, gelatin, starch, glycerin, &c.) also require occasionally to be determined. Some of these determinations present grave difficulties, and a few are not capable of being effected with accuracy in the present condition of proximate analysis.

In analysing soaps too much care cannot be taken to obtain a fairly representative sample. In the case of hard soaps this is best effected by cutting a transverse slice from the middle of the bar or cake. When convenient, this may at once be weighed, dissolved, and the solution made up to a difinite measure, a known volume being then taken for each determination. The determination of the moisture of soap is considered on page 243.

The table on next page presents a method for the recognition and determination of the most frequently occurring constituents of soap, the more important of which are subsequently further considered in separate paragraphs.

Carbolic and Cresylic Acids may be detected and estimated as described in Volume I. page 315.

Boric and Silicic Acids may be determined by the methods of mineral analysis, either in the ignited soap or in the aqueous liquid produced by decomposing the soap with dilute acid.

Gelatin may be detected by the chemical and physical characters of the residue left on dissolving the soap in alcohol (see next page). It may be approximately estimated from the ammonia yielded on igniting this residue with soda-lime, 21 parts of ammonia corresponding to 100 of gelatin.

Dissolve 10 grammes of the soap by digestion on the water-bath with rectified spirit of ·83 sp. gravity. Filter boiling hot, and wash the residue with hot spirit.

RESIDUE may contain alkaline carbonate, sulphate, silicate, borate; sand, clay, steatite, heavy spar, gypsum, hydrated alumina, gelatin, starch, colouring matters, &c. If the residue be considerable, dry it at 100° and weigh. Boil weighed residue with water, and filter, decant, or strain.

RESIDUE may contain sand, *native silicates and sulphates* insoluble in HCl; and hydrated *alumina* (from use of alum), bone *phosphate, lime*, soluble *silica*, *colouring matters*, &c., soluble in hydrochloric acid.

SOLUTION.—Test portions for *gelatin* with tannin, for *starch* with iodine, &c. Titrate aliquot part of solution with standard HCl, and calculate alkali found to *carbonate*,* then add excess of HCl, and evaporate to dryness. (Immerse slip of tumeric paper in acid liquid towards end of evaporation. Red-brown coloration indicates *borate*). Redissolve in dilute HCl, and filter off and weigh any *silica* from soluble *silicates*. Filtrate may be used for determining soluble *sulphates*, by precipitation with $BaCl_2$.

* In presence of soluble silicates or borates, the carbonate must be estimated from the CO_2 evolved, not from the alkalinity of the liquid.

SOLUTION.—Pass carbonic acid to saturation. Filter if necessary.

PRECIPITATE consists of Na_2CO_3 or K_2CO_3 produced from free alkali of sample. Titrate with decinormal acid. Each 1 c.c. neutralised represents ·0040 grms. free NaHO, or ·0056 of free KHO in soap operated on. See also p. 243, *et seq.*

SOLUTION.—Add about 30 c.c. of water, and evaporate in water-bath till the alcohol is expelled. Dilute with hot water, transfer to a suitable vessel (see page 246), and add standard acid in moderate excess, agitating thoroughly all the time. Note the measure of standard acid employed. Separate the aqueous liquid from the oily layer of fatty acids, &c., as described on page 246, *et seq.*

OILY LAYER contains *fatty acids* and any *hydrocarbon oil*, *resin*, *carbolic* or *cresylic acid*, *thymol*, &c. contained in the original soap. Treat as described on p. 153, *et seq.*

AQUEOUS SOLUTION.—Determine excess of acid by titrating with standard alkali. Deduct this from the measure of acid used for decomposition. The remainder is the measure of standard acid equivalent to the alkali combined with the fatty and resin acids of the soap. Each 1 c.c. of normal acid thus utilised is equivalent to ·047 grammes K_2O, or ·031 grammes Na_2O in the soap operated upon.

STARCH may be detected in the residue insoluble in alcohol by its reaction with iodine. It may be approximately estimated, if necessary, in the manner indicated under "Starch."

WATER.—The accurate determination of the water of soap requires considerable care. If the soap be a solid one a fairly representative sample should be reduced to fine shavings by scraping with a knife. A known weight is then exposed for some time to a temperature of 40° or 50° C., the heat being gradually raised to 100° C., and continued at that temperature as long as loss of weight is observed. The soap should not be allowed to melt. A better method is to dissolve about 2 grammes of the soap in the minimum quantity of hot strong alcohol, and to pour the liquid on a known weight of clean dry sand, which is then exposed with frequent stirring to a temperature of 110° C. The water in soap may also be estimated by difference.

ALKALI.—The alkali of soap may exist in several conditions, thus:—(*a*) alkali combined with the fatty acids is an essential constituent of the soap; (*b*) free caustic alkali may be present; (*c*) an alkaline carbonate may exist in the soap; (*d*) sulphates and chlorides of the alkali-metals may be present, owing to their existence in the alkali used for saponification. Chlorides may also be due to the precipitation of the soap with brine, or, in "marine soap," to the introduction of salt water; (*e*) alkaline silicate may be present owing to its intentional addition in concentrated solution. The sulphates and chlorides may usually be ignored.

Caustic alkalies and alkaline carbonates are indicated by the production of a brownish-red or brownish-yellow precipitate on adding mercuric chloride to an aqueous solution of the soap. In their absence the precipitate produced is purely white. This test may also be applied to a freshly-cut surface of the soap. Mercurous nitrate is said to be preferable to mercuric chloride, free alkali causing a grey or black coloration. A more delicate test consists on applying an alcoholic solution of phenol-phthaleïn to a freshly-cut surface of the soap, when a red coloration is produced, the intensity of which is proportionate to the free alkali present.

If free or carbonated alkali be found by either of the above tests, the quantity may be ascertained by solution in alcohol,* as described in the table (page 242). Instead of precipitating the caustic alkali by a stream of carbonic acid, the quantity present may be directly ascertained by titrating the alcoholic solution* by decinormal sulphuric acid, using phenol-phthaleïn as an indicator. The disappearance of the pink tint which the phenol-phthaleïn communicates to the liquid sharply marks the termination of the reaction. The solution may be concentrated to get rid of the alcohol, and a further addition of standard acid made to precipitate the fatty acids.

A method which is sometimes used for determining the free alkali in soap is based on the precipitation of the aqueous solution by strong brine, and titration of the filtrate with standard acid. The process is clumsy and inaccurate.

In soaps containing soluble silicates the determination of the proportion of alkali existing in each form is difficult. By dissolving the sample in alcohol, as directed in the table, the free caustic alkali and soap pass into solution, while the residue contains the alkaline carbonate and silicate. As the silicate is not of constant composition, though usually approximately corresponding to the formula $Na_2O,2SiO_2$, it is impossible to deduce the alkali existing as silicate by determining the amount of silica; but, if desired, it may be ascertained by difference, by determining the carbonic acid evolved on treating the aqueous solution of the residue in alcohol with dilute acid. This estimation will give the means of calculating the alkali existing as carbonate, and the remainder of the alkali in the portion of the soap insoluble in alcohol must exist as silicate (see page 252).

A useful approximation to the amount of alkali existing in combination with the fatty acids may be made by multiplying the weight of these found by the factor ·115. The product is the amount of soda, Na_2O, in combination with them. Or if potash be the alkali required to be found, the figure thus obtained may be multiplied by $\frac{47}{31}$. With soaps

* The alcohol used must be freed from every trace of free acid, by cautiously adding dilute soda to the hot spirit till phenol-phthaleïn is coloured faintly pink.

made with both alkalies, resin, or coco-nut oil, the method is quite unreliable. It is therefore safer and better to make a direct estimation of the alkali required to combine with the fatty acids, by taking a known weight of the latter, dissolving in rectified spirit, and titrating the solution with standard alkali and phenol-phthaleïn as described on page 156. This plan also leads to a knowledge of the combining equivalent of the fatty acids, and hence throws light on their nature.

In the absence of notable quantities of free alkali or of alkaline silicates or carbonates, and for many technical purposes, it is sufficient to determine the *total alkali* of the sample. This, together with a determination of the fatty acids, may be effected in the following manner:—10 grammes' weight of the sample, or a volume of solution corresponding to this weight, is dissolved in hot water. The solution is then treated with a known measure of standard acid, with rapid stirring. The acid must be added in quantity sufficient to produce a decided acid reaction. The precipitated fatty acids form an oily layer on the surface of the aqueous liquid, while any silica, produced by the decomposition of alkaline silicate, and any insoluble mineral matters settle to the bottom or remain suspended in the lower portion. When the separation is sufficiently perfect the fatty acids are removed by one of the modes of treatment described on page 246. The aqueous liquid, or an aliquot part of it, is then titrated with standard alkali. The excess of acid is thus ascertained; this is deducted from the total measure used for decomposing the soap, and the difference represents the acid which is equivalent to and was neutralised by the alkali of the soap. Each 1 c.c. of normal acid thus utilised corresponds to ·031 grammes of Na_2O, or ·047 grammes of K_2O in the 10 grammes of soap employed.

It has been proposed to effect the titration directly on the original aqueous solution of the soap, without separating the fatty acids, by using e o s i n as the indicator instead of litmus. The point of neutrality is marked by the decolorisation of the liquid, but the reaction is not very sharp.

In cases in which it is desired to ascertain the proportions in which p o t a s h and s o d a exist in a mixed soap, the

sample must be carefully ignited and the alkalies determined in the ash by the ordinary methods of inorganic analysis. In the case of mixed soap, ignition also furnishes a ready means of arriving at the total amount of alkali, the weight of the ash representing the alkalies as carbonates, *plus* any other alkaline salts and mineral matter. A better method is to decompose the aqueous solution of the soap by an excess of oxalic acid, separating the fatty acids, evaporating the aqueous liquid to dryness, redissolving the residue in water, and filtering from any silica, re-evaporating, igniting, and weighing the resultant alkaline carbonates. By then titrating them with acid, the relative amounts of potash and soda may be ascertained by the principles of indirect analysis.

CHLORIDES may be determined by dissolving 10 grammes of the soap in water, precipitating the fatty acids with a slight excess of dilute sulphuric acid, separating, neutralising the filtrate by sodium carbonate, and titrating with decinormal nitrate of silver, using neutral potassium chromate as an indicator. 1 c.c. of decinormal silver nitrate corresponds to ·00585 grammes NaCl, or ·00746 of KCl.

SULPHATES may be determined as described in the table, or the aqueous solution of the soap may be decomposed by a slight excess of dilute hydrochloric acid, the fatty acids separated, and the sulphates precipitated from the aqueous liquid by adding barium chloride.

TREATMENT OF THE FATTY ACIDS.—The oily layer separated from a solution of soap on treatment with an acid consists of a mixture of the fatty and resin acids produced by the reaction, together with any hydrocarbon oils present in the original sample, and any unsaponified fat pre-existing in the soap. The separation of these admixtures is described on page 153, *et seq.*

The treatment of the oily layer requires some care. If the soap be chiefly a stearate or palmitate, as when made from tallow or palm oil, the fatty acids are solid when cold, and there is no better plan than to effect their precipitation in a vessel of such shape that the cake can be directly removed, wiped with blotting paper, and weighed. Another method of treating solid fatty acids is to cause their precipitation in a

conical flask. When cold the cake can be detached from the sides of the flask without fracture by gently agitating the liquid, which may then be poured out very completely. This plan allows of the fatty acids being washed by agitation once or more with boiling water, the cake being reformed on cooling; the washings are added to the main solution, being first passed through a filter, if requisite, to separate any suspended particles of fatty acids. This mode of operating is due to Muter, and is described in detail on page 233.

If the layer of fatty acids refuse to solidify at any moderate temperature (as is the case with the product obtained from olein soaps), or if the cake be deficient in consistency, the following plan may be adopted:—

The precipitation of the fatty acids is conducted in a globular or cylindrical separator furnished with a glass tap (see fig. 6, p. 165), the volume of the liquid being brought to about 100 to 120 c.c. About 20 c.c. of ether is then added, and the whole well shaken together, and then left at rest. When separation is complete, the aqueous layer is cautiously and slowly drawn off through the tap, and the ethereal layer washed by agitation with cold water, the washings being slowly tapped off in their turn. The aqueous liquid having been got rid of to the last drop, the ethereal solution is run off into a tared flask or beaker. The separator is rinsed with a little more ether, which is added to the main quantity, and the solution of fatty acids is then evaporated or distilled at a steam-heat, and the residue weighed as soon as it no longer smells of ether. Too long an application of heat is unadvisable, and in the case of fatty acids from coco-nut or palm-nut oil soap the temperature should never *approach* 100° C. If a flask be used, a current of filtered air should be passed through it towards the close of the operation. Any globules of water which may have been introduced through faulty manipulation may be got rid of in the manner described in the footnote on page 106. Some operators prefer to dispense with the use of ether, except for ultimately rinsing the separator, evaporating the ethereal solution and adding the small weight of residual fatty acids to that of the main quantity. There is considerable advantage in this course in

the analysis of soaps made from coco-nut or palm-nut oil. If preferred, recently distilled carbon disulphide may be substituted for the ether, in which case it must be used in sufficient quantity to cause the solution of the fatty acids in it to settle readily to the bottom of the aqueous liquid, when it may be drawn off and cautiously evaporated.

Solution in ether or carbon disulphide is applicable to all fatty acids, whatever their fusibility.

Another plan is to add to the hot liquid, containing the liberated fatty acids, a weight of dry bleached bees'-wax equal to that of the soap operated on. The fatty acids become amalgamated with the wax, and, on cooling, a firm coherent cake is formed, which may be at once wiped and weighed. The weight of wax added being deducted from that of the cake, that of the fatty acids present is at once found. This method is convenient and fairly accurate, but is inapplicable if the fatty acids are to be further examined for hydrocarbon oils or resin.

The methods of determining fatty acids hitherto described assume they are wholly insoluble in water. This is true of the fatty acids derived from the saponification of most oils, but coco-nut oil, palm-nut oil, and butter-fat yield acids of which a notable proportion will dissolve in water or distil with vapour of water at 100° C. Hence, if either of these fats have been used in manufacturing the soap, the fatty acids will be estimated below the truth. The loss is small in the case of the acids from coco-nut and palm-nut oils, but considerable in the case of butter. For the accurate determination of the fatty acids in such soaps, the fatty acids should be separated from the soap solution by adding a slight excess of hydrochloric acid, and then thoroughly washed in the manner described on page 233, dried at a very gentle heat and weighed. The aqueous liquid, containing the soluble fatty acids, is then made up to a definite measure, and an aliquot part of the solution exactly neutralised with soda, evaporated to dryness, and the residue ignited. The ash is then titrated with standard acid, of which it will neutralise a volume proportionate to the organic salts converted into carbonate on ignition. Each 1 c.c. of normal

acid required represents 0·144 gramme of soluble fatty acid reckoned as caprylic acid, $C_8H_{16}O_2$.*

The fact that the soaps produced by the saponification of coco-nut and palm-nut oils are not readily precipitated by solution of common salt may be employed for the detecting the presence of these oils in soap. The soap should be dissolved in water, and the fatty acids liberated by acidulating the solution, and separated without special washing or the use of ether. Ten grammes of the fatty acids should next be treated with 40 c.c. of a normal solution of caustic soda, or a volume just sufficient to dissolve them completely. The whole is then boiled, and the weight of the liquid brought to 50 grammes by evaporation or cautious addition of water. A saturated solution of common salt (previously boiled with a few drops of sodium carbonate and filtered from any precipitate) is then run in gradually from a burette, the liquid being constantly stirred and kept gently boiling. The addition is continued until the soap suddenly precipitates, a point which is usually sharply marked. The soap from ordinary oils is precipitated when from 8 to 10 c.c. of the salt solution has been added, but that from coco-nut oil requires an addition of more than 50 c.c. Mixtures of the fatty acids from coco-nut or palm-nut oil with those from other oils will of course require a volume of brine intermediate between these two limits.†

RESIN in soap may be detected by the dark colour of the liquid obtained when the aqueous solution of the soap is

* Another possible method of determining the total fatty acids in coco-nut and palm-nut oil soaps is as follows:—Separate the fatty acids in the ordinary manner, but in as concentrated a solution as possible. Agitate the aqueous liquid with a little ether, separate, and extract any dissolved fatty acids from the ether by agitating with dilute caustic soda solution. Employ the alkaline solution obtained to neutralise the main quantity of fatty acids, and add a few drops of phenol-phthaleïn, and then more caustic soda solution drop by drop till the pink colour just remains permanent. Then precipitate the hot liquid with a slight excess of magnesium sulphate, filter, wash with hot water, dry the percipitate at 100° C., and weigh. Ignite the precipitate and weigh the residual MgO. The difference is the weight of fatty anhydrides forming insoluble salts with magnesia. Evaporate filtrate, dry the residue at 100° C. and weigh. Ignite and weigh again. The difference is the weight of fatty anhydrides forming soluble salts with magnesia.

† This method may be employed for detecting other oils in coco-nut and palm-nut oils, the sample being first saponified as directed on page 120.

treated with brine and caustic soda, and the precipitate separated. Its determination is exceedingly difficult. The mixed fatty and resin acids may be treated in the manner described on page 160, when an approximation to the truth may be obtained.* An alternative method, which is simple, convenient, and capable of yielding roughly approximate results, consists in determining the density of the mixed fatty and resin acids at 100° C. They are first heated for ten minutes to about 130° C. to drive off any traces of water and ether, and are then poured into a small specific gravity bottle furnished with a perforated stopper. The stopper is inserted, and the bottle plunged up to the neck in hot water, which is then kept rapidly boiling for six or seven minutes, so as to enable the contents of the bottle to become thoroughly heated. The exterior of the stopper is wiped clean while the bottle is still immersed in the boiling water, the bottle withdrawn, dried, and weighed when cool. The weight of the contents, divided by the weight of distilled water at 15° C., which the bottle has been found to contain, gives the specific gravity of the fatty acids at 100°C. The following results, obtained in the author's laboratory, show the density of the acids from different sources, taken in this manner:—

Source of the Fatty Acids.	Density at 100° C. (compared with Water at 15° C.)	
Olive oil	·862	
Cotton-seed oil	·867	
Rape oil	·868	
Linseed oil	·855	=·8565.
Palm oil	·841	
Palm-nut oil	·840	
Tallow	·862	
Rosin	1·046	

If D be the specific gravity of the mixed acids from a sample, and R the resin acids in 1 gramme of the mixture, then R can be approximately calculated from the following formula:—

$$R = \frac{D - \cdot 856}{\cdot 19}.$$

* Mr C. Hope has obtained very encouraging results by Barfoed's method. *Zeit. Anal. Chem.* xiv. 20; and *Journ. Chem. Soc.* xxix. 773.

When the origin of the fatty acids is known the number representing the density should be substituted for the mean value ·856.

MINERAL OIL, ROSIN OIL, and COAL-TAR OIL are sometimes introduced into soap to a considerable extent. Although quite incapable of undergoing saponification, they may nevertheless exist in soap in notable proportion without their presence being suspected; for if not used in excessive amount, they remain in perfect solution when the soap is dissolved in water or alcohol, and, on decomposing the solution with an acid, they pass wholly into the oily layer of fatty and resin acids.

The presence of these hydrocarbon oils in soap may sometimes be detected by the fluorescence exhibited by the ethereal solution of the fatty acids. If in considerable quantity, they may be partially separated by subjecting the dry soap to a gradually increasing heat, when the hydrocarbon oils will distil off, together with any other volatile matter which may be present.

The most satisfactory means of detecting and determining hydrocarbon oils in soap is to extract them by agitating the aqueous solution of the sample with ether. Either the solution of 10 grammes of the soap in about 120 c.c. of warm water may be at once treated with ether, or the fatty acids may, after weighing, be saponified, and the soap obtained dissolved and treated in the same way. The details of the operation are fully described on page 165.

UNSAPONIFIED FAT will be extracted along with the hydrocarbons when the soap is submitted to the foregoing mode of treatment. It may be separated from hydrocarbon oils by treating the matter extracted by ether with alcoholic soda, as described on page 165.

GLYCERIN or GLYCEROL may be determined in soap by either of the methods described in Volume I. page 127.

In estimating glycerin it is desirable to bear in mind the following facts:—

(*a*) Glycerin is apt to volatilise with vapour of water. Hence the evaporation of aqueous solutions of glycerin should be avoided as far as possible, and all necessary concentrations should be effected at the lowest practicable temperature.

(*b*) At 100° to 110° C., glycerin is sensibly volatile in an open dish, but when heated in a small flask, or in a dish in the drying oven, the loss is very small.

(*c*) Glycerol forms a compound with lime, which is only sparingly soluble in alcohol.

A volumetric method for the indirect estimation of glycerin in soap and the ley resulting from the saponification of fats has been recently described by Dr Muter.* One gramme of absolute glycerin, or a volume of a solution which from its density is known to contain this quantity, is washed into a graduated cylinder of 250 c.c. capacity, having a tap in the side at about 50 c.c. from the bottom (see footnote, page 227). 50 c.c. of a solution of one part of caustic potash in two of water is next added, and then a weak solution of cupric sulphate added gradually, and with constant shaking, until a fair amount of cupric hydrate remains undissolved. The whole is then made up to a definite volume, and the tube closed and set aside. When the liquid has become perfectly clear, a known volume is run off into a beaker, and just neutralised with nitric acid. A definite volume of ammonia solution is next added, and the liquid titrated with a standard solution of potassium cyanide. The complete decolorisation of the liquid indicates the termination of the reaction. A blank experiment is then made in exactly the same manner as before, the glycerin being omitted, and the volume of cyanide solution required deducted from that previously used. The difference gives the number of cubic centimetres of cyanide corresponding to the weight of glycerin in the volume of blue liquid titrated. An aqueous liquid containing an unknown amount of glycerin, treated in a similar manner, will decolorise a volume of cyanide solution corresponding to the glycerin present.

The foregoing method is based on the assumption that the solvent action of a solution of potash on cupric hydrate is directly proportionate to the amount of glycerol in the liquid.

Interpretation of the Results of Analyses of Soaps.—The process of ordinary saponification consists of the decomposition of the glyceride by caustic alkali, with

* *Analyst*, vi. 41.

consequent formation of glycerin and a soap or salt of the alkali-metal. Thus, the following formula represents the saponification of stearin by soda:—

$$\left.\begin{matrix}(C_3H_5)'''\\(C_{18}H_{35}O)_3\end{matrix}\right\}O_3+3NaHO=\left.\begin{matrix}(C_3H_5)'''\\H_3\end{matrix}\right\}O_3+3(NaC_{18}H_{35}O,O).$$

When the resulting soap is decomposed by an acid, as occurs in the course of an analysis, free stearic acid is produced, together with a chloride (or other salt) of alkali-metal.

$$Na,C_{18}H_{35}O_2+HCl=NaCl+H,C_{18}H_{35}O_2.$$

Calculating from this formula, it is found that, on decomposition with acid, sodium stearate yields 92·8 per cent. of fatty acid. Similarly, the alkali in the soap would be stated to be 10·13 per cent., so that the analysis would be—

Stearic acid . . .	92·81	per cent.
Soda (Na_2O) . . .	10·13	„
	102·94	„

Here there is an error of nearly three per cent. in excess, owing to the hydrolysis which takes place in decomposition. It is evident that if the basic constituent of a soap be stated as anhydrous alkali, a correction must be made in the actual weight of fatty acid found to bring it to the corresponding anhydride.* 612 parts of stearic acid, $C_{18}H_{36}O_2$, correspond to 594 of stearic anhydride, $C_{36}H_{70}O_3$, and the proportions of the

* In a complete analysis of a soda soap, the constituents should be stated in the following manner :—

	Per Cent.	Per Cent.
*Fatty anhydrides	—	—
Soda existing as soap . . .	—	
Silica	—	—
Soda existing as silicate . . .	—	
Sodium carbonate	—	
Sodium hydrate (caustic soda, NaHO) .	—	
Sodium sulphate	—	
Sodium chloride	—	
Lime	—	
Oxide of iron, &c.	—	
Water	—	
	—	

* = Fatty acids — per cent.

respective anhydrides corresponding to palmitic and oleic acids are not greatly different from the above. Hence the necessary correction of the observed weight of fatty acids to the corresponding quantity of fatty anhydrides may be made by multiplying by the factor ·97, 100 parts of $C_{18}H_{36}O_2$ representing approximately 97 parts of $C_{36}H_{70}O_3$.

There are not many published analyses of soaps on which much reliance can be placed. In the great majority of cases, the observers appear to have been content to state the amount of fatty acids, and alkali as deduced from the ash, the remainder being entered as "water, &c." Such meagre and inexact information as is supplied by such "determinations" is of very little value. The author is indebted to Mr Cornelius Hope for the very valuable analytical data contained in the table on next page. Sample No. 10 was prepared by the "cold process," and hence contained the glycerin produced by the saponification. This accounts for the sum of the estimated constituents being only 95·19. Samples 3, 4, and 12 were the only three which contained free caustic alkali, and in these it only reached the insignificant proportion of ·16, ·26, and ·15 per cent of NaHO respectively. Mr Hope points out that a striking feature of the analyses is the variable composition of the silicate as existing in the soap, although as added it is tolerably constant in composition. This is due to the property possessed both by rosin and fats of taking alkali from sodium silicate.

A well-made mottled or marbled soap should not contain more than 35 to 38 per cent. of water, and in good white soap the proportion should not be higher than 45 per cent. Not unfrequently, however, the amount is as high as 55 to 60 per cent., and occasionally upwards of 80 per cent. is present. This is especially the case with soaps made with coco-nut oil, which is frequently employed on this account. Coco-nut and palm-nut oil soaps have, however, a special value of their own, on account of their producing a lather with salt water.*

* A sample of "marine soap" for emigrants' use, manufactured from palm-nut oil, gave Mr C. Hope the following results on analysis :—Fatty anhydrides, 19·42 ; soda existing as soap, 3·11 ; silica, 9·00 ; soda existing as silicate, 3·98 ; sodium chloride, 5·13 ; sodium sulphate, 0·35 ; sodium carbonate, 2·35; sodium hydrate, 0·65 ; lime, oxide of iron, &c., 0·16 ; water, 53·32 ; glycerin (by calculation), 2·80 ; total, 100·27. Fatty acids, 20·02 per cent.

Table of Analyses of Soaps.

Description of Soap.	Origin.	Fatty and Resin Anhydrides.	Soda (Na_2O) existing as Soap.	Silica.	Soda existing as Silicate.	Sodium Carbonate and Hydrate.	Sodium Chloride and Sulphate.	Lime, Oxide of Iron, &c.	Water.	Total.	Fatty and Resin Acids.
1. "White," No. 1 . .	Tallow.	69·06	8·98	0·01	None.	·27	·65	·07	21·14	100·18	71·20
2. ,, No. 2 . .	Tallow and cocoa-nut oil.	60·50	6·82	0·06	None.	·06	·23	·16	32·20	100·03	62·36
3. ,, No. 3 . .	Do.	55·71	6·90	0·03	None.	·92	·18	·08	36·54	100·36	57·44
4. ,, No. 4 . .	Do.	44·27	6·23	7·02	2·36	·75	·66	·34	38·14	99·77	45·64
5. "Cold water," No. 1.	Tallow, rosin, and cotton-seed oil.	71·30	7·98	1·07	0·48	·75	·66	·16	17·44	99·84	73·50
6. ,, ,, No. 2.	Do.	49·95	7·00	2·34	1·01	·33	·51	·50	38·18	99·82	51·50
7. "Olive oil," No. 1 .	...	71·20	7·58	0·06	0·03	·22	·83	·20	19·70	99·62	73·40
8. "Marseilles," No. 1.	Chiefly olive oil.	62·66	7·27	0·06	0·03	·77	1·06	·16	28·20	100·12	64·60
9. "Palm oil," No. 1 .	...	59·28	6·65	0·42	0·01	·39	·60	·16	32·35	99·86	61·08
10. "Mottled" . . .	Palm-nut oil.	38·89	5·76	6·40	1·29	1·62	·50	·03	38·70	95·19	40·10
11. "Satinet" . . .	Tallow and rosin.	59·92	6·76	0·02	None.	·92	·78	·05	31·30	99·75	61·77
12. Glasgow "Almond"	Do.	42·41	4·14	5·64	1·59	2·76	·37	·14	42·88	99·93	43·72
13. "Pale rosin," No. 1.	Do.	60·90	7·22	0·04	None.	·10	·58	·02	31·22	100·08	62·78
14. ,, ,, No. 2.	Do.	48·20	5·00	0·42	0·18	·15	·75	·10	45·00	99·80	49·65
15. ,, ,, No. 3.	Do.	39·92	4·70	0·62	0·25	·20	1·66	·15	52·40	99·90	41·15
16. "Milling" . . .	...	63·06	7·25	0·02	None.	·10	1·80	·30	27·47	100·00	64·95
17. "Yellow" (for foreign markets) . . .	...	10·90	1·36	0·03	None.	Trace.	3·13	·14	84·00	99·56	11·20

These oils are sometimes employed alone, but are more frequently used in admixture with palm or olive oil.

THE COLOURING MATTER of soap consists of sulphide of iron, ochre, ultramarine, &c. These remain as a residue on dissolving the soap in water. The insoluble matter ought never to exceed 1 per cent. even in mottled soap, and should be less in other varieties.

EXTRANEOUS ADDITIONS to soap are made either with the object of causing the product to hold more water; as direct additions to the weight; or with the more legitimate view of introducing some constituent of detergent or medicinal value. Dextrin, starch, Irish moss, and gelatin are purely adulterants, as also are kaolin, barytes, and other insoluble earthy matters. On the other hand soluble silicates, borates, and carbonates have marked detergent properties, and hence may serve a useful purpose. Soaps containing free carbolic acid, thymol, &c., are also legitimate products of undoubted remedial value, but the same cannot be said of certain other articles of recent production.

SUGARS.

UNDER the generic name of sugars are included a large number of bodies occurring naturally in the animal or vegetable kingdoms, or produced from the so-called glucosides by the action of ferments or dilute acids.

The sugars constitute a series of closely-allied bodies, in many cases distinguishable from each other only with considerable difficulty, while their quantitative separation is frequently impossible in the present condition of chemistry.

As a class, the sugars are more or less sweet bodies, readily soluble in water. In many cases their solutions exert a powerful rotatory action on a ray of polarised light. Some of the sugars readily reduce alkaline solutions of copper and silver, while other species possess this power to a very limited extent.

In differentiating the numerous species of sugar two characters are of special importance; first, the extent and direction of their action on polarised light; secondly, their activity as reducing agents, especially with reference to their action on a hot alkaline solution of a cupric salt. These two methods of examination are so important, and of such extended application, that they are described in detail in special articles commencing on pages 264 and 283 respectively.

CLASSIFICATION OF SUGARS.

In the following table are given the distinguishing chemical and physical characters of the principal sugars. It will be seen that they may be classified under three groups—saccharoids, or unfermentable sugars; glucoses; and saccharoses.

In order to abridge the descriptions as much as possible, initial letters are used in the table, the characters given after them referring to the properties or reactions of the sugars when examined or treated in the respective manners indicated below :—

(*a*) Specific gravity of the sugar.

(*b*) Character of the crystals and general appearance of the sugar.

(*c*) Action of heat on the sugar.

(*d*) Solubility of the sugar in water.

(*e*) Solubility of the sugar in alcohol.

(*f*) Products of the action of moderately concentrated nitric acid on the sugar.

(*g*) Reaction of the sugar with concentrated sulphuric acid.

(*h*) Products formed by boiling the sugar with diluted sulphuric acid.

(*i*) Effect of yeast on the warm aqueous solution of the sugar.

(*j*) Products of the action of cheese and chalk on the aqueous solution of the sugar.

(*k*) Reaction of the sugar with strong solution of caustic alkali.

(*l*) Effect on Fehling's copper solution, when heated to 100° C. with an aqueous solution of the sugar (see page 286).

(*m*) Reaction of the sugar on ammonio-nitrate of silver at 100° C.

(*n*) Reaction of the aqueous solution of the sugar with ammoniacal acetate of lead.

In addition to the properties mentioned in the following tables, many of the sugars form characteristic crystalline compounds with metallic chlorides and other salts.

In most cases, the characters given in the tables are sufficiently definite and precise to serve as descriptions of the various sugars ; exceptions will, however, be made in the cases of bodies of such special importance as to require consideration in separate articles.

I. SACCHAROIDS, or NON-FERMENTABLE SUGARS.—This group includes the hexatomic alcohols mannite, dulcite, and sorbite, $C_6H_{14}O_6=C_6H_8(OH)_6$; and some unimportant bodies differing from these by the elements of water. They are not capable of undergoing fermentation either with yeast or with cheese and chalk.

Name.	Origin and Principal Modes of Formation.	Formula.	Sp. Rotatory Power.	Other Characters.
Mannite, or Mannitol.	Manna; reduction of glucose.	$C_6H_{14}O_6$	0, or *very* slightly left-handed.	(*b*) Anhydrous, four-sided trimetric prisms. (*c*) Fuses at 166°; at about 200° boils and distils with but slight decomposition. (*d*) Soluble in 6½ parts, cold; solution slightly sweet. (*e*) Soluble. (*f*) Saccharic and oxalic acids. (*g*) Sulphomannitic acid. (*h*) Unaffected. (*i*) and (*j*) Not fermentable, or only very slowly. (*k*) Not coloured. (*l*) Not reduced. (*m*) Reduced.
Dulcite, or Dulcitol.	*Melampyrum nemorosum*; action of nascent hydrogen on galactose.	$C_6H_{14}O_6$	0	(*b*) Anhydrous warty masses or hard monoclinic prisms. (*c*) Fuses at 188°. (*d*) Cold, 3·7 per cent. (*e*) Very slightly soluble. (*f*) Mucic acid (*not* saccharic acid). (*g*) Not carbonised. (*i*) and (*j*) Not fermentable. (*k*) Not affected. (*l*) Not reduced. (*n*) Not precipitated.
Sorbite.	Berries of mountain ash.	$C_6H_{14}O_6+\frac{1}{2}$ Aq.	0	(*c*) Becomes anhydrous; melts at 110°. (*g*) Not carbonised. (*i*) and (*j*) Not fermentable. (*k*) No coloration; distinction from sorbin. (*l*) Not reduced.
Iso-dulcite.	Action of dilute acids on quercitron.	$C_6H_{14}O_6$, or $C_6H_{12}O_5+$Aq.	S=+7·6°	(*b*) Crystals resemble cane sugar. (*c*) Melts with loss of water between 105° and 110°. (*d*) 50 per cent. in the cold; solution sweet. (*e*) Soluble. (*g*) Turns brown. (*i*) and (*j*) Not fermentable. (*k*) Turns brown. (*l*) Reduced.
Quercite, or Quercitol.	Acorns.	$C_6H_{12}O_5$	S=+33·5	(*b*) Transparent monoclinic prisms. (*c*) Fuses at 235°. (*d*) and (*e*) Soluble. (*f*) Oxalic acid. (*g*) Not coloured. (*i*) and (*j*) Not fermentable. (*k*) Not coloured. (*l*) Not reduced.
Pinite.	*Pinus Lambertiana*.	$C_6H_{12}O_5$	Sj=+58·6	(*a*) 1·52. (*b*) Radiated crystalline nodules. (*d*) Very soluble; solution very sweet. (*e*) Sparingly soluble. (*f*) Mucic acid. (*i*) and (*j*) Not fermentable. (*l*) Not reduced. (*n*) Precipitated.
Erythro-mannite.	Lichens.	...	0	(*b*) Pyramidal prisms. (*c*) Fuses at 118°. (*d*) and (*e*) Soluble. (*f*) Forms *no* mucic acid. (*i*) and (*j*) Not fermentable. (*l*) Not reduced. (*n*) Not precipitated.

II. GLUCOSES.—These sugars usually contain two atoms of hydrogen less than the members of Group I. (saccharoïds), and hence may be regarded as the aldehydes of hexatomic alcohols. In fact, ordinary dextrose, $C_6H_{12}O_6$, may be converted into mannite, $C_6H_{14}O_6$, by the action of nascent hydrogen, just as acetic aldehyde may be reduced to ordinary alcohol by the same means. The first three of the glucoses described in the following table present few chemical differences, but are distinguished by their action on polarised light and some other characters. On oxidation, they yield saccharic acid. Galactose differs from them in yielding mucic acid. The first four glucoses in the table readily undergo the alcoholic fermentation in contact with yeast, and reduce Fehling's solution and ammonio-nitrate of silver; but inosite, sorbyn, and eucalyn do not undergo the alcoholic fermentation with yeast, though they yield lactic and butyric acids under the influence of cheese and chalk. The body produced by "inverting" cane sugar is a mixture of equal parts of dextrose and lævulose (see page 281).

Name.	Origin and Principal Modes of Formation.	Formula	Sp. Rotatory Power.	Other Characters.
Sucro-dextrose, dextro-glucose, dextrose, grape-sugar, starch-sugar.	Honey, sweet fruits, diabetic urine, action of dilute acids on starch and glucosides.	$C_6H_{12}O_6+Aq.$	$S_D = +51{\cdot}9$ $Sj = +57{\cdot}6$ (See pages 274 and 839.)	(*b*) From aqueous solution, in granular warty masses containing 1 Aq.; crystallises from alcohol in anhydrous microscopic needles. (*c*) Becomes anhydrous below 100° C.; melts at 140°; at 170 yields glucosan, $C_6H_{10}O_5$. (*d*) Cold, 100 per cent., hot in all proportions; solution less sweet than that of cane sugar. (*e*) Soluble. (*f*) Saccharic acid. (*g*) Forms sulpho-saccharic acid, without charring. (*h*) Not affected till after long time. (*i*) Easily undergoes vinous fermentation. (*k*) Turns brown. (*l*) 10CuO reduced. (*m*) Reduced.
Sucro-lævulose, lævo-glucose, lævulose, mucoid sugar.	Honey, together with sucrose and dextrose; fruits; obtained pure by the action of dilute acids on inulin.	$C_6H_{12}O_6$	$S_D = -98$ at 15° C. $Sj = -108{\cdot}8$ at 15° C. (See page 281.)	(*b*) Syrupy liquid, forming with difficulty an anhydrous amorphous solid. (*c*) At about 170° yields lævulosan, $C_6H_{10}O_5$. (*d*) Solution much sweeter than that of dextrose. (*e*) More soluble than dextrose. Lævulose closely resembles dextrose in other characters, but is more easily altered by heat and acids, and offers greater resistance to alkalies and ferments. Its reducing power on Sacchse's solution (see page) is less than that of dextrose. By the action of chlorine, lævulose forms glycolic acid, dextrose giving dextronic acid.

Mannitose.	Oxidation of mannite.	$C_6H_{12}O_6$	0	(*b*) Syrupy. (*e*) Soluble. In other characters mannitose closely resembles dextrose.
Galactose, lactose.	Action of dilute acids on milk sugar.	$C_6H_{12}O_6$	α Sj=139·6 β Sj=83·2	(*c*) Sparingly soluble in cold alcohol. (*f*) Yields mucic acid. Resembles dextrose in other reactions, but has less powerful reducing action on Fehling's solution. Probably consists of a mixture of two dextro-rotatory glucoses.
Arabinose, pectinose.	Action of dilute acid on arabin.	$C_5H_{10}O_5$	Sj=+118° affected by temperature.	(*b*) Very brittle glistening masses. Anhydrous. (*d*) Very soluble hot, crystallising on cooling; solution sweet, but less so than cane sugar. (*f*) Oxalic acid. (*g*) Chars. (*i*) Not fermentable. (*k*) Turns yellow. (*l*) $\delta\frac{1}{2}$ molecules of CuO reduced.
Inosite, inosol, phaseomannite.	Muscle, kidney beans, cochineal.	$C_6H_{12}O_6+2$ Aq.	0	(*b*) Cauliflower-like masses," or monoclinic prisms resembling gypsum. (*c*) When rendered anhydrous melts at 210° C. (*d*) Water at 19° C. dissolves 16 per cent. of its weight; solution sweet. (*e*) Insoluble. (*f*) Evaporated nearly to dryness, and ammonia and $CaCl_2$ added, and again evaporated gives rose-red colour. (*g*) Not charred even at 100° C. (*i*) Not fermentable. (*j*) Forms lactic, butyric, and carbonic acids. (*g*), (*h*), and (*k*) Not affected even at 100° C. (*l*) Not reduced.
Sorbinose, sorbin.	Ripe mountain-ash berries.	$C_6H_{12}O_6$	S(?)=−46·9	(*b*) Hard trimetric prisms, or rhombic octahedra. (*d*) Easily soluble (200 per cent.); solution very sweet. (*e*) Almost insoluble. (*f*) Tartaric, racemic, and aposorbic acids. (*h*) Not affected. (*i*) Not fermentable. (*j*) Lactic and butyric acids, and alcohol. (*k*) Turns yellow. (*l*) Reduced. (*n*) Precipitated. Yields glycolic acid by the action of chlorine.
Eucalyptose, eucalyn.	Fermentation of melli-tose.	$C_6H_{12}O_6+1$ Aq.	Sj=+65°	(*b*) Uncrystallisable syrup, rendered anhydrous at 100° C. (*f*) Oxalic acid. (*g*) Chars. (*h*) No action. (*i*) Not fermentable. (*j*) Lactic and butyric acids. (*l*) Reduced.
Dambose.	Action of hydriodic acid on dambonite.	$C_6H_{12}O_6$	0	(*b*) Anhydrous six-sided prisms (distinction from inosite). (*c*) Melts at 212°. (*d*) Easily soluble (*i*) Not fermentable.
Bornesite.	Borneo caoutchouc.	$C_6\left\{\begin{matrix}H_{11}\\CH_3\end{matrix}\right\}O_6$	S_D=+32°	(*c*) Melts at 175°. (*g*) and (*k*) After boiling with dilute sulphuric acid reduces Fehling's solution.
Dambonite.	Gaboon caoutchouc.	$C_6\left\{\begin{matrix}H_{10}\\(CH_3)_2\end{matrix}\right\}O_6$	0	(*c*) Melts at 205°. (*h*) No action. (*k*) Reduced.

III. SACCHAROSES.* $C_{12}H_{22}O_{11}$ ($=2C_6H_{12}O_6-H_2O$). These sugars are related to the glucoses (Group II.) in the same manner as di-ethylenic alcohol is to glycol, or di-glycerin to glycerin (glycerol). They differ chemically from the glucoses by being less powerful reducing agents, and hence having, with the exception of maltose and lactose, little or no action on Fehling's solution; in being charred by sulphuric acid; and in not being capable of *direct* fermentation, though by the action of yeast, or by boiling with dilute acids, they are converted with greater or less facility into glucoses, and then undergo fermentation; the alcohol produced being about 51 to 51·5 per cent. of the weight of the original saccharose employed, against a production of only 48 to 49 per cent. from glucoses.

Name.	Origin and Principal Modes of Formation.	Formula.	Sp. Rotatory Power.	Other Characters.
Sucrose, saccharose, cane sugar.	Sugar cane, maple, white beet, maize, date-palm.	$C_{12}H_{22}O_{11}$	$S_D=+66·5°$ $S_j=+73·8°$ (See page 271.)	(*a*) 1·588. (*b*) Monoclinic prisms, or sparkling crystalline masses. (*c*) Melts at about 160° C., yielding dextrose and lævulosan. (*d*) Cold 300 per cent., hot in all proportions. (*e*) Insoluble in absolute alcohol. (*f*) Oxalic and saccharic acids. (*g*) Chars. (*h*) Forms inverted sugar, a mixture of dextro- and lævo-glucose. (*i*) The same, then alcoholic fermentation. (*k*) Not darkened. (*l*) Not reduced. (*m*) Precipitate of $C_{12}H_{18}Pb_2''O_{11}$.
Lactin, lactose, milk-sugar.	Milk of mammals.	$C_{12}H_{22}O_{11}+1$ Aq.	α Variety $S_D=+80°$ β variety $S_D=+52·7°$ (For crystals containing 1 Aq.)	(*a*) 1·525. (*b*) Hard trimetric prisms, or saccharoïd masses. containing 1 Aq. (*c*) Becomes anhydrous at about 130° and at 180° chars. (*d*) α form cold, 17 per cent.; β form, cold, 28 per cent., hot 40 per cent. (*e*) Soluble. (*f*) Mucic, oxalic, and saccharic acids. (*g*) Charred. (*h*) Yields galactose. (*i*) First galactose, then vinous fermentation. (*j*) lactic acid, alcohol, &c. (*k*) Little affected. (*l*) 7 CuO reduced. (*m*) Reduced. (*n*) Precipitated.
Maltose, malt-sugar.	Malt; together with dextrin, by the limited action of dilute acids on starch.	$C_{12}H_{22}O_{11}$	$S_D=+139·2$ $S_j=+154·5$ (See page 328.)	(*b*) Indefinitely crystalline in hard white crusts or minute needles containing 1 Aq. expelled at 110° C. (*c*) Much less soluble than dextrose. (*d*) Very soluble. (*i*) Yields dextrose, then vinous fermentation. (*l*) About 6 CuO reduced. In general properties closely resembles dextro-glucose.

Melitose, eucalypton.	Eucalyptus.	$C_{12}H_{22}O_{11}+3Aq.$	Sj = +102° (For anhydrous substance.)	(*b*) Thin interlaced needles. (*c*) Gives off 2 Aq. at 100° C., and becomes anhydrous at 130°. (*d*) Cold 11 per cent.; hot, easily soluble. (*e*) Soluble. (*f*) Mucic and much oxalic acid. (*h*) Glucose and eucalyn. (*i*) Glucose and eucalyn, the glucose then fermenting. (*l*) Not reduced. (*n*) Precipitated.
Melizitose	Larch (*Laria Europea*).	$C_{12}H_{22}O_{11}$	S_D=+88·8° Sj=+94·8°	(*b*) Small brilliant monoclinic prisms containing 1 Aq. readily took. (*c*) The anhydrous sugar fuses below 140° without alteration; decomposes at about 200°. (*d*) Easily soluble. (*f*) Oxalic but *no* mucic acid. (*g*) Chars. (*h*) Fermentable glucose. (*i*) Slowly and with difficulty undergoes vinous fermentation. (*k*) Not darkened. (*l*) Not reduced.
Mycose, trehalose.	Ergot, mushrooms, Trehala manna.	$C_{12}H_{22}O_{11}+2Aq.$	S_D=+200° Sj=+222° (For anhydrous substance.)	(*b*) Shining rhombic prisms, or rectangular octahedra. (*c*) Melts at 100° to 110°, and loses 2 Aq., solidifying again; when anhydrous melts at 210° without decomposition. (*d*) Extremely soluble. (*e*) Soluble in boiling alcohol, almost insoluble in cold. (*f*) Oxalic and saccharic acids, but no mucic acid. (*g*) Colourless in the cold, chars at 100° C. (*h*) Inverted by long boiling, yielding a fermentable glucose. (*i*) Slow and imperfect vinous fermentation. (*k*) Not darkenod. (*l*) Not reduced. (*m*) Not precipitated.
Synanthrose.	*Dahlia variabilis*, Jerusalem artichoke.	$C_{12}H_{22}O_{11}$ or perhaps $C_{12}H_{22}O_{10}+Aq.$	0	(*b*) Amorphous, very deliquescent. (*c*) At 140° turns brown, yielding caramel, &c. (*d*) and (*e*) Easily soluble, solutions faintly sweet. (*g* and *k*) Not coloured in the cold. (*h*) Dextrose and a lævo-rotatory glucose. The inverted products have a rotatory power of Sj= −54·1° at 17°, said to be unaffected by temperature. (*i*) Glucoses, followed by slow vinous fermentation. (*l*) Not reduced. (*n*) Not precipitated.

* It has been recently proposed to use the termination *on* for the sugars of this group, and hence the generic name would be saccharons, and mycon, lacton, and malton the names of species belonging to the group; the termination *ose* being limited to the glucoses.

The general methods by which sugars are isolated in the proximate analysis of animal and vegetable substances depend much on the nature of the associated bodies. Principles of separation commonly utilised are—the removal of albuminoid bodies by heat or precipitation; the precipitation of dextrin and other gummy matters by alcohol; the removal of organic acids and various other matters by acetate of lead; concentration of the saccharine fluid with a view to promoting crystallisation; and the detection and estimation of the sugars present by their reactions as reducing agents (page 283), and their relations to polarised light. A third mode of determination is based on the specific gravity of the saccharine solution. These methods of examination are described in detail in the next three articles.

RELATIONS OF THE SUGARS TO POLARISED LIGHT.

The greater number of sugars possess the property of altering the plane of polarisation of a ray of light. The power is possessed not merely by the solid sugars but also by their solutions, the rotatory action exerted by the latter being approximately, but not strictly, proportional to their concentration, or in other words to the number of molecules of dissolved sugar which the ray of light is caused to traverse.

Construction of Polarimeters.—In all modifications of the polarising saccharimeter, the polariser, or optical means of obtaining a beam of polarised light, consists of a double-refracting prism of calcite. In some cases a double image prism is used, but in others the extraordinary ray only is employed.

The analyser is composed of a single-image prism, and a Galilean telescope is frequently employed as an eye-piece. On rotating the analyser through 90° the field becomes perfectly dark, but on introducing between the analyser and polariser a tube filled with sugar solution the light again passes. If white light be used the transmitted tint varies with the strength of the solution of sugar and the length of the tube interposed, and rotation of the analyser merely causes an alteration in the colour of the transmitted light,

a phenomenon due to the fact that rays of differing refrangibility are rotated unequally. If monochromatic light be employed, a certain angular rotation of the analyser will suffice wholly to extinguish the light from the field of view, and hence by measuring the angle through which the analyser must be rotated to restore darkness, an estimate of the strength of the interposed liquid in sugar may be obtained. Quartz is well known to possess very powerful rotatory action on polarised light, a plate 3·75 millimetres in thickness (=0·148 inch) rotating the plane of polarisation of the mean yellow ray through 90 degrees. Some specimens of quartz possess right-handed rotation, and others are *lævo*-rotatory to an equal extent. Hence, a double plate composed of equal thicknesses of the two varieties possesses no rotatory power. If a plate be composed of semicircles of right and left-handed quartz, each 3·75 millimetres in thickness, and such a plate be placed between the Nicol's prisms while their principal sections are parallel, the field becomes tinted of a peculiar purple, or corn-flower colour, known as the *teinte du passage* or transition tint. The least rotation of the analyser causes one-half of the circle to incline to red and the other half to violet, and the interposition of a tube of sugar solution or other rotating liquid produces a similar effect, while the restored uniformity of tint necessitates a rotation of the analyser through an angle dependent on the strength and thickness of the polarising liquid used.

M. Soleil has applied these principles in a very ingenious manner in his well-known saccharimeters, the construction of which is illustrated and described in Watt's *Dictionary of Chemistry*, and other standard works. The Soleil instrument, however, shares with all others dependent on an observation of the transition-tint the disadvantage that the *teinte du passage* is not always the same for different eyes, and that the errors inherent in the construction of the instrument become greatly intensified if the solution under observation be not strictly free from colour.

In the case of coloured liquids, therefore, or in the event of the observer being somewhat colour-blind, it is far better to employ some instrument constructed for observation with the monochromatic sodium flame. In the polaristrobometer or

shadow-polariscope of Wild, a Savart double plate of quartz is placed behind the analysing prism and the solution-tube; the field appears crossed by dark bands or striæ which can be caused to disappear by rotating the analyser, so that at the conclusion of the observation, or in the absence of an active rotating liquid, the field appears uniform. The rotating power of the interposed liquid is read off on a divided circle.

In using this and other polarimeters employing monochromatic light, the source of illumination is a bunsen flame rendered luminous by inserting in it a loop of platinum wire holding a bead of sodium carbonate or a platinum trough containing previously melted sodium chloride. A desirable addition is a transparent plate of potassium bichromate fixed on the end of the instrument nearest to the flame.

Hofmann's saccharimeter is an instrument very similar to Wild's.

Laurent's polarimeter is one of the simplest and best. One-half of the field of vision is covered by a very thin plate of quartz, which allows some of the light to pass, even when the analyser and polariser (both of which are Nicol's prisms) are crossed. If the analyser be rotated so as to cause the quartz plate to become dark, light passes through the uncovered half of the field. In a position intermediate between these two, the two halves of the field appear equally dark, and this is the zero-point of the instrument. The slightest deviation from this neutral position causes one-half of the field to appear darker and the other half lighter than before. Hence, the change is a double one and the instrument very sensitive. Monochromatic light must be used. The more modern instruments have the divided circle graduated both in angular degrees and sugar units.*

* As a rule, in the Wild, Laurent, and Jellett-Cornu polarimeters, one-half the circle is divided into angular degrees, the other half bearing a sugar-scale. Thus, the Jellett-Cornu instruments made by Duboscq have 100 divisions, of such size that by taking 16·350 grammes of the sample each division of rotation represents 1 per cent. of sugar. The Laurent polarimeters made by Schmidt & Haensch of Berlin are provided with the Ventzke scale, for use with which 26·048 grammes is the standard quantity.

Ventzke-divisions can be calculated into their equivalent in Soleil-divisions by multiplying by the factor 1·593.

In the Jellett-Cornu polarimeter the polariser is a peculiarly cut crystal of calcite known as a Jellett's prism, the analyser being a Nicol. At a certain position of the latter, the two halves of the field appear equally illuminated. Monochromatic light is used,* and the indications are read off on a divided circle.†

Another very ingenious and highly accurate method has been described by Broch. It consists in observing the spectrum of the polarised light after transmission through the optically active liquid. A spectroscope is employed, having a Nicol's prism behind the slit, and a similar prism as analyser, the solution-tube being placed between them in the usual manner. The light is then refracted by a prism, and then observed through a telescope in the usual way. A dark band appears on the spectrum owing to the complete absorption of the light of some particular wave-length. The position of the band depends on the rotatory power exerted by the solution, and it gradually shifts from one end of the spectrum to the other as the analyser is rotated. The observation consists in adjusting the vertical spider-line in the eye-piece of the telescope, so that it coincides in position with the Fraunhöfer line D, and the analyser is then rotated until the centre of the black band is coincident with the spider-line. The light used is either sun-light reflected from a heliostat, or a luminous gas or lamp-flame containing a bead of sodium chloride or carbonate.

Professor Jellett has devised a form of instrument in which the rotation produced by an active solution is neutralised by that of turpentine of the opposite kind. A rack-work arrangement allows of the thickness of turpentine passed through being varied as required, and the indications are read off on a scale. The instrument is fully described in Thudichum and Dupré's work on "Wine," and is stated to give very accurate results.

* The use of monochromatic light, *desirable* in saccharimetry, becomes absolutely *essential* for obtaining accurate polarimetric determinations of tartaric acid. This is due to the fact that Biot's law, that the angles of rotation for the different simple colours are proportional to the squares of the indices of refraction and inversely as the squares of the wave-lengths, is true of quartz and saccharine liquids, but does not hold good for tartaric acid solutions.

† A cheap instrument on this construction is now made by Messrs Field of Birmingham, and offered at about five guineas.

Specific Rotatory Power of Sugars.—The specific rotatory power of an optically active substance is the angular rotation exerted by it on a ray of polarised light which is caused to traverse a thickness of 1 decimetre (=3·937 inches) of the pure substance.

The *absolute* specific rotatory power of a solid substance can only be observed if the body be obtainable in thick slices of considerable transparency. In default of these rarely attainable conditions, it is necessary to operate on a solution of known concentration, and from the *sensible* or *apparent* specific rotatory power observed, to calculate the *absolute* rotatory power of the substance in a solid state.

The sensible specific rotatory power of an active body is often seriously affected by change of temperature or by the concentration of the solution. In some cases the rotation is increased and in others diminished by dilution, so that the value obtained for a given solution does not represent the absolute specific rotatory power of the pure substance, but differs from it to an unknown extent, which is dependent on the influence which may be exerted by the optically inactive solvent. The statement of the specific rotatory power of a body in solution is therefore of value only when the strength of the solution and the nature of the solvent are also given. Moreover, Oudemanns has shown that the influence of two solvents is often very different from that of either alone. Thus, a solution of cinchonine in absolute alcohol has a rotatory power of +228° for the D line, while the chloroform solution rotates +212° only. Yet a solution of equal strength in a mixture of 87 per cent. of chloroform and 13 per cent. of alcohol has a rotation of +237°.*

For various reasons the most accurate results are obtainable by working with highly concentrated solutions, and hence a liquid should be chosen which possesses a high power of solution for the optically active body.

The foregoing considerations have not hitherto received the consideration they deserve, to which circumstance is probably

* Tollens has recently found that solutions of cane sugar in methyl alcohol, ethyl alcohol, and acetone exhibit sensibly higher rotatory power than aqueous solutions of the same strength.—*Ber.* xiii. 2297.

attributable the discordant statements on record as to the rotatory power of various optically active bodies.*

The sensible or apparent specific rotatory power of a substance is found by dividing the angular rotation observed in the polarimeter (a) by the length of the tube in decimetres (l), and by the concentration (c) or number of grammes in 100 c.c. of the liquid. Thus, if S represent the specific rotatory power, then—

$$S = \frac{a}{l \times \frac{c}{100}} = \frac{100a}{l \times c}.$$

In all determinations of specific rotatory power it is necessary to take into account the refrangibility of the light employed for the observation. Formerly, an approximately monochromatic light was obtained by interposing a plate of deep red glass, the rotation observed being taken as that of "the red ray." The use of a Bunsen flame in which a compound of sodium is heated, affords a strictly monochromatic light of the refrangibility of Fraunhöfer's line D in the solar spectrum. When the corn-flower or transition tint is observed the results correspond closely (in the case of sugar solutions) with those obtained by observing the rotation of the "mean yellow ray." This is due to the *teinte du passage* being complementary to, and hence equally rotated with, the mean yellow ray. In consequence of the difference in the rotating action of circularly polarising liquids on rays of varying refrangibility, it is desirable always to state the nature of the light used. This is usually done by affixing a small letter as index to the number repressing the specific rotatory power of the substance. Thus $[a]_R$ is symbolical of the specific rotatory power for the mean red ray; $[a]_J$ for the mean yellow, or transition tint; and $[a]_D$ for the monochromatic light of incandescent sodium vapour. These symbols being somewhat clumsy, the author has suggested their replacement by the symbols S_R, S_J, and S_D.

* Further information on this interesting subject will be found in Watt's *Dictionary of Chemistry*, vol. viii. p. 1209, *et seq.*

The following table by Biot shows the rotation of rays of different refrangibilities produced by a plate of quartz 1 millimetre in thickness:—

Colour of Ray.	Angular Rotation.		
	Degrees.	Minutes.	Seconds.
Extreme red	17	29	47
Red glass (Cu_2O)	18	25	0
Limit of red and orange	20	28	47
,, orange and yellow . . .	22	18	49
Mean yellow	24	0	0
Limit of yellow and green	25	40	31
,, green and blue	30	2	45
,, blue and indigo	34	34	18
,, indigo and violet	37	51	58
Extreme violet	44	4	58

The following values have been found by Broch for the rotation produced by a thickness of 1 millimetre of quartz on light of the refrangibilities of the chief lines of the solar spectrum:—

B.	C.	D.	E.	F.	G.
15° 18′	17° 15′	21° 40′	27° 48′	32° 30′	42° 12′

Girard and De Luynes have recently determined with great care the deviation produced by a plate of quartz 1 millimetre in thickness, and find an angular rotation of 21° 48′ = 21·8° for light of the refrangibility of the sodium line D, the possible error not exceeding 4′ = ·07°.*

The strength of a cane-sugar solution which will produce the same deviation, when examined in a tube 2 decimetres in length, as a plate of quartz 1 millimetre in thickness, has been determined by various observers. Clerget estimated it at 16·471 grammes of sucrose in each 100 c.c. of solution. Dubrunfaut reduced the amount to 16·390 grammes, while the weight 16·350 grammes was the result of the investigations of a commission consisting of Pouillet, Barreswil, Schlösing, and Duboscq. The directions now issued with the instrument specify the last-named amount as that to be used in verifying the scale. Recently Girard and De Luynes have

* *Compt. Rend.* lxxx. 1354.

given 19·190 grammes of cane sugar per 100 c.c. as the equivalent of 1 millimetre of quartz. Tollens,* in a very elaborate paper, gives 16·337 grammes as the standard amount.† The deviation of the D line produced by 1 millimetre of quartz, is 21° 40′, according to Broch, or 21° 48′ according to Girard and De Luynes. The mean of these two determinations is 21° 44′ = 21·73°. Employing this figure in the formula for specific rotatory power given on page 269, the value of S_D for cane sugar in solutions containing about 16 grammes per 100 c.c., is found as follows:—

$$S_D = \frac{100 \times 21{\cdot}73^\circ}{2 \times 16{\cdot}337} = 66{\cdot}50^\circ.$$

This result applies to the value of S_D for sugar solutions containing between 16 and 17 per cent. of sucrose. As stated already, the concentration of the solution sensibly affects the specific rotation, and not always in the same direction. Thus, strong solutions of sucrose cause a deviation less than the same amount of sugar would in more dilute solutions, while with dextrose the reverse is the case. On this account, recorded values for S must not be interpreted too strictly in cases in which no mention is made of the concentration of the solution. The importance of this point is well shown by the following determinations of Hesse,‡ of the value of S_D for cane sugar in solutions of various strengths:—

Grammes of Sucrose, per 100 c.c.	Value of S_D.
1	67·95
2	67·39
3	67·05
6	66·67
10	66·50
20	66·45

The exact apparent specific rotatory power may be found,

* *Ber. d. Deutch. Chem. Ges.* 1877, 1403.

† The corresponding amount for the Ventzke-Soleil instrument is 26·086 grammes in 100 c.c.

‡ *Annal. der Chemie*, clxxvi. 95.

for solutions varying from 1 to 10 grammes of cane sugar, per 100 c.c., by the following formula, in which c represents the number of grammes of sugar in each 100 c.c. of the solution—

$$S_D = +68{\cdot}65 - {\cdot}828c + {\cdot}115415c^2 - {\cdot}00541666c^3.$$

Beyond a concentration of 10 grammes of sugar per 100 c.c. of the solution, the decrease is pretty regularly ·005 for each unit of sugar.

The values of Tollens and Hesse for the specific rotation of cane sugar agree with those of Tuschmidt,* who obtained 66·42 (apparently for somewhat concentrated solutions), and Backhoven, who obtained the same result.† Schmitz, again, has found 66·42 and 66·53 as the value of S_D when $c=10$;‡ and, lastly, Tollens§ gives +66·48° as the correct value for S_{10D} in the case of cane sugar. These results all correspond closely, and point conclusively to a value of +66·5° for cane sugar in solutions of a concentration from 10 to 20 grammes per 100 c.c. It must be remembered that this is the *apparent* specific rotation for the concentration in question; the *absolute* value of S_D for cane sugar being, according to Tollens, +63·90°, and according to Schmitz, +64·16°.

Although the apparent specific rotatory power of cane sugar for the D line may be considered to be accurately ascertained, the same cannot be said of the value for the transition-tint. This is doubtless due in part to the fact that the transition-tint is not a ray of definite refrangibility, and even differs with different observers.

These are insurmountable difficulties in the way of obtaining a constant value for S_j, and hence all determinations made by instruments intended for observing the transition-tint must be regarded as only of secondary value. This is well shown by the following discordant factors proposed by different observers for calculating S_D to S_j in the case of cane sugar. For convenience, the former is uniformly taken as +66·5°, and the product obtained by multiplying

* *Journ. f. Pract. Chem.* [2], ii. 235.
† *Ibid.* [2], viii. 277.
‡ *Ber. d. Deutch. Chem. Ges.* 1877, 1414.
§ *Ibid.* 1403.

this constant by the factor or fraction, represents the value of S_J:—

S_D	× Factor	=	S_J	Authority.
66·5 ×	1·129	=	75·08	Landolt.
	$\frac{24}{21·67}$	=	73·65	Broch.
	$\frac{24}{21·80}$	=	73·21	Girard and De Luynes.
	$\frac{24}{21·54}$	=	74·09	Brown and Heron.
	1·091	=	72·55	Calderon.
	1·049	=	69·96	Weiss.

The factor of Weiss may be ignored. That of Calderon is remarkable. It is deduced from determinations made by him in Berthelot's laboratory with the view of revising that chemist's value for S_J(=73·8°). Calderon found, for 10 to 20 per cent. solutions of cane sugar, S_D=67·1 and S_J=73·2.* Brown and Heron do not state the grounds of their adoption of the ratio employed by them.

The mean of the more trustworthy of the above numbers gives a value for S_J not greatly different from +73·8°, which is that generally adopted. If this be accepted as the specific rotation of cane sugar for the transition-tint, then S_D and S_J may be calculated into each other by the following factors, which are those adopted in this work:—

$$\frac{S_J}{S_D}=\frac{73·8}{66·5}=1·110\text{; and}$$
$$\frac{S_D}{S_J}=\frac{66·5}{73·8}=·9011.$$

In the following table are given the most reliable determinations of specific rotation of some of the most important varieties of sugar. The optical properties of the rarer sugars are shown in the tables on page 259.† It will be observed that the figures

* *Comptes Rendus*, lxxxiii. 393.

† According to Thomsen, the rotatory power of the carbohydrates in solutions of the ideal concentration of $c=o$, multiplied by the molecular weight, is always some multiple of the constant number 19.—*Journ. Chem. Soc.* xlii. 147 and 245.

given below are the *apparent* or *sensible* specific rotatory powers *for solutions containing* 10 *per cent. or so* of the solid sugar. The figures printed in bolder type are the result of direct determinations, the others being calculated by means of the ratio—

$$\frac{S_J}{S_D}=1{\cdot}11\,.$$

The signs + and − signify *dextro-* and *lævo*-rotation respectively. It must not be forgotten that the crystals of sugars (other than cane) are not usually anhydrous when deposited from aqueous solutions. The formulæ given in the following table show the condition of hydration of the sugars to which the values for specific rotation apply :—

Variety of Sugar.	Formula.	Specific Rotatory Power.		Observer.
		S_D.	S_J.	
Cane sugar .	$C_{12}H_{22}O_{11}$	**+ 66·5**	**+ 73·8**	Hesse, Tollens, Berthelot.
Milk sugar . .	$C_{12}H_{22}O_{11}+H_2O$	α+ **60·0** β+ **52·7** β+ **53·1**	+ 88·8 + 58·5 + 58·9	Hesse. Hesse. Mills & Hogarth.
Maltose . . .	$C_{12}H_{22}O_{11}$	**+139·2**	**+154·5***	O'Sullivan, Steiner, Meissl.
Sucro-dextrose	$C_6H_{12}O_6$	α+91 to 100 β+ 51·9	+101 to 112 + **57·6**	Various. Average.
Lævulose . .	$C_6H_{12}O_6$	−98·0 at 15° C. −51·9 at 88° C.	−106·8 at 15° C. − 57·6 at 15° C.	Deduced (p. 275).
Invert sugar	$2C_6H_{12}O_6$*	−23·05 at 15° C. −0 at 88° C.	**−25·6** at 15° C. **−0** at 88° C.	Casamajor. Tuschmidt.

The average of the most reliable determinations of the specific rotatory power of sucro-dextrose gives a value of +57·6° for S_J (see "Dextrose," page 339).

According to Tuschmidt, Casamajor, and many other observers,† a solution of cane sugar which, *before* inversion, shows a deviation of +100 divisions, *after* inversion has a lævo-rotation of −36·5 divisions at 15° C.

The value given in the table for the specific rotation of invert sugar is based on this fact, also taking into account the

* See "Maltose," page 328.

† As expressed in the text the statement is Casamajor's. Tuschmidt gives the formula—$S\ t=-(27{\cdot}6-0{\cdot}32t)$. That is, the rotatory power of invert sugar is −27·6°, less ·32° for each degree Centigrade above zero. Thus, at 15° C. the rotation would be $-27{\cdot}6-(\cdot32+15)=-22{\cdot}8°$, against −23·05°, the number adopted in the test.

increase in the weight of solids caused by the inversion of the cane sugar to glucoses.*

From the value for invert sugar thus found, that of lævulose was calculated by the equation, $25{\cdot}6 \times 2 + 57{\cdot}6 = 108{\cdot}8$ at 15°C.†

Practical Optical Saccharimetry.—For the polarimetric determination of sugars, it is found convenient in practice to employ a constant weight of each sample. The weight to be taken varies from 16·19 to 26·07 grammes, according to the instrument to be employed, and to a lesser degree with each particular instrument. With Soleil's saccharimeter the standard weight is 16·350 grammes, and with other instruments, showing directly the percentage-content of real sugar in the sample, weights closely approximating to 16·337 grammes are usually employed. With polarimeters furnished with the Ventzke scale, however, the standard weight is 26·048 grammes. With instruments employing sodium light, and graduated only in angular degrees, 18·800 grammes is a more convenient weight to use.

Preparation of the Solution of Sugar for the Polarimeter.—Having carefully mixed the sample to obtain a fair average specimen, the standard quantity is weighed out and introduced carefully into a 100 c.c. flask. About 50 c.c. of water are then added, and the liquid carefully agitated until the whole of the sugar has passed into solution.

For accurate observation with the polariscope it is essential that the saccharine liquid should be as colourless as possible. The necessary clarification may be effected by means of animal charcoal, hydrated alumina, or basic acetate of lead.

Animal charcoal is employed by adding to the solution of the sugar (prepared as above described, and diluted to exactly 100 c.c.) about one-fourth of its bulk of powdered bone-black, which must be fresh and free from hygroscopic water. The liquid is well agitated with the black for a few

* The equation used was :—

$$S_j = \frac{-36{\cdot}5^\circ \times \frac{{\cdot}2173 \times 73{\cdot}8}{66{\cdot}5}}{2 \times \frac{16{\cdot}337}{100} \times \frac{100}{95}} = -25{\cdot}59^\circ \text{ at } 15\,^\circ\text{C.}$$

† The corresponding value for 14° C. is $-109{\cdot}6°$, against $-106°$ as generally taken.

minutes and then passed through a dry filter. This is a preferable mode of using charcoal to the French plan, in which the granular bone-black is placed in a vertical tube closed at the lower end by a plug of cotton-wool, and the sugar solution passed through the column of charcoal. In using this method, the first portions of the percolated liquid must be rejected, as the charcoal absorbs sugar as well as colouring matter. Indeed, it is highly probable that the tendency to absorption is the cause of many of the discrepancies in sugar assays, and hence it is desirable to avoid the source of error altogether by employing the following method of clarification, which is very efficacious, even under extremely unfavourable conditions:—Weigh out the normal quantity of sugar and dissolve it in about 50 c.c. of water in a flask holding 100 c.c., as described on last page. According to the quality of the sample the solution will be (1) colourless but cloudy, (2) yellow, (3) brown, or (4) almost black.

In the first case, add about 3 c.c. of a cream of hydrated alumina and one drop of basic acetate of lead solution.* In the second case, the same volume of alumina may be used, but the lead solution increased to 3 or 5 drops. In the third and fourth cases add about 2 c.c. of a 10 per cent. solution of sodium sulphite, and then the lead solution gradually, with constant shaking, till no further precipitate is produced.† Whichever mode of clarifying is adopted, the liquid is well agitated, and allowed to stand at rest for about 10 minutes, to ensure the complete separation of any precipitate. The

* This alumina cream is prepared by pouring a solution of alum into excess of a hot solution of washing-soda, collecting the precipitate in a linen bag, washing well with boiling water, and mixing it with enough water to form a thin cream.

The solution of basic acetate of lead is prepared by grinding together in a mortar ½ lb. of recently ignited litharge, 1 lb. of acetate of lead, and enough water to render the whole pasty. The mixture is next boiled with three pints of water, and the solution filtered and preserved in well closed bottles.

† If, as is often recommended, a considerable excess of lead solution be added, some of the precipitate is apt to be redissolved, and the solution becomes opalescent and filters with difficulty. It is also said that the presence of lead in the solution affects the polarimetric readings.

flask is then filled nearly to the mark with water, and the froth allowed to rise to the surface, when it is destroyed by the cautious addition of a few drops of spirit or a single drop of ether. Water is then added exactly to the mark, the contents of the flask thoroughly mixed by agitation, and the liquid filtered through a dry filter.

Another mode of clarification, recommended by Scheibler, and very simple and good in all ordinary cases, is as follows—Solutions of alum or aluminium sulphate and of basic lead acetate are prepared of equivalent strengths, so that on mixing equal measures and filtering no sulphate remains in solution. To the solution of sugar 5 c.c. of each of these liquids is added, the mixture shaken, made up to 100 c.c., and passed through a dry filter.

Some exceptionally dark cane sugars, and most beet-root molasses, are not sufficiently decolorised by either of the above methods. In such cases a double normal quantity should be weighed out, and the solution clarified by sodium sulphite and basic lead solution, as before described, a rather larger quantity of the latter liquid being employed. The solution is made up accurately to 100 c.c., filtered, and 50 c.c. of the filtrate treated with a saturated solution of sulphurous acid until the liquid smells strongly of the gas. About 2 grammes of purified animal-charcoal* are then added, the liquid well shaken, made up exactly to 100 c.c., and filtered. By proceeding in this manner, a perfectly colourless or lemon-yellow solution may be obtained from the worst samples.

ESTIMATION OF CANE SUGAR BY THE POLARIMETER.—The solution of sugar having been clarified, if necessary, by one of the foregoing methods, the tube of the polarimeter (2 decimetres in length) is rinsed with a little of it, and then completely filled with the liquid. A glass plate is then placed on the top, and secured by screwing home the brass cap. This being done, the cap should be somewhat loosened to avoid

* This is prepared by boiling 1 lb. of freshly ground bone-charcoal in half-a-gallon of common yellow hydrochloric acid diluted with one gallon of water. The liquid is filtered through a linen bag, and the residue washed with hot water till free from acid, dried and ignited to full redness in a closed crucible. It is bottled while still warm, and kept carefully dry.

any chance of pressure being exerted on the contents of the tube. The tube with its contained saccharine solution is then placed between the polariser and analyser of the saccharimeter, when an optical disturbance will be observed, the extent of which will depend on the amount and nature of the sugar in solution.

The polarimeter is then adjusted until the neutral point is reached, or in other words, until the optical disturbance produced by the introduction of the saccharine solution is compensated. The rotation required to produce this effect is then read off and recorded.

Polarimeters intended for use in saccharimetry are usually graduated so that the percentage of cane sugar in the sample examined is shown without calculation, which is not the case if the instrument be graduated in angular degrees only.

According to Biot, a plate of quartz 1 millimetre in thickness produces an angular rotation of exactly 24 degrees for the transition-tint. This rotation is taken as the standard in the Soleil and Soleil-Duboscq saccharimeters, and the 24 degrees are divided into 100 equal parts, so that each one of the divisions is equivalent to ·24 angular degrees. A cane sugar solution contained in a 2 decimetre tube must have a concentration variously estimated at 16·19 to 16·35 grammes in 100 c.c. of the liquid to produce a rotation equal to that caused by 1 millimetre of quartz. In practice, a solution of sugar, varying in strength from 16·19 to 16·35 grammes of the solid in each 100 c.c. according to the practice of the instrument-maker, is introduced into the polarimeter, and the point of neutrality marked as 100. The distance between this point and the zero-point is then divided into 100 equal parts. Hence with each particular saccharimeter should be employed a solution of sugar of the same concentration as that used for its graduation. By doing this, the percentage of cane sugar contained in any impure sample free from other active bodies can be ascertained by dissolving the standard weight to 100 c.c., and noting the number of divisions through which the light is rotated when the solution is interposed in a 2-decimetre tube. The saccharimeters employing sodium-light are usually graduated in a similar manner, but the 100 divisions correspond to about

21·73 angular degrees instead of 24°, as in those instruments using the transition-tint. In all cases, it is desirable to verify the standard weight of sugar said to cause a rotation through 100 divisions of the scale, and, if proved correct, this weight should be invariably employed in subsequent experiments. As stated on page 271, 16·337 grammes for 100 c.c. is the exact quantity of sugar producing a rotation in a 2-decimetre tube equivalent to that caused by 1 millimetre of quartz, and this quantity will be the same whether the instrument be constructed for the sodium-light or for the transition-tint.

The Ventzke-Soleil saccharimeter has divisions somewhat less open than the above, so that the standard weight of sugar to be taken is 26·048 grammes.

Most instruments are now graduated both in angular degrees and in percentages of cane sugar. If the polarimeters employed be graduated in the former manner only, the percentage of real sugar in a sample may be ascertained by comparing the rotatory power of its solution with that of an equally concentrated solution of pure sugar.* Thus, if the solutions be made by dissolving in water 20 grammes each of the standard sugar and the sample, and making the liquids up to 100 c.c. each, then, in a 2-decimetre tube the standard solution should give an angular rotation of +26·6 degrees for the sodium ray.† Hence, if the angular rotation produced by the solution of the sample was only 25·5 degrees, the percentage of sugar contained in it was 95·87, according to the proportion

$$\frac{25{\cdot}5 \times 100}{26{\cdot}6} = 95{\cdot}87.$$

Even this simple calculation may be avoided, for, if the weight of the sample taken be $\frac{25 \times 20}{26{\cdot}6} = 18{\cdot}80$ grammes, the angular rotation produced in a 2-decimetre tube will be exactly 25

* Sugar crystals, or white sugar-candy, crushed to powder, and dried first by pressure between layers of filter-paper and then by exposure for a short time to a temperature of 100° C., will furnish a very good standard.

† According to the equation on page 269, $66{\cdot}5 = \frac{100\,a}{l \times c} = \frac{100\,a}{2 \times 20}$; whence $a = 26{\cdot}6$.

degrees for the D line, and hence each degree of angular rotation will represent 4 per cent. of sugar in the sample.

POLARISING SACCHARIMETRY IN COMPLEX LIQUIDS.—So far the use of the polarimeter has only been described in its application to the determination of cane sugar in comparatively pure specimens, but if proper means be adopted it is capable of a far wider range of usefulness.

Most sugars possess more or less action on a ray of polarised light, the exact value of $[a]$ or S varying with each kind of sugar, and being also dependent in a minor degree upon the temperature, concentration of solution, and other conditions already alluded to (see page 268). It has also been found that the rotatory power varies in many cases with the length of time the sugar has been dissolved. Thus several sugars exist in two modifications, α and β, the former of which is present in newly-made solutions, but undergoes conversion into β in the course of a few hours at ordinary temperatures, or immediately on heating the liquid. The α modification always has a higher rotatory power than the β variety, while, in the case of milk sugar, and probably of other sugars existing in two forms, the solubility is exactly inverse.*

It will be evident, therefore, that while the polarimeter is capable of accurately indicating the proportion of cane sugar present in a liquid containing no other optically active substance, its readings may be below the truth, or actually negative if the liquid contain a notable amount of certain other varieties of sugar. Hence in such complex liquids a

* Hesse explains this curious fact in the following manner :—"The rotatory powers of the two modifications (of milk sugar) stand to one another as 3 to 2, consequently in inverse proportion to the solubility of the two forms. A freshly-prepared solution of milk sugar saturated at 10° C. contains, in 100 parts, 14·55 parts of sugar. In these proportions the molecules of sugar fill the given space so perfectly that any further molecules of sugar added to the solution find no room to dissolve. By boiling or standing there results a contraction in the building up of the molecules, so that the volume of each is reduced to two-thirds of its original expansion. The solution is then only two-thirds full, so that a further one-third part of substance in the same condition may find place in it. A light ray which passes through the volume of the first form must travel a path one-half longer than when it passes through the β form, and, correspondingly, in the first case it is more strongly affected by one half than in the latter." (See also page 327.)

single reading by the polarimeter is useless, but by a judicious application of chemistry the indications may still be relied on.

The different varieties of glucose are unaffected by heating with dilute acid, while cane sugar is, by such treatment, converted into a mixture of equal parts of sucro-dextrose or dextro-glucose, and sucro-lævulose or lævo-glucose. $C_{12}H_{22}O_{11}+H_2O=2C_6H_{12}O_6$. The product is called inverted- or invert-sugar, of which 100 parts are produced by the hydration or "hydrolysis" of 95 parts of cane sugar.

While the effect of increase of temperature on the rotatory power of cane sugar and sucro-dextrose is almost inappreciable, in the case of lævulose the temperature is a most important factor. The same remark applies to invert sugar, the lævulose of which diminishes in rotatory power to the same extent as if it were unmixed with dextrose. On this account the rotatory power of invert sugar decreases regularly with increase of temperature till at 88° C. it is optically neutral, and at still higher temperatures exerts a *dextro*-rotatory power.

Serious discrepancies exist in the rotatory power of sucro-dextrose as determined by different observers (see page 339), but fortunately any doubt as to the true rotatory power of this sugar does not affect the accuracy of ordinary sugar assays, for the change in rotatory power caused by the inversion of a solution of cane sugar has been accurately ascertained, irrespective of the exact measure of the rotatory powers of the two glucoses to the combined influence of which the effect is due. It has been found by various observers that a solution of cane sugar which *before inversion* causes a deviation of 100 divisions to the right, *after inversion* has a *lævo*-rotatory power of 39 divisions at 10° C., and consequently has undergone an optical change equivalent to a *rotation through* 139 *divisions*. Owing to the diminished optical power of lævulose at high temperatures, the change by inversion is less the higher the temperature at which it is observed, decreasing by 1 division for each increase of 2° C. Thus at 0° C., the change by inversion would equal 144 divisions, and the value for any higher temperature may be found by the equation:—

$$D=144-\frac{t}{2}.$$

Hence at 15° C., the change by inversion is 136·5 divisions for a solution previously reading + 100; or the number representing the change by inversion, *however expressed*, multiplied by the factor ·7326 $\left(=\frac{100}{136\cdot5}\right)$ shows the corresponding rotation caused by the *cane* sugar in the original solution, whence the proportion of cane sugar may be readily deduced.

The above factor and equation may be conveniently combined as follows:—C is that part of the rotation produced by the uninverted liquid which is really due to the cane sugar contained in it, and D is the *change* in the polarimetric reading caused by the process of inversion. Then:—

$$C=\frac{100\ D}{144-\frac{t}{2}}$$

Thus, if a saccharine solution show a rotation of + 23 angular degrees before inversion and after inversion a *lævo*-rotatory action of 7·2 degrees, at 16° C., then by the equation:—

$$C=\frac{100\times30\cdot2}{144-\frac{16}{2}}=\frac{3020}{136}=22\cdot26°.$$

Thus of the 23 angular degrees of rotation produced by the original sugar solution 22·26° were really due to cane sugar, and should be calculated to that substance, while the remaining + ·74° of rotation was due to dextrose or some other *dextro*-rotatory substance not capable of inversion by the means employed for the purpose.

The rotation due to cane sugar having been ascertained, the amount of that substance present in the solution may be found as described on page 279.

In the above arguments the fact is left out of consideration that inversion usually involves increase in the bulk of the saccharine liquid. In practice, the increase is neutralised by taking the reading of the *inverted* sugar in a tube 22 centimetres in length instead of 20, as with the original liquid. The 22 centimetre tube, intended for the observation of the

rotation of the inverted sugar, should be furnished with a short vertical tube to allow the insertion of a thermometer, so that the temperature of the liquid during the observation may be accurately ascertained.*

THE INVERSION OF SUGAR for polarimetric purposes is best accomplished in the following manner:—The sugar solution is clarified and made up to a definite volume in the manner described on page 275, and its rotating power observed by the polarimeter. 50 c.c. of the solution are then mixed with 5 c.c. of pure fuming hydrochloric acid of about 1·16 sp. gravity. This is best done in a flask having two marks on the neck, one at 50 c.c. and a second at 55 c.c. The flask is next heated on a water-bath till its contents have acquired a temperature of 68° C., an operation which should be arranged to occupy about ten minutes. The solution is then cooled down by immersing the flask in cold water, placed in the 22 centimetre tube, and its rotation observed by the polarimeter in the manner already described.

REACTIONS OF THE SUGARS AS REDUCING AGENTS.

Many species of sugar, including the different varieties of glucose, possess considerable activity as reducing agents, while in the case of other kinds, as cane sugar, the same property is comparatively feebly marked.

The reducing properties of sugars are best manifested and measured by their reactions on alkaline solution of certain heavy metals, such as silver, copper, and mercury. The reduction exercised on cupric salts is the best known and most important.

If a solution of cupric sulphate be mixed with a saccharine liquid in sufficient quantity, no precipitate of hydrated cupric oxide, CuO,H_2O, is produced on addition of caustic potash or soda. The liquid acquires a deep blue colour, but remains perfectly clear. On raising the fluid to the boiling point, no

* The increase in the volume of the liquid can be avoided by inverting with crystallised oxalic acid. A good plan of avoiding change of temperature is to employ a polarising tube surrounded with cold water, on the plan of a Liebig's condenser.

visible change occurs if the liquid contained cane sugar only, but if any variety of glucose be present, a yellow precipitate of hydrated cuprous oxide is produced which quickly turns to anhydrous Cu_2O, and acquires an orange-red colour. If the glucose be present in excess the blue colour of the solution entirely disappears. Instead of relying on the saccharine matter for the prevention of the precipitation of the blue cupric hydrate by the alkali it is far better to employ tartaric acid or a tartrate (see below).

The reducing action of certain varieties of sugar on alkaline solutions of copper has been applied by different chemists in an almost infinite variety of ways, the precipitated cuprous oxide being weighed as such by several, by others converted into metallic copper or cupric oxide, by others again redissolved and estimated volumetrically. Some operators make the original process a volumetric one. The great majority of these modified processes are merely of historical interest and require no detailed description.*

Preparation and use of Fehling's Copper Solution.—The alkaline solution of copper most commonly em-

* The reduction of copper solutions by glucose appears first to have been utilised by Trömmer. Frommherz suggested the employment of a citrate to keep the cupric oxide in solution. Modifications of the ordinary alkaline tartrate solution have been devised by Barreswil, Poggiale, Rosenthal, Chevalier, Boussingault, Reveil, Fehling, Strohl, Violette, Magneshahens, Lowenthal, Joulie, Possoz, &c. Loewe employed glycerin instead of a tartrate. Various treatments of the precipitated cuprous oxide have been proposed by the following chemists :—Mohr dissolves the oxide in hydrochloric acid and titrates with permanganate. Brunner dissolves in an acid solution of ferric chloride and estimates the reduced iron by bichromate or permanganate. Champion and Pellet dissolve the precipitate in hydrochloric acid and chlorate of potassium, boil off free chlorine, and titrate the liquid with stannous chloride. Girard and Soxhlet reduce the cuprous oxide in hydrogen and weigh the metallic copper. Muter dries the cuprous oxide at 100° C., and weighs it as Cu_2O. O'Sullivan and other operators ignite the precipitate strongly and weigh as CuO. Ferdinard-Jean dissolves the cuprous oxide in hydrochloric acid, and weighs the metallic silver precipitated on adding ammoniacal silver nitrate. Maumené uses an excess of copper solution, filters, adds ammonia to the filtrate, and estimates the residual copper by titration with sodium sulphide, for which Perrot substitutes potassium cyanide. Lastly, Pavy adds ammonia to the alkaline cupric solution and runs in the sugar solution till the hot liquid is decolorised.

ployed is that recommended by Fehling, which is prepared in the following manner:—34·64 grammes of pure crystallised sulphate of copper (free from iron and moisture) are dissolved in about 200 c.c. of distilled water. Commercial caustic soda of good quality is treated with a small quantity of cold water, so that only about three-fourths of it is dissolved. The lye is filtered through clean sand or glass-wool, and diluted to a specific gravity of 1·14. In 480 c.c. of this solution are dissolved 173 grammes of recrystallised Rochelle salt (potassium sodium tartrate),* the copper solution added to the alkaline liquid and the whole diluted to exactly 1 litre. The "Fehling's solution" thus prepared should be carefully preserved from air and light, as it is apt to undergo some obscure change which renders its indications unreliable. Hence before use it is desirable to ascertain its condition by diluting a quantity with an equal measure of water and heating the liquid to boiling for a few minutes. It ought to remain perfectly clear. The tendency to change can be conveniently avoided by making up the alkaline solution of Rochelle salt to 500 c.c., and the cupric sulphate solution to an equal bulk, and preserving them separately. For use, the two solutions are mixed in equal volumes.

When intended to be used for the gravimetric estimation of glucose, the *exact* strength of the Fehling's solution is of little importance, but when it is to be employed volumetrically its accuracy should be ascertained by titrating 10 c.c. with a standard solution of inverted sugar. 0·475 grammes of dry cane sugar, after being inverted (see page 283), ought to be capable of exactly reducing 100 c.c. of Fehling's solution.

The following figures show the reducing power of sugars on Fehling's copper solution:†—

Two molecules of glucose ($2C_6H_{12}O_6 = 360$) reduce 10CuO (=794·0)
One molecule of lactose ($C_{12}H_{22}O_{11} = 342$) reduces 7CuO (=555·8)
One molecule of maltose ($C_{12}H_{22}O_{11} = 342$) reduces about 6CuO.

* Much of the Rochelle salt of commerce is very impure. It is safest to prepare it by dissolving commercial cream of tartar in hot water, adding carbonate of sodium till the liquid remains slightly alkaline after boiling, filtering from the precipitated calcium carbonate, and crystallising the Rochelle salt from the clear liquid.

† See the reference to Soxhlet's researches on page 293. The exact reaction

·950 of Gramme Pure Sugar Inverted & diluted up to 200 C.C Water. 10 C.C of this solution neutralizes exactly 10 C C of Copper Liquid.

For the detection of a reducing sugar all that is necessary is to heat the clear solution to the boiling point with twice its measure of Fehling's solution. If a yellow or orange precipitate or turbidity is produced, a reducing sugar or some substance giving a similar reaction is present. Cane sugar does not react with Fehling's solution till it has been "inverted" by heating with acid. The following bodies resemble the producing sugars in their reaction with hot Fehling's solution:—aldehyde, chloral, pyrogallic acid, gallotannic acid, arsenious acid. Dextrin, gum-arabic, alcohol, acetic acid, oxalic acid, tartaric acid, citric acid, gallic acid, glycerin, urea, uric acid, sulphurous acid, &c., do not reduce Fehling's solution at a temperature approaching ebullition.

If a saccharine liquid be much coloured it is difficult or impossible properly to recognise the reaction with Fehling's solution. Coloration of the liquid is still more objectionable if the sugar is to be quantitatively determined, in particular by the volumetric method. In such cases the sugar solution must be clarified by one of the methods employed for the preparation of a solution for the polarimeter (see page 275), but it must be borne in mind that, if lead has been employed, it must be *completely* removed from the solution, or the results of the Fehling's test will be worthless.

To prepare the clarified sugar solution containing lead for the copper test, a quantity of it judged to contain from ·2 to ·5 grammes of glucose is accurately measured and placed in a 100 c.c. flask. A strong solution of sulphurous acid is next added, until the lead is completely precipitated, when a little washed alumina is added, the fluid diluted to the mark with water, agitated, and filtered. The clear filtrate is then ready for addition to the cupric solution as described below.

The inversion of cane sugar to render it determinable by copper solution may be affected as described on

of reducing sugars on Fehling's solution is not known, but among the products are—1. Acetic and formic acids. 2. Certain non-volatile acids, especially tartronic; an acid forming uncrystallisable salts; and an acid decomposed with formation of humus-like products on heating its alkaline solution. 3. A gum-like substance.

quantity of Pure Sugar be requisite, it will require a proportionate quantity more of impure Sugar or in the proportion 96 : 100 :: 99

page 283, taking care that the liquid is first clarified if necessary, and then freed from lead as described above. By operating in this manner a very satisfactory solution is obtained, and excessive colour is avoided. The acid liquid must be rendered neutral by carbonate of sodium before adding it to the Fehling's solution.

GRAVIMETRIC DETERMINATION OF REDUCING SUGARS BY FEHLING'S SOLUTION.*—25 to 30 c.c. of Fehling's solution, prepared as described on page 285, should be placed in a beaker of about 5 or 6 ounces' capacity, and diluted with 50 c.c. of boiling, well-boiled water. The beaker is placed in a larger one in which water is kept constantly boiling. At the end of six or seven minutes (the liquid being still perfectly clear) a known weight or measure of the glucose-holding liquid, previously clarified, inverted, and neutralised if necessary (see last page), is added to the hot Fehling's solution, and the water kept boiling in the outer beaker for twelve to fourteen minutes. If the blue colour of the solution be completely destroyed within the first few minutes, it can be restored by quickly adding more of the Fehling's solution, but it is much safer to commence the assay again, using a smaller amount of the saccharine liquid. After twelve to fourteen minutes† the precipitated cuprous oxide is rapidly filtered, washed with boiling well-boiled water, dried, and ignited in porcelain. Strong ignition for five or six minutes in an open crucible ensures the conversion of the red precipitate into the black cupric oxide (CuO), and treatment with nitric acid is hence rarely necessary. The oxide of copper must be cooled under a dessicator and weighed as rapidly as possible, as it is extremely hygroscopic.

Although the above method is very satisfactory, some chemists may prefer to redissolve the precipitate, either before or after ignition, and deposit the metallic copper on the inside of a platinum crucible by electrolysis.

* The details here given are taken from a paper by O'Sullivan (*Journ. Chem. Soc.* xxx. 131).

† A longer time causes too high a result if dextrin or cane sugar be present, but is without effect on solutions of pure glucose.

The determination of milk sugar by Fehling's solution requires close adherence to several precautions to ensure accuracy. The process has recently been subjected to a critical examination by Rodewald and Tollens.* Their results are generally confirmed by Muter,† but the latter chemist indicates, in addition, certain points, by attention to which the method is further increased in accuracy. According to Muter, constant results cannot be ensured unless the whole liquid be diluted to such a point as to reduce to insignificance the tendency of the alkali to act on the sugar, while the Fehling's solution is employed in sufficient quantity to instantaneously perform the whole reaction, and both the sugar and the Fehling's solution are actually boiling when mixed. Under such conditions the proportion of copper reduced is said to be rigidly 7Cu for $C_{12}H_{22}O_{11}$, as stated on page 285.

The experimental details by which the above equivalent may be ensured are as follow:—The solution is diluted with hot water until it does not contain more than 0·1 per cent. of milk sugar, and the liquid is brought to brisk ebullition in a large beaker. A very slight excess of boiling hot Fehling's solution is then added,‡ and the whole kept boiling for three minutes and allowed to settle. In a few minutes the precipitate will have subsided, so that the slightly blue liquid can be almost wholly poured off. 50 c.c. of boiling water are poured on the precipitate, and the liquid rapidly filtered, and the precipitate washed with boiling water till free from any trace of free alkali. Muter then moistens the precipitate with two drops of petroleum spirit, drys it in a water-oven, and weighs as Cu_2O, but it is evident that any of the alternative methods of after-treatment may be substituted for the direct weighing of the cuprous oxide. Muter's plan involves the necessity of using a weighed filter, which is apt to suffer from the action of the strongly alkaline liquid.

The following factors may be employed for calculating the weight of copper or copper oxide obtained to the correspond-

* *Deut. Chem. Ges. Ber.* xi. 2076. † *Analyst*, v. 35.

‡ It is evident that the measure of Fehling's solution required must be approximately ascertained by previous trials.

ing quantities of the principal kinds of sugar. (See also page 293).

	Glucose, $C_6H_{12}O_6$.	Cane Sugar, $C_{12}H_{22}O_{11}$ (after inversion).	Milk Sugar, $C_{12}H_{22}O_{11}$.	Malt Sugar, $C_{12}H_{22}O_{11}$.
Cu . .	·5634	·5395	·7698	·3408
Cu_2O . .	·5042	·4790	·9835	·3025 *
CuO . .	·4535	·4308	·6147	·2721

Thus, if one gramme of a sample of cane sugar has been weighed out, inverted, and precipitated as above described, and the resultant CuO weighed 1·9800 grammes, then the total quantity of sugar (expressed as cane sugar) is—

$$1{\cdot}98 \times {\cdot}4308 = {\cdot}85298 = 85{\cdot}3 \text{ per cent.}$$

Soxhlet has recently † thrown doubt on the gravimetric determination of sugar by Fehling's solution. Further information respecting his conclusions will be found on page 293.

VOLUMETRIC DETERMINATION OF REDUCING SUGARS BY FEHLING'S SOLUTION.—This operation is conducted in much the same manner as the gravimetric process, but the saccharine liquid is diluted till it contains only about ½ per cent. of glucose, and is then run in from a burette. It is essential that the sugar solution be added to the cupric test and not the reverse. The following are the details of the operation:—The saccharine solution, if necessary after being clarified, inverted, and neutralised as described on page 286, is placed in a burette. Exactly 10 c.c. of the Fehling's solution are measured into a wide test-tube or small flask supported vertically by a clip. 30 c.c. of water are added, and a few fragments of tobacco-pipe stem dropped in to prevent bumping. Raise the liquid to boiling by applying a small flame, and run in the sugar solution, 2 c.c. at a time, boiling between each addition. When the blue colour of the liquid has nearly

* The factors here given for maltose are based on the results of Brown and Heron (*Journ. Chem. Soc.* xxxv. 609). For further information see page 328.

† *Chem. Centr.* 1878, 218 and 236.

disappeared, the sugar solution should be added more cautiously, but it is desirable to effect the titration as rapidly as possible. The end of the reaction is reached when, on removing the flame and allowing the cuprous oxide to settle, the supernatant fluid appears colourless, or faintly yellow when viewed against a white surface. If any doubt be felt as to the termination of the reaction, a few drops of the liquid may be filtered through a small filter into a mixture of acetic acid and dilute potassium ferrocyanide, contained in a porcelain crucible or placed on a white plate. If copper be still present in the liquid, more or less brown coloration will be observed.

The following are the weights of the principal kinds of sugar which, it is generally assumed, will reduce 10 c.c. of Fehling's solution prepared as described on page 285. Soxhlet's figures are given on page 292:—

10 c.c. Fehling solution	=	·0500	gramme	of dextrose, lævulose, or invert sugar.
10 c.c. ,, ,,	=	·0475	,,	cane sugar (after inversion).
10 c.c. ,, ,,	=	·07143	,,	milk sugar (lactose).
10 c.c. ,, ,,	=	·0807*	,,	malt sugar (maltose).

The results obtained by using Fehling's solution volumetrically are not generally so accurate as those of the gravimetric method. The operation should be *quickly* conducted.†

Titration of Reducing Sugars by Pavy's Ammoniacal Cupric Solution.—This modification of the ordinary mode of using Fehling's solution is based on the fact that in presence of a sufficient excess of ammonia the cuprous oxide is not precipitated, but forms a *colourless* solution, so that the end of the reaction is indicated by the decolorisation of the blue liquid. As the ammoniacal cuprous solution is extremely oxidisable, the blue colour being restored by oxidation, it is necessary to avoid access of air. This is best done by attaching the nose of the Mohr's burette containing the sugar solution to a tube passing through the india-rubber

* See page 289, and note on page 328.

† In presence of much albuminous or other impurity in the sugar solution, the cuprous oxide refuses to settle, but remains suspended in a fine state of division, rendering the whole liquid muddy. Efficient previous clarification will always prevent this inconvenience and render unnecessary the filtration of a few drops of the turbid liquid, with subsequent testing for copper, by acidulating and adding sulphuretted hydrogen or potassium ferrocyanide.

stopper of a flask containing the copper solution. A second tube conveys the steam and ammoniacal gas into a flask of cold water. It is desirable to allow the end of the tube to dip into a little mercury placed at the bottom of the water, so as to prevent any tendency to "suck back." A still better arrangement is to pass (by a third tube) a slow current of hydrogen or coal-gas through the flask containing the boiling copper solution.

To prepare the ammonical solution, 120 c.c. of the ordinary Fehling's solution (see page 285) should be mixed with 300 c.c. of strong ammonia (sp. gr. ·880), and with 400 c.c. more of the caustic soda solution of 1·14 sp. gr. The mixture is then made up to 1 litre. 100 c.c. measure of this solution has the same oxidising power on glucose as 10 c.c. of the ordinary Fehling's solution,—that is, it corresponds to ·050 gramme.

In carrying out the process, 100 c.c. of the above solution are placed in the flask, a few fragments of pumice or tobacco-pipe added, the tubes and burette adjusted, and the liquid raised to the boil. The sugar solution is then gradually run in from the burette, the boiling being continued regularly. The process is at an end when the blue colour of the liquid is wholly destroyed. The end-reaction is very sharply marked, but the reduction occurs more slowly than with the ordinary Fehling's solution. The process is often a very useful one, especially for the rapid assay of impure saccharine liquids such as beer-worts.

Pavy's solution is said to possess a different oxidising power on maltose (see page 329) and lactose from that exerted by Fehling's test. Its reaction on glucose is, under the above-described conditions, only $\frac{5}{6}$ths of that exerted by Fehling's solution. Hence 120 c.c. of the latter are employed in making the ammoniacal solution, instead of 100, as would be the case if they were strictly equivalent.

Determination of Sugars by other Reducible Liquids.—Other methods for the determination of reducing sugars have been based on the reduction of an alkaline solution of potassio-mercuric cyanide (Knapp); of an alkaline solution of potassio-mercuric iodide (Sachsse); of mercuric acetate (Hager); of an alkaline solution of bismuth (Frangni); and

of an alkaline solution of potassium ferricyanide (Gentèle).* Müller and Hager have shown that Knapp's process is very valuable for determining sugar in diabetic urine. The method of applying it is fully described on page 355.

Sachsse's original solution is prepared by dissolving 18 grammes of pure dry mercuric iodide in a solution of 25 grammes of potassium iodide. To this a solution of 80 grammes of caustic potash is added, and the solution diluted to 1 litre. 40 c.c. of this solution are boiled in a basin, and a standard solution of the sugar gradually added. The end of the reaction is attained when a drop of the supernatant liquid ceases to give a brown colour with a drop of a very alkaline solution of stannous chloride. The end of the reaction is well defined, and the results are accurate when pure dextrose or inverted sugar is worked with, though differing with each. In presence of cane sugar the results are quite erroneous. By reducing the proportion of caustic potash from 80 grammes to 10 grammes per litre, Heinrich finds that glucose may be accurately determined in presence of very varying amounts of cane sugar. Neither Knapp's nor Sachsse's solution can advantageously replace that of Fehling for ordinary purposes, but occasionally they are capable of being applied with great advantage. This is owing to the fact that they are unequally affected by the different kinds of reducing sugars, and even the two mercurial solutions exhibit essential differences in this respect. The subject has been recently investigated by Soxhlet† who gives the following table. The numbers must not be interpreted too rigidly, but regarded as roughly comparative rather than absolute determinations of reducing power.

	Fehling.	Knapp.	Sachsse.
Dextrose	100	100	100
Invert Sugar	96·2	99·0 (100 ?)	124·5
Lævulose	92·4	102·2 (100 ?)	148·6
Milk Sugar	70·3	64·9	70·9
Lacto-glucose	93·2	83·0	74·8
Inverted-milk Sugar . .	96·2	90·0	85·5
Maltose	61·0	63·8	65·0

* *Journ. Chem. Soc.* xxxii. 226; xxxiv. 246; xxxvi. 180.

† *Journ. Pract. Chem.* [2], xxi. 227; and *Journ. Chem. Soc.* xxxviii. 758.

Some of Soxhlet's results are not accepted as accurate (see page 295), and further investigation of the subject is much wanted. His observations are very suggestive of possible means of differentiating various sugars.

Influence of Variable Conditions on the Reducing Power of Sugar Solutions.—In all experiments on the reducing power of sugar on metallic solutions, it is important to operate as far as possible under constant conditions. Apparently unimportant variations, as time occupied in the experiment, amount of free alkali, presence of excess of the metallic solution, concentration of the liquid, and other conditions liable to change with every experiment, are all factors more or less concerned in the results obtained, and rigidly accurate results thus become impossible in many cases likely to occur in the practical analysis of saccharine liquids. The variations due to some of the above causes have been recently studied by Soxhlet,* a very full abstract of whose original paper has been published in English by C. H. Hutchinson.† Soxhlet finds that the reducing power of sugar for alkaline copper solutions is only constant under exactly the same conditions, and that if the same amount of sugar act in one case on an amount of copper solution which it is just able to reduce, and in another on an excessive quantity, the reducing equivalent will in the first case be found to be considerably less than in the second. Evidently, therefore, if a solution of sugar be added by small quantities at a time to a copper solution, as in an ordinary volumetric estimation, the amount of reduction effected by the first quantities added will be greater than that produced by the last. To avoid the error due to this cause Soxhlet employs the sugar and copper solutions in the exact proportions necessary for their mutual reaction, ascertaining the volumes requisite by a series of approximating experiments.‡

* *Journ. Pract. Chem.* [2], xxi. 227–317. † *Pharm. Journ.* [3], xi. 721.

‡ These were made by adding to a carefully measured quantity of Fehling's solution (prepared fresh daily), at the boiling point, a certain amount of a one per cent. or half per cent. solution of the sugar. The reaction was allowed to continue for a specified time, when the liquid was passed through a plaited filter, and a portion of the filtrate acidulated with acetic acid, and tested with potassium ferrocyanide. If a reddish brown coloration or precipitate resulted,

The following results were obtained by Soxhlet by operating in the manner described. The sugar solutions contained 1 gramme of the solid in 100 c.c. The figures represent the weight of the sugars in grammes required for the reduction of 100 c.c. of Fehling's solution, used undiluted or mixed with one, two, three, or four measures of water.

Kind of Sugar.	Time of Heating in Minutes.	Weight of Sugar oxidised by 100 c.c. of Fehling's Solution.				
		Undiluted.	Equal Bulk of Water.	Two Measures Water.	Three Measures Water.	Four Measures Water.
Dextrose (anhydrous)	2	·4750	·4825	·4880	·4920	·4940
Invert Sugar	2	·4940	·5030	·5090	·5140	.5150
Lævulose (calculated)	2	·5130	·5235	·5300	·5360	·5260
Milk Sugar (dried at 100°	6	·676	unaffected by dilution.			·676
Lacto-glucose (dried at 100°	2	·511	...	...	...	·533
Maltose . .	3 to 4	·778	...	...	...	·740

It will be seen from Soxhlet's results that dilution of the Fehling's solution very sensibly affects the reducing power exerted by the sugar. Thus one equivalent of invert sugar in 1 per cent. solution reduces 10·1 equivalents of CuO when the undiluted cupric solution is employed, but 9·7 equivalents only when the Fehling's solution is diluted with four measures of water. It will also be observed that Soxhlet's results show a slight but very sensible difference between the reducing power of dextrose and of invert sugar, and this difference becomes more marked when the reducing power of lævulose is calculated therefrom. This difference, if a real one, is of an exceedingly important nature, as it is calculated to vitiate very many of the analyses of saccharine matters on record. It is therefore greatly to be regretted that Soxhlet's

the experiment was repeated, a somewhat larger quantity of sugar solution being employed, and so on until a measure of sugar solution was found that would exactly suffice for the decomposition of the copper solution, while if 0·1 c.c. less of sugar solution were employed, a sensible quantity of copper was found in the filtrate. Hence the volume of sugar solution required was ascertained to within 0·1 c.c.

conclusions are very seriously diminished in value by the questionable method adopted by him for effecting inversion.*

The same objection applies to Soxhlet's experiments on the reducing power of invert sugar on the mercurial solutions of Knapp and Sachsse (see page 292). In these cases also he found that the reducing equivalent was notably influenced by the concentration of the solution and the proportion of alkali present, and that any other variation in the conditions of working was also liable to influence the amount of mercury reduced.

SPECIFIC GRAVITY OF SACCHARINE SOLUTIONS.

An aqueous solution of cane sugar, containing 10 grammes of the solid in each 100 c.c., has a density of 1·0386 at 15·5° C. (=60° F.). The weight of water in 100 c.c. of this solution is 103·86 − 10·00 = 93·86 grammes. As this would occupy 93·86 c.c., the volume occupied by the 10 grammes of sugar is 6·14 c.c., whence the specific gravity of the sugar in a state of solution is $\frac{1}{6{\cdot}14} = 1{\cdot}628$,—a figure which agrees closely with those obtained in a similar manner for other carbohydrates.

The following table shows the sp. gravity of solutions of sugars and allied substances under three different conditions, namely:—

(*a*) Solutions containing 4·21 per cent. of carbon, which is the proportion present in a solution containing 10 per cent. by weight of cane sugar;

(*b*) Solutions containing 10 grammes of the solid in 100 grammes *weight* of liquid; and,

* This was done by dissolving 9·5 grammes of purified cane sugar in 700 c.c. of water, adding 100 c.c. of one-fifth normal hydrochloric acid, and heating on the water bath for thirty minutes. The solution was then exactly neutralised by caustic soda, and diluted with water to 1000 c.c. Soxhlet found that ·5 gramme (=·475 of cane sugar) of inverted sugar so obtained reduced 101·2 c.c. of undiluted Fehling's solution, while with more prolonged heating with the same amount of acid the product reduced 100·5 c.c. of copper solution, and this was further reduced to 100·2 when 300 c.c. measure of the standard acid was employed, and the heating continued for ninety minutes.

(*c*) Solutions containing 10 grammes of the solid in 100 c.c. *measure* of the liquid.

The figures refer in all cases to densities at 15·5° C. (=60° F.), water at the same temperature being taken as 1000.*

Substance in Solution.	Formula.	Specific gravity of solution containing			Observer.
		a. 4·21 per cent. of carbon.	*b.* 10 grammes solid per 100 grammes.	*c.* 10 grammes solid per 100 c.c.	
Invert Sugar .	$2C_6H_{12}O_6$	1042·4	1040·3	1038·8	G. H. and R.†
Cane Sugar . .	$C_{12}H_{22}O_{11}$	{1040·6 {1040·1	1040·6 1040·1	1039·0 1038·6	G. H. and R.† Brown and Heron.‡
Malt Sugar . .	$C_{12}H_{22}O_{11}$	1040·8	1040·8	1039·3	Brown and Heron.‡
Pale Malt Extract	...	1041·2	...	...	G. H. and R.†
Brown Malt Extract	...	1041·2	...	...	G. H. and R.†
Malt Extract .	...	...	1040·4	1038·9	Muspratt.
Starch Paste .	$xC_{12}H_{20}O_{10}$	1039·1	1041·3	1039·7	Brown and Heron.‡
Dextrin . .	$yC_{12}H_{20}O_{10}$	1038·3	1040·0	1038·5	O'Sullivan.§
Caramel . .	$C_{12}H_{18}O_9$ (?)	1034·9	1039·0	1037·5	G. H. and R.‡

From these figures it appears that solutions of different carbohydrates of equal concentration have almost identical specific gravities. In other words, the density of the solution depends on the amount of solid dissolved, *not* on the percentage of carbon in the liquid. As a consequence of this fact it is found that solutions of maltose or cane sugar increase very sensibly in density on inversion by dilute acid or a small quantity of yeast.

The density of solutions of dextrin and the chief kinds of sugar being almost identical, it follows that the sum of them present in an aqueous solution may be found by allowing an increase of 3·86 in density for each 1 gramme of sugar or other carbohydrate in 100 c.c. of the liquid. For very dilute solutions this figure is correct,‖ but for those containing over 12 of solids for 100 volumes—such as brewers' worts—the

* Throughout the section on the specific gravity of saccharine solutions water is taken as 1000, instead of 1·000, as in other parts of the volume.

† *Report on Original Gravities*, 1852, by Graham, Hofmann, and Redwood.

‡ *Journ. Chem. Soc.* xxx. 130. § *Ibid.* xxxv. 569, *et seq.*

‖ Brown and Heron (*Journ. Chem. Soc.* xxxv. 664) have laid down a curve by which the strength of cane-sugar solutions can be readily ascertained in all cases of less density than 1150.

factor $\frac{1}{3{\cdot}85}$ gives still closer results. If W be the weight of solid in carbohydrate in 100 c.c., and D be the density of the solution at 60° F. (compared with water as 1000), then the value of W may be found by the equation—

$$W = \frac{D - 1000}{3{\cdot}85}.$$

From the number thus found for W (=the number of grammes of solids in 100 c.c.) the weight of solid carbohydrates in 100 *parts by weight* of the liquid (w) may be found by multiplying W by 1000, and dividing the product by the density of the liquid—

$$w = \frac{1000 \times W}{D}.$$

The sp. gravity of standard wort is fixed by law at 1057 at a temperature of 60° F.* Hence, such wort contains 14·8 grammes of solids for 100 c.c., or 148 lbs. per 100 gallons ;† for—

$$W = \frac{1057 - 1000}{3{\cdot}85} = 14{\cdot}8.$$

This result gives, by the second equation, 14·0 parts of solids in 100 parts by weight of the liquid; for—

$$w = \frac{14800}{1057} = 14{\cdot}0.$$

For all saccharine solutions of moderate strength the foregoing formulæ will answer every purpose. Solutions of invert sugar respond to the formulæ up to about 20 per cent. of contained solid, but more concentrated solutions should be diluted with a known proportion of water before applying the method.

* Inland Revenue Act, 1880.

† It is surprising how difficult it is for an unscientific mind to grasp the true relations between weight and volume. Thus, the provisions of the Inland Revenue Act relating to density were at first wholly incomprehensible to the majority of brewers. A very common fallacy was to suppose that a barrel of wort which weighed 20 lbs. more than the same barrel would if filled with water must necessarily contain 20 lbs. only of dry extract.

Tables showing the densities of concentrated solutions of cane sugar have been published by Gerlach, Scheibler, Balling, and Brix. The following figures are chiefly those of Gerlach, and will answer every purpose :—

Cane Sugar per cent. by weight.	Sp. Gravity at 17·5° C.	Cane Sugar per cent. by weight.	Sp. Gravity at 17·5° C.	Cane Sugar per cent. by weight.	Sp. Gravity at 17·5° C.
10	1·0401	35	1·1540	60	1·2899
11	·0443	36	·1590	61	·2959
12	·0485	37	·1641	62	·3019
13	·0527	38	·1691	63	·3079
14	·0570	39	·1742	64	·3139
15	·0613	40	·1794	65	·3200
16	·0656	41	·1845	66	·3262
17	·0700	42	·1897	67	·3324
18	·0744	43	·1950	68	·3386
19	·0788	44	·2003	69	·3449
20	·0832	45	·2056	70	·3512
21	·0877	46	·2109	71	·3575
22	·0922	47	·2163	72	·3639
23	·0968	48	·2218	73	·3703
24	·1014	49	·2272	74	·3768
25	·1060	50	·2327	75	·3833
26	·1106	51	·2383	80	·4159
27	·1153	52	·2439	85	·4499
28	·1200	53	·2495	90	·4849
29	·1248	54	·2552	95	·5209
30	·1296	55	·2609	99	·5504
31	·1344	56	·2666		
32	·1393	57	·2724		
33	·1442	58	·2782		
34	.1491	59	·2840		

Correction of Densities of Saccharine Solutions for Temperature.—In breweries it is often convenient to ascertain the density of the wort at a temperature above that of 60° F. (=15·5° C.), in which case the specific gravity as observed by the hydrometer can be calculated into the corresponding number for a temperature of 60° F., in the following manner :—

To unity add ·004 for every degree of specific gravity above 1000 (g) shown by the hot wort, and ·01 for each Fahrenheit degree of temperature (t) above 60° F. Multiply the sum of these by $\frac{1}{10}$th of the number of Fahrenheit degrees above 60° F. and the product, added to the density of the hot wort, will give a number representing the specific gravity of the

liquid at 60° F. The rule is expressed by the following formula:—

$$G=\left(1+\frac{(g-1000)4}{1000}+\frac{t-60}{100}\right)\frac{t-60}{10}+g.$$

Thus, if the wort be found to have a density of 1052·0 at a temperature of 110° F., then by the formula:—

$$G=\left(1+\frac{(1052-1000)4}{1000}+\frac{110-60}{100}\right)\frac{110-60}{10}+1052.$$

$$G=(1+\cdot208+\cdot5)5+1052.$$

$$G=1\cdot708\times5+1052.$$

$$G=1060\cdot54.$$

The formula may be simplified if for $g-1000$ be substituted e, the excess of density over 1000 at the observed temperature; and for t be substituted f, the excess of temperature above 60° F. The formula then becomes—

$$G=\left(1+\frac{4e}{1000}+\frac{f}{100}\right)\frac{f}{10}+g.$$

Corrections of densities of cane sugar solutions for temperature may be made by the same formula.

Interpretation of the Indications of Beaumé's Hydrometer.—The instrument almost exclusively employed by sugar manufacturers for ascertaining the density of saccharine solutions is Beaumé's hydrometer for liquids heavier than water. As originally constructed, the point to which the instrument sunk when immersed in a solution of 15 parts of common salt in 85 parts by weight of water was taken as 15 degrees. The interval between this point and that at which the hydrometer stood when immersed in pure water was divided into 15 equal parts, and a scale of similar equal parts extended as far as was necessary. According to this scale concentrated sulphuric acid of 1845 sp. gravity marked 69½ degrees. Gay-Lussac proposed a modified scale, according to which the same density corresponded to 66 degrees. Of late years, all the instruments made in *England*, at any rate, have been graduated to a scale intermediate between those two. On such instruments a liquid of 1480

specific gravity marks 48 degrees, and hence the actual specific gravity may be calculated by the following formula:*—

$$\text{Sp. gravity} = \frac{148{,}000}{148 - \text{deg. Beaumé.}}$$

Thus, if a liquid mark 12 degrees Beaumé, the actual specific gravity will be 1088·2; for—

$$\frac{148{,}000}{148-12} = 1088{\cdot}2.$$

Interpretation of the Indications of Bates' Brewers' Saccharometer.—In testing the strength of the worts in breweries, a hydrometer or saccharometer is employed, the indications of which are expressed in pounds per barrel, and may be translated into absolute specific gravities by dividing the number of "saccharometer-pounds" by ·36 and adding 1000.

A barrel (=36 gallons) of water weighing 360 pounds, a saccharine solution a barrel of which weighs (360+20=) 380 pounds is said to have "a saccharometer-gravity of 20 pounds per barrel." The real specific gravity of such wort would be 1055·5; for 360 : 380 = 1000 : 1055·5.

Similarly, a wort of 1057 specific gravity, which is the standard strength of beer wort on which the duty of 6s. 3d. per barrel is levied, has a saccharometer-gravity of 20·52 pounds per barrel; for

$$1057 - 1000 = 57; \text{ and } 57 \times {\cdot}36 = 20{\cdot}52.$$

It is assumed by the Excise that 1 quarter of malt will yield to water sufficient saccharine matter to produce 4 barrels (144 gallons) of standard wort of 1057 specific gravity. It is also assumed that 336 pounds of any description of corn, or 216 pounds of sugar, are the equivalent of 1 quarter of malt (of an average weight of 336 lbs.) and hence are also capable of producing 4 barrels of wort of 1057 specific gravity.

* The basis of the formula here given and the history of the present Beaumé scale are derived from an interesting paper by G. W. Wigner. (*Analyst*, v. 138). The indications of Beaumé's hydrometer for liquids lighter than water may be calculated into degrees of specific gravity by the formula $\frac{140{,}000}{130 + \text{deg. B.}}$ = sp. gravity.

Determination of the Original Gravity of Beer Worts.—As the duty on beer (as was formerly that on malt) is calculated from the strength of the wort as indicated by its specific gravity, it becomes necessary to allow a rebate or drawback when the beer is exported. If the wort could always be examined in an unfermented state, it would merely be necessary to ascertain its density and gauge its measure to obtain the data for calculating the allowance to be made. But, by the process of fermentation, the specific gravity of the wort is diminished to an extent dependent on the amount of alcohol formed. The weight of alcohol produced being approximately 50 per cent. of the saccharine matter destroyed by the fermentation, it is evident that a determination of the alcohol in the fermented liquid would give the means of ascertaining the quantity of sugar destroyed, and hence of making the necessary correction for the reduction in the density of the wort (technically called its "attenuation") caused by the fermentation.

The practical details of the methods of determining the original gravities of beer-worts have been very carefully investigated by Messrs Graham, Hofmann, and Redwood,* and their results show that the desired information can be obtained with great accuracy in the following manner:—

1. Distillation method. A known measure of the beer (4 fluid ounces, or 100 c.c.) is distilled without addition of soda or tannin in an apparatus furnished with a good condensing arrangement, as described on page 94, Vol. I. When about half the liquid has passed over, the distillate is diluted with water till it occupies, at 60° F., the exact original bulk of beer taken, when its specific gravity is carefully observed. The difference between 1000 and the gravity of the distillate is called the "spirit indication" of the beer. Reference is next made to the following table, from which is ascertained the number of "degrees of gravity lost" by the attenuation of the wort.

The figures in the table are identical with those in Schedule I. of the Inland Revenue Act, 1880, and were deduced from actual experiments on malt-worts fermented

* *Report on Original Gravities*, 1852.

under normal conditions, in the manner detailed in Graham, Hofmann, and Redwood's Report.

Degrees of Spirit Indication.	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
0	...	·3	·6	·9	1·2	1·5	1·8	2·1	2·4	2·7
1	3·0	3·3	3·7	4·1	4·4	4·8	5·1	5·5	5·9	6·2
2	6·6	7·0	7·4	7·8	8·2	8·6	9·0	9·4	9·8	10·2
3	10·7	11·1	11·5	12·0	12·4	12·9	13·3	13·8	14·2	14·7
4	15·1	15·5	16·0	16·4	16·8	17·3	17·7	18·2	18·6	19·1
5	19·5	19·9	20·4	20·9	21·3	21·8	22·2	22·7	23·1	23·6
6	24·1	24·6	25·0	25·5	26·0	26·4	26·9	27·4	27·8	28·3
7	28·8	29·2	29·7	30·2	30·7	31·2	31·7	32·2	32·7	33·2
8	33·7	34·3	34·8	35·4	35·9	36·5	37·0	37·5	38·0	38·6
9	39·1	39·7	40·2	40·7	41·2	41·7	42·2	42·7	43·2	43·7
10	44·2	44·7	45·1	45·6	46·0	46·5	47·0	47·5	48·0	48·5
11	49·0	49·6	50·1	50·6	51·2	51·7	52·2	52·7	53·3	53·8
12	54·3	54·9	55·4	55·9	56·4	56·9	57·4	57·9	58·4	58·9
13	59·4	60·0	60·5	61·1	61·6	62·2	62·7	63·3	63·8	64·3
14	64·8	65·4	65·9	66·5	67·1	67·6	68·2	68·7	69·3	69·9
15	70·5	71·1	71·7	72·3	72·9	73·5	74·1	74·4	75·3	75·9

These conditions included the formation of one part of acetic acid ($C_2H_4O_2$)* in 1000 measures of the beer, and hence no correction is necessary in the case of beers containing about this proportion, but the free acid in old and hard beer is often very sensibly in excess of the above-named amount, and in such cases its percentage must be determined by titrating the beer with standard alkali.† Any excess of acetic acid thus found, above the 0·1 per cent. normally present, must be calculated into alcohol and duly allowed for. This is most readily done by the following equation, in which a represents the percentage of acetic acid (or more strictly speaking, the grammes of free acid reckoned as acetic per 100 c.c. of the beer).

$$1{\cdot}3a - {\cdot}14 = \text{spirit-indication.}$$

* As a matter of fact, the normal acidity of beer is due more to succinic and lactic acids than to acetic acid.

† This may be effected as described on pages 189 and 190 Vol. I.; or the standard solution of caustic soda may be replaced by standard ammonia. This is made by diluting ordinary solution of ammonia with distilled water till it has a density of ·9986 at 60° F. 100 c.c. of such a solution will exactly neutralise 1 gramme of acetic acid ($C_2H_4O_2$) or 1·050 grammes of crystallised oxalic acid, and hence 100 fluid grains are equivalent to 1 grain. If 100 c.c. of beer be employed for the titration each 1 c.c. of ammonia employed represents 0·01 per cent of free acid.

The value 1·3*a* gives the spirit-indication corresponding to the whole free acid present, and hence from that has to be subtracted ·14, the spirit-indication of the natural ·1 per cent. of free acid. Thus, if a beer be found to contain ·48 of free acid calculated as acetic, then the correction of the spirit-indication will be—

$$1{\cdot}3(\cdot48) - \cdot14 = \cdot484.$$

Hence the figure ·484 (or practically ·48) will require to be added to the "spirit-indication" ascertained from the gravity of the distillate of the beer. Except in the case of decidedly sour beers, such as would be very unlikely to be exported, the correction for excess of acetic acid is generally so trifling that it may be neglected.*

It remains to dilute the "extract," or liquid left in the retort, with water, till it measures exactly the original bulk of the beer taken, when its specific gravity is to be carefully taken. This is called the "extract-gravity."

The original gravity of the wort is then ascertained by adding the degrees of gravity lost to the density of the extract. The mode of calculation will be seen from the following example:—

Specific gravity of water at 60° F.	1000·0
Specific gravity of distillate at 60° F.	989·0
Difference="spirit indication"	11·0
Allowance for alcohol corresponding to ·20 per cent. *excess* of acid	·26
Corrected spirit indication	11·26
Equal, by table, to "gravity lost"	50·4
To which add sp. gravity of "extract"	1041·3
"Original gravity" of wort	1091·7

* The directions in the Inland Revenue Act of 1880 for ascertaining the original gravity of worts in which fermentation has commenced are as follows. It will be observed that the question of acidity is wholly ignored, as the process is intended to be employed for the examination of recently-fermented worts:—

"1. A sample is to be taken from any part of such worts, and a definite

The table already given (page 302) is the only one legalised for the determination of original gravities, and is used by the Excise without correction whether the wort be derived wholly or partly from starch- or cane sugar, or simply from malt. This practice gives the brewer the advantage of any error. But for private purposes it is well to bear in mind that while the table is accurate when applied to beers brewed wholly or partly from starch-sugar instead of malt, it is deficient in accuracy when used for beer brewed from cane sugar, unless a deduction of ·35° be made from the spirit indication before referring to the table. With this correction, necessitated by the increase in density undergone by cane sugar solutions on inversion, the table already given furnishes accurate results.

2. Evaporation method. In employing this process, the specific gravity of the original beer is first carefully ascertained, taking care to agitate the liquid well to eliminate as much carbonic acid as possible. The "extract gravity" is next determined. For this purpose there is no occasion to boil the sample in a closed vessel, as it is not required to collect the volatilised spirit. It is simply necessary to evaporate sufficiently to ensure the entire expulsion of the alcohol, and then allow the liquid to cool, and make it up exactly to the original bulk of the beer taken. The density is then observed, and the corresponding "spirit-indication" ascertained by subtracting the density of the original beer from that of the "extract." The necessary allowance, if any, for excess of acid above 0·1 per cent. must next be made as in the distillation method, and from the corrected spirit indication the corresponding number of degrees of gravity lost is ascer-

quantity thereof by measure at the temperature of 60° Fahrenheit shall be distilled:

"2. The distillate and residue shall each be made up with distilled water to the original measure of the quantity before distillation, and the gravity of each shall be ascertained:

"3. The number of degrees by which the gravity of the distillate is less than the gravity of distilled water shall be deemed the spirit-indication of the distillate:

"4. The degrees of original gravity standing opposite to such spirit-indication in the table in the first schedule to this Act added to the specific gravity of the residue shall be deemed the original gravity of the worts."

tained by reference to the table already given. The result thus obtained is not in strict accordance with that by the distillation method, and requires to be corrected by an addition of $\frac{1}{40}$ to the "degrees of gravity lost" as ascertained by the table. Thus, if the corrected spirit indication be 9·4, corresponding to 41·2 degrees of gravity lost, the last figure requires a correction of $\frac{41{\cdot}2}{40} = 1{\cdot}03$, which, added to 41·2, raises it to the corrected number, 42·03 degrees. The following example illustrates the whole mode of calculation:—

Specific gravity of "extract" . .	1044·7
Specific gravity of original beer . .	1035·2
Difference="spirit-indication" .	9·5
Allowance for excess of acidity . .	0·1
Corrected spirit-indication .	9·6
Corresponding "gravity lost" (by table)	42·2
Correction of $\frac{1}{40}$ of above number .	1·055
Corrected gravity lost . .	43·25
Specific gravity of extract . . .	1044·7
Original gravity of wort . .	1087·95

The results by the evaporation process are not generally so reliable or so constant on repetition as those by the distillation method, but they are obtained with great facility, the only additional operation necessary being the determination of the density of the original beer, and hence the calculation should never be omitted, as it furnishes a valuable check on the distillation process. If the wort is a solution of cane sugar, a deduction of ·35 should be made from the spirit-indication, as described on the last page.

Other methods of determining the original density of beer-worts have been devised by Balling and others, but practically the processes already described are amply sufficient for the purpose.

CANE SUGAR.

Sucrose. Saccharose. Saccharon. Cannose. Diglucosic Alcohol. $C_{12}H_{22}O_{11}$.

French—Sucre de Canne. *German*—Zucker.

Cane sugar is found ready-formed in many grasses, in the sap of several forest trees, in the root of the beet and the mallow, and in several other plants. Most sweet fruits contain saccharose together with invert sugar, but some contain only the former. The nectar of flowers contains both cannose and invert sugar, but the presence of cane sugar in honey is somewhat doubtful (see page 350).

The sugar of commerce is principally obtained from the sugar cane (*Saccharum officinarum*), but almost equally large quantities are manufactured on the Continent from the white beet (*Beta maritima*), smaller amounts being also obtained from the palm and sugar maple, which last yields about 5 per cent. of its weight. Sugar cane contains from 12 to 20 per cent. of sucrose, and the white beet from 7 to 11, or occasionally 14 per cent.*

* The following analyses show the general composition of the sugar cane :—

Locality and Kind of Cane.	Water.	Sugar.	Woody Fibre.	Salts.	Authority.
Martinique . .	72·1	18·0	9·9		Peligot.
Guadaloupe . .	72·0	17·8	9·8	0·4	Dupuy.
Havana . . .	77·0	12·0	11·0	...	Casaseca.
Cuba . . .	65·9	17·7	16·4	...	Casaseca.
Mauritius . . .	69·0	20·0	10·0	1·0	Icery.
Ribbon cane . .	76·73	13·39	9·07	·39	Avequin.
Tahiti . . .	76·08	14·28	8·87	·35	Avequin.

The following is a more detailed analysis by Payen of Otaheite cane at maturity :—

Water	71·04	per cent.
Sugar	18·00	,,
Cellulose, ligneous matter, pectin, and pectic acid .	9·56	,,
Albuminous matters	0·55	,,
Cerosin ; red, green and yellow colouring matters ; fatty matter; resins ; essential oil ; aromatic matter ; and a deliquescent substance . . .	0·37	,,
Insoluble salts, 0·12 ; soluble, 0·16, consisting of phosphates, sulphates, chlorides, oxalates, acetates, malates, &c.	0·28	,,
	100·00	,,

Cane-juice has usually a density of 1070 to 1090, but has been met with as low as 1046 and as high as 1110. It is an opaque, frothy, yellowish green liquid. On filtration it yields a pale yellow fluid, which is nearly pure syrup, the greenish scum containing chlorophyll, a peculiar wax called cerosin, albuminous matters, fibre, and a considerable proportion of

The following is an analysis by Payen of the white or sugar beet :—

Water	82·7 per cent.
Sugar	11·3 ,,
Cellulose	0·8 ,,
Albuminous matters	1·5 ,,
Fatty matter	0·1 ,,
Pectin matters, asparagine, aspartic acid, betain ($C_{15}H_{33}N_3O_6$), &c. ; oxalates, nitrates, phosphates &c.	3·7 ,,
	100·0 ,,

According to Casaseca, the lower portions of the sugar cane are the richest in sugar, the centre being of about the average composition. This is shown by the following analysis by Gill of carefully sampled good average cane from the Aska district, Madras :—

	A. Two feet top.	B. Two feet middle.	C. Two feet root.
Megass proper.	7·63 per cent.	8·47 per cent.	8·30 per cent.
Juice	92·37 ,,	91·58 ,,	91·70 ,,
Containing, Cane Sugar	10·63%	13·31%	13·37%
,, Glucose	2·64%	1·51%	1·54%

The expressed juice had the following composition :—

	A.	B.	C.
Cane Sugar	11·51	14·55	14·58
Glucose	2·86	1·65	1·68
Ash	·33	·28	·25
Unknown	·50	·92	·49
Apparent solids	15·20	17·40	17·00
Water	84·80	82·60	83·00
	100·00	100·00	100·00

The megass referred to above contains little but woody fibre, as the sugar is extracted in the Aska district by the diffusion process. Ordinary megass or mill-trash after passing the rollers retains 8 or 10 per cent. of sugar and 50 per cent. of water.

The ash of the sugar cane contains about 50 of silica, 5 to 8 of phosphoric acid, and very variable proportions of potash. Soda appears to be a constant constituent.

ash. The pure or nearly colourless juice, from which the green matter has been separated, contains :—

Water.	Sugar.	Organic Matter precipitated by lead salts.	Salts.	Total.
81·00	18·20	0·45	0·35	100·00

The juice of the white beet contains a much larger proportion of foreign matters in proportion to the sugar, a fact which renders the manufacture of sugar from beet-root much more troublesome than from cane.*

Cane sugar forms large transparent colourless crystals, having the form of a monoclinic prism; they have a specific gravity of about 1·6, and are unchangeable in the air.

Cane sugar possesses a powerful rotatory action on a ray of polarised light; the apparent rotatory power in 10 per cent. solutions being + 66·5° for the D line, and + 73·8° for the transition-tint. The optical properties of cane sugar are fully described in the section on the "Relations of the Sugars to Polarised Light" (see page 264).

At a temperature of about 160° C. (320° F.) cane sugar melts, and on cooling forms a transparent amber-coloured solid known as barley sugar. This modification gradually loses its transparency from spontaneous crystallisation, but the change may be retarded, though not altogether prevented, by the addition of a small proportion of vinegar to the melted sugar.†

* The process of manufacturing sugar from the cane is shortly as follows :— The cane is crushed between rollers and the expressed juice allowed to flow into a large vessel in which it is heated nearly to its boiling point. Lime is then added, when a coagulum is formed which consists chiefly of earthy phosphates, a peculiar albuminous principle, and mechanical impurities. The clear liquid is rapidly evaporated, and, when sufficiently concentrated, transferred to a shallow vessel to crystallise. The crystals are drained from the dark-coloured syrup known as molasses or treacle, and form the raw or muscovado sugar of commerce. From this intermediate product refined sugar is obtained by redissolving the crystals in hot water, clarifying by filtration through animal charcoal, evaporating under reduced pressure, crystallising, &c. Loaf-sugar, white-crystals, and sugar-candy are all practically pure sucrose.

† Barley sugar appears to be a definite allotropic modification of cane sugar, comparable to viscous sulphur.

When heated a little above 160° C. cane sugar is converted without loss of weight into a mixture of dextrose and lævulosan. $C_{12}H_{22}O_{11} = C_6H_{12}O_6 + C_6H_{10}O_5$.* At a higher temperature water is given off, the dextrose being probably converted into glucosan, $C_6H_{10}O_5$, and at about 210° more water is lost and a brown substance called caramel is produced, to which the formula $C_{12}H_{18}O_9$ has been attributed, but which probably consists of a mixture of several compounds, all resulting from the "cumulative resolution" of the sugar. At a higher temperature inflammable gases are evolved, the decomposition being attended with a highly characteristic smell.

Cane sugar is soluble in about one-third of its weight of cold water, forming a very sweet, viscid liquid known as syrup. In boiling water it is soluble in all proportions.† An aqueous solution of sugar on being subjected to prolonged ebullition acquires an acid reaction, usually becoming less viscid and losing irrecoverably its power of crystallisation. The liquid then contains invert sugar (see page 311).

Cane sugar is almost insoluble in absolute alcohol, but dissolves in rectified spirits of wine with moderate facility, and readily in weaker alcoholic liquids.

Sucrose is insoluble in ether, chloroform, carbon disulphide, petroleum spirit, or oil of turpentine, but dissolves in glycerin, and all aqueous liquids.

The reaction of dilute acids on cane sugar results in the formation of a mixture of glucoses called invert sugar (see page 311).

Strong sulphuric acid acts violently on cane sugar, charring it, and causing abundant evolution of gas.

Nitric acid acts upon cane sugar in a manner dependent on its concentration and other conditions. With one part of sugar and three of nitric acid of 1·25 to 1·30 sp. gravity, the product formed at 50° C. is wholly saccharic acid,

* On dissolving the product in water and fermenting the solution with yeast, the dextrose is destroyed and the lævulosan may be obtained by evaporating the liquid as an uncrystallisable syrup, which appears to become converted into lævulose on boiling with water or dilute acids.

† For information respecting the density of aqueous solutions of cane sugar (see page 295, *et seq.*).

$C_6H_{10}O_8$, but at a boiling heat oxalic acid, $C_2H_2O_4$, is the chief product. If stronger nitric acid be employed, these bodies undergo further oxidation with formation of carbonic acid. Cold fuming nitric acid converts cane sugar into nitrosaccharose, which probably contains $C_{12}H_{18}(NO_2)_4O_{11}$.

When cane sugar is rubbed in a mortar with caustic potash or soda it undergoes no visible change, a property which distinguishes it from the glucoses. Similarly, the solution of cane sugar undergoes no immediate change when mixed with alkali and raised to the boiling point. The rotatory power of the alkaline liquid is temporarily diminished, but is restored to its original amount on neutralising the solution by an acid.

According to Wanklyn, when boiled with a strongly alkaline solution of potassium permanganate, cane sugar is oxidised in a very definite manner with formation of oxalic and carbonic acids, the reaction being—

$$C_{12}H_{22}O_{11}+O_{20}=4C_2H_2O_4+7H_2O+4CO_2.$$

Cane sugar does not immediately reduce Fehling's solution at a boiling temperature, but on prolonged ebullition precipitation of cuprous oxide gradually occurs.

Cane sugar possesses considerable solvent powers for certain metallic oxides, with which it forms compounds called sucrates. Thus, lime, magnesia and litharge dissolve with some facility in syrup, but are completely reprecipitated by passing a current of carbonic acid gas through the liquid. On mixing syrup with a concentrated solution of baryta, a crystalline precipitate is obtained, having the composition $C_{12}H_{22}BaO_{12}=BaO,C_{12}H_{22}O_{11}$, or $C_{12}H_{21}(Ba.OH)O_{11}$. This compound may be re-crystallised from boiling water, separating in brilliant scales resembling boric acid. Its sparing solubility in cold water has been utilised in the treatment of saccharine juices, pure cane sugar being readily obtainable by decomposing the barium sucrate by sulphuric acid.

Cane sugar resembles tartaric and citric acids in its power of preventing the precipitation of ferric and cupric oxides by alkalies (see page 283).

With sodium chloride cane sugar forms a crystallisable

compound of the formula $C_{12}H_{22}O_{11}+NaCl+2H_2O$. A solution of this body has a less powerful rotatory action on polarised light than corresponds to the sugar contained in it, whilst the optical power of a solution of the compound $2C_{12}H_{22}O_{11}+3NaI+3H_2O$ is directly proportional to that of the contained sugar.

Inversion of Cane Sugar. Invert Sugar.—When an aqueous solution of cane sugar is boiled for a long time it gradually becomes less viscid, acquires an acid reaction, and loses irrecoverably its power of crystallisation. This change in properties is attended by the assimilation of the elements of water, with formation of the mixture of sucro-dextrose and sucro-lævulose known as inverted or invert sugar. $C_{12}H_{22}O_{11}+H_2O=2C_6H_{12}O_6$.* The inversion of cane sugar is accompanied by an increase in the density of the solution.† Inversion is effected much more readily in the presence of a small quantity of free acid, the rate of change depending mainly on the proportion of acid used, its chemical activity, and the temperature employed in the operation. Thus, dilute sulphuric and hydrochloric acids effect the inversion of cane sugar at the ordinary temperature after some time, and the change is almost instantaneous at a temperature of 65 to 70° C. On the other hand, acetic, tartaric, citric, and sulphurous acids act very slowly at ordinary temperatures. Concentrated solutions of sugar are completely inverted with considerable difficulty.

The inversion of cane sugar is often an important step in the analysis of saccharine liquids. The best means of effecting it is described in detail on page 283.

By the prolonged action of dilute acids on sugar the hydrolysis goes a step further, with formation of an unfermentable body of the formula $C_6H_{14}O_7$.

Fermentation of Sugar.—Cane sugar is not *directly*

* Cane sugar is inverted on a commercial scale for brewers' purposes. The product, sometimes mixed with cane or starch sugar, is known as "invert sugar," "saccharum," "malt saccharum," &c. It may be analysed in the same manner as honey (see page 351).

† The property of inversion by yeast or dilute acids is not limited to cane sugar, but appears to be common to all the saccharoses. In some cases two dissimilar glucoses result, in others apparently only one.

fermentable, but, when its aqueous solution is mixed with yeast or an infusion of malt, and exposed to a temperature of about 30° C., the sucrose is changed to invert sugar,* the density of the liquid increases, and the inverted sugar subsequently ferments, with production of alcohol and carbon dioxide, according to the following equations:—

$$\underset{\text{Cane Sugar.}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Invert Sugar.}}{2C_6H_{12}O_6}; \text{ and}$$

$$C_6H_{12}O_6 = \underset{\text{Alcohol.}}{2C_2H_6O_2} + \underset{\text{Carbon Dioxide.}}{2CO_2}.$$

These, however, are not the sole products. Traces of the higher homologues of ethylic alcohol are probably always produced, and Pasteur has shown that glycerol (glycerin), $C_3H_8O_3$, and succinic acid are constant products of the vinous fermentation.† The proportion of succinic acid formed varies from 0·6 to 0·9 per cent. of the weight of the cane sugar fermented, and the glycerin from 3·2 to 3·7 per cent. Thus, 100 grammes of sugar-candy, fermented with 1·198 grammes of dry yeast, gave 0·673 grammes of succinic acid and 3·64 grammes of glycerin, or a total of 4·13 grammes. In consequence of the constant formation of these, and traces of other products, the proportion of alcohol produced is not 54·97 per cent. of the weight of the cane sugar taken, as would be the case if the above formula were rigidly correct, but only 51 per cent., or 51½ per cent. at the outside.

The action of yeast cells (*Torula cerevisiæ*) on sugar is prevented by too great concentration of the solution, whether due to alkaline chlorides, gelatin, glycerin, or sugar itself. The presence of strong mineral acids, even in small proportion, prevents or retards the vinous fermentation, phosphoric acid alone acting favourably. Fermentation is also prevented by very small quantities of carbolic, salicylic, and sulphurous acids, or other antiseptics.

* If the proportion of yeast is very small, the change never goes beyond the formation of invert sugar.

† However good in quality white sugar made from beet-root may be, on fermentation it always produces an alcoholic liquid having a disagreeable taste. Hence the white sugar used in the manufacture of champagne ought always to be prepared from the cane.

When a solution of cane sugar is mixed with fresh sour cheese, or with milk and chalk, and the liquid is exposed to a temperature of 25 to 30° C. for some weeks, with frequent agitation, the sugar is converted into lactic acid, $C_3H_6O_3$, and ultimately into butyric acid, $C_4H_8O_2$, with evolution of hydrogen and carbon dioxide. A similar abnormal or lactous fermentation is apt to occur in the manufacture of beer, if the yeast used contains an undue proportion of the lactous ferment, *Penicillium glaucum*. Similarly the beer is apt to develop acetic acid in presence of excess of *Mycoderma aceti*.

Under certain conditions cane sugar is apt to undergo the mucous fermentation, by which it is converted into mannite, $C_6H_{14}O_6$, gum, $C_6H_{10}O_5$, and carbonic acid, the average production being about 51 per cent. of mannite and 45½ per cent. of gum. Beet-root juice and certain white wines are especially apt to undergo the mucous fermentation.

Detection of Cane Sugar.—Cane sugar is detected more readily by its physical properties than by its chemical reactions. The following are the leading characters of service in the recognition of cane sugar:—

1. The sweet taste of the substance or solution.
2. The dextro-rotatory action of the solution on polarised light (see page 277).
3. The form of the crystals (see page 308).
4. The characteristic odour produced on heating the solid substance (see page 309).
5. The production of saccharic and oxalic acids by the action of moderately concentrated nitric acid.
6. The formation of alcohol by the prolonged action of yeast on the warm solution.
7. The increase in the reducing power of the liquid on Fehling's test after inversion of the sugar by treatment with dilute acid (page 286), and the change in the rotatory power of the solution by inversion (see page 280).

For information respecting the distinctive tests for cane sugar, milk sugar, and glucose, see page 343.

The greater number of the foregoing properties and reac-

tions of cane sugar receive more precise recognition in the following section on the

Determination of Cane Sugar.—Cane sugar may be determined by a variety of methods, which may be conveniently classified according to the principles on which they are based.

1. DETERMINATION OF SUGAR BY THE DENSITY OF THE SOLUTION.

For the employment of this method it is, of course, essential that the solvent should be water and that sensible quantities of foreign matters should be absent; if volatile, like alcohol, they may be removed by distillation. The method is constantly applied in sugar-works, not so much for ascertaining the amount of sugar in the juice as to obtain an estimate of the foreign matters associated with it; the actual sugar being really determined by other methods, and a corresponding deduction made from the percentage of "apparent sugar" present.* On page 295, *et seq.*, full directions are given for deducing the contents of cane sugar contained in aqueous saccharine solutions of various densities.

The percentage of sugar by weight having been ascertained, the number of pounds of sugar per gallon of the syrup may be found by multiplying the specific gravity by one-tenth of the percentage by weight.

2. DETERMINATION OF CANE SUGAR BY WEIGHING AS SUCH.

This method is employed in Payen's and Scheibler's methods of sugar-assaying (see page 320), and in a few other cases.

3. DETERMINATION OF SUGAR BY FERMENTATION.

In this case the saccharine liquid is treated with an amount of yeast equal to about 3 per cent. of the weight of sugar supposed to be present, and kept at a temperature of about 30° C. (=86° F.) for sixteen to twenty-four hours, care being taken that alcohol is not lost by evaporation. The liquid is then distilled, and the alcohol in the distillate estimated as described in Vol. I. page 94. If necessary, the liquid must be rendered neutral, or faintly acid, before fermentation. 51 parts by weight of alcohol produced represent 100 parts of cane sugar. This method of determining sugar is occasion-

* See also page 319.

ally of considerable value, though the results are only approximate.

4. DETERMINATION OF SACCHAROSE BY ITS REDUCING ACTION.

For this purpose the sugar is inverted by heating it with hydrochloric acid (page 283), the solution neutralised, and the resultant glucose determined by one of the processes described in the section on the reducing action of sugars (see page 283).

For every 100 parts of glucose found, 95 parts of cane sugar must be reckoned.

5. DETERMINATION OF SACCHAROSE BY THE POLARIMETER.

This method of determination has been fully described in the section on the "Relations of the Sugars to Polarised Light" (see page 275).

Assay of Commercial and Raw Sugar (Saccharose).—Commercial saccharose is rarely met with in a state of perfect purity, unless very extreme care has been employed in its manufacture. Though but seldom intentionally adulterated, the crude product is liable to such excessive natural variations of quality that its commercial assay is often of considerable importance.

The following analyses, chiefly by Dr Wallace, clearly show the composition of commercial sugar from several sources and in various conditions of purity:—

	Cane Sugar.	Glucose.	Extractive Matters.	Insoluble Matter.	Ash.	Water.
West India . .	94·4	2·2	0·3	0·1	0·2	2·8
Beet-sugar . .	95·7	0·3	0·4	...	1·6	2·0
Beet-sugar*. .	89·15	...	3·96	...	2·63	4·26
Date-sugar . .	95·4	1·8	0·4	1·7	0·2	0·8
Lumps . .	97·3	0·5	..	...	0·2	2·0
Pieces . .	87·7	6·0	0·5	...	0·8	5·0
Bastards . .	68·3	15·0	1·2	...	1·5	14·0
Green syrup .	62·7	8·0	0·6	...	1·0	27·7
Golden syrup .	39·6	33·0	2·8	...	2·5	22·7
Molasses . .	48·0	18·0	1·5	...	1·4	31·1
Treacle . .	32·5	37·2	3·5	...	3·5	23·4
Beetroot molasses*	50·9	1·1	16·1	...	12·9	19·0

* This analysis is by Haughton Gill.

The following are analyses by Hassall of raw and refined sugars (Finzel's crystals):—

	Cane Sugar.	Glucose.	Insoluble Matter.	Ash.*	Water.
Raw Sugar . . .	89·22	3·69	0·12	1·13	5·84
Refined Sugar . . .	99·90	None	None	·02	·08
Refined Sugar . . .	99·86	None	None	·01	·13

The foregoing analyses clearly show what are the chief items to be considered in the assay of commercial and raw

* The following analyses are illustrative of the composition of the ash of sugar:—

	No. 1. Cane.	No. 2. Cane, Sulphated.	No. 3. Beet, Sulphated.
Potash	29·10	28·79	34·19
Soda	1·94	0·87	11·12
Lime	15·10	8·83	3·60
Magnesia	3·76	2·73	0·16
Ferric Oxide	0·56	6·90	0·28
Alumina	0·65		
Silica	12·38	8·29	1·78
Phosphoric Acid . . .	5·59	...	...
Sulphuric Acid	23·75	43·65	48·85
Carbonic Acid	4·06	...	...
Chlorine	4·15	...	...
	101·03	100·06	99·96
Less, Oxygen equivalent to Chlorine . . .	·93		
	100·10		

No. 1 is the ash of cane sugar from Demerara, the original sample yielding 1·38 per cent. of ash. The analyst is Dr Wallace. Nos. 2 and 3 are by J. W. Macdonald, and represent the composition of the sulphated ash (see page 317) produced in the analysis of many samples of cane and beet sugar. Hence they may be taken as fairly representing the average composition of the ash, at least so far as the bases are concerned, for any carbonates and chlorides were converted into sulphates by the action of the sulphuric acid employed in the incineration, and phosphoric acid was not tested for. But I have recently received samples of sulphated ash through Mr Macdonald, and find 2·90 per cent. of P_2O_5 in the cane sugar ash, and only 0·24 per cent. in the ash of beet sugar. In the treatment of beet juice it is usual to employ an excess of lime,

sugars. For the determination of the principal constituents the following are the most approved methods:—

WATER is estimated in granular cane sugars by exposing 5 grammes of the sample in a thin layer to a temperature of 60° C., weighing every hour until there is no further loss. Twelve hours are frequently required for complete dessication. Beet sugars and good cane sugars may be dried at 100° C., two hours being sufficient. Sugars containing much glucose generally give too high a moisture if dried at 100° C., owing to a partial conversion of the glucose into glucosan and caramel.

The estimation of water in treacle, beet and cane juice, &c., is tedious, owing to the low temperature which must be employed, and to the formation of a skin on the surface of the liquid. To avoid this, 5 grammes (or a known weight) of the sample should be dissolved in water, and the solution made up to 100 c.c. 10 c.c. of this solution (=·5 gramme of the original sample) are poured over about 12 or 15 grammes of previously ignited silver-sand contained in a flat dish. The whole is dried at a temperature not exceeding 60° C. until constant, the increase in weight being due to the dry sugar in ·5 gramme of the sample. By conducting the dessication in a partial vacuum,* from which the moisture is removed by sulphuric acid or chloride of calcium, the operation may be finished in a few hours.

ASH. If not already wet or viscous, moisten the sample all over with the least possible quantity of water, and then with a little pure and concentrated sulphuric acid. Heat the whole gently till the frothing ceases and the mass forms a dry cinder. Ignite the charred mass in a muffle at a very low red heat, moistening the residue again with sulphuric acid, when the ignition approaches completion. Continue the ignition at

which is afterwards removed by carbonic acid. Hence the phosphates of the juice would be precipitated almost entirely at an early stage of the manufacture. The proportion of phosphoric acid in the ash of a sugar might perhaps furnish an indirect indication whether the article was manufactured from cane or from beet. Raw beet sugar, however, is readily distinguished from that derived from the cane by the appearance, flavour, and the small proportion of glucose, owing to the destruction of the greater part by the employment of a large excess of lime.

* Laugier dries the sample at 50° C. in a current of purified hydrogen or coal-gas.

a low temperature till the carbon is wholly consumed, then heat to bright redness for ten minutes, and weigh when cold. From the residue thus obtained deduct one-tenth of its weight, when the remainder will be the actual ash of the sample.* If sand be present in sensible quantity, it must be estimated by dissolving the ash in hydrochloric acid and weighing the insoluble residue. This must be deducted from the total ash before making the correction of one-tenth.

ALBUMINOID MATTERS are easily determined directly. When requisite their amount may be estimated by burning a known weight of the sugar with soda-lime. The percentage of nitrogen found, multiplied by 6·33, gives the percentage of albuminoid matters.

"Albuminoid and extractive matters" are usually estimated indirectly by subtracting the sum of the percentages of all other constituents from 100·00.

GLUCOSE may be estimated by Fehling's, Pavy's, Knapp's or Sachsse's method (see page 283, *et seq.*). Fehling's solution applied gravimetrically gives very satisfactory results, but requires a somewhat longer time than some of the volumetric methods. These latter, on the other hand, require that the solution should be tolerably free from colour.

VALUATION OF SUGAR from the results of analysis. In valuing crude sugars it is usual to assume that every unit of ash prevents five units of cane sugar from crystallising, and that each unit of glucose prevents the crystallisation of an equal weight of cane-sugar. Hence a deduction equal to the percentage of glucose found, *plus* five times the percentage of ash, must be made from the content of cane-sugar found by analysis, in order to obtain the percentage of crystallisable sugar in the sample.† This per-

* If sulphuric acid be not used, complete incineration is very difficult; the ash obtained is very fusible, or light and easily blown away; and, as it consists largely of potassium carbonate, it is very deliquescent, and hence difficult to weigh accurately. The correction of one-tenth for the increase in weight caused by the conversion of the carbonates into sulphates is not strictly accurate, but is a trade-practice very generally adopted. For the composition of the sulphated ash see page 316.

† An amended allowance has been recently proposed. *Twice* the glucose, *plus* four times the ash, is deducted from the cane sugar found.

centage of crystallisable sugar is called the "refining value" of the sample. The results of the above calculation are not always in strict accordance with the truth, though for beet-sugar the variations are not great. Schultz considers that the out-turn of refined beet-sugar is equal to the total sugar *minus* twice the amount of total soluble impurities.

A rapid approximate valuation of sugar may be obtained by making a perfectly saturated solution of the sample in water at 17·5° C., and ascertaining the density of the liquid. In the case of pure cane sugar this will not exceed 1·3300; but the specific gravity increases with the proportion of foreign substances. The following table is given by E. Anthon:*—

Specific gravity.	Percentage composition of solution saturated at 17·5° C.		
	Sugar.	Other substances.	Water.
1·3300	66·66	0·00	33·34
1·3322	64·85	2·66	32·49
1·3384	63·70	5·29	31·01
1·3446	62·65	7·76	29·68
1·3509	61·42	10·13	28·45
1·3572	60·28	12·48	27·24
1·3636	59·14	14·67	26·19
1·3700	58·00	16·82	25·18
1·3764	56·85	18·87	24·28
1·3829	55·70	20·77	23·53
1·3894	54·56	22·59	22·85
1·3959	53·42	24·36	22·22
1·4025	52·28	25·98	21·74
1·4092	51·14	27·56	21·30
1·4159	50·00	29·00	21·00

A very convenient and instructive method of assaying a juice or syrup is to determine the specific gravity, and thence deduce the quantity of total soluble solids, or "apparent sugar," assuming them all to have the same density in solution as cane sugar. The quantity of real sugar present is then determined by other means, and the difference gives the percentage of "solids not sugar." The percentage of real sugar contained in 100 parts of "apparent sugar" or "apparent solids" is called the "apparent purity co-effi-

* *Jahresb.* 1868, page 957.

cient" of the juice or syrup, and furnishes a very useful datum in practice.

DIRECT DETERMINATION OF CRYSTALLISED SUGAR. Instead of arriving at the proportion of crystallisable sugar in a sample by estimating the cane sugar present, and deducting from that amount weights equal respectively to the glucose and to five times the ash, Payen proposed to ascertain the amount of crystallised sugar actually contained in the sample, it being assumed that the sample would contain in a crystallised state all sugar capable of being crystallised in presence of the impurities, and that this quantity could be actually obtained in a purified condition. Payen's method has been much improved by Scheibler, who operates as follows:—

Three strengths of alcohol, having specific gravities respectively of ·8488 (No. 1), ·8265 (No. 2), and ·8118 (No. 3), are first carefully prepared, and No. 1 is mixed with 5 per cent. by measure of ordinary acetic acid. All three of these liquids are completely saturated with cane sugar by keeping them in bottles filled with lumps of the best white sugar free from powder. Twenty grammes of the sample are weighed out, and placed in a Mohr's burette having a plug of cotton—or glass-wool at the lower end. The orifice is provided with a compression clamp or glass tap, which is connected by india-rubber tubing with a flask, in which a partial vacuum can be obtained by a Bunsen pump or other means. A tube filled with pumice, moistened with sulphuric acid, is attached by a cork to the upper part of the burette, and a current of warm air drawn through the apparatus for some time to remove as much of the water as possible. (This part of the process may be omitted if the original sample be tolerably dry.) The drying-tube is next removed, and the burette filled with the sugar-saturated alcohol No. 1 (sp. gravity before saturation, ·8488). This is allowed to percolate slowly through the sugar till it runs into the flask colourless, or nearly so. The liquid is then just sucked out, and the residual sugar rinsed successively with No. 2, No. 3, and finally with absolute alcohol. The drying-tube is again attached, and warm air sucked through the apparatus till the sugar is thoroughly dried, when it is removed and weighed; or it may be washed out (without

being dried) with water, the solution made up to 100 c.c., clarified and polarised. It is very desirable to enclose the burette in a cylindrical lamp-glass or similar contrivance by which it can be surrounded with water, which can be kept at 60° C. during the preliminary and final dryings in a current of air, while by filling the cylinder with water at 60° F. (= 15·5° C.), a constant temperature is readily maintained during the treatment with alcohol. The results yielded by this process are very constant and reliable if care be taken to conduct the operation at the temperature at which the alcohols were saturated, and if the sugar be well air-dried before being washed. Although yielding good results with cane sugars and superior beet sugars, the results obtained with low beets (second and third runnings) are somewhat fallacious.* The method assumes that all the sugar in solution in the adhering molasses will pass into the final residue of molasses.

The foregoing method of assaying raw sugar has been recently criticised by Casamajor,† who, without seriously invalidating the results obtained by it, has suggested the following mode of estimating crystallised sugar:—"Methyl alcohol"—by which it is presumed the author of the process means commercial wood-spirit—of ·8533 sp. gravity at 60° F. (= 15·5° C.), is saturated with cane sugar in the same manner as Payen's solutions. By this treatment it increases to ·8710 sp. gravity. If not strictly of this density, it must be made so by appropriate addition of water or wood-spirit, allowing time for the difference in the amount of sugar to become precipitated or dissolved. 19·8 grammes of the sample are then triturated in a mortar with exactly 50 c.c. of the above solution; and when all lumps and crystals are broken up, and the action is supposed complete, the liquid is passed through a dry filter, and the density carefully taken by a hydrometer or specific gravity bottle. From the specific gravity thus

* The process has been recently investigated by Wichelhaus, Eissfeld, and Stammer, who, from numerous experiments on various kinds of raw sugar, found the method gave fairly constant and accurate results, the largest variation being 1½ per cent.—*Bied. Centr.* 1879, p. 542.

† *Chem. News*, xl. 74, 97, 107, 131.

found (reduced if necessary to 60° F.) the corresponding percentage of alcohol by volume is ascertained (see Vol. I. p. 90), and to this figure is added 22·9,* the sum of the two being the percentage of crystallised sugar in the sample. If the trituration of the sugar with the spirit has to be conducted at a temperature in excess of 15·5° C. (=60° F.), 0·1 grammes less of the sugar should be taken for every increase of 5° C. Thus, if the temperature of the laboratory be 25·5° C., the standard weight of the sample should be 19·8 grammes instead of 19·6.

ADULTERATIONS OF COMMERCIAL CANE SUGAR.—The gross impurities and intentional adulterations of raw cane sugar are sometimes very considerable. Thus the raw product may contain woody fibre from the crushed cane, often much gritty sand, sporules of fungus, colonies of *Acarus sacchari* or sugar-mite, and occasionally, when in bulk, stones, old iron, and other make-weights. Starch sugar is occasionally used as an adulterant of refined sugar (see next page).

Intentional additions of sand and earthy matters are occasionally made to raw sugars, but it is very doubtful if such a fraud has ever been actually practised by a retail dealer. Formerly, when coarse brown sugar was more frequently used than is now the case, the opportunity and inducements to adulterate were much greater than at present.

The presence of sand and earthy matters is of course indicated by an excessive proportion of ash, and the incomplete solubility of the sample in water.

Fungus spores are objectionable from the extreme rapidity with which, under suitable conditions, they develop into a spreading vegetable growth, especially in presence of nitrogenous matter. Such sugar is apt to undergo fermentation and turn sour, and preserves made with it soon spoil.

The *Acarus sacchari*, or sugar-mite, is a small animal closely resembling the itch-insect, and, like it, capable of burrowing under the skin and producing an irritating pustular

* This figure is the difference between 100·0 and the percentage of alcohol by volume corresponding to the specific gravity of the standard solution.

disease called the "grocer's itch," which frequently attacks those constantly employed in handling raw sugars.

The sugar acarus is possessed of great vitality, resisting the action of warm water for many hours. It is sometimes visible to the naked eye, and was found by Hassall in 69 out of 72 samples of brown sugar purchased at retail shops in London, while Dr Cameron estimated that as many as 100,000 acari were present in each pound of the sugar supplied to one of the Dublin workhouses. The acarus is wholly eliminated by the process of refining to which white and crystallised sugar are subjected. The sugar mite is best detected by dissolving the sample of sugar in warm water, when the insect will be found adhering to the sides of the glass, or at the surface or bottom of the liquid. By observing any suspected particles with a low microscopic power, the acarus may be readily identified.*

The addition of starch-glucose to cane sugar has often been mentioned, but the practice is certainly far from common.† It would never pay to introduce glucose into a solution of cane sugar, as the presence of, say 10 per cent., would prevent an equal weight of cane sugar from being obtained in a crystallised state, and hence the sophistication would result in a loss rather than a gain. The only way in which starch sugar can be used as an adulterant of cane sugar so as to yield a profit is to mix the two substances in a solid state. The intentional addition of small proportions of glucose would not pay for the trouble, and hence, in searching for starch sugar as an adulterant, the traces of glucose occasionally normally present in refined cane sugar may be safely neglected.

The detection and estimation of glucose in cane sugar may be readily effected by the use of Fehling's solution (see page 286, *et seq.*). The proportion may also be accurately ascertained by observing the rotatory power of the original solution and then that of the inverted liquid (see page 280). By this means the cane sugar is estimated, and the sum of this amount

* Hassall has published drawings of the sugar acarus and sporules of fungus found in raw sugar.—*Food and its Adulterations*, 1876, p. 240, *et seq.*

† A case of adulteration of cane sugar by starch sugar was recently described by Casamajor.—*Chem. News*, xli. 221.

and the water, subtracted from 100·0, gives the percentage of glucose in the sample.

If the sense of taste be first deadened by placing a pinch of pure powdered cane sugar on the tongue, and then, while the taste remains, a portion of the suspected sample be tested in the same way, the bitterish taste of starch sugar will be distinctly perceived if the specimen under examination be adulterated.*

The employment of Casamajor's alcohol method (see page 321) does not give an accurate estimation of starch sugar in admixture with sucrose, in consequence of the difficult solubility of dextrose in wood-spirit.

If the sample suspected to contain starch sugar be placed in a beaker and stirred for a few seconds with rather less than its own weight of cold water, any glucose will be seen floating in the liquid as white specks resembling crushed wheat.

A better plan is to prepare a saturated solution of dry starch sugar in "methylic alcohol" of ·935 sp. gravity.† The sample to be tested is thoroughly dried and then stirred for two minutes with the spirit saturated with starch sugar. The cane sugar dissolves, while any admixture of dextrose remains insoluble. The residue is separated by decanting the liquid, and washed first with more of the spirit, and then with strong methyl alcohol. The process is probably capable of yielding approximate quantitative results.‡

Molasses or Treacle.—The physical characters of this secondary product of the manufacture of cane sugar are well known.

The production of molasses is due to the long-continued heating of the saccharine juice, but the quality varies with the nature and culture of the sugar-yielding plant, and with many other circumstances. "Refiners' molasses," the syrup obtained in the refining of sugar, retains a considerable

* This test may also be employed for detecting the presence of chloride of tin and other impurities in molasses or sugars, even when the proportion is very minute.—Casamajor, *Chem. News*, xli. 222.

† 100 c.c. of such spirit will dissolve 57 grammes of starch sugar, yielding a solution of 1·25 sp. gravity.

‡ Casamajor, *Chem. News*, xliii. 326.

amount of sucrose, the proportion being about 35 per cent. in cane sugar molasses, and as much as 50 per cent. in that from beetroot. This is prevented from crystallising by the impurities present in the raw sugar (see page 318). The molasses from raw cane sugar contains also about 30 per cent. of invert sugar, from which beetroot molasses is comparatively free, but the latter contains raffinose, $C_6H_{14}O_7$, a peculiar non-rotating glucose, with aspartic acid* and various other bodies. The proportion of salts contained in beetroot molasses is usually 12 to 14 per cent., whereas refiners' treacle from raw cane sugar rarely contains half that proportion.†

Analyses of various kinds of molasses are given on page 315. Beetroot molasses contains most of the foreign substances, such as caramel, aspartic acid, and salts, that are contained in cane sugar molasses. According to Payen, beetroot molasses averages the following composition:—Sugar, 49·4; non-saccharine solids, 33·5; water, 17·1 per cent.

The commercial analysis and assay of molasses may be effected as described on page 315, *et seq.*

Rum is obtained by the fermentation of cane sugar molasses, with subsequent distillation.

Beetroot molasses is also subjected to fermentation and distillation. The residue of the distillation, termed vinasse, is remarkable for the bodies it yields on dry distillation. Besides the ordinary products obtained by the distillation

* Aspartic or asparaginic acid, $C_4H_7NO_4$, results from the action of dilute acids on asparagine, $C_4H_8N_2O_3$. Both asparagine and aspartic acid exert *lævo*-rotatory action in alkaline solutions and *dextro*-rotatory action in acid solutions.

Aspartic acid reduces Fehling's solution.

Vanillin has been recently recognised in beet sugar molasses.

† Messrs Duncan and Newlands have devised an ingenious process for treating molasses, with the result of recovering from it both cane sugar and potash. The molasses is treated with crude sulphate of alumina, which causes the precipitation of potash-alum in the form of fine crystals, which are removed and purified by re-crystallisation. In the saccharine liquid the excess of alumina is precipitated and the free acid neutralised by chalk or lime, the liquid boiled, filtered, and decolorised by animal charcoal in the usual way. The potash salts and other impurities having been thus got rid of, an abundant crop of cane-sugar crystals is obtained on concentrating the liquid.

of wood or coal, the ammoniacal liquor from the dry distillation of vinasse contains a notable proportion of trimethylamine $(CH_3)_3N$, together with some allied products.*

Sugar Confectionery.—The various forms of sweets now so extensively manufactured rarely require analytical examination except for the detection of poisonous colouring materials, and the use of these has greatly declined of late years.

Among the red colouring matters of sugar confectionery red lead and vermillion have been observed, but in the great majority of cases harmless lakes are used, or else a minute quantity of aniline red.

Chromate of lead is not unfrequently employed as a yellow colouring agent, but gamboge is the usual pigment. Greens have been found to be produced by a mixture of chromate of lead and prussian blue, and arsenite of copper and other cuprous pigments have also been met with.

The blue mineral colouring matters are usually harmless, consisting of prussian blue or ultramarine.

The detection of the injurious colouring matters in confectionery belongs to mineral analysis and requires no detailed description here.

The essences used for flavouring confectionery are now usually of artificial origin. Their nature is described in Vol. I. page 160.† There is no evidence that the use of artificial fruit-essences, in the minute proportion necessary, is in any way injurious.

MILK-SUGAR.

Lactose. Lacton. Lactin. $C_{12}H_{22}O_{11}$.

French—Sucre de Lait. *German*—Milchzucker.

This variety of sugar is met with only in the milk of the

* *Journ. Chem. Soc.* xxxvi. 912, and xxxviii. 159. See also an interesting lecture by H. E. Roscoe, on "A New Chemical Industry," *Chem. News.* vol. xxxix. p. 107.

† A valuable article on artificial fruit-essences, by J. H. Maisch, and of later date than the publication of Vol. I., will be found in *The American Journal of Pharmacy* for March 1879, and in the *Year Book of Pharmacy*, 1879, p. 270.

mammalia, herbivorous animals secreting a larger proportion than the carnivora. Lactose is the most constant constituent of milk, about 5 per cent. being present in human milk and 4 per cent. in the milk of most of the herbivora.

Milk-sugar is usually prepared by curdling the milk with rennet or dilute sulphuric acid, removing the coagulum and evaporating the whey to a thin syrup. The crystals, which gradually separate, are purified by crystallisation from hot water, re-solution, filtration through animal charcoal, and re-crystallisation.

Milk-sugar crystallises in hard, white, semi-transparent, hemihedral rhombic (or trimetric ?) prisms or saccharoid masses of the composition, $C_{12}H_{22}O_{11}+H_2O$.* The crystals are unaltered at 100°C., but are rendered anhydrous by heating to 130°C. The anhydrous sugar is not further altered at 160°C., but at 170° to 180° it turns brown and yields lactocaramel, with the loss of the elements of water.

A freshly-prepared saturated solution of milk-sugar in cold water contains 14·55 per cent. of the crystallised sugar, but after standing (or immediately on boiling), the solution is found to contain 21·64 per cent., or half as much more. This change in solubility appears to be related to the size of the molecules, for the specific rotatory power of the two modifications of sugar which may be assumed to exist in the solutions is in inverse proportion to the solubility in water.† Thus a freshly-prepared solution is supposed to contain the α modification, and a solution which has been kept the β variety, the value of S_D for the α variety is $+80°$, and for the β kind $+52·7°$. As the latter modification is more soluble than the former in the proportion of about 3 to 2, it follows that saturated solutions of either modification will exert the same angular rotation on a ray of polarised light.‡

When boiled with dilute sulphuric acid, milk-sugar undergoes hydrolysis, a glucose known as lactose or galactose,

* On rapidly boiling down a solution of milk-sugar in a metallic dish, the solution suddenly solidifies to a porous mass of small anhydrous crystals. These are readily soluble in water, giving a solution rotating $+52·7°$.

† See note on page 280.

‡ Mills and Howarth confirm the above value of S for α and β lactin, but differ considerably from Hesse respecting the *solubility* of milk-sugar.

$C_6H_{12}O_6$, being formed. Recent researches have shown that, as in the inversion of cane sugar, the action of dilute acid on milk-sugar really results in the formation of two isomeric glucoses, corresponding with sucro-dextrose and sucro-lævulose. In the cases of the products from milk-sugar, however, both the glucoses are dextro-rotatory. Their freshly-prepared solutions exert a stronger rotatory action than after standing or heating. After heating, the specific rotatory powers are as follows:—

For *a* Lacto-glucose, . . . $S_D = 92{\cdot}8$.
For *β* Lacto-glucose, . . . $S_D = 62{\cdot}8$.

It is by no means certain that these values are correct. *β* lacto-glucose presents very close resemblances to sucro-dextrose, with which it is probably identical.

The leading properties and chemical reactions of milk-sugar are given on pages 262 and 343. In some of its characters it approximates to cane- and in others to grape-sugar.

MALT-SUGAR.

Maltose. Malton. $C_{12}H_{22}O_{11}$.

The sources and leading properties of this sugar are given on page 262. It has been but recently isolated in a state of purity, the existing knowledge respecting it being largely due to the researches of Mr C. O'Sullivan.* By this and other chemists it has been definitely proved that the action of diastase or dilute acids on starchy matters (*e.g.*, malt, maize, rice) gives rise to a production of maltose and dextrin as intermediate products (see page 330), glucose being produced only at a more advanced stage of the hydrolysis. Hence malt-worts do not contain dextrose or other variety of glucose, as commonly supposed, but a mixture of dextrin ($nC_6H_{10}O_5$) and maltose, $C_{12}H_{22}O_{11}$.

Anhydrous maltose has a specific rotatory power of $+139{\cdot}2°$ for the sodium-ray, and of $+154{\cdot}2°$ for the transition-tint.†

* *Journ. Chem. Soc.* xxix. 479, and xxx. 125.

† O'Sullivan's earlier experiments on the apparent specific rotation of anhydrous maltose gave the value Sj = +150°, but more recently he has adopted a number between +154° and +155° (*Journ. Chem. Soc.* xxxv. 771).

When heated with dilute acid, maltose gradually undergoes hydrolysis, the solution increasing in density and diminishing in rotatory power. Boiling for five minutes with dilute sulphuric acid scarcely causes any change, but complete inversion ensues in six or eight hours at the ordinary pressure, or in ten or fifteen minutes under a pressure of atmospheres. It is doubtful whether the product of the inversion is ordinary sucro-dextrose or one or more dextro-rotatory glucoses distinct from this. Malt extract does not invert maltose.

Like cane-sugar, maltose is incapable of direct fermentation, but by the continued action of yeast it is converted into glucose, and then yields alcohol to the amount of 51 to 51½ per cent. of the original maltose.*

Maltose resembles the glucoses in reducing hot Fehling's solution without previous inversion, but the amount of copper precipitate is only 62 per cent. of that reduced by an equal weight of glucose according to Brown and Heron,† but $\frac{65}{100}$ according to C. O'Sullivan.‡ Soxhlet states that the equivalent is $\frac{61}{100}$ when the sugar is contained in a 1 per cent. solution, and the Fehling reagent is undiluted and employed in the exact proportion necessary; $\frac{64{\cdot}1}{100}$ when the latter is diluted with four volumes of water; and $\frac{65{\cdot}3}{100}$ when twice as much of this diluted Fehling's solution is used as is required for the reaction.§

According to J. Steiner, the reducing action of maltose on Pavy's ammoniacal cupric solution is the same as upon the ordinary Fehling's reagent. Thus 20 c.c. of Fehling's solution

Brown and Heron obtained the number +153·1°, apparently with 5 per cent. solutions. Steiner found $S_D = +138{\cdot}9°$ with 11 per cent. solutions, and Meissl obtained the value $S_D = +139{\cdot}3°$ for solutions containing 20 per cent. of maltose. The mean of the two last determinations is the value adopted in the test. See also p. 274.

* If a mixture of maltose and dextrose be fermented with yeast, the whole of the glucose disappears before the former sugar is touched.

† *Journ. Chem. Soc.* xxxv. p. 619. ‡ *Ibid.* xxx. 126.

§ *Journ. Pract. Chem.* [2], xxi. 227, *et seq.*

requires the same measure of maltose solution for its reduction, whether it be used direct or previously mixed with 40 c.c. of strong ammonia, and titrated as described on page 291.* On the other hand, the addition of more caustic soda in presence of ammonia increases the oxidising power of the cupric solution to a notable extent.†

The action of maltose on the mercurial solutions of Sachsse and Knapp is described on page 292.

The relative proportions of maltose and dextrin, produced by the action of malt extract or dilute acids on starch, vary with the temperature employed for hydrolysis; but the normal reaction may be represented in its simplest form as follows:—

$$\underset{\text{Starch.}}{C_{18}H_{30}O_{15}} + H_2O = \underset{\text{Dextrin.}}{C_6H_{10}O_5} + \underset{\text{Maltose.}}{C_{12}H_{22}O_{11}}.$$

This equation corresponds to a formation of 33·33 of dextrin and 68·40 of maltose from 100·00 of starch, and represents the approximate proportions of the leading constituents of a well-made beer-wort, and also of the commercial product known as "dextrin-maltose."

The detection of maltose and its distinction from the other principal sugars are considered on page 343. Its estimation is based on the same principles as those applied to the determination of other sugars—namely, the density of the solution, the cupric-oxide reducing power, and the action of the liquid on polarised light. The estimation of maltose in "dextrin-maltose" and commercial "glucose" is described on page 346; its determination in beer-wort on page 333. The information in these two sections will indicate the methods employed for the estimation of maltose in all cases of practical interest.

Commercial Analysis of Malt.—The brewing value of a sample of malt is chiefly dependent on three factors—namely, the proportion of diastase contained in it, the quantity of soluble or extractive matter it will yield to water, and lastly, the quality of this extractive matter.‡

Well-malted barley is always yellow, occasionally inter-

* Yoshida, *Chem. News*, xliii. 29. † *Chem. News*, xliii. 45.

‡ The following description of the characters of malt is abstracted from a paper by J. Steiner in the *Brewers' Journal*.

mixed with a speck of brown; while a yellowish grey tint is always objectionable. On breaking the malt, the interior should be of a pure white colour, unless the drying has been intentionally carried so far as partially to caramelise the sugar.

The taste of malt is an important criterion of its quality. It should always have an agreeable, sweet taste, and the rapid perception of sweetness proves the presence of a sufficient proportion of diastase.

Malt ought to float on cold water. It should not be very hard, being easily bruised between the fingers, but should be crisp, not soft. These characters indicate whether a sample is "steely," or incompletely malted.

Good malt is plump, long and narrow corns yielding little extract. The *acrospire* should be from two-thirds to three-fourths of the length of the corn, but in no case should it protrude, otherwise too much albuminous matter will be extracted in mashing.

False ferments may be recognised by washing about five grammes of the sample in a little water and examining these washings, after about a quarter of an hour's standing, under the microscope. Lactic ferments are certain to be present, but they should not be numerous, or dart about in a very active manner, or the converting power of the diastose will be deficient, and the fermentative activity and purity of the yeast will suffer in consequence.

Moisture may be determined by drying a known weight of the sample in the water-oven till no further loss of weight ensues. Malt is very hygroscopic, and hence care must be taken that the moisture is determined in such a manner as fairly to represent the bulk. Freshly-made English malt contains from 2½ to 3½ per cent. of moisture, which increases gradually with keeping to about 5 or 6 per cent. German and Austrian malt is not so highly dried as English, and thus often contains 5 or 6 per cent. of moisture even when freshly made, while in Bavarian malt the moisture often rises as high as 10 per cent.

Extractive matter in malt is best determined by a miniature mashing process, in which the conditions are rigidly adhered to for all samples, so as to make the test strictly comparative, and to afford a criterion of the probable

behaviour of the malt on a large scale. The extraction is best conducted in the following manner:—The malt is crushed in a small coffee-mill, the fluted rollers of which are so fixed as to produce a grist which will pass through a sieve having apertures $\frac{1}{16}$th inch in diameter. 50 grammes of the product are then weighed out as rapidly as possible (to avoid accession of moisture), and treated in a weighed beaker with 250 c.c. of warm distilled water of such a temperature that the initial heat of the mixture may be from 50° to 52° C. The beaker containing the mash is placed in a water-bath, and the contents maintained at the same temperature for a quarter of an hour. The heat is then gradually raised till the immersed thermometer registers 59° or 60° C., and the temperature is then kept constant till a drop taken from the liquid ceases to give a blue colour with iodine solution, and nearly ceases to give a brown. This shows that all the starch and nearly all the erythrodextrin have suffered hydrolysis,—a point which will be reached in about twenty minutes. The heat is then increased to about 70° C., in order to complete the saccharification, when the water in the bath is boiled for five minutes. This step, which completes the process of mashing, should be arrived at in about 100 minutes from the commencement of the operation. The beaker is then cooled, and the contents weighed. The liquid is diluted with water till the whole weighs 400 grammes, or eight times the weight of the original malt. The infusion is now passed through a dry filter, and the density of the clear liquid taken at 60° F. (=15·5° C.) in the usual way by a specific gravity bottle. The excess of density over that of water (taken as 1000) multiplied by 2078, and divided by the density of the infusion, will give the percentage of dry extract yielded by the malt.*

* This method is based on the fact that each gramme of malt-extract per 100 c.c. of infusion raises the density of the liquid by 3·85 degrees (water being 1000). The figure 2078 is the product of $\frac{8 \times 1000}{3{\cdot}85}$; and hence the percentage of extractive matter in the malt is found by the equation—

$$\frac{\text{excess of density above } 1000 \times 2078}{\text{density}} = \text{per cent. of extract.}$$

Thus, if the specific gravity of the infusion was found to be 1035; then $\frac{35 \times 2078}{1035} = 70{\cdot}27$ per cent. of extract in the malt.

By the Inland Revenue Act of 1880, a bushel of average malt is assumed to weigh 42 pounds, and two such bushels (=84 pounds) are considered to be capable of yielding one barrel (=36 gallons) of wort of the standard density of 1057. Wort of this density contains 14 per cent. by weight, or 148 pounds per 100 gallons, of solid extract. Hence the solid extract in 36 gallons of the wort will be 53·28 lbs, which is equal to a yield of 63·43 per cent. on the malt.*

The solid matter of ordinary malt-solution contains about 63 per cent of maltose, but when obtained in the manner directed the proportion is not unfrequently somewhat higher. The remainder of the solid matter consists of dextrin, certain indeterminate carbohydrates, albuminoid matters, the soluble constituents of the ash, &c. Notable traces of soluble starch may sometimes be present, if the mashing has been imperfectly or hurriedly conducted.

If desired, a further examination of the infusion may be made with a view of ascertaining the proportions of the leading constituents. The colour and flavour of the liquid should also be noted.

The proportion of maltose present in the infusion may be determined by Fehling's solution, which is by preference employed gravimetrically in the manner described on page 287.

The maltose being known, the percentage of dextrin is deducible from the rotatory action of the infusion on polarised light. The liquid should, if necessary, be decolorised as described on page 275, and the rotation then carefully observed. In order to ascertain how much of the observed effect is produced by dextrin, the rotation due to the maltose present is first calculated. The number of grammes of maltose in 100 c.c. of the infusion having been ascertained by precipitation with Fehling's solution, the number thus found is divided by 2·71, when the dividend is the angular rotation

* The Inland Revenue Act assumes that 28 pounds weight of any kind of sugar is equivalent in saccharine power to a bushel (=42 pounds) of standard malt, and hence that sugars contain 95·1 per cent. of soluble solid matter. This assumption is of course far from being true of the different varieties of commercial glucose (see page 344).

which was due to the maltose of the infusion. The figure thus obtained, if deducted from the total angular rotation observed, gives the rotation due to dextrin. The angle found, multiplied by 3·86, gives the grammes of dextrin in 100 c.c. of the solution. These instructions are based on the assumption that the polarimeter is one in which monochromatic light is employed, and that the infusion is observed in a tube 2 decimetres in length. By dividing the grammes per 100 c.c. by the density of the infusion (water = 1) the actual percentage by weight of the maltose and dextrin in the infusion will be ascertained.

The nitrogenous matters of malt are of considerable importance. Malt contains both soluble and insoluble nitrogenous compounds, the latter of which remain with the draff or grains, while the former pass into the wort, and remain to some extent in the finished beer. The presence of too large a proportion of albuminoids renders beer liable to change and "turn," while too little is disadvantageous in other respects. The coagulation of the albumen materially assists the clarification of the hot wort. The fulness on the palate, the viscosity, and the nourishing properties of beer are characters largely dependent on the albuminoids. The proportion of albuminoids in malting barley should be fully 10 per cent., but in practice it varies from 6 or 7 up to 17 per cent.

The total nitrogen of malt is best ascertained by igniting it with soda-lime in the usual way. The nitrogen found may be calculated to albuminoids by multiplying it by the factor 6·33. The insoluble nitrogen is ascertained from a combustion of the draff with soda-lime, and the difference between this result and the total gives the soluble nitrogen.

Draff or insoluble matter may be determined by washing, drying, and weighing the residue left undissolved in the mashing operation. It may also be ascertained by subtracting the sum of the solid extract and moisture from 100. It is found, however, in practice that the solid extract, moisture, and draff by direct weighing always amount to more than 100. This is due to the fact that the starch takes up the elements of water during the mashing, and yields

more than its own weight of maltose. Hence care should be taken to describe the soluble matter as "extractive matter yielded by mashing the malt," and not as "extractive matter contained in the malt."

Ash may be determined by carefully incinerating 5 or 10 grammes of the malt sample in a muffle, at as low a temperature as possible. In some cases it is of interest to ascertain separately the mineral constituents of the draff and the infusion.

The acidity of malt is an important character in judging of its soundness. The normal proportion of free acid (calculated as lactic acid) is not more than 0·2, or at the most 0·3 per cent.; 0·4 per cent. is unusually high, and denotes unsoundness. Such malt should never be used for brewing beers intended for exportation or long keeping. The acidity of malt is readily ascertained by treating 50 grammes of crushed malt with 100 c.c. of cold water and stirring the mixture occasionally during half an hour. The liquid is then passed through a dry filter, and, when the greater part has run through, 50 c.c. are titrated with litmus and decinormal soda, or standard Excise ammonia. Each 1 c.c. of decinormal soda used for the neutralisation corresponds to ·0090 grammes of lactic acid, $C_3H_6O_3$, in the solution operated on.

The diastastic or fermentative power of malt can be measured in the following manner:—50 grammes' weight of the crushed sample is treated with 500 c.c. of cold water, the mixture being occasionally stirred during one hour. The solution is then heated to 60° C., kept at that temperature for half an hour, and the solution filtered through a dry filter. Two quantities of bread of 50 grammes each, taken from the same loaf, are treated with 300 c.c. of water at 40°C. To one of these quantities 200 c.c. of the malt infusion (=20 grammes of malt) is added, and to the other 200 c.c. of water. Both mixtures are then rendered faintly alkaline by a few drops of bicarbonate of sodium, and kept at 40° C. for three hours, when the liquids are filtered. 50 c.c. of each of the filtrates is then evaporated to dryness at a steam heat and the residue weighed. The difference between the weights of the two extracts shows the amount of matter rendered soluble by

the diastase in 2 grammes of malt. The result so obtained requires a correction for the weight of solid matter in the malt extract added. This may be avoided by adding to the filtrate from the blank experiment, during evaporation, 20 c.c. of the infusion of malt, this being the quantity contained in the 50 c.c. evaporated in the other experiment.

Another method is as follows:—Into each of three flasks of about 250 c.c. capacity is put 0·1 gramme of starch, previously dried at 100° C. 100 c.c. of water is next added to each quantity, and the liquids raised to the boiling point so as thoroughly to gelatinise the starch. To one of the flasks is added 10 c.c. of a 10 per cent. infusion of malt, prepared as above described, the other quantities being treated with 15 and 20 c.c. of malt infusion respecting. The flasks are then maintained at a temperature of about 50° C. for three hours, when a drop or two from each is tested on a porcelain plate with a solution of iodine. If no blue or brown coloration is produced by one of the flasks, it is evident that the proportion of diastase in the malt infusion added was sufficient to convert 0·1 gramme of starch into achro-dextrin and maltose. If a colour be produced in the other cases, the conversion is clearly incomplete, and a further addition of malt solution should be made, and the heating repeated for three hours more. By proceeding in this manner, it is easy, with a little practice, to hit the exact point at which sufficient malt infusion has been added.

Dunstan and Dimmock, who devised the above method, have applied it to the examination of various specimens of commercial malt extract.* Of fourteen samples examined, only three were found to have any converting power on starch, the activity of the diastase of the remaining specimens having doubtless been destroyed by evaporation of the malt-solution at too high a temperature. Of the three active samples of malt extract (*i.e.*, evaporated malt solution), 17·3, 29·0, and 34·0 parts respectively were required for the conversion of 1 part of starch. The proportions of water varied from 19 to 86 per cent., the latter sample containing 4·1 per cent. of alcohol.

* *Pharm. Journ.* [3], ix. 733, 735.

The following analyses by Oudemanns illustrate the composition of unmalted barley as compared with malt dried in different ways. Apparently the constituents are calculated on the moisture-free samples.

	Barley.	Malt.		
	Air-dried.	Air-dried.	Pale Kiln-dried.	High Kiln-dried.
Starch . . .	67·0	58·1	58·6	47·6
Dextrin . . .	5·6	8·0	6·6	10·2
Sugar	0·0	0·5	0·7	0·9
Cellulose, &c. . .	9·6	14·4	10·8	11·5
Albuminoids, &c. .	12·1	13·6	10·4	10·5
Fat	2·6	2·2	2·4	2·6
Ash	3·1	3·2	2·7	2·7
Torrefaction Products	0·0	0·0	7·8	14·0
	100·0	100·0	100·0	100·0

The "grains," "draff," or exhausted malt will have a composition varying within certain limits according to skill with which the process of mashing or infusion was conducted. The draff from highly dried malt contains a smaller proportion of starch than that from pale malt. Grains usually contain from 4 to 6 per cent. of albuminoids, from 5 to 10 of starch, &c., 6 to 10 of cellulose and lignin, and nearly 80 of water.

GLUCOSES. $C_6H_{12}O_6$.

The generic and specific characters of the principal kinds of glucose are described in the tables on pages 260 and 343. The action of the glucoses as reducing agents is fully discussed in the section commencing on page 283. The fermentation of glucose is considered on page 312.

With the exception of the two varieties produced by the inversion of cane sugar, and existing ready formed in honey and other natural products, the glucoses are very unimportant.

Dextrose. Dextro-glucose. Sucro-dextrose.

French—Sucre de raisin. *German*—Traubenzucker.

This species of glucose, often called grape sugar, or

starch sugar, may be produced in various ways, of which the following are the chief:—

(*a*) By the hydrolysis of starch, dextrin, cane sugar (together with lævulose), or some gums, by means of dilute acids, diastose, or a small proportion of yeast (see pages 311 and 345).

(*b*) By treating linen rags or similar vegetable matter with sulphuric acid (see page 359).

(*c*) By decomposing the so-called glucosides (*e.g.*, salicin, gallotannic acid, amygdalin, phloridzin, &c.), by treatment with dilute acids or certain ferments.*

Dextrose occurs ready-formed, together with lævulose, in honey (see page 350). It also occurs, unmixed with lævulose or cane sugar, in diabetic urine.†

Dextrose is found ready-formed in various fruits. The following figures exemplify the usual proportions:—

	Per Cent.		Per Cent.
Peach . . .	1·57	Cranberry . .	7·45
Apricot . . .	1·80	Pear . . .	8·02–10·8
Plum . . .	2·12	Apple . . .	7·38–8·37
Raspberry . .	4·00	Sour Cherry . .	8·77
Blackberry . .	4·44	Sweet Cherry . .	10·79
Strawberry . .	5·73	Grape . . .	14·93
Bilberry . . .	5·78	Currant . .	6·10

Dextrose usually crystallises from its aqueous solution in granular, hemispherical, warty masses containing $C_6H_{12}O_6 + H_2O$. It becomes anhydrous below 100° C. Dextrose is less soluble in cold water than cane sugar, requiring $1\frac{1}{3}$ times its own weight, but it dissolves in all proportions in boiling water, forming a syrup of a sweetening power much inferior to a solution of cane sugar,‡ or one of lævulose of the same strength.

* The dextro-rotatory glucoses obtained by the action of dilute acids on the glucosides are generally assumed to be identical with sucro-dextrose, or grape sugar, but the researches of Hesse and others have thrown considerable doubt upon the accuracy of this view (see page 339).

† Hoppe-Seyler has concluded from his observations of the specific rotatory power of the dextro-glucose prepared from diabetic urine, and many times re-crystallised from alcohol, that all varieties of dextrose prepared from other sources have been contaminated with more or less dextrin, but it is more probable that the discrepancy in the value of $[a]$ or S for dextrose, as determined by various observers, is really due to the existence of several varieties of this glucose. In other words, there is considerable doubt of the identity of diabetic dextrose or "diabetose" with sucro-dextrose.

‡ It is said that two parts of cane sugar possess the same sweetening power as five of dextrose. This statement appears to require verification.

Considerable discrepancies exist in the determinations of the specific rotatory power of dextrose as ascertained by different observers. In certain cases it is even doubtful whether the recorded numbers apply to anhydrous or to crystallised dextrose. The following table shows the value of S_D and S_j* for anhydrous dextrose according to the observations of various chemists. The figures refer to a solution which has been either heated or kept for some hours, a freshly-prepared solution of dextrose in cold water having a rotatory power about twice as great as that shown in the table. The values printed in prominent type are those obtained by direct observation; the others by calculation, on the assumption that $S_j = S_D \times 1{\cdot}11$. The figures having H. affixed are obtained by calculation from the observed rotation of the *hydrated* dextrose:—

APPARENT SPECIFIC ROTATORY POWER OF β MODIFICATION OF DEXTRO-GLUCOSE IN SOLUTION, AS DETERMINED BY DIFFERENT OBSERVERS.

Source of Sugar.	Value for Anhydrous Sugar of		Concentration of Solution employed.	Observer.
	S_D or $[a]_D$.	Sj or $[a]j$.		
Sucrose	50·5	+56·0°	?	Berthelot.
	51·7	57·4	?	Béchamp.
	52·9	58·65	5–10	Brown & Heron.
	51·9	57·6	?	O'Sullivan.
	51·3	57·0	?	Schmidt.
Starch	53·02	58·85	10	Tollens.
Diabetic Urine.	56·4	62·6	4·5–26	Hoppe-Seyler.
Starch	51·67	57·3	3	Hesse.
	51·51 (H.)	52·2	12	,,
Grapes	52·16	57·9	3	,,
	51·80	57·5	?	,,
Honey	50·97 (H.)	56·6	12	,,
	51·7	57·3	?	,,
Salicin	51·8	57·4	2½–12	,,
	52·4 (H.)	58·2	12	,,
Amygdalin	54·2 (H.)	60·1	2	,,
Phloridzin	43·7 (H.)	48·5	6	,,
VALUE ADOPTED	51·9	57·6	10–20	AVERAGE.

It will be seen from these results that it is very doubtful whether the dextro-glucoses obtained from diabetic urine and from some of the glucosides (*e.g.*, phloridzin) are identical with

* For an explanation of these symbols see page 269.

the sucro-dextrose from starch, honey, or grapes. The mean of the more reliable values of S_j for anhydrous sucro-dextrose is about +57·6°, which number has been adopted as the value of S_j for sucro-dextrose. The number +51·9° is obtained as the value of S_D, by multiplying 56·6 by the factor ·9011, the origin of which is described on page 273.

If dextrose be heated with a solution of caustic alkali, the liquid rapidly becomes coloured yellow or brown, and on continued heating a humus-like substance separates. A similar change occurs slowly at the ordinary temperature. According to Peligot, the product is an amorphous body called glucic acid, but the reaction is still very obscure. Hoppe-Seyler obtained ordinary lactic acid, formic acid, pyrocatechol, and indefinite bodies. On mixing alcoholic solutions of dextrose and caustic potash, a white gelatinous precipitate is formed which speedily turns brown.

A solution of dextrose dissolves the alkaline earths forming yellow solutions precipitable by alcohol. By boiling with excess of lime dextrose is rapidly acted on and destroyed.* Dextrose, when pure, is not precipitated by neutral or basic lead acetate, but gives a white precipitate with an ammoniacal solution of normal lead acetate.

The reaction of dextrose with alkaline solutions of copper is described on page 283, *et seq.*

When quite pure, dextrose is not readily charred by concentrated sulphuric acid, but combines with it to form an acid-ethereal salt, decomposed by water.

By the action of nascent hydrogen dextrose is converted into mannite or mannitol, $C_6H_{14}O_7$.

* Peligot has recently isolated from the products of the action of lime on glucose a body called saccharin, not capable of inversion or fermentation, and having a rotatory power for the sodium ray of +92·8°. Saccharin melts at 160°, and is volatile almost without decomposition. It decomposes carbonates when boiled with them, forming saccharinates, from which the free acid cannot be obtained, as it splits up into water and saccharin. Peligot considers saccharin isomeric with cane sugar ($C_{12}H_{22}O_{11}$), but Scheibler gives the formula $C_6H_{10}O_5$, and regards it as the anhydride of saccharinic acid, $C_6H_{12}O_6$, which forms a series of very soluble salts, those of potassium and ammonium being crystalline. The existence of saccharin probably accounts for the anomalous results obtained by the polariscopic analysis of many saccharine products.—*Compt. Rend.* lxxxix. 918, xc. 1141; *Ber.* xiii. 1826, 2212.

Lævulose. Lævo-glucose. Sucro-lævulose. — This variety of sugar occurs together with dextrose in honey and many fruits. A variety of lævulose is produced by the action of dilute acids on inulin, but its identity with sucro-lævulose is doubtful. Lævulose is obtained, together with an equal weight of dextrose, by the action of dilute acids, diastase, or a limited quantity of yeast on cane sugar (see page 311). Lævulose is not a product of the action of dilute acids on any known glucoside.

The principal physical and chemical properties of lævulose are described on page 260. It presents a close general resemblance to dextrose, the following being the chief differences of analytical value:—

(1) Lævulose is not crystallisable, and is more soluble in alcohol than dextrose.

(2) The aqueous solution of lævulose is much sweeter than one of dextrose of the same strength.

(3) The specific rotatory power of lævulose is $-98°$ for the D line at 15° C., decreasing with a rise of temperature; while the value of S_D for dextrose is $+51{\cdot}9°$, unaffected by temperature.

(4) Mixed in ice-cold 5 per cent. solution with 120 per cent. of its weight of fine-powdered slaked lime (which should be added gradually, the vessel being immersed in ice-cold water), a milky liquid is obtained, which gradually becomes pasty from the formation of a difficultly-soluble calcium lævulosate, $CaO,C_6H_{12}O_6,H_2O$, while dextrose on similar treatment yields a freely soluble compound,* which can be separated by filtration through linen. The residue, after being washed and strongly pressed, may be suspended in water and decomposed by oxalic or carbonic acid, when a solution of pure lævulose is obtained, which yields *anhydrous* lævulose by evaporation in vacuo over sulphuric acid.

(5) The respective reducing actions of dextrose and lævulose on Fehling's copper solution are usually assumed to be identical. According to Soxhlet, however, the reducing

* If invert sugar or honey is to be treated for lævulose, the proportions of lime and water must be modified accordingly: 10 parts of invert sugar, 6 of slaked lime, and 100 of water are then the right proportions.

action of the former is sensibly greater than that of the latter (see page 294).

(6) The reducing action of dextrose on Knapp's mercurial solution is sensibly the same as that of lævulose, but the latter glucose exerts a far stronger reducing action on the solution of Sachsse, equal amounts of the dextrose and lævulose reducing 100 and 148·6 c.c. of Sachsse's solution respectively (see page 292).

Detection of Glucoses.—All the varieties of glucose appear to be very similar in their leading chemical properties, though differing from each other in certain minor respects and in their physical characters. (These differences are described in the table on page 260.) The reactions on next page present a selection from the very numerous tests proposed for the detection of glucose. For convenience of reference, the reactions under similar conditions of maltose, and cane- and milk- sugar, are given in parallel columns.* The facts stated under glucose are intended to apply to sucro-dextrose, sucro-lævulose, or to the mixture of the two called invert sugar. They have not invariably been verified for the glucoses from other sources.

A number of other liquids besides solutions of copper are reduced by glucose, and more or less by maltose and lactose also. Thus, in alkaline solutions, glucose, maltose, and lactose reduce blue indigo to white indigo, ferricyanides to ferro-cyanides, mercuric cyanide or Nessler's solution to metallic mercury, and so forth.

Reaction 1 cannot be regarded as a conclusive test for cane sugar except in the certain absence of other substances likely to be charred by sulphuric acid. The change in the rotatory power by boiling with acid (reaction 3) is almost the only satisfactory method of detecting cane sugar in presence of glucose, unless actual crystals of the former can be observed under the microscope. The change in the reducing action on Fehling's solution after inversion proves the previous presence in the solution either of cane sugar or other saccharose, or of a glucoside.

* I have not thought it necessary to repeat the statements made on previous pages with respect to the physical characters of the sugars.

TABLE OF REACTIONS OF THE MORE IMPORTANT SUGARS.

	Glucoses, $C_6H_{12}O_6$.	Maltose, $C_{12}H_{22}O_{11}$.	Cane Sugar, $C_{12}H_{22}O_{11}$.	Milk Sugar, $C_{12}H_{22}O_{11}+H_2O$.
1. Moisten the solid sugar with water, and stir in the cold with concentrated sulphuric acid (1·85 sp. gr.).	Not affected when pure.	...	Chars.	
2. Triturate the solid sugar with caustic soda, or boil it with a 3 per cent. caustic soda solution for one minute.	Brown coloration.	...	Not affected.	Not affected.
3. Observe the rotatory power of the original solution again, after inversion by method described on page 283, correcting for change of volume.	Rotatory power unchanged. $S_D = +51·9$ for dextrose.	Dextro - rotatory power diminished from $= +135°$ to $+54·6$ in same liquid.	Dextro - rotatory power changed to lævorotatory, $+66·5°$ becoming $-24·3°$ in same liquid.	Dextro - rotatory power increased, $+52·7°$ becoming $+77·8°$.
4. To the aqueous solution, add a few drops of cupric sulphate and excess of caustic soda; or to the neutral solution add Fehling's solution and heat to the point. (The latter modification is the preferable.) See page 283, *et seq.*	Deep blue liquid, giving yellow or red precipitate on heating. K = 100.	Deep blue liquid, giving yellow or red precipitate on heating. K = 62.	Deep blue liquid, unchanged by heating. K = 0.	Deep blue liquid, giving yellow or red precipitate on heating. K = 70.
5. To a few drops of Fehling's solution, add caustic soda and ammonia, heat to boiling, and add the liquid to be tested for sugar.	The solution is decolorised.	The solution is decolorised.	No change.	The solution is decolorised.
6. Boil the solution for two minutes with 1 c.c. of a liquid containing 4 per cent. of cupric acetate, and 1 per cent. acetic acid ($C_2H_4O_2$).	Red precipitate of cuprous oxide.	...	No change.	No change.

Glycerin and dextrin do not reduce Fehling's solution on heating to boiling, though they share with the sugars the power of preventing the precipitation of cupric solutions by alkalies.

For the behaviour of other bodies with Fehling's solution, and for details respecting the quantitative employment of the test see page 286, *et seq.*

Glucose is best distinguished from milk sugar by reaction 6. Unless applied quantitatively, the test is incompetent to detect the latter in presence of the former, but the necessity for so doing does not occur in practice. For the detection of glucose as an adulterant of cane sugar see page 323. Mixtures of glucose and maltose are considered on page 346.

Determination of Glucoses.—The general principles on which the determination of glucoses is based have already been considered in the sections devoted to the relations of the sugars to polarised light (page 264); the action of the sugars as reducing agents (page 283); and the assay of commercial cane sugar (page 315). In practice we employ methods based on the specific gravity of the solution (see pages 295 and 297); the reducing action of glucoses on solutions of copper or mercury (pages 286 and 291); and, occasionally, fermentation (page 314). The determination of glucoses by the polarimeter is not always very satisfactory, and is rendered especially unreliable in the assay of commercial cane sugars and saccharine liquids, by the presence in these of one or more little-known varieties of glucose of different optical activity from either ordinary dextrose or lævulose. In determining glucose it is generally assumed that with all methods, except the optical one and that with Sachsse's solution, it is a matter of indifference whether the modification of glucose present be dextrose, lævulose, or a mixture of the two. On this point, however, it is desirable to bear in mind the observations on page 294.

Analysis of Commercial Glucose.—Under the names of glucose, saccharum, saccharine, starch sugar, and other more fanciful cognomens, are manufactured and sold a variety of products of which dextrose is the leading constituent. Commercial glucoses are employed by brewers as substitutes for malt and cane sugar, and large quantities are also used by manufacturers of fancy sugars and preserves.

Glucose occurs in commerce in two forms, one a hard sub-crystalline body, and the other a thick syrupy liquid. The latter contains a much larger proportion of dextrin than the former.*

Commercial glucose is produced by the action of dilute sulphuric acid on starch or starchy matter, or occasionally woody fibre. The substances most commonly employed are maize and rice. The ground grain, or the starch from the same, is either boiled with the acid in an open tank, or heated with it in strong copper cylinders under high pressure. If the first method be adopted, and the process arrested as soon as a cold sample of the liquid ceases to give a blue colour with iodine, the product contains a large proportion of dextrin; but if a high pressure be employed, and the action pushed further, dextrose is the chief product. In either mode of operating, maltose is formed together with the other products. The acid is subsequently removed by neutralisation with chalk or whiting,† and the glucose obtained in a solid state, or as a viscous liquid of about 1·42 specific gravity, by evaporating the clear solution.

The following analyses of commercial glucoses were quoted by W. G. Valentin in a lecture before the Society of Arts.

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
Glucose ($C_6H_{12}O_6$) . .	80·0	58·85	67·44	63·42	61·46
Maltose ($C_{12}H_{22}O_{11}$) . .	None.	14·11	10·96	13·50	13·20
Dextrin ($C_6H_{10}O_5$) . .	None.	1·70	None.	None.	None.
Unfermentable carbohydrates ($C_6H_{14}O_7$), with a little albuminoids .	8·20	9·38	4·30	8·40	8·60
Mineral matter . .	1·30	1·40	1·60	1·50	1·60
Water	10·50	14·56	15·70	13·18	15·20
	100·00	100·00	100·00	100·00	100·00
Total Solid Matter . .	89·5	85·44	84·30	86·82	84·80
Matter of use to the brewer	80·0	74·66	78·40	76·92	74·60

* In America the solid product is called "grape sugar," the term "glucose" being popularly applied to the syrupy liquid.

† The solution of dextrose retains a considerable quantity of dissolved calcium sulphate. More complete separation occurs on concentration to about 1·24 sp. gravity, and a further deposition occurs when the solution is fermented.

No. 1 was somewhat brown, very hard, and of English manufacture.

No. 2 was pale straw-coloured, softish, French.

No. 3, whitish, somewhat hard, English.

No. 4, whitish, somewhat hard, German.

No. 5, white, somewhat hard, German.

These analyses are unusually elaborate, and for commercial purposes there is no occasion to enter so much into detail. Many analysts limit their statements to the proportions of water, ash, dextrin, and glucose, ignoring the maltose altogether. This practice is very objectionable, as, in an analysis so stated, not only is the maltose classed as dextrose, but the amount of dextrin is also seriously in error. This is well seen by the following results obtained by the author from a commercial glucose. Column A. shows the composition on the assumption that all the reducing sugar is glucose, the remaining optically active matter being dextrin. Column B. gives a more correct analysis of the material.

	A.	B.
Water . . .	17·77	17·77
Mineral matter . .	·63	·63
Glucose . . .	72·60	64·94
Maltose . . .	...	12·35
Dextrin . . .	9·00	4·31
	100·00	100·00
Total solid matter	82·23	82·23

The following data, obtained by the analysis of the above sample, illustrate the mode of deducing the relative proportions of glucose, maltose, and dextrin in such products :—

(*a*) On ignition, the sample left 0·63 per cent. of ash.

(*b*) The specific gravity of a solution of 20 grammes of the sample diluted to 100 c.c., was 1063·32 at 60° F.

This figure, divided by 3·85 (see page 296) gives—

Total solids . .	82·23	per cent.
Less, Ash . . .	·63	„
Carbohydrates . .	81·60	„

(*c*) By Fehling's test (see page 287) the sample was found to have a reducing-power equivalent to 72·6 per cent. of glucose. The reducing-power of maltose may be taken as $\frac{62}{100}$ that of glucose.

(*d*) A solution of 20 grammes per 100 c.c., observed in a 2 decimetre tube, caused an angular rotation of +23·7° for the sodium line D. Hence the value of S_D for the sample was +59·25°.*

The values of S_D for dextro-glucose, maltose, and dextrin, are respectively +52°, +139°, and +193°, ignoring fractional parts of a degree.

Let S be the apparent specific rotatory power, and K the cupric oxide reducing-power of the sample, and *g*, *m*, and *d* the respective amounts of glucose, maltose, and dextrin contained in 1 gramme of the sample. Then, from the above data, the following equations result:—

1. $g+m+d=·816$
2. $g+·62m=K=·726$
3. $52g+139m+193d=S_D=59·25.$

From these—

$g=·726-·62m.$

$d+g=·816-m$

$d+·726-·62m=·816-m$

and $d=·09-·38m.$

Substituting the above values for *g* and *d* in equation 3, we get—

$$52(·726-·62m)+139m+193(·09-·38m)=59·25.$$

Simplifying this—

$$37·752-32·24m+139m+17·37-73·34m=59·25.$$

Simplifying again, and transposing, we get—

$$33·42m=4·128\text{; whence,}$$

$$m=·1235.$$

The value of *m* being found, those of *g* and *d* are easily derived from equations 1 and 2. Thus—

$$g=·726-·62\ (·1235)=·726-·07657=·64943.$$

$$d=·816-m-g=·816-·1235-·6494=·0431.$$

* $S_D=\frac{23·7}{2\times\frac{20}{100}}=59·25°$. See page 269.

As these values represent the respective weights of glucose, maltose, and dextrin in one gramme of the sample, the percentages will be 64·94, 12·35, and 4·31, accordingly; together making up 81·60 per cent.

From the above example it is evident that the glucose, maltose, and dextrin in a sample are readily deduced from the solution-density, and the results of the Fehling's test and polariscopic reading.

Although the total percentage of matter useful to the brewer is the same whether the sugar be wholly dextro-glucose, or in large part maltose, the quality of the material, as measured by the character of the beer produced, is very different, beer brewed from maltose being greatly superior to a glucose-beer. The latter is apt to be thin and deficient in head, very clean, and of a vinous character. Maltose gives a beer of full body, good head, soft and creamy on the palate. It keeps well, and, owing to the gradual after-fermentation which occurs, continues brisk and sparkling. These remarks apply to beer brewed from acid-made maltose as well as to malt-brewed beer.

On account of the superiority of maltose over glucose as a brewing material, it is desirable to limit the action of the dilute acid used for converting the starchy matter. In practice it is found that a mixture of two parts of maltose and one of dextrin is the most generally suitable for brewers' purposes. This product, which has been introduced under the name of "dextrin-maltose," is obtained if the action of the acid be arrested when the specific rotatory power of the solids has decreased to about $+171°$ for the transition-tint, or $+151°$ for the sodium-ray.*

The dextrin of brewing materials is of value for giving "body" to the beer. A less proportion is desired for "running" ales than for heavier or "stock" ales. "Confectioners' glucose" is a viscid colourless liquid resembling glycerin. It contains a very large proportion of dextrin.

* The cupric-oxide reducing-power of the solid carbohydrates in the above product should be about ·42 of that of anhydrous dextrose or invert sugar. The amount of solids present is ascertained by removing the sulphuric acid by baryta-water, and taking the density of the solution (see page 296).

An approximately accurate determination of the dextrin of commercial glucose can be made by mixing the clear solution of the sample with ten volumes of absolute alcohol, the precipitate being regarded as "dextrin."

Some chemists state as "maltose" the percentage of the sample which undergoes inversion to glucose by boiling for five minutes with very dilute acid, but, as a matter of fact, maltose is scarcely affected by this treatment.

The "dextrin," according to the same chemists, is the portion of the sample which becomes inverted by heating under pressure with dilute sulphuric acid for six hours.

"Intermediate carbohydrates," or more probably over-hydrated carbohydrates, are those which are incapable of inversion or of fermentation with yeast.*

Although it may occasionally be of service to determine the "dextrin" and other constituents by such arbitrary methods as these, it is extremely doubtful whether the results obtained really represent the composition of the original sample, and certainly for all practical purposes it is sufficient to class the carbohydrates as glucose, maltose, and dextrin, which may be effected in the manner already described (page 346).

Inverted cane sugar is now made largely for brewers' use, being sold under the names of "invert" or "inverse sugar," "saccharum," "malt saccharum," &c. Starch sugar and cane sugar are often added. The analysis of such products may be effected in the same manner as that of honey (see page 351), but it is generally sufficient to estimate the sugar by Fehling's solution before and after inversion. These estimations give the data for calculating the cane or uninverted sugar of the sample, and the total glucose, without distinguishing between the dextrose and lævulose.

If desired, the water in commercial glucose can be determined directly, as in cane sugar (see page 317). The

* Landbeck has recently described an unfermentable, poisonous, bitter substance giving many of the reactions of colchicine, and which is sometimes present to a considerable extent in commercial glucose and badly fermented beer.—*Pharm. Journ.* [3], xi. 832.

amount in a solid sample should not exceed 16 or 17 per cent.

The ash of glucose usually consists almost wholly of calcium sulphate. It should not exceed 1 per cent. of the weight of the sample, and should be almost wholly free from iron, which is objectionable in brewing materials.

The nitrogenous matter of glucose can be determined if desired by ignition with soda-lime. The amount of nitrogen found multiplied by 6·33 gives the albuminoid matter. Fair comparative results may be obtained by Wanklyn's "albuminoid ammonia" process. Mere traces of nitrogenous matter should be present in good glucose, though it is true that some favourite commercial brands contain a notable proportion of albuminoids.

Free Acid ought to be wholly absent from commercial glucose, though many specimens possess normally a slightly acid reaction which is probably due to acid phosphates.

Honey.—Honey is essentially a strong aqueous solution of mixed lævulose and dextrose. It is sometimes stated to contain sucrose as a normal constituent, but the presence of this sugar in genuine honey is extremely doubtful, at least in sensible quantity.* The following analyses of authentic specimens of genuine honey are by Dr J. Campbell Brown.† The figures originally published are slightly corrected with Dr Brown's concurrence, the value of S_j for sucro-dextrose being taken as 57·6, and that of lævulose as 109·6 (see page 275). With the corrected values, the small quantities of cane sugar, found by indirect analysis to be present in some of the samples, disappear entirely, except in the case of the Jamaica sample, and in that case Dr Brown thinks it as probable that the appearance of cane sugar as a constituent is as probably due to error of experiment as to its actual presence in the specimen. The doubt thrown by Soxhlet on the assumed equal reducing value of dextrose and lævulose (see page 294) also affects the question of the presence or absence of cane sugar.

* On the other hand, the nectar of plants contains a considerable proportion of an invertible sugar, probably cane sugar.—*Chem. News*, xxxviii. 93.

† *Analyst*, iii. 269.

Locality.	Lævulose.	Dextrose.	Sucrose.	Wax, Pollen, and Insoluble Matter.	Ash.	Water expelled at 100° C.	Water expelled at considerably above 100° C, and loss.
English .	37·04	36·11	None.	Good trace.	·15	19·10	7·60
Welsh . .	37·66	39·24	None.	Trace.	·14	16·40	6·56
Normandy	37·36	42·02	None.	Slight trace.	·17	15·50	4·95
German .	33·56	36·16	None.	Trace.	·17	19·11	11·00
Greek . .	40·43	31·77	None.	·05	·15	19·80	7·80
Lisbon .	37·69	34·51	None.	Nearly 1·0	·14	18·80	6·86
Jamaica .	33·60	34·80	2·2 (?)	2·1	·25	19·46	7·58
California	38·29	35·57	None.	Good trace.	·11	17·90	8·13
Mexican .	36·39	35·04	None.	Trace.	·97	18·47	10·03

The specific gravity of honey is about 1·41, but varies somewhat with the proportion of water.

In analysing honey, the ash, water, and insoluble matter may be determined as described under sugar (page 317). The insoluble matter consists of wax, pollen, &c., and should be carefully examined under the microscope. A fair determination of the total water may be obtained by ascertaining the density of a 10 per cent. or 20 per cent. solution of the sample (see page 346).

Cane sugar can be best sought for in honey by carefully ascertaining the polarising and cupric-oxide reducing power of a solution of the sample of definite strength, and then making the same determinations after inversion. In the absence of cane sugar there will be no sensible alteration by inversion.

The total glucose may be determined by Fehling's solution (see page 287). Let the percentage thus found be called *g*. The proportions of dextrose (*d*) and lævulose (*l*) may then be deduced from the results of the optical examination as follows:—

Suppose a sample of honey has given the following analytical results:—

Total glucose by cupric oxide reduction = 70 per cent.

Cane sugar, as deduced from the difference in the Fehling reaction and rotatory power before and after inversion, = 2 per cent.

Specific rotatory power of sample $= -17{\cdot}5°$ at 14° C.; a solution of 20 grammes made up to 100 c.c. having given a rotation of $-7{\cdot}00$ angular degrees for the transition-tint, in a tube 2 decimetres in length (see page 269).

Let c be the cane sugar, d the dextrose, and l the lævulose in 1 gramme of the sample. Then $c = {\cdot}02$; $d + l = {\cdot}70$; and $l = {\cdot}70 - d$.

The values of S_j for sucrose, dextrose, and lævulose, are, respectively, $+73{\cdot}8$, $+57{\cdot}6$, and $-109{\cdot}6$ (at 14° C.), and the specific rotatory power of the sample must be the algebraic sum of the effects of these three multiplied by the proportions in which they are present. This gives the equation:—

$$73{\cdot}8\,c + 57{\cdot}6d + (-109{\cdot}6)l = -17{\cdot}5.$$

c being ·02, and l being $\cdot 70 - d$, we obtain—

$$1{\cdot}476 + 57{\cdot}6d = -17{\cdot}5 + 76{\cdot}72 - 109{\cdot}6d;\ \text{whence,}$$

$$166{\cdot}2d = 57{\cdot}74;\ \text{and}$$

$$d = {\cdot}3474.$$

The percentage of dextrose being thus found to be 34·74, that of lævulose must be 35·26.

In J. Campbell Brown's analyses it will be observed that the dextrose and lævulose are approximately equal in amount. Hence any considerable adulteration by dextrose would be detectable, but the addition of invert sugar would be wholly unrecognisable unless its presence could be inferred from the amount and composition of the ash.

In a substance called t a z m a, found in Ethiopia, allied to honey, and said to be the product of an insect like a large mosquito, A. Villiers found 32 per cent. of g l u c o s e (the dextrose being somewhat in excess), *no* cane sugar, and 27·9 per cent. of a kind of d e x t r i n.*

A microscopical examination of honey is occasionally of value. Under the microscope, crystals of glucose, scales from butterflies' wings, spores of fungi, and different kinds of pollen may be observed. The latter, if sufficiently identified, might lead to a knowledge of the country whence the honey was derived.

* *Compt. Rend.* lxxxviii. 292; *Journ. Chem. Soc.* xxxvi. 450.

Fictitious honey is sometimes manufactured from glucose and certain flavouring materials.

The following method of distinguishing genuine from adulterated honey is said to be trustworthy :—Mix the honey with an equal quantity (? weight or measure) of water, then add strong spirit (sp. gr. ·86), stirring constantly till a permanent turbidity is produced. In honey adulterated with glucose syrup or dextrin a heavy gummy deposit will soon form, while, with genuine honey, but a slight milkiness is produced. This test might answer for the detection of commercial glucose containing dextrin, but would probably be useless in cases in which invert sugar had been added. The addition of glucose, whether starch sugar or inverted cane sugar, will be almost certainly indicated by the increased proportion of ash, and by the presence in it of a notable proportion of calcium sulphate. Molasses, which is said to be occasionally added to honey, might be detected by the presence of chlorides in the excessive ash (not sulphated), and by the large proportion of cane sugar. Starch and flour are readily detected, as they remain insoluble when the honey is dissolved in cold water or spirit. Gelatin, if present, would also be left, and would be recognisable by its odour on ignition and its reaction with tannin.

Examination of Diabetic Urine.—Various methods of examining urine for sugar have been devised. The subject is of considerable importance, as the presence of dextrose in sensible quantities in the urine is a constant symptom of the disease known as *diabetes mellitus*. Diabetic urine is usually of high density, often reaching 1·040, pale in colour, and apt to froth on agitation. Occasionally it is almost a pure solution of dextrose. The proportion of sugar in diabetic urine may be determined approximately by the polarimeter, but the results are deficient in accuracy owing to the presence of other optically active bodies. On the whole, the processes based on the reduction of metallic solutions by the glucose give the best results; the solution most generally and deservedly employed being that of Fehling. Before applying the test, it is desirable to remove albumen, if present, by heating the slightly acid or acidified urine to boiling, and filtering from

any precipitate. The liquid should then be rendered distinctly alkaline by caustic soda or potash, filtered from any precipitate of phosphates, &c., and the copper solution then employed in the following manner:—

Heat to boiling in a test-tube 10 c.c. of Fehling's solution, prepared as described on page 285,* previously introducing a few small fragments of clay tobacco-pipe to prevent bumping. When boiling, add ½ to 1 c.c. of the urine, previously treated as indicated above. If sugar be abundant, as in a decidedly diabetic urine, a yellowish or brick-red opacity and deposit will be produced. If a negative reaction is obtained, test for traces of sugar by adding 7 c.c. or 8 c.c. of the urine to the hot liquid, heating again to ebullition, and then setting the tube aside for some time. If no turbidity is produced as the mixture cools, the urine is either quite free from sugar, or at any rate contains less than 0·025 per cent. If the quantity of sugar present is small—that is, under 0·5 per cent.—the precipitation of the yellow or red cuprous oxide does not take place immediately, but occurs as the liquid cools, the appearance being somewhat peculiar. The liquid first loses its transparency, and passes from a clear bluish-green to an opaque, light-greenish colour. This green milky appearance is quite characteristic of dextrose.

By applying the above test quantitatively (see page 287), the determination of glucose in urine may be readily effected, but it must be borne in mind that traces of sugar are found normally, or at least very commonly, in urine, and hence too great a stress should not be laid on the presence of an insignificant proportion.

Pavy's solution (see page 290) may also be used for the determination of the glucose in diabetic urine, though it cannot be employed for the detection of small quantities of the sugar. Müller and Hagen determine the sugar volumetrically by Knapp's method, the process being conducted in the following manner:—

* It is absolutely essential that the Fehling's solution used should remain perfectly clear when diluted with its own volume of water, and boiled for a few minutes. If prepared as directed, no difficulty will be experienced in this respect.

A standard solution is prepared by dissolving 10 grammes of pure dry mercuric cyanide in water, adding 100 c.c. of caustic soda solution of 1·145 sp. gravity, and diluting the liquid to 1000 c.c. 10 c.c. of this liquid are reduced by 0·025 grammes of diabetic sugar (dextrose). 10 c.c. of the standard solution are diluted with 20 to 30 c.c. of water, and the liquid heated to the point of boiling. The urine, previously diluted with water to five or ten times its volume, is then run in from a burette till the whole of the mercury is precipitated. When the precipitate has settled, a drop of the supernatant liquid, which has a more or less yellow colour, is transferred by a glass tube to a piece of *thin, pure white,* Swedish filter-paper. The paper is held over a bottle containing fuming hydrochloric acid, and then over a vessel containing strong solution of sulphuretted hydrogen. The slightest trace of mercury is shown by the production of a light-brown or yellow stain. It is desirable to compare a drop of the original liquid side by side which has been subjected to the treatment with the acid gases. By thus working, the slightest trace of mercury remaining in the liquid may be detected. Of course it is desirable to repeat the determination. The above method is available for the assay of diabetic urine containing as little as 0·1 per cent. of sugar, while Fehling's solution cannot be applied quantitatively when less than 0·5 per cent. of sugar is present, owing to the incomplete separation of the cuprous oxide in presence of certain obscure foreign matters contained in urine. Knapp's method has the advantage of being applicable in all cases, and the standard solution undergoes no change on keeping. Albumin should be removed before titration, by heating the urine to boiling, and filtering.

Bodies other than sugar, capable of reducing both Fehling's and Knapp's solutions, are sometimes present in urine, but their exact amount and nature are not known.

Determination of Glucose in Blood.—This question has been recently investigated by Dr Pavy,* who first mixes the liquid with an excess of solution of sodium sulphate, and then heats it to boiling to coagulate the albuminoids. The liquid is filtered and the sugar determined

* *Proc. Royal Society*, xxvi. pp. 314 and 346.

gravimetrically by Fehling's solution, as described on page 285. Dr Pavy has deduced some interesting facts from his experiments.

Glucosides.—The name glucoside is applied to numerous bodies possessing the common property of yielding glucose, $C_6H_{12}O_6$, as one of the products of their treatment with water and a dilute acid. Thus, salicin when boiled with dilute sulphuric acid yields dextro-glucose and the alcohol-like body saligenol or saligenin.

$$C_{13}H_{18}O_7 + H_2O = C_6H_{12}O_6 + C_7H_7O.OH.$$

A similar decomposition of the glucosides often occurs by the agency of certain peculiar ferments occurring in the plant together with the glucoside. These ferments have a very limited power of producing such decompositions, their influence being exerted only on a few glucosides of closely-related composition.

The nature of the glucoses obtained from the glucosides has been identified with sucro-dextrose in a few instances (see page 339), but in the majority of cases the exact nature of the resultant glucose is quite uncertain.

Some of the glucosides are of interest from a pharmaceutical and toxicological point of view, but none of them except tannin and the glucoside of mustard (see Vol. I. pp. 56 and 282) commonly require to be assayed, or are of sufficient importance to necessitate special description. Their analytical character have in most cases been but very imperfectly studied. From the alkaloids they may, as a rule, be separated by acidulating the aqueous liquid with sulphuric acid, and agitating with a mixture of chloroform and ether, which extracts the glucosides without affecting the sulphates of the majority of the alkaloids. The alkaloids which cannot thus be separated are usually weak bases. Their names are given on page 404, and other reactions by which the alkaloids are distinguished and separated from the glucosides will be found in the same section.

STARCH AND ITS ISOMERS.

In the vegetable kingdom, and to a minor extent in the animal kingdom, there exist a number of carbohydrates having in common a composition represented by the empirical formula $C_6H_{10}O_5$. These carbohydrates are non-volatile bodies, and, with perhaps one or two exceptions, are amorphous. They usually exert a marked rotatory action on a ray of polarised light. They are neutral in action, and form but few definite compounds or metallic derivatives. They are very numerous, and apparently capable of isomeric modification. Owing to their physical characters, and feebly-marked chemical affinities, it is often extremely difficult to obtain them in a state of purity.

None of the members of the group reduce Fehling's solution when boiled with it. By treatment with acids they yield reducing sugars among other products, and then reduce the cupric solution.

The members of the group are many of them of little practical interest, and their analytical reactions have been very incompletely studied. Hence, the more important members only are treated in the following sections. In the article on "Cellulose" will be found tables for the general proximate analysis of plant-products; and under the head of "Gums" a short description of pectinous matters.

CELLULOSE. $C_6H_{10}O_5$.

Cellulose constitutes the essential part of the solid framework or cellular tissue of plants, and hence is an especially characteristic product of the vegetable kingdom. The outer

coating of Ascidian animals is, however, identical with cellulose.

Cellulose occurs nearly pure in cotton, linen, and the pith of elder and other plants. Swedish filter-paper, linen rags, and cotton-wool are still purer forms of cellulose.

Cellulose is closely related to starch, and is most probably directly formed from it; but it is more stable than starch, and is not readily rendered soluble.

Cellulose is a white, tasteless, odourless, non-volatile body of about 1·45 specific gravity. It is insoluble in water and all ordinary menstrua, but can be dissolved by a solution of cuprammonium hydrate.* On treatment with this solvent, the cellulose becomes gelatinous, and on agitation gradually dissolves, forming a viscid solution which may be filtered after dilution with water. On neutralising the filtrate with hydrochloric acid the cellulose is separated in a flocculent state resembling hydrated alumina. When dried, it forms a brittle horn-like mass. Carbonic acid also precipitates the solution, as do sugar, salt, and even copious dilution with water.

According to Fremy three varieties of cellulose† exist, distinguished by their behaviour with the cupric solution; thus—

(*a*) CELLULOSE, constituting the greater part of cotton and the utricular tissue of certain fruits, is dissolved by the cupric reagent.

(*b*) PARACELLULOSE, forming the epidermis of leaves and the utricular tissue of certain roots, is not soluble in the cupric solution till after treatment with hot hydrochloric acid.

(*c*) METACELLULOSE, or f u n g i n, is found chiefly in agarics and lichens, and is not dissolved by the cupric reagent even after treatment with acid.

Cellulose is not altered by cold dilute alkaline solutions, but in concentrated caustic potash or soda it swells up and

* This reagent may be prepared by leaving copper-turnings partially immersed in ammonia, and with access of air. Or cupric hydrate may be precipitated from a cold solution of cupric sulphate by adding excess of caustic soda, and the well-washed precipitate dissolved in ammonia.

† All three varieties are soluble without coloration in cold sulphuric acid of 1·78 sp. gravity.

gradually dissolves, being apparently converted into dextrin and ultimately into sugars. Cellulose absorbs an appreciable amount of barium hydrate when immersed in dilute baryta water.

By heating to a high temperature with caustic potash cellulose yields methylic alcohol and potassium oxalate.

Cellulose undergoes gradual change by prolonged boiling with dilute acids, and is even affected by boiling water alone, especially if heated under pressure.

Cold concentrated hydrochloric or sulphuric acid dissolves cellulose, converting it first into a body which gives a blue colour with iodine, and swells up in water without dissolving; a dextrinoid substance is next formed, and if the liquid be then largely diluted and boiled, sugars are formed which reduce Fehling's solution. If cellulose be heated with concentrated sulphuric acid, charring at once occurs. By treating cellulose with cold sulphuric acid previously diluted with half its measure of water, it is converted into a substance which, after washing with cold water, is extraordinarily tough. This fact is utilised for the production of "parchment paper." Chloride of zinc may be substituted for the sulphuric acid.

When boiled with moderately concentrated nitric acid, cellulose yields much oxalic acid. By treatment with cold nitric acid, it is converted into nitro-substitution products of a composition dependent on the strength of the acid employed. These are described more in detail on page 365..

If cotton-wool or filter-paper be heated at 180° C. for several hours with about six or eight parts of acetic anhydride, it is entirely dissolved and converted into a triacetate, $C_6H_7(C_2H_3O)_3O_5$, which may be separated by pouring the syrup into water; it is a white powder, optically inactive, soluble in strong acetic or sulphuric acid, and very readily converted into cellulose and potassium acetate by boiling with dilute caustic potash.

Cellulose is not coloured by iodine solution alone, or at most only assumes a yellow or brownish colour, but in

presence of hydriodic acid, potassium or zinc iodide, zinc chloride, sulphuric or phosphoric acid, it is coloured blue by iodine. Concentrated sulphuric acid and zinc chloride especially favour the production of the blue colour. If cellulose be first treated with one of the above reagents, and then freed from it by washing, no blue colour is produced on adding solution of iodine.

Recognition of Vegetable Fibres.—As vegetable fibres, when thoroughly bleached, all consist of nearly pure cellulose, chemical tests are not available for distinguishing one kind from another; but owing to the impossibility of wholly removing the incrusting matter on the large scale, it is possible to distinguish between certain fibres, such as cotton and linen.

When flax fibre (linen) is immersed in a boiling solution of equal parts of caustic potash and water for about a minute, then removed and pressed between folds of filter paper, it assumes a dark yellow colour, whilst cotton when similarly treated either remains white or becomes a very bright yellow. The same solution of potash employed cold colours raw flax orange-yellow, whilst raw cotton becomes grey.

When flax or a tissue made from it is immersed in oil, and then strongly pressed to remove the excess of the liquid, it remains transparent, while cotton similarly treated becomes opaque.

Phormium tenax, or New Zealand flax, may be distinguished from ordinary flax or hemp by the red colour produced on immersing it in nitric acid of 1·32 sp. gravity, containing lower oxides of nitrogen. A reddish colour is also developed if New Zealand flax be immersed first in strong chlorine water and then in ammonia.

By far the best and most reliable means of differentiating vegetable fibres is to examine their structure with a microscopic power of 120 to 150 diameters.

The filaments of cotton appear under the microscope as transparent tubes about ·04 millimetres in diameter, flattened and twisted round their axis, and tapering off to a closed point at end. A section of the filament resembles somewhat a figure of 8, the tube, originally cylindrical, having collapsed most in the middle, forming semi-tubes on each side, which

give to the fibre when viewed in certain lights the appearance of a flat ribbon with a hem or border at each edge. The uniform transparency of the filament is impaired by small irregular figures, in all probability wrinkles or creases arising from the dessication of the tube. The twisted and corkscrew form of the dried filament of cotton distinguishes it from all other vegetable fibres, and is characteristic of the fully ripe and mature pod, M. Bauer having ascertained that the fibres of the unripe seed are simply untwisted cylindrical tubes, which never twist afterwards if separated from the plant; but when the seeds ripen, even before the capsule bursts, the cylindrical tubes collapse in the middle, and assume the form already described. This form and character the fibres always retain, undergoing no change through the various operations of spinning, weaving, bleaching, printing, and dyeing, nor in all the subsequent domestic processes of washing, &c., and even the reduction of the rags to pulp for the manufacture of paper effects no change in the structure of the fibres.

Linen, or flax fibre, appears under the microscope as hollow cylindrical tubes, open at both ends, and having a diameter of about ·02 of a millimetre. Their surface is smooth, the inner tube very narrow, and joints or septa appear at intervals, but they are not furnished with hairy appendices as is the case with hemp. The jointed structure of flax is only perceptible under a very excellent instrument, and with judicious management of the light.

Hemp fibre resembles that of flax, but has a mean diameter of about ·04 mm., and exhibits small hairy appendages at the joints.

With manilla the fibrous bundles are oval, nearly opaque, and surrounded by a considerable quantity of dried-up celluiar tissue composed of rectangular cells. The bundles are smooth, very few partly detached ultimate fibres are seen, and no spiral tissue.

Sizal forms oval fibrous bundles surrounded by cellular tissue; a few smooth ultimate fibres projecting from the bundles. Sizal is more translucent than manilla, and is characterised by the large quantity of spiral fibres mixed up in the bundles.

In machine-dressed New Zealand flax the bundles

are translucent and irregularly covered with tissue. Spiral fibres can be detected in the bundles, but less numerous than with sizal. The bundles are flat, and numerous ultimate fibres project from them. In Maori-prepared *Phormium* the bundles are almost wholly free from tissue, and there are no spiral fibres.

In examining fibres under the microscope the tissue should be cut up with sharp scissors, placed on a glass slide, moistened with water, and covered with a piece of thin glass.*

Analysis of Woody Tissues and Determination of Cellulose.—Cellulose is associated in woody tissues with ligneous, cuticular, and intercellular bodies. These have the following analytical characters:—

LIGNIN, VASCULOSE, or ligneous matter, cements the fibres and cells together, and constitutes the heavy part of woody tissue. Lignin contains more carbon than cellulose. Lignin is insoluble in cold sulphuric acid of 1·78 specific gravity, and in ammonio-cupric oxide solution. It is also undissolved by alkalies under ordinary conditions, but dissolves when heated with them under pressure. Treatment with dilute nitric acid, chlorine, or bromine readily converts it into bodies soluble in dilute alkalies, and partly even in water and alcohol.

The presence of lignin in vegetable tissues, such as hemp, flax, or paper, may be detected by moistening the substance with a half per cent. solution of phloroglucin, and then adding hydrochloric acid, when an intense red or violet coloration will be produced if lignin be present.

CUTOSE, or cuticular substance, constitutes cork and the fine transparent membrane covering the exposed parts of vegetables. It contains a high percentage of carbon, and yields suberic acid, $C_8H_{14}O_4$, on oxidation by nitric acid of 1·20 sp. gravity. Cutose is insoluble in sulphuric acid of 1·78 sp. gravity, and in the cupric solution which dissolves cellulose. On the other hand, it dissolves in hot dilute solution of sodium hydrate or carbonate.

PECTOSE occurs in the utricular tissues of fruits and roots.

* For the characters of vegetable fibres detailed in the text I am almost entirely indebted to Crookes's *Handbook of Dyeing and Calico-Printing*. Further information will be found in Bowman's *Structure of the Cotton-Fibre in its Relation to Technical Applications*.

It is insoluble in water, but is converted into soluble pectin (see page 380) by boiling with dilute hydrochloric acid. The solution obtained is precipitated by alcohol.

CALCIUM PECTATE forms part of the membrane which binds the cells together. On treatment with cold dilute hydrochloric acid, pectic acid is liberated, and this may be dissolved in dilute alkali and reprecipitated by an acid.*

MINERAL MATTERS are of course found in the ash left on igniting the tissue.

DETERMINATION OF CELLULOSE.—In consequence of its association with bodies of a closely allied nature, the accurate determination of cellulose is often a tedious operation, and some, at least, of the processes prescribed for the purpose yield arbitrary rather than accurate results.

From starch, cellulose is best separated by boiling the substance with water containing 1 per cent. by measure of sulphuric acid. The liquid is filtered when a drop taken out gives no coloration with iodine solution. In cases where the use of acid is objected to, the substance should be boiled with water, and the unfiltered liquid mixed with an equal measure of cold infusion of malt. The starch will be wholly dissolved by keeping the liquid at a temperature of 60° C. for a short time.

The separation of cellulose from sugar, dextrin, and

* The following table shows the general outline of the method of analysing the *insoluble* portion of woody tissues :—

<table>
<tr><td colspan="4">Treat the substance with cold, very dilute hydrochloric acid. Wash and treat the residue with cold dilute caustic soda solution.</td></tr>
<tr><td rowspan="4">Solution contains alkaline pectate, from which insoluble pectic acid may be precipitated by adding HCl.</td><td colspan="3">Residue.—Boil with dilute hydrochloric acid.</td></tr>
<tr><td rowspan="3">Solution.–Precipitate pectin by addition of alcohol.</td><td colspan="2">Residue.—Treat with cold sulphuric acid of 1·78 specific gravity.</td></tr>
<tr><td rowspan="2">Solution contains products formed from the cellulose.</td><td colspan="2">Residue.—Boil with dilute caustic soda solution.</td></tr>
<tr><td>Solution contains cutose.</td><td>Residue consists of lignin, soluble in alkali after treatment with dilute nitric acid.</td></tr>
</table>

other substances soluble in water presents no difficulty. Albuminoids may be separated by treatment with warm water containing 1 per cent. of caustic alkali. They may be determined by igniting the substance with soda-lime.

For the determination of cellulose in wood, vegetable fibres, and substances to be used for the manufacture of paper, Müller recommends the following process:—5 grammes of the finely-divided substance are boiled four or five times with water, using 100 c.c. each time. The residue is dried at 100° C., weighed, and exhausted with a mixture of equal measures of benzene and strong alcohol, to remove fat, wax, resin, &c. The residue is again dried, and boiled several times with water, to every 100 c.c. of which 1 c.c. of strong ammonia has been added. This treatment removes colouring matter and pectous substances. The residue is further bruised in a mortar if necessary, and is then treated in a closed bottle with 250 c.c. of water, and 20 c.c. of bromine water containing 4 c.c. of bromine to the litre. In the case of the purer bark-fibres, such as flax and hemp, the yellow colour of the liquid only slowly disappears, but with straw and woods decolorisation occurs in a few minutes. When this takes place, more bromine water is added, and this is repeated till the yellow colour remains and bromine can be detected in the liquid after twelve hours. The liquid is then filtered, and the residue washed with water and heated to boiling with a litre of water containing 5 c.c. of strong ammonia. The liquid and tissue are usually coloured brown by this treatment. The undissolved matter is filtered off, washed, and again treated with bromine water. When the action seems complete, the residue is again heated with ammoniacal water. This second treatment is sufficient with the purer fibres, but the operation must be repeated as often as the residue imparts a brownish tint to the alkaline liquid. The cellulose is thus obtained as a pure white body. It is washed with water, and then with boiling alcohol, after which treatment it may be dried at 100° C. and weighed.

Bevan and Cross* substitute a treatment with chlorine gas for the repeated digestion with dilute bromine water prescribed in the foregoing process. A single repetition of the

* *Chem. News*, xlii. 77.

treatment is then always sufficient, and the results obtained are concordant with those given by the bromine process. Bevan and Cross also find that by boiling the chlorinated fibre for a few minutes in a 5 per cent. solution of sodium sulphite, and then in a 1 per cent. solution of caustic potash, pure cellulose is at once obtained,—the results by this method being 5 per cent. higher than those yielded by Müller's process.

Nitro-cellulose.—Nitric acid of 1·2 specific gravity has little or no action on cellulose in the cold, but when heated converts it into oxalic acid, $C_2H_2O_4$, and other products.

With cold nitric acid of greater strength cellulose is converted into various nitro-substitution products, the constitution of which depends on the strength of the acid employed.

Thus, with acid of moderate strength mononitro-cellulose, $C_6H_9(NO_2)O_5$, is the chief product. With a mixture of equal volumes of strong sulphuric acid (1·85 sp. gravity) and nitric acid of 1·42 sp. gravity, dinitro-cellulose $C_6H_8(NO_2)_2O_5$, is obtained. This body is the pyro-xylin of the Pharmacopœia, and differs from the mono- and the trinitro-derivatives by being soluble in a mixture of three measures of ether and one of rectified spirit, employed in the proportion of 48 c.c. to 1 gramme of pyro-xylin. The solution thus obtained is known as collodion (*Collodium*, B.P.), and is a colourless liquid which, on exposure to the air, rapidly evaporates, leaving a transparent film of dinitro-cellulose, insoluble in water or rectified spirit.

Pyroxylin is also soluble in acetone and in glacial acetic acid, and is precipitated in very voluminous flocks on diluting either of these solutions with water.

TRINITRO-CELLULOSE, $C_6H_7(NO_2)_3O_5$,* is obtained by treating cellulose in the cold with the strongest nitric acid (1·52 sp. gravity) mixed with two or three times its bulk of concentrated sulphuric acid. The product is thrown into water and washed with scrupulous care. Trinitro-cellulose retains

* Curiously discrepant statements are made as to the action of solvents in the nitro-celluloses. Several chemists, in addition, deny that any more highly nitrated product can be obtained than corresponds to the formula $C_{12}H_{15}(NO_2)_5O_{10}$, but Abel has shown that the preparations to which this formula was ascribed had been imperfectly purified. On the whole, the balance of evidence seems in favour of the formula given in the text.

the form and appearance of the original cellulose from which it is prepared, but is found to have lost the property of depolarising light. It is somewhat hygroscopic, and becomes highly electrical when rubbed or pulled out briskly. Trinitro-cellulose is insoluble in water, alcohol, ether, and all mixtures of alcohol with ether. It is dissolved, however, by a mixture of ether, ammonia, and potash, and, according to some, by methyl or ethyl acetate (acetic ether). In dilute acids it is insolnble.

Trinitro-cellulose, if dry, inflames when a light is applied, and burns very rapidly with a large, luminous, and wholly smokeless flame. When subjected to strong percussion it detonates with extreme violence, whether it be wet or dry.

Gun-cotton, when carefully made, consists almost wholly of trinitro-cellulose. It may be purified from foreign matters and lower nitro-derivatives by treatment with ether-alcohol (3 to 1).

The various nitro-celluloses are soluble in strong caustic soda, undergoing partial saponification with formation of cellulose and sodium nitrate. By the action of reducing agents, such as potassium sulphydrate or ferrous chloride, they are reconverted into cellulose, even by digestion at the ordinary temperature. By boiling with a solution of stannous oxide in caustic potash, gun-cotton is dissolved, with conversion into cellulose which is precipitated in flocks on neutralising the solution.

THE ASSAY OF GUN-COTTON is sometimes of importance with a view of judging of its tendency to decompose. Pure trinitro-cellulose will keep indefinitely, but the presence of free acid, dinitro-cellulose, or fatty or waxy matters renders it more or less unstable, and, therefore, unsafe.

Free acid may be detected by treating 20 grammes' weight of the gun-cotton with 50 c.c. of cold water. After twelve hours the water may be pressed out, filtered, and tested with litmus paper. If any trace of acidity be detected 25 c.c. of the liquid may then be titrated with decinormal caustic alkali. The remainder of the liquid may be employed to ascertain the nature of the free acid. If sulphuric acid, on evaporating the liquid to dryness at 100° C. a small frag-

ment of immersed filter paper will be charred. If nitric acid be the free acid it may be detected by mixing the liquid with an equal bulk of pure sulphuric acid, cooling thoroughly, and placing a crystal of ferrous sulphate in the mixture. A brown tint will be developed in the neighbourhood of the crystal, if any nitric acid or nitrates be present.

Dinitro-cellulose and foreign nitro-compounds may be detected by treating 5 grammes of the sample previously dried at 100° C. with 100 c.c. of a mixture of three parts of ether and one of rectified spirit. The mixture is shaken frequently during twelve hours, and is then rapidly filtered through loosely-packed glass-wool, the filtrate evaporated at a gentle heat, and the residue weighed.

Unaltered cellulose may be estimated by treating the gun-cotton left undissolved by the ether-alcohol with acetic ether, which dissolves the trinitro-cellulose and leaves the unchanged cotton. An alternative plan is to prepare a solution of sodium stannite by adding caustic soda to a solution of stannous chloride till the precipitate at first formed is just redissolved. The liquid thus obtained, when boiled with gun-cotton, dissolves the nitro-compounds, without affecting the unchanged cellulose.

The nitric peroxide, NO_2, contained in samples of nitro-cellulose may be determined by reducing the substance with a ferrous salt, and measuring the nitric oxide, NO, evolved.* A flask of 250 c.c. capacity is fitted with a caoutchouc stopper, through which pass two tubes, one leading to a pneumatic trough, while the other is a funnel-tube drawn out to a point and provided with a tap. The portion of this tube below the tap is filled with distilled water, while the funnel itself contains about 50 c.c. of a mixture of hydrochloric and sulphuric acids. 0·5 gramme of the sample is placed in the flask, together with about 5 grammes of ammonio-ferrous sulphate and 50 c.c. of water. The flask is then closed and

* It is probable that the nitric peroxide in gun-cotton might be determined by treating the sample with sulphuric acid and mercury, as in Crum's process of estimating nitrates in water. If conducted in a nitrometer, and the volume of gas compared with that yielded by a standard sample or nitre solution, as suggested by me (*Analyst*, vol. v.), the process would be very simple.

the liquid boiled till the air is expelled. The acids in the funnel are then allowed to run slowly into the flask, when the boiling is continued as long as gas is evolved. The nitric oxide gas liberated is collected over soda solution, its volume measured, corrected for pressure and temperature, and calculated to weight.*

The number of cubic centimetres of gas at 0° C. and 760 mm. pressure multiplied by 0·62693, gives the weight of nitrogen in milligrammes, which, multiplied by 1·72649, gives the equivalent weight of NO_2.

STARCH. $nC_6H_{10}O_5$.†

French—Fécule. *German*—Stärke.

Starch is found in cells in every part of plants, except in the top of the bud and the extremity of the rootlets. Although an especially characteristic product of the vegetable kingdom, starch-like substances are also met with in certain parts of animals.

Pure starch is a white, glistening, tasteless and odourless powder. It is fixed in the air, and is incapable of crystallisation or volatilisation. Ordinary air-dried starch contains about 18 per cent. of water, a proportion corresponding to the formula $C_6H_{10}O_5 + 2H_2O$.† When dried in vacuo the product contains $C_6H_{10}O_5 + H_2O$, and by heating to 100° or 110° C. in a current of dry air anhydrous starch is obtained as a highly hygroscopic powder.

Anhydrous starch may be heated to 160° C. without change, but by exposure to a temperature of 200° for an hour it is rendered completely soluble in water, being converted into dextrin and other products (see page 376). Commercial starch undergoes a similar change at a lower temperature.

Starch is not dissolved without change by any known liquid. It is quite unacted on by cold water, alcohol, or

* Champion and Pellet, *Comp. Rend.* lxxxiii. 707.

† Sachsse regards ordinary starch as a hydrate of the composition $C_{36}H_{60}O_{30}H_2O + 12Aq$. From the experiments of Brown and Heron this formula should probably be doubled.

ether. When heated with water to a temperature varying from 50 to 90° C., according to the origin of the starch, it swells up and forms a paste. When the mixture is largely diluted with hot water almost perfect solution seems to occur, though it is doubtful how far this is really the case. The solution is strongly dextro-rotatory ($S_j = +216°$), and contains soluble starch.

When boiled with dilute acids starch is readily converted into a mixture of dextrin and maltose, prolonged treatment resulting in further hydrolysis and formation of dextrose (see page 329). A solution of starch undergoes a similar change when treated with malt extract, even in the cold, but solid starch is unaffected by malt extract.

By treatment with cold nitric acid starch yields nitro-derivatives, but on heating with the reagent it is converted into oxalic acid and other products.

When treated with a solution of caustic potash or soda containing 1½ to 2 per cent. of the alkali, starch swells up enormously and forms a tenacious paste which is soluble in water, the solution yielding, with cupric sulphate, a blue precipitate which does not blacken on boiling, and is soluble in pure water.

Ammonia does not gelatinise starch.

SOLUBLE STARCH is produced by boiling starch with water. A solution is thus obtained which may be rendered quite clear by addition of a little caustic alkali. It is strongly dextro-rotatory. Starch solution is one of the most perfect colloids known, and has a very high viscosity.

Soluble starch is not only obtained by boiling starch with water, but also by heating it to 100° C. with glacial acetic acid, or to 190° with glycerol. It is the first product of the action of dilute acids or malt-extract on starch. It is uncertain whether it is chemically or only mechanically distinct from the insoluble form of starch. Starch solution is perfectly neutral to litmus, but yields sparingly soluble precipitates with lime and baryta water. With an ammoniacal solution of lead acetate it yields a precipitate having a composition represented approximately by the formula $C_{12}H_{18}Pb_2''O_{11}$. Tannin gives a white precipitate with starch

solution, which disappears on warming, and is re-formed as the liquid cools. Soluble starch is completely precipitated by adding alcohol to its aqueous solution. On exposure to the air solution of starch gradually decomposes with formation of lactic acid.

The most characteristic reaction of starch solution is the violet or indigo-blue coloration which it gives with iodine. The coloured body does not appear to be a definite compound of starch with iodine, and hence is best called iodised starch. The best form in which to employ the reagent is as a very dilute solution of iodine in iodide of potassium. The starch solution should be perfectly cold. On heating the liquid it is decolorised, but on cooling the blue colour is restored, though not with the same intensity as before. In employing the reaction as a test for starch it is necessary to remember that it is only produced by *free* iodine. Hence any free alkali should be neutralised by cautious addition of cold dilute acid, and any reducing or oxidising agent got rid of if possible. The best way of testing for starch is to add the iodine solution gradually to the slightly acid liquid until either a blue colour appears or the liquid remains permanently coloured yellow by the free iodine. If the latter effect is produced and yet no blue coloration is obtained no starch can be present.

The only organic body liable to interfere when the test is performed in the foregoing manner is erythro-dextrin, which itself produces an intense reddish brown coloration with iodine, which is apt to mask a feeble starch-reaction. The affinity of iodine for starch is, however, greater than its affinity for erythro-dextrin, and hence if a very little iodine solution be employed, the blue colour due to starch will be alone developed, the brown coloration becoming apparent on a further addition of the reagent. By cautiously adding very dilute ammonia, or gradually heating the liquid, the brown colour can be destroyed while the blue remains.*

* Neither the brown colour of a solution of iodised erythro-dextrin nor the blue of iodised starch shows any absorption bands when examined by the spectroscope. According to Bondonneau, iodised starch has a definite composition represented by the formula $(C_6H_{10}O_5)I_5$.

Structure of Starch Corpuscles.—Starch occurs in plants in the form of minute granules which generally possess a concentrically stratified structure, similar to that of an onion. These granules consist chiefly of a body called granulose, together with a closely allied substance known as starch-cellulose, and water and traces of mineral matter. Starch-cellulose occurs in largest proportion in the outer layers of the granule, and probably constitutes the whole of the external coating. Owing to this protective coating, starch granules are wholly unacted on by cold water, as the internal granulose, though slightly soluble, is highly colloidal. When the outer layer of the granule is ruptured, as by grinding the starch with sand, water acts readily on it, and the liquid gives an intense blue colour with starch. By treating starch paste with malt extract, the insoluble starch-cellulose may be obtained pure, and then is found to give only a dirty yellow colour with iodine. By boiling with water, starch-cellulose is mostly converted into soluble starch, leaving, however, a portion which obstinately resists the action of water, but is readily dissolved by dilute alkali. By repeated alternate treatment of potato-starch in the cold with very dilute alkali and acid, the cellulose may be removed, when the residue dissolves in hot water to form a perfectly clear solution. Solid starch corpuscles, when treated with iodine solution, are coloured intensely blue, the reagent readily penetrating the coating of cellulose and thus reaching the granulose.

Young small corpuscles of starch appears to be invariably spherical, but as they grow older they may become lenticular, ovoid, or polygonal. The shape and size of the starch corpuscles are often highly characteristic of the plant by which they were produced, and this fact is frequently taken advantage of for identifying the presence of starch from particular sources.

When a sample is to be examined under the microscope for the identification of its starch, a minute quantity should be placed on a glass slide with the point of a knife. If in a powdered state, or readily reducible to powder, a preferable plan is to stir the sample with a dry glass rod, and tap the rod on the glass slide. A drop of distilled water should then be added, and if the unpowdered structure be employed it should

be broken up by careful mashing with the point of a knife. A glass cover is then put on, and any superfluous moisture removed by blotting paper. The specimen is now ready for observation. Somewhat oblique light should always be employed, and the power should vary from $\frac{1}{2}$ to $\frac{1}{5}$ inch, using a B eye-piece furnished with a micrometer-scale, the value of the divisions of which have been previously ascertained. Too high a magnifying power should be avoided, especially in a first examination.

The points to be observed in the microscopic observation of starches are—(*a*) The shape and size of the granules. (*b*) The position and character of the *hilum*. (*c*) The concentric markings. The two first observations are tolerably simple, but the examination for rings requires care, the markings being rarely visible without very cautious manipulation of the illumination and movement of the fine-adjustment, and then only in a few granules at the same time. Natal arrowroot and turmeric starches are almost the only two which show well-developed rings on nearly every granule. Wheat, on the other hand, shows no rings, even in the best light. When the hilum is situated near the centre of the granule, the rings are usually complete, but when the hilum is near one end of the granule only a segment of each ring is visible.

Although the size of starch-granules is a highly important character, it must be remembered that great variation occurs between individual granules, and that it is only the general or average size of the corpuscles which is usually recorded. Variation in size of the starch-granules is very marked in the case of the potato, in which the corpuscles range from 0·0025 of an inch in length down to less than 0·0002.

Examination with polarised light, either with or without the use of a selenite plate, is a valuable auxiliary means of identifying starches, but the statements made in many books, as the black cross being observable in the case of certain starches only, must be considered as merely applicable to the precise conditions under which the observations referred to were made. With proper manipulation, all starches appear to show the black cross, and an ignorance of this fact has led many into error. For observation of starches by polarised light it is

often desirable to employ a highly-refracting mounting medium, and for such purposes water may be advantageously replaced by diluted glycerin, glycerin jelly, canada balsam, oil of anise, carbon disulphide, &c.

Much has been written on the microscopic appearance of starches, and some observers profess to be able to distinguish starch of almost every origin. To the observer who has not made a special study of the morphology of starches, these distinctions are in many cases wholly unrecognisable, and as the minute points of difference are almost incapable either of description or delineation, the only safe method of discriminating starches is by a careful comparison of the sample with specimens of known origin and purity, making the observations under exactly similar conditions as to illumination, magnifying power, and mounting medium. These standard specimens should not be permanently mounted, but kept in a dry state, and a minute quantity mixed with water or other medium when required for use. As a rule it is quite unnecessary to prepare the pure starches for comparison, a direct employment of the air-dried tissue answering every purpose.

A very complete tabular scheme for the recognition of starches by the microscope has been devised by Dr Muter. Of course, it in no way enables the observer to dispense with the requisite experience in observation, but it much facilitates the recognition by drawing the attention to the more characteristic features of the starches.*

Detection and Determination of Starch.—For the detection of starch existing in the solid state, no other means are so good as the microscopic recognition of the corpuscles,

* The general scheme of this work, combined with the limited space at disposal, prevents a reproduction of Dr Muter's tables. They were originally published in the *Analyst* (vol. i. p. 172), and are reprinted, with some useful practical observations, in Muter's *Organic Materia Medica* (2d edition). The best plates showing the microscopic appearance of starches are those in the original edition of Pareira's *Materia Medica*. They have been recently republished in Attfield's *Chemistry* (9th edition). Hassall's work on *Food and its Adulterations* contains numerous woodcuts showing the microscopic character of starches.

Valuable articles on the identification of starches has been published by H. Pocklington (*Pharm. Journ.* 3d series, vol. iii. p. 663; vol. iv. p. 352; vol. vi. pp. 501, 662, 741), and J. W. Tripe (*Analyst*, vol. iv. p. 221).

the origin of which may usually be identified in the manner already described. The microscopic examination may be advantageously supplemented by adding a drop of iodine solution to the slide, when each of the true starch granules will assume a blue colour, which renders their recognition easy. In some cases, as when roasted coffee is mixed with beans or acorns, the microscopic detection of the starch becomes difficult, but may still be effected in the following manner. The coffee is boiled with water for a few minutes, and the solution is decanted or filtered from the insoluble matter. The liquid is next thoroughly cooled, and cold dilute sulphuric acid is added. A solution of potassium permanganate is then gradually added till the brown colour is nearly or entirely destroyed, when the decolorised liquid is tested with iodine. A blue colour is obtainable in this way with coffee containing only 1 per cent. of roasted acorns.

Sometimes it is desirable to remove the colouring matter from the solid substance before examining it for starch. If cold water fail to effect this, alcohol should be tried, and subsequently other solvents. The cases are rare, however, in which the starch cannot be observed microscopically after successive treatment of the substance with cold water and alcohol.

In solution, the iodine reaction is the only satisfactory means of recognising starch. The best mode of operating has been already described (see page 370).

The determination of starch is effected in different ways according to the nature of the substance in which it occurs. In wheat-flour a convenient plan is to place a weighed quantity of the sample in a sieve, and allow a stream of water to trickle over it, kneading well all the time. When the water runs away clear, it is allowed to stand, and, when the starch has all settled out, the water is poured off and the deposited starch collected, dried at 110°, and weighed.

In plant-products, such as wheaten-flour, oat-meal, cocoa, &c., the determination of starch may be effected as described on page 384. Methods based on the conversion of the starch into dextrose by boiling with dilute acid are not very satisfactory, owing to the difficulty of effecting the transformation perfectly. The change to dextrin and maltose is easily made,

but these intermediate products undergo further change but very slowly, and no ready means exist of ascertaining the completion of the reaction.

When starch only is to be determined in plant-products the method described on page 384 may be simplified as follows:— Any fat and essential oil having been removed by treatment with ether, the substance is treated with a saturated solution of salicylic acid in cold water. This will dissolve alkaline salts, sugar, dextrin, &c. The liquid is filtered, and the residue washed with decinormal caustic soda (4 grammes NaHO per litre) to remove salicylic acid and albuminoids. The residue is rinsed off the filter with warm water, and treated with a known measure of recently-prepared and filtered cold infusion of malt, of which the specific gravity has been previously ascertained. The mixture is kept at a temperature of about 60° C., with occasional stirring, until a drop taken out with a glass rod and added to a drop of diluted iodine solution on a porcelain plate shows no blue or brown coloration. The solution is then filtered, made up to a definite volume, and its specific gravity accurately ascertained. From the excess of the density over water is subtracted the density due to the infusion of malt used, allowance being made for the increased volume of the liquid, when the difference represents the density due to the starch dissolved, and this number divided by 3·99 ($=3{\cdot}85 \times 1{\cdot}037$) gives the number of grammes of starch in each 100 c.c. of the solution.*

For technical purposes it is sometimes desired to determine the proportion of starch existing in potatoes. This can be done with approximate accuracy by ascertaining the specific gravity of the tuber. The unpeeled potatoes, freed from dirt,

* Thus, suppose 50 grammes of the sample be taken, and, after treatment with ether, and salicylic acid and soda solutions in the manner described, the residue be treated with 200 c.c. of water and 50 c.c. of infusion of malt of 1060 sp. gravity; the liquid being subsequently made up to 300 c.c. and found to have a density of 1068. Then, the correction due to the malt-extract will be $\frac{(1060-1000)\times 50}{300} = 10$; this, subtracted from the difference between the density of the solution and that of water ($1068-1000=68$), leaves 58 as the excess-density caused by the solution of the starch of the sample; and this figure, divided by 3·99, gives 14·535 grammes for 100 c.c., which is 43·605 grammes of starch in the 50 grammes taken, or 87·31 per cent. of starch in the sample.

are placed in a solution of salt, which is then diluted with water till some of the individual tubers sink, while others just float. The density of the saline solution, as ascertained by a hydrometer, is then equal to the average specific gravity of the potatoes. A more accurate method consists in taking 5 kilogrammes of the potatoes, and then weighing in water. The weight in water divided into the original weight in air gives the specific gravity. Tables have been compiled for ascertaining the percentage of starch from the specific gravity of the potatoes. The most complete table is that of Heidepriem,* for which may be substituted the following formulæ, in which W is the weight of 5 kilogrammes of potatoes immersed in water.

$(W-285)\cdot052+7\cdot13=$ percentage of starch; and
$(W-285)\cdot052+14\cdot35=$ percentage of solid matter.

DEXTRIN.

Amylin. $C_6H_{10}O_5$.

Dextrin is a product obtained by treating starch or amylaceous bodies in certain ways. The following modes of treatment cause a formation of dextrin:—

(*a*) By heating starch or flour to a temperature varying from 110° to 150° C., till it acquires a yellow or brownish colour. The change is greatly facilitated by moistening the starch with dilute nitric acid, and then slowly drying the paste and heating it for some time to about 200° C.

(*b*) By boiling starch with dilute sulphuric acid till the cooled liquid no longer gives any coloration with solution of iodine.

(*c*) By treating gelatinised starch with warm water and a small quantity of yeast or malt-extract.

Process *a* is largely employed for the manufacture of solid dextrin, which is known in commerce by the name of British gum, gommeline, starch gum, &c. Processes *b* or *c* result in a simultaneous formation of maltose, as described on page 328; *b* is used for the preparation of

* The table from which I have deduced the formulæ in the text is printed in full in the *Journ. Chem. Soc.* vol. xxxii. p. 234, and in *Watts' Dictionary*, vol. viii. part 2, p. 1670.

commercial glucose, and *c* is the reaction which takes place in mashing malt for the manufacture of beer.

Several, and not impossibly many, varieties of dextrin exist, all being apparently formed by the breaking up of the highly complex starch molecule by treatment with dilute acids or ferments. There is no known method of distinguishing the different varieties with certainty, except that one kind, or possibly class, of dextrin gives a reddish-brown colour with solution of iodine, while the other kind or class produces no coloration. The erythro-dextrin, or the kind giving the brown colour with iodine, is an intermediate product of the formation of achro-dextrin from starch.

The best method of applying the iodine reaction as a test for erythro-dextrin is to divide a very weak solution of iodine in iodide of potassium into two parts, and place the slightly yellow liquid in adjacent test tubes or glass cylinders. On then adding the solution to be tested to one, and an equal measure of water to the other, any brownish coloration will be readily observed. In presence of starch, the blue colour is apt to obscure the brown tint produced by the erythro-dextrin. This may be avoided to some extent by employing the iodine solution somewhat in excess, so as to get a full development of the brown colour.

Commercial dextrin is a white, yellowish, or brownish amorphous solid. It is tasteless or slightly sweet, odourless, and non-volatile. Dextrin is very deliquescent, and dissolves in an equal weight of cold water to form a syrupy liquid which is miscible with 1½ measures of proof spirit. By strong spirit, if used in sufficient quantity, dextrin is completely separated from its aqueous solutions.

Cold concentrated sulphuric acid dissolves dry dextrin without colour, but charring takes place on warming. By boiling with dilute acids, dextrin yields maltose and ultimately dextrose (see page 349). Hot nitric acid of 1·35 sp. gravity converts dextrin into oxalic acid, whereas the natural gums yield mucic acid under similar conditions.

Dextrin is distinguished from starch by its solubility in cold water; from soluble starch by yielding no blue colour with iodine when tested as described on page 370,

and no precipitate with baryta water; from maltose and dextrose by not reducing Fehling's solution; from starch, soluble starch, gelatin, and egg-albumen by not yielding a precipitate with tannin; from albumen by not being coagulated by heat or mineral acids.

Dextrin is separated from starch and cellulose by solution in cold water; coagulable albuminoids may then be separated by raising the faintly acid solution to boiling. An ammoniacal solution of acetate of lead added to the cold and dilute liquid will then precipitate the dextrin, leaving the sugar in solution. The precipitate may be dried at 100° C., and has the formula, $PbO,C_6H_{10}O_5$. A less accurate method consists in precipitating the dextrin by means of a large proportion of alcohol, washing the precipitate with rectified spirit, and drying it at 110° C. After weighing, the dextrin should be ignited, and the resultant ash deducted from the total weight obtained.

The proportion of dextrin present in a solution also containing maltose and dextrose may be determined by observing the rotatory action of the liquid, together with its specific gravity and reducing action on Fehling's solution. The method is described on page 346.

COMMERCIAL DEXTRIN often contains unaltered starch, which may be recognised by the microscope and its insolubility in cold water. Soluble starch, detected by the blue colour produced by iodine, is often present, and for some purposes as much as 15 per cent. is unobjectionable. Reducing sugars (maltose) are nearly always present, and may be detected and estimated as described on page 346.

Caramel is the cause of the brownish colour of samples of dextrin.

Dextrin syrups are largely employed by confectioners. They may be examined in the same manner as glucose (page 344).

GUMS.

French—Gommes. *German*—Gommi.

Gums are a peculiar class of bodies occurring in the juices of plants. They are perfectly non-volatile, have little or no taste, are uncrystallisable, and eminently colloidal. These

properties render their purification very difficult, and hence but little is known of their chemical relationships. They appear, however, all to belong to the class of carbohydrates; that is, they all contain 6, or a multiple of 6, atoms of carbon, associated with hydrogen and oxygen in the proportion in which these elements exist in water.

The analytical characters of the gums as a class are indicated by the following facts, which are also applied to their separation from similar bodies.

Gums are either soluble in, or swell up in contact with cold water, a character which distinguishes them from starch, cellulose, and resins. They differ from the sugars by being incapable of fermentation by yeast, and from the sugars and resins by their insolubility in alcohol. From dextrin the gums soluble in water are distinguished by the lævo-rotatory power of their solutions, and by yielding mucic acid by treatment with moderately concentrated nitric acid.* From erythro-dextrin and starch the gums differ by giving no colour with solution of iodine, and from albuminoids they are distinguished by not yielding ammonia when ignited with soda-lime.

The gums having been very imperfectly studied, it is impossible to arrange them with any degree of scientific accuracy. They may, however, be conveniently classified according to their behaviour when treated with cold water and dilute acids. Thus the gums of which gum arabic is the type are dissolved by cold water, and are not readily precipitated by acids. Pectin forms a jelly when its aqueous solution is faintly acidified, while gum tragacanth merely swells up when treated with cold water, without undergoing notable solution.

The following table shows the leading properties of the principal members of the family of gums. Gum arabic and gum tragacanth are described more fully on pages 381 and 382.

* According to Nägeli and Cramer, quince-mucilage yields no mucic acid by treatment with nitric acid. Mucic acid, $C_6H_{10}O_8$, is a crystalline body very sparingly soluble in cold water or alcohol, and hence it separates as a sandy crystalline powder on diluting and cooling the liquid obtained by boiling the gum with nitric acid of 1·35 sp. gravity. Mucic acid gives a crimson coloration when treated with concentrated sulphuric acid.

Table showing the Leading Properties of Gums.

Name.	Chief Source or Mode of Formation.	Characteristic Properties.
Arabin . . .	Gum arabic, and the soluble portion of other gums.	Formula doubtful. *Lævo*-rotatory. (See also page 381.)
Metarabin . } Pararabin . }	Roots of carrot, beet, &c.	Insoluble in water. Metarabin is converted into arabin by treatment with dilute *alkali*. Pararabin undergoes a similar change by treatment with *acids*.
Cerasin . . .	The insoluble part of cherry-tree gum, peach gum, &c.	Said to be metagummate of calcium. By long-continued boiling with water it yields arabin.
Pectin . . .	By the action of a natural ferment on pectose, an insoluble body existing in unripe fruits. Exists ready-formed in ripe fruits, and very largely in Irish moss.	Optically inactive. Soluble in water, the solution gelatinising on adding either acid or alkali. Also precipitated by alcohol, but not by neutral lead acetate till after boiling the solution, by which parapectin is formed. By boiling with acid, forms metapectin, which is acid to litmus and precipitated by barium chloride. By treatment with bases all varieties of pectin yield pectates, which, on addition of hydrochloric acid, give insoluble pectic acid.
Bassorin . . . Tragacanthin . .	Gum bassora, and Gum tragacanth.	Insoluble in cold water, but swells up. By prolonged action of boiling water, yields pectin. By boiling with very dilute hydrochloric acid, yields pectic acid, insoluble in cold water.
Vegetable mucilage	Occurs largely in linseed, marsh-mallow root, quince seed, elm bark, &c.	Yield a dextro-rotatory reducing sugar and a dextrinoid body by boiling with dilute acids. Very little understood.

Gum Arabic.—Gum Acacia.

Gum arabic is the dried exudation from the bark of various species of *Acaciæ*. The finest kind is "picked Turkey gum," which occurs in commerce in lumps of various sizes, colourless, and full of minute cracks. Gum Senegal forms yellowish lumps, not having the minute cracks of the better variety. It is less readily soluble than true gum arabic, and its solution soon becomes very dark in colour.

Gum arabic consists essentially of the calcium salt of arabin or arabic acid, which may be obtained pure by dialysing a solution of the gum previously acidulated with hydrochloric acid. The colloid liquid thus obtained is *lævo*-rotatory, and is not precipitated by pure alcohol, but is thrown down if a trace of any acid or salt be present. After being evaporated to dryness and heated to 100° C., the arabin does not re-dissolve, even in hot water, but swells up into a gelatinous mass, which gradually dissolves on treatment with soda, or lime or baryta water, yielding a liquid undistinguishable from that of ordinary gum arabic.

Gum arabic, when dried at 100° C., has a density of 1·525. Its aqueous solutions have the density common to other carbohydrates (see page 296). It is slightly soluble in dilute spirit, but quite insoluble in liquids containing over 60 per cent. of alcohol, and hence is precipitated from its aqueous solution by addition of much alcohol.

Gum arabic, in aqueous solution, is not precipitated by neutral lead acetate, but with the basic acetate it forms a white jelly. Its solution is also precipitated by potassic silicate, mercuric chloride, ammonium oxalate, and borax.

Assay of Gum Arabic.—Gum arabic should not contain more than about 4 per cent. of ash. It should be soluble almost without residue in cold water. The solution should be free from starch and dextrin, as indicated by the negative reaction with iodine solution. It should not reduce Fehling's solution when heated to boiling with it, any red precipitate being due to the presence of a reducing sugar, probably introduced as an impurity in an admixture of dextrin.

The inferior kinds of gum are largely employed as thicken-

ing agents in calico-printing. Good gum neither tarnishes nor alters delicate colours, and does not weaken the mordants. The action of gums on delicate colours may be ascertained by printing a solution of the sample mixed with cochineal-pink or fuchsine upon pure wool; the fabric is then steamed and washed, when, if the gum be pure, there will be no trace of yellowness apparent. Too great an acidity of the gum gives it a solvent action on mordants, and hence renders it unsuitable for use.

The relative viscosity of samples of gum is an important character in judging of their quality. This may be tested by making solutions of 10 grammes of each sample in a little warm water, diluting the liquids to 100 c.c. and ascertaining the rate at which the solutions flow from a glass tube drawn out to a fine orifice. The apparatus described on page 142 may be employed for the purpose; a recently prepared solution of gum of the best quality being used as a standard.

Gum Tragacanth is a white or yellowish substance which swells up in water, but is only very slightly soluble. According to Giraud it usually contains about 60 per cent. of a pectinous body which yields pectic acid by boiling with water containing 1 per cent. of hydrochloric acid; from 8 to 10 per cent. of soluble gum, probably arabin; 5 to 6 per cent. of starch and cellulose; 3 per cent. of ash; 20 per cent. of water; and traces of nitrogenous bodies.

Before being used for calico-printing, gum tragacanth is swelled by soaking in cold water for twenty-four hours, and afterwards boiled with water for six hours, when a thick homogeneous solution results, which, however, has but little cohesive power. The comparative viscosity of the liquid can be ascertained as described above.

PROXIMATE ANALYSIS OF PLANTS.

The quantitative separation, and even the qualitative detection, of the various constituents of plants is often attended with great difficulty. Owing to the immense variety of bodies

met with in the vegetable kingdom, it is impossible to prescribe any detailed method which shall be suitable for use in all cases. It is, however, possible to devise a scheme of general proximate analysis which will be of great assistance in the examination of plant-products. This has been done in a very able manner by Professor A. B. Prescott,* and it is from the methods prescribed by him that the following tables of analysis have been drawn up. It must be distinctly understood that the scheme is intended to facilitate the systematic analysis of vegetable substances, and that bodies of certain kinds having by its aid been proved to be present should be isolated or determined by the special methods to be found under the heads of cellulose, starch, dextrin, sugars, cinchona barks, tannin, &c.

MOISTURE is determined by drying a known weight of the finely-divided substance at 100 to 120° C. The loss of weight represents water, and sometimes a little volatile oil. In some cases it is necessary to dry the substance at a lower temperature, or to employ a current of dry coal-gas or carbon dioxide.

MINERAL MATTER is determined by igniting a weighed portion of the substance at the lowest possible red heat. Complete destruction of the carbon is sometimes very difficult, but may be facilitated by treating the ash with a few drops of a strong solution of ammonium nitrate. Too high a temperature should be carefully avoided, as it causes fusion in many cases, and volatilisation of alkaline salts in almost all.†

TOTAL NITROGEN is determined by ignition with soda-lime. The amount found may, if required, be calculated to its equivalent in albuminoids by multiplying it by the factor 6·33.

ACTION OF SOLVENTS.—The substance is then submitted to a systematic treatment with solvents and reagents in the manner prescribed in the following tables:—

* *Pharm. Journ.* [3], x. 793.

† When it is not desired to determine the salt-radicals in the ash it is sometimes very convenient to add sulphuric acid before or during the process of ignition, as in the determination of the ash in sugar (see page 317).

Treat 5 grammes of the finely-divided substance with benzene wholly distilling at 86° C., or failing this with chloroform. The treatment should be continued for six hours, and be conducted in a Xoxheth's extractor, or other suitable apparatus for re-percolation.

A. Solution may contain alkaloids, glucosides, free organic acids, chlorophyll, some resins, fixed oils, fats and waxes, camphors, volatile oils, but no mineral matter.

Residue.—Dry at 100° C., weigh and treat with redistilled methylated spirit of ·848 sp. gravity for twelve hours in a Xoxheth's tube. See figure on page 127.

B. Solution may contain mineral matters, tannin, organic acids, alkaloids, glucosides, some extractive and colouring matters, resins, sugars.

Residue.—Dry at 100° C., weigh and treat with a known measure of cold water. Macerate, with frequent agitation, for eight or ten hours. Then filter through fine washed linen, or paper if possible.

C. Solution may contain soluble albuminoids, gum; and, in the analysis of fruits and fleshy roots, pectin bodies, salts of organic acids, dextrinoid bodies, and colouring matters.

Residue.—Wash with alcohol, dry at 100°, and weigh. Then treat with 500 c.c. of water, and 5 c.c. of concentrated sulphuric acid, and heat till a drop of the liquid gives no colour with iodine.

D. Solution may contain dextrin and maltose from conversion of starch; also albuminoids, and occasionally organic acids, either as salts or free.

Residue.—Wash thoroughly, dry at 110° C. and weigh. Boil for two hours with 500 c.c. of a 2 per cent. of caustic soda. Filter through washed linen.

E. Solution may contain albuminous matters, pectous matters, cutose, humus, and products of decomposition.

Residue.—Wash thoroughly in succession with hot water, alcohol and ether. Dry at 110° C. and weigh. Treat with dilute bromine water and ammonia, as directed on page 364.

F. Solution.—Lignin and colouring matters.

Residue.—Weigh as cellulose.

A. Solution in Benzene or Chloroform.—Evaporate carefully to dryness, and weigh the residue. Then treat with water; again evaporate to dryness at 100°, heat to 110°, and weigh again.

<table>
<tr>
<td>VOLATILISED. — Volatile oils, camphors (partially), volatile alkaloids. The last may be detected by the alkaline reaction of the aqueous liquid, and their loss avoided by adding a drop of hydrochloric acid before evaporation.</td>
<td colspan="3">RESIDUE.—Treat with a moderate quantity of warm water, and when cold filter through fine paper by Bunsen pump.</td>
</tr>
<tr>
<td></td>
<td>SOLUTION.—Divide into two equal portions a. and b.—
a. Evaporate to dryness, and weigh total extract. Ignite, and weigh ash.
b. Test portions for alkaloids and glucosides by special reagents; and for organic acids by solutions of barium, calcium, iron, lead, and silver.</td>
<td colspan="2">RESIDUE.—Remove from the filter and vessels used by benzene or chloroform, and agitate solution with warm, very dilute hydrochloric acid, and separate by means of a tapped funnel. (See figure on page 165.)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ACID SOLUTION. —Test for alkaloids and glucosides.</td>
<td>BENZENE SOLUTION. — Evaporate to dryness, and treat residue several times with spirit of ·848 sp. gr. Filter through paper.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SOLUTION may contain camphors, resins, chlorophyll, certain fixed oils (e.g. castor oil). Camphors are recognisable by the smell; Chlorophyll by its absorption - spectrum.</td>
<td>RESIDUE consists of fixed oils, fats, wax, and, very rarely, resin.</td>
</tr>
</table>

B. Solution in Alcohol of ·848 Specific Gravity.—Concentrate to a small bulk, and remove, dry, and weigh any crystals or powder which may separate from the cooled liquid. Dilute the clear liquid to 200 c.c. by spirit of ·848 specific gravity, and divide into several aliquot parts (20, 20 and 160 c.c.).

<table>
<tr><td>20 c.c.—Evaporate to dryness, and weigh total extract. Ignite and weigh again to determine ash and total organic extract.</td><td>20 c.c.—Evaporate nearly to dryness; add water, filter, and evaporate filtrate to dryness. Residue is soluble extract, and on ignition leaves the soluble ash.</td><td colspan="4">160 c.c.—If much sugar or tannin be present (recognisable by the taste) employ process a; if but little of either of these be present use process b.</td></tr>
<tr><td></td><td></td><td colspan="2">(a) Evaporate nearly to dryness, add water, filter, and make up filtrate to 160 c.c.</td><td colspan="2">(b) Evaporate carefully to dryness, pulverise and treat residue with several considerable portions of absolute alcohol (specific gravity ·7938). Filter.</td></tr>
<tr><td></td><td></td><td>Residue may contain resins; colouring matters; albuminoids, especially from seeds; alkaloids, and glucosides.</td><td>Solution.—Divide into eight portions of 20 c.c. each.
1. Precipitate tannin with ammoniacal zinc acetate. The loss of weight by carefully igniting the weighed precipitate dried at 120° represents tannin.
2. Add neutral lead acetate. Loss of weight on ignition represents tannic, gallic, and other organic acids, colouring and extractive matters, and, rarely, albuminoids.
3 and 4. Precipitate by basic lead acetate, and treat as in 2. After separating lead, treat one half of filtrate with Fehling's solution to estimate glucose; invert other portions and determine glucose; the difference gives glucose formed from glucosides and sucrose.
5 and 6. Treat with basic lead acetate and filter. Decompose both precipitate and filtrate with H_2S, testing the first for organic acids, and latter for alkaloids and glucosides.
7 and 8. Use in case of accident to other portions.</td><td>Solution.—Evaporate nearly to dryness, and add water.</td><td>Residue.—Treat with water.</td></tr>
<tr><td></td><td></td><td></td><td></td><td>Solution.—Add basic acetate of lead. Loss of weight on ignition represents tannin, organic acids, and some extractives. Filtrate may contain alkaloids, glucosides, extractive and colouring matters.</td><td>Residue may contain—1. Alkaloids, glucosides (rarely), and extractives soluble in dilute HCl.
2. Matters insoluble in dilute HCl.
3. Acid resins and colours, soluble in dilute ammonia.
4. Neutral resins, colours, and nitrogenous matters insoluble in dilute ammonia.</td><td>Solution.—Add basic lead acetate. Loss of weight on igniting precipitate represents colours, extractives, organic acids, albuminoids (rarely). Filtrate; remove lead, and determine glucose by Fehling's solution, and glucosides and sucrose by increased reduction after inversion.</td><td>Residue.—Treat with dilute HCl.
1. Dissolved; some alkaloids and glucosides.
2. Insoluble; some resins, and colouring and extractive matters. Dissolve in alcohol; evaporate to dryness, and weigh.</td></tr>
</table>

C. Solution in Cold Water.—Make up liquid to known volume and divide into aliquot portions.

1. Determine *total solid matter* by evaporating and drying residue at 110° C. Determine *ash* by ignition.
2. Add solution of iodine. A blue colour indicates *soluble starch ;* a reddish-brown colour, *erythro-dextrin.*
3. Add ammonium oxalate. A white precipitate indicates calcium, probably as calcium *arabinate.*
4. Evaporate known volume, ignite residue with soda-lime, and multiply nitrogen found by 6·33 to estimate *albumin.*
5. Add dilute hydrochloric acid. A gelatinous precipitate consists of *pectin* or *pectic acid ;* if the liquid be filtered and treated with twice its measure of alcohol, a further precipitate may consist of *arabin* or *dextrin.*

D. Solution in Dilute Acid.—Boil with excess of barium carbonate, exactly neutralise last traces of acid by cautious addition of baryta-water, filter, concentrate, and bring volume to exactly 50 c.c. Then ascertain specific gravity, and divide excess above 1000 by 8. The figure thus obtained is the weight of starch in the 5 grammes of substance taken. If the density indicates but a small proportion of starch, boil half the solution with 1 c.c. HCl. for six hours, replacing the water as it evaporates, then neutralise and estimate glucose by Fehling's solution. Amount found, multiplied by 0·9, gives *starch.* Test portion of solution by adding tannin. A white or buff precipitate indicates *albuminoids.*

E. Solution in Dilute Alkali.—Add slight excess of hydrochloric acid. A precipitate may contain *pectic acid* and other bodies, *colouring matters,* &c. Further precipitation usually occurs on adding alcohol.

COMPOSITION OF CEREALS, &c.

A very large number of analyses of wheat and other grains have been published by different chemists, but unfortunately many of tham are of doubtful value, owing to the defective methods of analysis employed.

The following is the average composition of the cereal grains, according to Graham :—

	Old Wheat.	Barley.	Oats.	Rye.	Maize.	Rice.
Water . .	11·1	12·0	14·2	14·3	11·5	10·8
Starch . .	62·3	52·7	56·1	54·9	54·8	78·8
Fat . . .	1·2	2·6	4·6	2·0	4·7	0·1
Cellulose . .	8·3	11·5	1·0	6·4	14·9	0·2
Gum and Sugar.	3·8	4·2	5·7	11·3	2·9	1·6
Albuminoids .	10·9	13·2	16·0	8·8	8·9	7·2
Ash * . .	1·6	2·8	2·2	1·8	1·6	0·9
Loss, &c. . .	0·8	1·0	0·2	0·5	0·7	0·4
	100·0	100·0	100·0	100·0	100·0	100·0

A. H. Church gives the following analyses by himself in illustration of the composition of representative specimens of the cereal grains and products therefrom.

	White English Wheat.	Fine Wheat Flour.	Wheat Bran.	Scotch Oatmeal.†	Pearl Barley.‡	Rye Flour	Cleaned Rice.	Maize.	Millet.	Dari.
Water . . .	14·5	13·0	14·0	5·0	14·6	13·0	14·6	14·5	13·0	12·2
Albuminoids and other nitrogenous bodies.	11·0	10·5	15·0	16·1	6·2	10·5	7·5	9·0	15·3	8·2
Starch, with traces of Dextrin, &c. . .	69·0	74·3	44·0	63·0	76·0	71·0	76·0	64·5	61·6	70·6
Fat	1·2	0·8	4·0	10·1	1·3	1·6	0·5	5·0	5·0	4 2
Cellulose and Lignose	2·6	0·7	17·0	3·7	0·8	2·3	0·9	5·0	3·5	3·1
Mineral matter * .	1·7	0·7	6·0	2·1	1·1	1·6	0·5	2·0	1·6	1·7
	100·0	100·0	100·0	100·0	100·0	100·0	100·0	100·0	100·0	100·0

* The composition of the ash of cereals is considered on page 394.

† 100 lbs. of oats yield about 60 of oatmeal and 26 of husks, the remainder being water and loss.

‡ The product called pearl barley constitutes only about one-third of the whole seed.

For convenience of comparison, the following analyses of other vegetable products are given. They are selected from among a large number published in Church's valuable work on *Food*.

	Buck-wheat.	Peas.	Haricot Beans.	Lentils.	Earth-nuts, Shelled.
Water	13·4	14·3	14·0	14·5	7·5
Albuminoids, &c.	15·2	22·4	23·0	24·0	24·5
Starch, &c.	63·6	51·3	52·3	49·0	11·7
Fat	3·4	2·5	2·3	2·6	50·0
Cellulose and Lignose	2·1	6·5	5·5	6·9	4·5
Mineral matter	2·3	3·0	2·9	3·0	1·8
	100·0	100·0	100·0	100·0	100·0

	Potatoes.	White Turnips.	Carrots.	Beetroot, Red.	Yam.
Water	75·0	92·8	89·0	82·0	79·6
Albuminoids, &c.	2·3	0·5	0·5	0·4	2·2
Sugar	...	...	4·5	10·0	} 16·3
Starch	15·4	...	...	...	
Dextrin, Gum, and Pectose	2·0	4·0	0·5	3·4	
Fat	0·3	0·1	0·2	0·1	0·5
Cellulose and Lignose	1·0	1·8	4·3	3·0	0·9
Mineral matter	1·0	0·8	1·0	0·9	1·5

Albuminoids of Cereals.—The bodies known to chemists by the generic name of albuminoid bodies or protein compounds have, on an average, the following percentage composition:—Carbon, 53·3; hydrogen, 7·1; nitrogen, 15·7; oxygen, 22·1; and sulphur, 1·8. These proportions were calculated by Lieberkühn to the empirical formula $C_{72}H_{112}N_{18}O_{22}S$.

In analyses of cereals it is usual to calculate the proportion of albuminoids present from the percentage of nitrogen found, and to take little notice of the nature of the albuminoid or nitrogenous matter present. Such a plan is very misleading if the analysis is used to judge of the suitability of a cereal for bread-making, or as an article of diet generally, and hence it is desirable to acquire a more complete knowledge of the nature and amount of the nitrogenous bodies present than is

obtainable from a mere determination of the nitrogen, and the calculation of the amount found to its equivalent in albuminoids.

When wheaten flour is kneaded in a stream of water the starch is gradually washed away, and there remains a sticky cohesive mass which is very rich in nitrogen. The "crude gluten" so obtained consists of a mixture of vegetable fibrin and glutin, with small quantities of fat and mineral matter.

VEGETABLE FIBRIN is insoluble in water or alcohol. It readily undergoes decomposition in the moist state, first producing soluble albuminoid bodies and ultimately offensive products. Fibrin constitutes about 80 per cent. of "crude gluten," and may be obtained pure by digesting it in moderately strong alcohol, which dissolves out

GLUTIN; a body slightly soluble also in cold water, but insoluble in absolute alcohol.

VEGETABLE ALBUMIN, and LEGUMIN or Vegetable Casein are soluble in cold water, and hence pass into solution when the flour is kneaded in the manner described. The albumin may be coagulated by boiling the liquid, and the legumin precipitated from the filtrate by adding acetic acid.

CEREALIN is an albuminoid occurring especially in the husk or bran of wheat and other cereals. It has a powerful fermentative action on starch, rapidly converting it into dextrin and other soluble bodies. Cerealin is precipitated by alcohol and acids.

Other soluble nitrogenous bodies besides cerealin have a marked power of converting starch, and seeds or meals containing them in large proportion are unsuited for making bread. Thus, if barley meal be kneaded with water in the manner already described, but very little crude gluten will be obtained, although barley is richer than wheat in total nitrogen. Barley flour, consequently, if made into bread yields a heavy, doughy mass. Rye flour, which is very rich in total nitrogen, leaves little or no crude gluten when kneaded, and hence does not yield the tough, elastic dough so characteristic of wheat flour. The same is true of oat flour and maize flour.

The presence of cerealin in bran renders whole meal unsuitable for making bread by fermentation with yeast, though "ærated bread" can be prepared from it. The cerealin acts like malt-extract, causing a rapid conversion of the starch into dextrin and sugar, and hence all admixture of the flour with bran should be carefully avoided.*

On account of the different characters possessed by the nitrogenous matters of wheat flour, it is sometimes of advantage to separate the crude gluten and ascertain its physical characters. The examination of the gluten is facilitated by the use of the *aleurometer*, an instrument devised by Bolland. It consists of a copper or brass cylinder, furnished with a piston. 15 grammes weight of freshly-separated gluten is placed in the cylinder, and the piston pushed down till it registers 25°. The cylinder is then heated to 150° C. for ten minutes, when the gluten will be found to have expanded and forced up the piston to an extent dependent on its quality. Good flour yields a gluten which will swell to four times its original volume. With damaged flour the gluten does not swell much, but becomes viscous or nearly fluid, adheres to the cylinder, and sometimes exhales a disagreeable odour, whereas good gluten has merely the odour of hot bread. If the gluten does not indicate at least 25° on the aleurometer it may be considered unfit for bread-making.†

To determine the proportion of gluten obtainable from flour 30 grammes of the sample should be triturated in a mortar with 50 grammes of water. The dough produced should leave the mortar without leaving a trace behind. The mass is placed in a fine linen cloth, which is then tied up and gently kneaded with the fingers, while a fine stream of water is permitted to flow on to it. The kneading and washing are continued until the water which runs away is found to be clear, and hence

* The use of whole meal is often advocated on account of the high proportion of nitrogenous matter and ash-constituents present in it, but, as pointed out by Dr Graham, the admixture of oatmeal with wheat flour might be advocated on precisely similar grounds. The indigestibility of the bran wholly neutralises any advantage supposed to be derivable from its superior nutritive value.

† Bolland's aleurometer is obtainable from Messrs Clarke & Denham, 69 Mark Lane, E.C.

free from starch. The gluten is then removed from the cloth and dried slowly at 110 to 120° C. Gluten from good flour is elastic and but little coloured; that from damaged or inferior flour adheres to the cloth, is with difficulty united into a single mass, and has less consistency and a higher colour than the product from good flour.*

Graham has suggested the following method of making rough comparative estimates of the soluble albuminoids of different samples of flour:—1 ounce of each of the specimens is treated with 4 ounces of cold water, and the mixtures allowed to stand for one hour or some other constant time. The liquids are then filtered, the first portions being rejected, and half an ounce of each of the clear filtrates collected. Each of the solutions thus obtained is then treated with an equal measure of methylated spirit, when a precipitate of soluble albuminoids will be produced, the amount of which will depend on the quality of the flour, the best specimens giving the smallest precipitates.

The albuminoids of wheat and other cereals may therefore be classed broadly as soluble and insoluble, the latter being of service in the formation of a firm elastic gluten, and the former being rather detrimental than otherwise in the production of bread. It has been pointed out by Graham that a constant ratio exists between the proportion of soluble albuminoids and the dextrin and sugar found on analysing the flour, and that the longer the flour be digested in cold water the greater the proportion of soluble albuminoids, and hence of dextrin and sugar, becomes.

* The following alternative method of determining the gluten of flour is taken from Wanklyn and Cooper's valuable little book on *Bread Analysis*:—10 grammes' weight of the sample is mixed on a porcelain plate with 4 c.c. of water, so as to obtain a homogeneous dough. This is placed in a conical measure or other suitable vessel, 50 c.c. of water added, and the dough manipulated with a spatula so as to expel the starch-granules. The water is decanted off, a fresh quantity added, and the kneading repeated till no more starch is extracted from the gluten. The mass is then removed and kneaded in a little ether, after which it is spread out in a thin layer on a platinum dish and dried in the water-oven till the weight is constant. The crude gluten contains ash equal to about ·3 per cent. on the flour, and fat equivalent to 1·00 of the flour. These may, of course, be directly determined in the crude gluten, if desired.

Wigner has pointed out * that wheat contains certain nitrogenous matters not coagulable even by carbolic acid. These bodies consist partly of nitrates, but a portion is present in some indefinite condition.

Wanklyn has applied his well-known albuminoid ammonia process to the determination of the nitrogenised principles of flour.† For the estimation of the total albuminoids 1 gramme of the sample is dissolved in 20 c.c. of a 5 per cent. solution of caustic potash, and the liquid diluted to 1 litre. 10 or 20 c.c. measure of this solution is next distilled with 50 c.c. of the alkaline solution of permanganate and 500 of ammonia-free water, the distillate being nesslerised in the usual way. The soluble albuminoids are determined in a similar manner, except that 10 grammes of the sample are taken and mixed up thoroughly with cold water, the mixture diluted to 100 c.c., filtered, 10 c.c. of the filtrate diluted to 100 c.c., and 10 c.c. of the dilute liquid (=·1 gramme of flour) distilled with permanganate. *Assuming* that the ammonia corresponds to ten times its weight of albuminoids, sound flour yields about 1 per cent. of albumin, &c. to cold water, while the total albuminoids range from 9·2 to 11·7 per cent. Pea-flour gave 23; rice, 6·2; maize, 10·3; oats, 10·0; barley, 11·0; malt, 5·0; and arrow-root, 0·8 per cent. of total albuminoids, calculated at ten times the ammonia yielded on distillation with alkaline permanganate.

Mineral Constituents of Cereals.—The following table shows the percentage of ash or mineral matter contained in nine different fractions obtained by grinding wheat containing 1·634 per cent. of mineral matter. The numbers given are the average results of the examination of twenty-eight samples, the experiments extending to the products of three separate years. It appears therefore that of the total ash of the grain, amounting to 1·634 per cent. of its weight, ·483 occurs in the first three products ("fine flour"), and that in the first five taken together the ash amounts to ·723. These three products constitute upwards of 80 per cent. of the weight of the original grain, and their mixture fairly represents the

* *Analyst*, iii. 288, 303, 358.

† *Philosophical Magazine*, May 1877.

composition of good seconds flour, with an ash of ·86 per cent. Even with the addition of products 6 and 7 of the following table, the ash of the flour only amounts to about ·9 per cent. Hence it may safely be assumed that no sample of flour in which bran is not very notably present ever yields a higher ash than 1·00 per cent. The ash of fine flour is more often below ·70 per cent. than in excess of that number:—

	Yield from 100 Parts of Meal.	Percentage of Ash in Products.	Distribution of Total Ash.
1. Fine Flour . . .	41·1	·69	·284
2. ,, ,, . . .	18·6	·71	·132
3. ,, ,, . . .	9·2	·73	·067
Products 1, 2, and 3 together	70·2*	·71	·483
4. "Tails" . . .	5·3	1·03	·054
5. "Fine Sharps" or Middlings"	8·8	2·12	·186
Products 1 to 5 together .	84·3	·86	·723
6. "Coarse Sharps" . .	3·4	4·18	·142
7. "Fine Pollard" . .	2·4	5·65	·136
8. "Coarse Pollard" . .	6·5	6·47	·420
9. "Long Bran" . .	3·0	7·11	·213
			1·634

The *amount* of ash of cereals is not influenced in any definite manner by the nature of the soil, and the same is true of the *composition* of the ash, the predominence of any particular constituent in the soil by no means leading to an excessive proportion of the same substance in the ash of the plant.

The difference in the proportion of ash yielded by the grain, chaff, and straw of cereals is strictly confined to the silica; if this be deducted, the remainders present no perceptible difference.

The percentage of ash yielded by barley and oats is some-

* There seems to be an error here, but a careful inspection of the original tables has failed to detect its nature. With the exception of the line commencing "Products 1 to 5 together," the numbers in which I have calculated, the figures are taken from the original paper by Lawes and Gilbert (*Journ. Chem. Soc.* x. 27).

what higher than that from wheat, whilst rye and maize yield about the same as wheat, and rice far less.*

Adulterations of Flour and Bread.—The adulterations to which bread and wheaten flour are liable are of two kinds—admixture of the flour or meal of other cereals, and addition of mineral substances. The first kind of sophistication can only be ascertained by a patient examination under the microscope (see page 371), and there are cases in which even this plan fails to be of service. Mineral adulterants may occasionally be used to increase the weight or bulk of the article, but such employment of them is now practically obsolete, and their use is limited to increasing the whiteness and apparent quality of the bread made from the flour. Alum is the addition usually made for this purpose, but plaster of Paris and similar materials are occasionally employed.

In the case of flour, a determination of the ash affords a sufficiently accurate means of detecting and determining mineral adulterants, with the exception of alum, which is usually employed in too small a quantity sensibly to affect

* The composition of the ash of the whole grain of wheat and other cereals has been studied by Lawes and Gilbert, Chevalier, Way and Ogston, &c. The following are the general practical conclusions deducible from the numerous analyses recorded :—

The proportion of potash is very variable, but useless as a means of distinguishing the ash of different grains. The lime ranges from 1 to 10 per cent. Baryta has been found in Egyptian wheat. The magnesia varies much, but in wheat-ash is pretty constant, fifty-three samples analysed by various chemists showing a range from 9·1 to 14·3, with a mean amount of 12·11 of MgO in 100 of ash. The ferric oxide in wheat ash was found by Way and Ogston to range from 0·1 to 3·3 per cent. Alumina is present only in minute traces, the proportion in genuine wheat flour-ash rarely exceeding 1 per cent, and even this is probably due to adherent dirt. The silica in the ash of wheat, rye, maize, and rice is generally very low, rarely reaching 5, and being usually less than 2 per cent. of the total. In barley ash, on the other hand, Chevalier found from 17·3 to 32·7, the usual amount being about 24 per cent., while the ash of oats contains from 40 to 50 per cent. of silica. Except in the larger proportion of silica the ashes of barley and oats resemble wheat ash in every essential respect. The phosphoric acid (P_2O_5) in wheat ash varies from 40 to 50 per cent., which is 10 per cent. more than is present in the ash of barley, and 20 per cent. in excess of the usual proportion in oats. On the other hand, the ash of maize or rye contains 40 to 50 per cent. of P_2O_5, and in rice ash the proportion is still larger. In estimating phosphoric acid in cereals it is necessary to fuse the ash with sodium carbonate, to convert the pyrophosphates into orthophosphates.

the percentage obtained. With wheaten flour any higher ash than 0·8 per cent. should be regarded with great suspicion, but in the case of oatmeal 2 per cent. or somewhat more is a normal proportion.

LOGWOOD TEST.—The readiest and most delicate test for alum in flour is based on the reaction produced by an alkaline solution of logwood. To prepare the tincture of logwood, 5 grammes of freshly-cut logwood chips or shavings should be digested in a closed bottle with 100 c.c. of methylated spirit.

To test for alum in flour, 10 grammes of the sample should be mixed in a glass basin or wide beaker with 10 c.c. of water. Then add 1 c.c. of the logwood tincture and an equal measure of a saturated aqueous solution of ammonium carbonate, and mix the whole together thoroughly. If the flour be pure, a pinkish colour is obtained; whereas, if alum be present, the pink is changed to lavender or actual blue. As a precaution, it is desirable to heat the paste in the water-oven for an hour or two, and note whether the blue colour remains.

To test for alum in bread, 5 c.c. of the logwood tincture should be diluted with 90 of water and 5 c.c. of saturated carbonate of ammonium solution added. Then without delay, the mixture is poured over about 10 grammes of the bread contained in a glass dish or clock-glass. After about five minutes, the liquid is drained away and the bread slightly washed and dried at 100° C. If alum be present, the bread will assume a lavender or dark-blue colour, which becomes still more marked on drying. With pure bread, the reddish colour first obtained fades to a buff or light brown. With care and a little practice the test is very satisfactory, and is so delicate that even 7 grains of alum to the 4 pound loaf can be detected. With moderate proportions of alum, the depth of colour produced will roughly indicate the amount of the adulterant present.

In employing the foregoing test it is very important that the tincture of logwood should be freshly prepared, and that the test should be made immediately after mixing the logwood tincture with the solution of ammonium carbonate. Inatten-

tion to these essential points has caused the failure of several chemists to obtain the blue coloration with specimens undoubtedly containing alum. The subsequent drying also should never be neglected. With proper care, the test is exceedingly delicate, 0·02 per cent. of alum causing a distinct shade of blue, while with three or four times this proportion the reaction is wholly beyond question.

In consequence of the ease with which the mineral adulterants of flour can be separated from the sample, it is rarely necessary to determine any of the constituents of the ash, but in the case of bread it will be found important.

CHLOROFORM TEST.—The best means of separating any mineral adulterants from flour is to place 100 grammes (or 4 ounces) of the sample in a dry cylindrical separator, furnished with a tap below and a stopper above. About 200 to 250 c.c. of methylated chloroform should then be added, and the whole thoroughly shaken together and then left at rest for some hours, or until the flour has risen to the surface of the chloroform. Any mineral adulterant present will then be found to have sunk to the bottom of the chloroform, and on running off a little of the liquid through the tap will pass with it. The small quantity of chloroform thus obtained may be diluted with more chloroform in a smaller separator, and again allowed to settle. The second deposit may still contain a little bran and other organic matters, but will consist chiefly of sand from the millstones, dirt, and any alum, plaster of Paris, or other mineral powder heavier than chloroform that happened to be in the flour. The deposit is tapped off, and the bulk of the chloroform having been got rid of by decantation or filtration, the last traces are driven off by a current of air assisted by very gentle heat, and the residue is weighed. It is next examined under a microscope, using a low power, with the view of detecting particles of alum or other crystalline matter. The residue is then dissolved in a little cold water, and the liquid filtered. The residue should be ignited and weighed. It will contain the dirt and millstone-dust of the sample, mixed with any plaster of Paris, chalk, barium sulphate, or

Fig. 7.

other mineral adulterant insoluble, or nearly insoluble, in water. If the amount found does not exceed 0·1 per cent. of the weight of flour it need not be further examined. The portion of the chloroform-deposit soluble in cold water will contain any alum present in the original flour. On evaporating the aqueous liquid to dryness the alum will be left, and may be recognised by its astringent taste, reaction with logwood (page 396), and the form of any crystals which may have been produced. Its amount may be accurately ascertained by determining the sulphates or aluminium, and calculating to the equivalent in alum. In the case of bread, oatmeal, and other products obtained by adding water to the ground cereal, the chloroform treatment is not available for the detection of mineral adulterants. In this case it is necessary to estimate the ash, and not unfrequently to make a partial analysis of it.

The mineral additions commonly made to bread and other preparations of the cereals include the following substances:— 1. Common salt. 2. The ingredients of common salt, added in the form of hydrochloric acid and sodium bicarbonate. 3. Baking powders; of very variable character, but usually containing sodium bicarbonate and tartaric acid. Acid phosphate of calcium and certain compounds of aluminium are also contained in some baking powders. 4. Lime water. 5. Magnesium carbonate. 6. Alum and equivalent preparations containing aluminium. 7. Plaster of Paris. 8. Whiting. 9. Barium sulphate.

Of this somewhat formidable list, the compounds of aluminium and the sulphates of barium and calcium are the only additions to which grave exception can be taken when only small proportions are used, though the earthy carbonates must be regarded as objectionable to some extent.

ALUM, or an equivalent preparation containing aluminium, is by far the most common mineral adulterant of bread. It can be detected with certainty, even when present in very small proportion, by the careful application of the logwood test described on page 396, which was originally proposed by Hadow, but was modified and greatly improved by Horsley, and more recently by J. Carter Bell.

DETERMINATION OF ALUM IN BREAD.—Of the constituents of alum, the only one which is of service for its determination in bread is the aluminium. Pure wheat grain appears to be wholly destitute of aluminium compounds, but commercial wheat flour to which no alum has been added is apt to contain small but sensible traces of aluminium derived from extraneous mineral matter. Such aluminium is present as silicate, and gives no blue colour with the logwood test. On the other hand, all the ordinary methods of quantitatively estimating the alum are incapable of distinguishing between the aluminium present as silicate and that existing in a soluble form. Hence it is usual to make a correction for the aluminium present as silicate. This is difficult to do with any approach to accuracy, but it may be taken as a rule that from the amount of alum calculated from the total aluminium in the bread should be subtracted a weight equal to the silica found, when the difference will be approximately the true amount of alum added.

The following method should be employed for the determination of the total alumina and silica in bread:—100 grammes' weight of the sample is dried at 100° C., and then incinerated. This is best done by heating it in a platinum tray (about 5 inches by 3) in a gas-muffle, but may also be effected in a platinum dish or large crucible placed over a bunsen. The heat should be moderate, so as to avoid fusion of the ash. The process is completed by adding pure sodium carbonate and a little nitre, and heating the mixture to fusion. The product is rinsed out with water into a beaker, acidulated with hydrochloric acid, and evaporated to dryness. The residue is taken up with dilute acid, and the liquid filtered from the silica, which is washed, dried, and weighed. To the solution, dilute ammonia is added till the precipitate barely redissolves on stirring, when a slightly acid solution of ammonium acetate is added, and the whole allowed to stand in the cold for twelve hours. The liquid is then filtered, the precipitate washed, and dissolved in the smallest quantity of hydrochloric acid. The solution so obtained is poured into an excess of an aqueous solution of *pure* caustic soda contained in a large platinum crucible. After heating for some time,

the liquid is considerably diluted and filtered. The filtrate is acidulated with hydrochloric acid, a few drops of sodium phosphate added, and then a slight excess of ammonia. The liquid is kept hot till all smell of ammonia is lost, when it is filtered, and the precipitated aluminium phosphate washed, ignited, and weighed. Its weight, multiplied by 3·686, gives the ammonium alum, or by 3·873 the potassium alum in the 100 grammes of bread taken. The amount so found requires a correction equal to the percentage of silica obtained.* By multiplying the percentage of alum by 280, the number of grains of alum per 4 lb. loaf will be obtained. The number of milligrammes of $AlPO_4$ per 100 grammes of the bread gives, without calculation, a close approximation to the number of grains of ammonium alum per 4 lb. loaf.

Throughout the foregoing process the use of porcelain vessels should be wholly avoided, and care should be taken that the alkaline liquids are not heated in glass. The caustic soda employed should be scrupulously free from alumina.*

PLASTER OF PARIS has been found in flour by Fairley, and has been met with by the author in muffins to the extent of 1 per cent. of their weight. In oat-cake it is said to be occasionally present to the extent of 10 per cent. and upwards. From flour, plaster of Paris is readily separated by treatment with chloroform.

The presence of plaster of Paris in bread is recognised by the high total ash, and the high proportion of calcium contained in it. The sulphates of the ash do not afford a means of accurately determining the amount of plaster present, as the albuminoids furnish a notable quantity of sulphates on igniting the cereals. On the other hand, mere traces of sulphates exist ready-formed in the cereals, and hence their determination in the unignited bread affords a means of

* I have recently endeavoured to devise a method of extracting alumina from bread in such a manner as to render unnecessary the questionable correction for the aluminium existing as silicate. My experiments in this direction are still incomplete, but I have obtained very encouraging results by a process based on the solution of the starch by malt extract, destruction of the soluble carbohydrates by yeast, acidulation of the liquid by nitric acid, followed by filtration, evaporation of the liquid, ignition of the residue, and precipitation of the aluminium as phosphate in the usual way.

estimating the plaster present. This method, though theoretically perfect, presents some difficulties in practice, owing to the difficulty of obtaining a solution of the sulphates fit for precipitation with barium chloride. The best way is to soak 12·20 grammes of the bread for some days in 1200 c.c. of cold distilled water till mould commences to form on the surface of the liquid. The solution is strained through coarse muslin, and the filtrate treated with 20 c.c. of carbolic acid distilled over a small quantity of lime. The whole is then raised to the boiling point and filtered through paper. 1 litre of the filtrate is then slightly acidulated with hydrochloric acid, and precipitated in the cold by barium chloride. 237 parts of $BaSO_4$ represent 136 of plaster of Paris. Experiments conducted in the author's laboratory with the view of testing the accuracy of this process gave very satisfactory results.

SULPHATE OF COPPER was formerly employed as an adulterant of bread, especially in foreign countries. This objectionable addition can be detected, even when present in but very minute proportion, by soaking the bread in a solution of potassium ferrocyanide acidulated with acetic acid, when a purplish or reddish brown coloration will be produced if copper be present. The amount of copper may be determined by moistening the bread with sulphuric acid, igniting, and estimating the metal in the ash.

Very minute proportions of copper have been stated to exist normally in wheat-ash, but it is doubtful whether its presence was not due to the practice, formerly very common, of steeping the corn in a solution of copper before sowing it.

ALKALOIDS AND ORGANIC BASES.

THIS important class of organic bodies includes numerous bases occurring naturally in the animal and vegetable kingdoms, as well as many others which are obtainable by destructive distillation, or by definite synthetical processes.

Without exception, the well-defined organic bases of any importance are compounds of nitrogen,* carbon and hydrogen being also essential constituents. Certain classes also contain oxygen, and the presence of this element appears to confer the property of non-volatility on the base. Sulphur is an occasional constituent.

The names of the alkaloids and organic bases are now invariably made to terminate in *ine*, and it is very desirable that this termination should be strictly confined to bodies of this class.† The termination *ia* is still employed for a few of the vegetable alkaloids (*e.g.*, morphia), and the name urea is retained for obvious reasons. The class of bodies known as glucosides—many of which, from an analytical point of view, present some similarity to the alkaloids—should receive names having the termination *in*.

Organic bases are usually classed as monamines, diamines, triamines, &c., according as they are derived from one, two, three, or more molecules of ammonia. They are further sub-classified as primary, secondary,

* Well-defined bases of great theoretical interest have been obtained, in which the nitrogen is replaced by phosphorus and other elements.

† The misuse by chemists of the termination *ine* has caused great confusion, which its employment to designate indefinite commercial products has increased. There is no excuse for writing benz*ine*, paraff*ine*, naphthal*ine*, or gelat*ine*; and glycer*ine* is also an undesirable title. The recommendations on nomenclature made by the Publication Committee of the *Journal of the Chemical Society* deserve more attention than they have hitherto received.

and tertiary amines, or as organic-ammonium hydroxides, according to the number of atoms of hydrogen which are replaced by organic radicals.*

For the purposes of this work it would be inconvenient to classify the organic bases in a strictly systematic manner. They will, therefore, be grouped under the following heads, and only the more important described in detail:—

1. CINCHONA BASES, including quinine, cinchonine, &c., are described in the section commencing on page 408.

2. OPIUM ALKALOIDS include morphine, codeine, and the other bases of opium.

3. STRYCHNOS ALKALOIDS; such as strychnine and brucine.

4. LESS IMPORTANT NON-VOLATILE BASES OF VEGETABLE ORIGIN, as aconitine, atropine, caffeine, &c.

5. VOLATILE ALKALOIDS OF VEGETABLE ORIGIN, including conine and nicotine.

6. ANILINE AND ITS HOMOLOGUES, comprising aniline, toluidine, &c.

7. BASIC ANILINE-DERIVATIVES, such as rosaniline.

Vegetable Alkaloids.—The bases of the first five of the above groups constitute the natural vegetable organic bases or alkaloids proper. The members of the first four groups all contain oxygen, and their molecular structure is, in most cases, but very imperfectly understood.

The vegetable alkaloids are found in all parts of the plant, and in many cases constitute their characteristic active principles. In nature, they usually occur in union with certain peculiar acids. Thus, morphine is associated with meconic acid, strychnine with igasuric acid, the

* Thus, aniline, or phenyl-amine, is a primary monamine, expressible by the formula $\left.\begin{matrix}(C_6H_5)'\\H\\H\end{matrix}\right\}N$; while the isomeric base picoline is a tertiary monamine, $(C_6H_7)'''N$, all three atoms of hydrogen being replaced by a triad radical. Methyl-ethyl-amyl-amine $\left.\begin{matrix}(CH_3)'\\(C_2H_5)'\\(C_5H_{11})'\end{matrix}\right\}N$, is a tertiary monamine, the three atoms of hydrogen being replaced by as many different radicals. Conine, the alkaloid of hemlock, is a secondary monamine of the formula $\left.\begin{matrix}(C_8H_{14})''\\H\end{matrix}\right\}N$, but the great majority of the natural alkaloids are tertiary amines.

cinchona-bases with kinic acid, and atropine with malic acid.

The natural alkaloids, or vegetable organic bases, are in many cases intensely poisonous, and others, as the alkaloids of tea, coffee, and cocoa, produce characteristic effects on the animal system.

Many of the natural alkaloids are powerfully alkaline in reaction, neutralise acids perfectly, and form series of well-defined and crystallisable salts.

With the exception of the volatile alkaloids (group 5), all the *natural* organic bases are solid. They are in most cases practically fixed, though caffeine and a few others can be sublimed. They are mostly but very slightly soluble in water, but are all dissolved by alcohol, and, as a rule, with great facility. Most of them are soluble in ether, and nearly all in chloroform.

As a rule, when the acidulated solution of the salt of an alkaloid is agitated with chloroform, ether, petroleum spirit, benzene, or amylic alcohol, the solvent does not remove the base from the aqueous liquid. This behaviour distinguishes alkaloids from glucosides; but caffeine, colchicine, delphinine, narcotine, papaverine, piperine, thebaine, and theobromine resemble the glucosides by being partially or wholly removed from their acidulated solutions by agitation with chloroform, while amylic alcohol extracts berberine and veratrine in addition to the foregoing bases.

On the other hand, when one of the above immiscible solvents is agitated with the aqueous solution of an alkaloidal salt to which a moderate excess of caustic soda or ammonia has been previously added, the base will be wholly or partially removed from the aqueous liquid, if the solvent be one capable of dissolving the alkaloid present. This behaviour of the alkaloids with immiscible solvents is of the utmost value for their isolation and determination.

THE ISOLATION OF ALKALOIDS in a tolerably pure condition is a process which almost always precedes the application of special tests for their identification. A good example of the separation of alkaloids from woody fibre and tannin-matters is furnished by the process for the assay of cinchona-barks

(page 448); the separation of alkaloids from resinous, gummy, and colouring matters is exemplified in the methods for the assay of opium (page 471); while the isolation of strychnine in toxicological investigations is a good illustration of the methods employed for the separation of alkaloids from albuminous, starchy, and fatty matters (see page 492). The last method is of pretty general applicability in toxicological investigations, provided that it be remembered that (1) many alkaloids are far less stable than strychnine, and hence are apt to be destroyed if the solutions are evaporated at too high a temperature; (2) that certain alkaloids are extracted by chloroform and amylic alcohol even from their acidulated solutions; (3) that curarine, morphine and solanine are nearly or wholly insoluble in ether or chloroform, and hence cannot be certainly extracted by agitating their alkaline solutions with either of these solvents; (4) that, whenever possible, the chemical tests for the isolated alkaloids should be supplemented by physiological tests; (5) that during the process of putrefaction certain cadaveric alkaloids ("ptomaines") are liable to be formed which simulate some of the reactions of the vegetable bases, but are distinguishable from most of them, except morphia, by the property of reducing ferricyanides to ferrocyanides, and therefore forming Prussian blue from a mixture of ferric chloride with potassium ferricyanide.

The following is an outline of the general methods employed for the isolation of alkaloids from plants:—(1.) The powdered substance is made into a paste with water and lime or magnesia, and the mixture dried and extracted with alcohol, chloroform, or petroleum spirit. (2.) The substance is mixed with water and lead acetate, the soluble acetate of the alkaloid separated from the insoluble lead salts by filtration, the lead precipitated from the filtrate by sulphuric acid or sulphuretted hydrogen, and the alkaloid separated by adding soda or ammonia. (3.) The substance is exhausted with alcohol, either with or without the assistance of a dilute acid, the alcohol removed by distillation, the liquid filtered, and the filtrate treated with soda or ammonia for the precipitation of the alkaloid.

The alkaloids having been obtained in a state of approximate purity by one of the foregoing methods, they may be further treated according to the following principles:—

(*a*) Colouring matters may be removed by agitating the solution with a small quantity of animal charcoal, but this agent must be used very sparingly, or the alkaloid may be wholly removed from solution. The alkaloid thus taken up may be recovered by boiling the charcoal with alcohol. The absorption of alkaloids by charcoal has been employed for their removal from beer and similar liquids.

(*b*) Fatty and resinous matters may be removed by agitating the acidulated solution of the alkaloid with petroleum spirit. (Piperine and some glucosides are also extracted.)

(*c*) Many colouring matters, and tannic and various other organic acids may be removed by treating the neutral solution with lead acetate, and filtering.

(*d*) From sugars, gums, salts, and extractive matters generally, the great majority of the alkaloids can be separated by agitating the solution with ammonia, and chloroform or a mixture of chloroform and ether. On separating the chloroform from the aqueous liquid, which retains the sugar, gum, and salts, and agitating it with dilute sulphuric acid, the alkaloid passes into the acid liquid, while colouring matters, fats, resins, and glucosides remain in the chloroform.

(*e*) A valuable means of concentrating alkaloids and obtaining them in a state of approximate purity is to precipitate the neutral or slightly acidulated solution with picric acid, potassio-iodide of mercury, or phospho-molybdic acid. The first of these is the best for cinchona bases (page 450), the second for opium bases and emetine (page 465), and the third for strychnine (page 485).

By a judicious application of the above principles it is generally an easy matter to isolate alkaloids in a nearly pure condition, or at any rate in such a state as to allow of the special tests being successfully applied. The systematic scheme for the proximate analysis of plants, detailed on page 384, *et seq.*, will also be of service in the isolation of alkaloids.

The volatile vegetable bases require a somewhat modified treatment, the nature of which will be described in the sequel.

REACTIONS OF VEGETABLE ALKALOIDS.—The behaviour of the alkaloids with solvents has been already detailed. Their reactions with certain general reagents are sometimes important, and are characteristic of particular bases. A very great number of reagents have been proposed as general tests for alkaloids, the following being the most valuable:—

(*a*) Strong sulphuric acid added to the solid alkaloid gives some characteristic reactions. On adding an oxidising agent, strychnine and some other bases give strongly-marked colour-reactions (see pages 458, 459, and 464).

(*b*) Strong nitric acid is useful as a test for morphia and some other alkaloids (see pages 459 and 463).

(*c*) Picric acid produces no precipitate in solutions (acidulated with sulphuric acid) of aniline, caffeine, morphine, pseudomorphine, solanine, theobromine, or the glucosides; and aconitine and atropine are precipitated in concentrated solutions only. (Atropine and morphine are precipitated in neutral solutions.) Copious precipitates are produced by picric acid in acidulated solutions of berberine, colchicine, delphinine, emetine, the cinchona alkaloids, opium alkaloids (except morphine and pseudomorphine), veratrine, &c. The alkaloids may be extracted from their picrates by agitating the precipitate with soda, and chloroform or other suitable solvent. Picric acid is occasionally employed for the estimation of the alkaloids in cinchona bark (see page 450).

(*d*) The hydrochlorides of the alkaloids form double salts with platinic chloride analogous to the chloroplatinate of ammonium. Aniline, digitaline, physostigmine and solanine are not precipitated; and aconitine, atropine, codeine, hyoscyamine, narcotine, nicotine, and veratrine only from concentrated solutions. The remaining alkaloids yield insoluble, or sparingly soluble chloroplatinates, most of which dissolve in cold dilute hydrochloric acid. Auric chloride also yields double salts with the hydrochlorides of organic bases, and occasionally serves to distinguish between closely similar alkaloids (see tables of cinchona bases, page 412 *et seq.*).

(*e*) A solution of potassio-iodide of mercury (Mayer)

precipitates most of the alkaloids very perfectly, the compounds produced being usually yellowish white. Caffeine, colchicine, and theobromine, as also digitalin and most glucosides, are not precipitated. The alkaloid may be extracted by triturating the precipitate with stannous chloride and excess of soda solution, and then agitating the mixture with chloroform or other suitable solvent. Mayer's reagent may be used for the volumetric determination of the alkaloids. The following are the weights of the alkaloids in milligrammes said to be precipitated by 1 c.c. of the Mayer's solution:—Aconitine, 26·8; atropine, 14·5; brucine, 23·3; cinchonine, 10·2; conine, 4·2; emetine, 18·9; morphine, 20·0; narcotine, 21·3; nicotine, 4·0; quinine, 10·8; quinidine, 12·0; strychnine, 16·7; veratrine, 26·9. The end of the reaction is somewhat difficult to observe, the process being best conducted as described on page 465. For the assay of ipecacuanha and some other drugs the method is a useful one.

(*e*) Sonnenschein's Reagent, a nitric acid solution of phosphomolybdic acid,* gives very insoluble precipitates with nearly all the alkaloids, and hence is of great service for removing them from complex organic mixtures. The precipitation should be effected in a slightly acid solution, and the precipitate washed with water containing the reagent. The precipitates are soluble in ammonia, usually with production of green or blue colour in the cases of atropine, aconitine, berberine, codeine, colchicine, conine, morphine, nicotine, and physostigmine. From the alkaline liquid the alkaloid can be dissolved out by agitating without delay with chloroform or other suitable solvent.

Other reagents of occasional value as tests for alkaloids are ferric chloride (pages 459 and 463), iodic acid (page 462), solution of iodine in iodide of potassium (page 420),

* Sonnenschein's reagent is prepared from the yellow precipitate produced on adding a phosphate to an acid solution of ammonium molybdate. The precipitate is collected, well washed with water containing nitric acid, and dissolved in a hot solution of sodium carbonate. The solution is evaporated to dryness, and the residue gently ignited till all ammonium salts have volatilised. The residue is moistened with nitric acid, and again gently ignited. One part of the residue is then dissolved in a mixture of one part of nitric acid (1·42 sp. gr.) and nine parts of water.

bromine or chlorine water and ammonia (page 418), tannin, and many others.

The colour-reactions of the alkaloids are numerous, and, in some cases, characteristic, but they should always, when possible, be confirmed by treating a portion of the pure alkaloid side by side with the sample.

CINCHONA ALKALOIDS.

The various species of the family of plants known as the *Cinchonaceæ* yield an extraordinary number of closely analogous alkaloids. These bases exist chiefly, though not wholly, in the bark of the trees, and are remarkable for their valuable febrifuge properties.

The cinchona alkaloids all have well-defined basic characters, some of them being sufficiently powerful to displace ammonia from its compounds. Their salts are usually crystallisable.

In the free state, the cinchona alkaloids are colourless or faintly-yellow solids, often readily fusible, but not volatile without decomposition. They have generally but little solubility in water, but dissolve more readily in alcohol, and generally with great facility in ether and chloroform. Such as are soluble in the last two liquids are removed from their alkaline solutions by agitation with ether or chloroform, but in no case will ether or chloroform remove them from an aqueous *solution* acidulated with sulphuric or hydrochloric acid. On the other hand, the anhydrous sulphates of many of the cinchona alkaloids are soluble in chloroform, and still more readily in a mixture of chloroform and absolute alcohol. This fact is sometimes utilised for detecting adulterations.

The solutions of some of the cinchona alkaloids in excess of dilute sulphuric acid exhibit a strong blue fluorescence, which is visible even in very dilute liquids. This fluorescence is destroyed by adding an excess of chloride of sodium or other haloid salt.

The solutions of the cinchona alkaloids exert a well-marked rotatory action on polarised light, the rotation being in some cases right- and in others left-handed. Unfortunately, the specific rotation is affected in a remarkable manner by

the solvent employed, and by the proportion of free acid present, so as to render the polariscopic indications practically useless for quantitative determinations even of the unmixed alkaloids.*

On adding a fixed alkali or alkaline carbonate to the solution of one of the cinchona bases, the sparingly soluble alkaloid is usually separated in a free state. Ammonia produces the same effect as the fixed alkalies, but the alkaloid is in some cases soluble in an excess of the precipitant. On agitating the alkaline liquid with chloroform, the alkaloid is dissolved, and may be recovered in a free state by separating the chloroform, and evaporating it to dryness at a steam-heat. By adding more chloroform to the aqueous liquid, and repeating the agitation, the complete extraction of the alkaloid may be ensured, and the process made quantitative (see page 419). Ether may be substituted for chloroform in the case of quinine and other alkaloids readily dissolved by it.

The cinchona bases are tertiary amines; for when treated with iodide of methyl or iodide of ethyl they form additive-compounds which are converted by treatment with oxide of silver into powerful soluble bases analogous to the hydroxide of tetra-ethyl-ammonium.

Many of the cinchona alkaloids form two series of salts; neutral (improperly called "basic") and acid salts.

The neutral sulphates of the cinchona alkaloids, have, when anhydrous, the general formula $A_2H_2SO_4$. They are generally very sparingly soluble in water, but the corresponding acid or bisulphates (AH_2SO_4) are generally readily soluble. In some cases still more acid sulphates are known.

The sulphates of many of the cinchona bases possess the property of combining with iodine, the compounds produced being in some cases of a very complicated character. Certain of these "iodosulphates" possess the remarkable optical properties of the tourmaline (see page 421).

When any salt of one of the natural cinchona bases is heated for a prolonged period to a high temperature, the alkaloid undergoes a curious change. It becomes incapable of crystallising, a property sometimes extending to its salts. The

* Hesse, *Annalen*, clxxvi. 203, and *Watt's Dictionary*, viii. 1224.

change occurs most readily by exposing the acid sulphate of the alkaloid to a temperature of 100° till anhydrous, and then increasing the heat for some time to about 130° C. No means are at present known by which the modified alkaloid can be restored to its original crystallisable condition.

With platinic chloride the hydrochlorides of the bases form chloroplatinates of the general formula $A,2HCl,PtCl_4$. With auric chloride they also form double salts, many of which are liable to speedy decomposition with separation of finely-divided metallic gold.

Certain of the cinchona-bases give a deep green coloration or precipitate when their solutions are treated with chlorine- or bromine-water, and ammonia subsequently added. This reaction is known as the "thalleioquin test" (see also page 418).

The cinchona bases are mostly very completely precipitated by tannic and picric acids, potassio-mercuric iodide, and certain other reagents. These reactions are sometimes used for their detection and separation.

List of Cinchona Bases.

The following is a complete list of the alkaloids hitherto isolated from the various species of cinchona bark, or produced from the natural cinchona bases by the action of heat. The more important alkaloids are not fully described, as they will be considered more in detail in the sequel.

The information given in the table under the various letters of the alphabet has reference to the following characters:—

(*a*) Crystalline form and general characters. (*b*) Whether dextro- (R) or lævo-rotatory (L). (*c*) Solubility in chloroform. (*d*) Solubility in ether. (*e*) Formula of the crystallised sulphate (A signifies 1 atom of alkaloid). (*f*) Characters of the acid sulphate. (*g*) Optical characters of the solution of the alkaloid in excess of dilute sulphuric acid. (*h*) Reaction of the acidulated solution of the alkaloid with platinic chloride. (*i*) Reaction of the acidulated solution of the alkaloid with auric chloride.

Table of Cinchona Bases.

Name.	Chief Source or Mode of Formation.	Formula.	Other Characters.
Quinine.	Various species of cinchona bark, see page 447.	$C_{20}H_{24}N_2O_2$.	See page 316, *et seq.*
Quinidine, Conchinine, Conquinine.	Various cinchona barks, but never in large proportion.	$C_{20}H_{24}N_2O_2$.	(*a*) Crystallises with various proportions of water. (*b*) R. (*c*) and (*d*) Soluble. (*e*) $A_2H_2SO_4+2Aq.$ (*f*) $AH_2SO_4+4Aq.$, readily soluble. (*g*) Solution fluorescent. See page 439.
Quinicine.	By melting the acid sulphate or other salts of quinine or quinidine. Never present in cinchona bark.	$C_{20}H_{24}N_2O_2$.	(*a*) Free base is amorphous, but many of the salts crystallisable. (*b*) R. (*d*) Very soluble. See page 443.
Apodiquinicine, Diconchinine.	The chief constituent of commercial "quinoïdine." Probably exists in many barks.	$C_{40}H_{28}N_4O_3$ $(=2C_{20}H_{24}N_2O_2-H_2O)$.	(*a*) Amorphous, as are all its salts. (*b*) R. (*d*) Very soluble. (*g*) Solution fluorescent. See page 444.
Cinchonidine.	*Cinchona rubra*, and some other species, often in considerable quantity.	$C_{20}H_{24}N_2O$.	(*a*) Crystallises from alcohol in anhydrous needles or shining prisms. (*b*) L. (*c*) Soluble. (*d*) 1 in 150. (*e*) $A_2H_2SO_4+6Aq.$, nearly insoluble in chloroform, but swells with it to a jelly-like mass. (*f*) $AH_2SO_4+5Aq.$, readily soluble. (*g*) Solutions not fluorescent. See page 439.
Cinchonine.	Various species of cinchona bark; almost always present. See page 437.	$C_{20}H_{24}N_2O$.	(*a*) Crystallises from strong alcohol in shining anhydrous prisms. (*b*) R. (*c*) Slightly soluble. (*d*) Nearly insoluble. (*e*) $A_2H_2SO_4+2Aq.$, $AH_2SO_4+4Aq.$, very soluble. (*g*) Not fluorescent. See page 437.
Cinchonicine.	By heating sulphate of cinchonidine or cinchonine. Never present in cinchona bark.	$C_{20}H_{24}N_2O$.	(*a*) Amorphous. (*b*) R. (*c*) and (*d*) Very soluble. Some of the salts are crystallisable. See page 444.

Dicinchonine.	Contained in the "quinoïdine" from barks rich in cinchonine.	$C_{40}H_{48}N_2O_2$.	(*a*) Amorphous. Never yet obtained pure. Very little known.
Homocinchonidine, Conquinidine, Cinchovatine.	*C. ovata*; closely resembles cinchonidine.	$C_{19}H_{22}N_2O$.	(*a*) Crystallises from strong alcohol in large prisms, and from diluted alcohol in scales. (*b*) L. (*e*) $A_2H_2SO_4 + 6Aq$. (*f*) Very deliquescent needles, of gelatinous appearance, melting if moist at about 30° C. If carefully dried resembles magnesia, and swells to a jelly-like mass with chloroform.
Homocinchonine.	*C. rosulenta.*	$C_{19}H_{22}N_2O$.	(*a*) Crystallises from alcohol in large prisms. (*d*) L. (*e*) $A_2H_2SO_4 + 6Aq$., amorphous mass or slender needles.
Homocinchonicine.	By heating the sulphate of homocinchonidine.	$C_{19}H_{22}N_2O$.	(*a*) Amorphous, but forms a crystalline oxalate, very similar to that of cinchonicine.
Dihomocinchonicine, Dihomocinchonine.	*C. rosulenta.*	$C_{38}H_{44}N_4O_2$.	(*a*) Amorphous, and forms only amorphous salts. (*b*) Strongly R.
Quinamine.	*C. succirubra, rosulenta, calisaya,* &c.	$C_{19}H_{24}N_2O_2$.	(*a*) Crystallises from hot dilute alcohol; melts at 172° C. (*b*) R. (*d*) Soluble. (*e*) Difficultly crystallisable; *very soluble.* (*h*) Precipitated from concentrated solutions only. See p. 442.
Quinidamine Conquinamine.	Sources same as above	$C_{19}H_{24}N_2O_2$.	(*a*) Crystallises in long shining prisms, melting at 123° C. (*b*) R, more strongly than quinamine. (*h*) Precipitated from concentrated solutions only. (*i*) Yellow ppte, changing to purple.
Quinamidine, Apoquinamine, Quinamicine, and Protoquinamicine.	Produced by the action of acids or heat on quinamine or quinidamine.	$C_{19}H_{24}N_2O_2$. $C_{19}H_{22}N_2O$. $C_{19}H_{24}N_2O_2$. $C_{17}H_{20}N_2O_2$.	Amorphous bases.
Paricine.	*C. succirubra.*	$C_{16}H_{18}N_2O$.	(*a*) Pale yellow, amorphous powder. (*d*) Soluble with yellow colour. Salts are amorphous. (*i*) Yellowish turbidity, not turning purple.
Ultra-quinine.	*C. cuprea.*	(?)	Resembles quinine, but crystallises from ether. (*Pharm. Journ.* [3], xii. 497.)

Name.	Chief Source or Mode of Formation.	Formula.	Other Characters.
Paytine.	Contained in the white bark of Payta. Probably identical with Aspidospermine from Quebracho bark.	$C_{21}H_{24}N_2O$.	(*a*) Crystallises with 1 Aqua in fine prisms. (*b*) L. (*h*) More easily precipitated than are quinamine, quinidamine, and quinamidine. (*i*) Yellow amorphous precipitate, soon turning purple.
Paytamine.	Occurs in Payta bark.	$C_{21}H_{24}N_2O$.	(*a*) Amorphous. (*d*) Easily soluble. (*h*) Precipitated. (*i*) Purple colour.
Cusconine.	Occurs in Cusco bark.	$C_{23}H_{26}N_2O_4$.	(*a*) Crystallises readily from alcohol, with 2Aq. (*b*) L. (*c*) Very soluble. (*d*) Sparingly soluble. (*e*) $A_2H_2SO_4$. (*f*) Crystallises from alcohol in laminæ. (*g*) Gelatinous, and uncrystallisable, as are most other salts. (*h*) Amorphous dark yellow ppte. (*i*) Yellowish flocculent ppte. With Fröhde's reagent cusconine gives dark blue colour, turning olive-green on heating, and blue again on cooling.
Aricine.	With cusconine in Cusco bark.	$C_{23}H_{26}N_2O_4$.	(*a*) White shining prisms, melting at 188° C. (*b*) L. (*c*) Very easily. (*d*) Soluble. (*e*) $A_2H_2SO_4$. (*f*) Forms white gelatinous mass composed of delicate needles. (*g*) Sparingly soluble, white prisms. (*h*) Amorphous sparingly soluble, orange ppte. (*i*) Dirty yellow. amorphous. With Fröhde's reagent behaves like cusconine. Distinguished from it and all other alkaloids by forming a crystalline acetate, nearly insoluble in cold water. Also by its sparingly soluble, crystalline, acid oxalate, that of cusconine being uncrystallisable. Aricine closely resembles cinchonine.
Cusconidine.	Occurs in Cusco bark.	(?)	(*a*) Amorphous.
Javanine.	Java Calisaya bark.	(?)	(*a*) Crystallises from water in rhombic scales. (*d*) Very soluble. (*g*) Dissolves in dilute sulphuric acid with intense yellow colour.

It will be seen that many of the alkaloids are capable of isomeric modifications. The better known cinchona alkaloids have the termination *ine*, as quinine and cinchonine, whilst their isomers end in *idine*. It appears probable, however, that the base usually termed cinchonidine presents the closest parallelism with quinine, and that cinchonine is the analogue of quinidine. In addition to the bases of the above type, there are formed by the action of heat on their salts a series of amorphous bases the names of which terminate in *icine*. Aricine is not one of this type, and hence is badly named. It will be observed that quinine has the composition of an oxy-cinchonine, and many similar relationships may be noticed.*

The more important properties of the leading cinchona alkaloids may be again summarised as follows:—

(*a*)
- *Hydrated* crystals are formed by Quinine, Quinidine, Paytine.
- *Anhydrous* ,, ,, Cinchonine, Cinchonidine, Quinamine.
- *No* ,, ,, Amorphous alkaloids.

(*b*)
- *Readily soluble* in ether, Quinine, Quinamine, Paytine, and Amorphous alkaloids.
- *Sparingly soluble* ,, Cinchonidine, Quinidine.
- *Almost insoluble* ,, Cinchonine.

---

* According to Skaup, however, cinchonine and cinchonidine have the composition $C_{19}H_{22}N_2O$. This is contradicted by Hesse.

The following arrangement in series shows the relationships in the chemical composition of some of the cinchona bases.

$C_{16}H_{18}N_2O + O = C_{16}H_{16}N_2O_2$.
Paricine. Unknown.
$C_{17}H_{20}N_2O_2$.
Protoquinamicine.
$C_{18}H_{22}N_2O_2$.
Unknown.
$C_{19}H_{24}N_2O_2 - H_2O = C_{19}H_{22}N_2O$.
Quinamine. Apoquinamine.
Quinamidine. Homocinchonidine.
Quinamicine. &c.
$C_{20}H_{26}N_2O_2 - H_2O = C_{20}H_{24}N_2O + O = C_{20}H_{24}N_2O_2$.
Unknown. Cinchonidine. Quinine.
Cinchonine, Quinidine
Cinchonicine. Quinicine.
$C_{21}H_{26}N_2O_2 - H_2O = C_{21}H_{24}N_2O$.
Unknown. Paytine.
Paytamine.

The foregoing arrangement includes all the known cinchona bases except cusconine and aricine, which have the formula $C_{23}H_{26}N_2O_4$, and are peculiar in containing 4 atoms of oxygen.

(c) { *Dextro-rotatory* solutions in alcohol are formed by Cinchonine, Quinidine, Quinamine and Amorphous Alkaloids.
Lævo-rotatory ,, Quinine, Cinchonidine, Paytine.

(d) { Dilute sulphuric acid solutions are *fluorescent* in the case of Quinine and Quinidine.
No fluorescence is exhibited by solutions of Cinchonine, Cinchonidine, Quinamine, or Amorphous Alkaloids.

(e) { *Thalleioquin is* formed by Quinine, Quinidine, Quinicine.
Thalleioquin is *not* formed by Cinchonine, Cinchonidine, Cinchonicine, Quinamine.

Analytical processes for the separation and approximate estimation of the principal cinchona bases are given in a tabular form on pages 452 and 454. Special methods for the separation of particular alkaloids will be found on pages 435, 441, 445, &c.

Quinine. Quinia. $C_{20}H_{24}N_2O_2$.

This is the most important of the cinchona bases, and appears to possess the most powerfully febrifuge properties. Its mode of preparation from the bark is based on the same principles as its determination in the same (see page 448).

Free quinine usually appears as an amorphous or resinous mass. In commerce the free alkaloid is usually met with as a coarse powder, having a brownish-yellow tint owing to a trace of colouring matter. It may also be obtained as a fine white powder, and is then quite pure.

From alcohol and some other solvents quinine may be obtained in crystals, but on the evaporation of its ethereal solution it separates as a gelatinous or resinoid mass, which is never crystalline.*

Quinine forms at least two hydrates, containing respectively 1 and 3 atoms of water, and apparently a dihydrate exists as well. The conditions of the formation of these hydrates are not well understood, and the circumstances under which they become anhydrous also require investigation. But their composition has little practical interest, as the author has proved by numerous experiments that the quinine obtained by the evaporation of its solution in chloroform or ether is rendered anhydrous if exposed at 100° C. till constant in weight, and that the same product is obtained in a very short time at 120°.

* This is an important character, as most other cinchona bases give crystalline ether-residues.

As obtained by the precipitation of the solution of one of its salts by an alkali, quinine forms a bulky white precipitate which coagulates into a resinoid mass by very slight elevation of temperature.

Quinine is very sparingly soluble in water, according to J. Regnauld the solubility at 15° C. being 1 part in 2024. According to Sestini, however, the solubility of the anhydrous alkaloid in water is 1 in 1667 at 20° and 1 in 902 at 100° C., the tri-hydrate requiring 1428 and 773 parts of water at the same temperatures.

In dilute solutions of the fixed alkalies quinine is not more soluble than in pure water, but ammonia exercises considerably greater solvent action. Certain ammonium and calcium salts notably increase the solubility of quinine in aqueous liquids.

Quinine dissolves in about two parts of alcohol of ·82 sp. gr., and is still more soluble in boiling alcohol. Crystallised quinine is stated to require from 22 to 30 parts of ether for solution, but nascent quinine dissolves in little more than its own weight of ether. Quinine is also very soluble in chloroform, and dissolves readily in benzene, petroleum spirit, and carbon disulphide.

Quinine exercises a powerful lævo-rotatory action on polarised light, the value of S_D being $-165{\cdot}8°$, for the solution of the free alkaloid in alcohol.

Quinine is a powerful base, its solutions having a marked alkaline reaction and neutralising the strongest acids.

Detection and Determination of Quinine.—The detection and estimation of quinine, when it occurs unmixed with other alkaloids or organic matter, is very readily effected, but the problem becomes more complex in the presence of other cinchona bases.

The following reactions are yielded by a solution of quinine in a moderate excess of dilute sulphuric acid:—

1. Solutions of quinine in dilute sulphuric acid exhibit a strong blue fluorescence. The effect is best observed in very dilute liquids, and is intensified by addition of excess of sulphuric acid. The hydrochloride and other haloid compounds of quinine (including the thiosulphate) exhibit no fluorescence

till excess of sulphuric acid is added, and the fluorescence of solutions of the sulphate is destroyed by very small quantities of hydrochloric acid or other chlorides. Under favourable conditions, the fluorescence of quinine becomes an extremely delicate test for the presence of the alkaloid. Fluorescence is also produced by quinidine and quinicine, but not by quinamine, cinchonine or its isomers, or the amorphous alkaloids. It is best observed as described on page 163.

2. If a solution of quinine, rendered as nearly neutral as possible, be treated first with chlorine or bromine, and then with excess of ammonia, a green substance called thalleioquin is produced, which in concentrated solutions forms a precipitate, and in more dilute a deep green liquid. When carefully applied the test is extremely delicate. Bromine is a more sensitive reagent than chlorine. The following is the best mode of applying the test:—To 10 c.c. of the solution of quinine add 3 c.c. of chlorine water, or ·5 c.c. of saturated bromine water. Agitate well, and then add one drop of strong ammonia solution, or sufficient to render the liquid distinctly alkaline. If the proportion of quinine exceed about 1 per 1000 of solution, a green substance is precipitated, soluble in absolute alcohol, but insoluble in ether or chloroform. In more dilute liquids, even if the proportion of quinine does not exceed 1 in 20,000, a deep green coloration is produced.

H. Trimble has proposed to use this reaction for the approximate colorimetric determination of quinine. He dissolves ·01 gramme of a quinine salt in 5 c.c. of fresh chlorine water, and adds 10 c.c. of ammonia solution. The sample is treated in the same way, and the proportion of quinine ascertained from the relative volumes of the liquids when coloured equally intensely.

The thalleioquin reaction is also given by quinidine and quinicine, but not by quinamine, or cinchonine and its isomers.

3. If, after the addition of chlorine or bromine water, the quinine solution be treated with a few drops of solution of potassium ferro- or ferri-cyanide, ammonia being *subsequently* added, a red coloration is produced instead of a green. The

reaction is not as delicate as the thalleioquin test, but affords useful confirmatory evidence of the presence of quinine.

4. On adding a fixed alkali, alkaline carbonate, or ammonia to a solution of a salt of quinine, a bulky white precipitate of the free alkaloid (more or less hydrated) is produced. The precipitate is very sparingly soluble in cold water or excess of these precipitants, with the exception of ammonia. The precipitate cannot be conveniently filtered off, washed, and weighed, as it is not wholly insoluble, and melts with very slight increase of temperature. Its state of hydration is also very uncertain. But, if the liquid containing the precipitated alkaloid be agitated with ether or chloroform, the quinine passes readily into complete solution, and may be obtained in the solid state by evaporating the solvent. The process is readily made quantitative by operating in the following manner:—

The quinine is brought into solution by treating the substance with dilute acid, and filtering from any insoluble matter. If any essential oils or glucosides be present, they may be removed by agitating the acid liquid with chloroform or ether, and removing the solvent when it has separated from the aqueous liquid. The latter is then brought to a measure of 30 to 40 c.c., placed in a burette or separator, thoroughly cooled, treated with excess of ammonia, and agitated without delay with half its bulk of ether. The ether dissolves the separated quinine, and on leaving the burette at rest for a few seconds, separates readily, and rises to the surface of the aqueous layer. Complete separation of the ethereal and aqueous liquids is facilitated by immersing the tube in very cold water. If any difficulty occur, the separation may be induced with certainty by adding more ether. The ethereal layer is next separated from the aqueous liquid. This may be effected by withdrawing the lighter liquid with a pipette, or allowing the denser to run out through the tap of the burette or separator. In either case the aqueous liquid should be agitated a second time with ether, and the operation again repeated if extreme accuracy be required. The ethereal solution of the quinine is evaporated in a small weighed beaker, and the residue dried at 120° C. for fifteen minutes, or the

alkaloid may be dried in the water-oven till constant in weight. By either mode of operating, the residue is readily obtained in a definite state, and may be regarded as anhydrous quinine, $C_{20}H_{24}N_2O_2$, mixed, of course, with any other alkaloid soluble in ether which may have been present in the original substance. The residue, after weighing, may be subjected to further treatment, with a view of detecting and estimating alkaloids other than quinine.

Chloroform may be substituted for the ether in the above process. It extracts the alkaloid equally well, but separates comparatively slowly from the aqueous liquid, several hours being frequently required for a sharp separation of the two layers. A mixture of equal measures of ether and chloroform separates readily, and gives good results. The determination of quinine by the above process is capable of yielding very accurate results, and is of very extensive and rapid applicability. The process is general for the estimation of any alkaloids readily soluble in ether or chloroform.

5. When quinine exists in a free state, as it is obtained in process 4 by the evaporation of its solution in ether or chloroform, it may be determined by titration with standard acid. Each 1 c.c. of decinormal sulphuric acid (=4·9 grammes of H_2SO_4 per litre) corresponds to ·0324 gramme of anhydrous quinine. The process is conducted by dissolving the ether-residue in hot alcohol, adding as much water as can be used without causing precipitation, and titrating with decinormal acid. The indicator may be litmus, but cochineal is decidedly preferable. Tolerably sharp readings are obtainable, but extreme care is necessary owing to the very high combining-weight of quinine ($C_{20}H_{24}N_2O_2$=324). The titration by standard acid, of course, merely indicates the total alkaloid present, in terms of quinine. The process furnishes a very useful check on the determination from the weight of the ether-residue, and brings the alkaloid into a convenient form for further examination by one of the following processes:—

6. On adding tincture of iodine to a solution of acid sulphate of quinine in dilute alcohol, a curious compound is produced, called, after its discoverer, Herepathite,

and having the formula $4C_{20}H_{24}N_2O_2,3H_2SO_4,2HI,I_4+3Aq.$* This body, called also the iodo-sulphate of quinine, or sulphate of iodo-quinine, is the type of a series of similar bodies formed by the action of iodine on the sulphates of the cinchona bases. Herepathite is but little soluble in cold water or dilute alcohol, and requires 1000 parts of hot water for solution; but it dissolves in boiling rectified spirit, and is deposited on cooling in tabular crystals, remarkable for their dichroism and their action on light, a thin film of herepathite polarising the transmitted light as completely as the tourmaline. Herepathite is re-converted into sulphate of quinine by treatment with sulphurous acid, sulphuretted hydrogen, and other reducing agents.

Iodosulphate of quinine possesses far less solubility than the corresponding compounds of the other cinchona bases. This fact has been utilised by De Vrij for the determination of quinine when in admixture with the other alkaloids. In the latest modification of his process, he precipitates the quinine by the very soluble iodosulphate of quinoïdine, which he prepares and employs in the following manner:†—

Two parts of sulphate of quinoïdine (Howard's "sulphate of amorphous quinine") are dissolved in eight parts of water containing 5 per cent. of sulphuric acid (the volumetric "normal" acid). To this solution, which must be *clear*, a solution of 1 part of iodine and 2 of iodide of potassium in 100 of water is *slowly* added with vigorous stirring, so that no part of the quinoïdine solution may come in contact with an excess of iodine. A flocculent, orange-coloured precipitate of iodosulphate of quinoïdine is formed, which by slight elevation of temperature coagulates to a dark brownish-red resinoid body. The yellowish liquid is poured off, and the precipitate heated to 100° with water, when the liquid is poured away. The adhering moisture is evaporated off at 100° C., when the iodosulphate remains as a soft and tenacious mass, which

* Herepathite may be readily prepared by dissolving the sulphate of quinine in ten parts of proof spirit containing 5 per cent. of sulphuric acid, and adding an alcoholic solution of iodine as long as a black precipitate is produced. The precipitate is filtered off, washed, and recrystallised from hot alcohol.

† *Pharm. Journ.* [3], vi. 461.

becomes brittle on cooling. One part of this substance is dissolved by heating with 6 parts of alcohol of 92 to 94 per cent.. The solution is allowed to cool, filtered, evaporated to dryness, and the residue dissolved in 5 parts of cold alcohol. When filtered, the solution thus obtained is ready for use.

To determine the proportion of real quinine in a sample of mixed cinchona bases, 1 part by weight of the alkaloid is dissolved in 40 parts of alcohol of 92 per cent., containing ·76 per cent. of sulphuric acid.* To this solution the iodosulphate of quinoïdine is added drop by drop from a burette, as long as a dark brownish-red precipitate of herepathite is formed.† As soon as all the quinine has been precipitated, and a slight excess of the reagent added, the liquor acquires an intense yellow colour. The beaker is now covered and heated on a water-bath till the liquid *begins* to boil.‡ It is then cooled and weighed. The liquid is next passed through a small filter and washed with a saturated solution of herepathite in alcohol of 92 per cent. The weight of the funnel with the moist filter is observed, and the filter is then allowed to dry. The loss of weight is the quantity of alcohol retained by the wet filter, and from this the weight of herepathite introduced can be ascertained.

The precipitated herepathite is next dried at 100° and weighed. The amount found is corrected by the addition of that remaining in solution, as ascertained by calculation from the weight of the liquid in which the precipitation was effected. 100 grammes of alcohol of 92 per cent. dissolve ·133 gramme of herepathite at 24·5 C., and ·125 gramme at 15° C.

The weight of herepathite found, multiplied by ·55055 gives

* This quantity of acid is sufficient to convert the bases into acid sulphates. An excess should be avoided. It is evident that the proper quantity will be used if there be added an additional measure of decinormal sulphuric acid equal to that required for the neutralisation of the ether-residue (page 420).

† The liquid must be continually stirred. An orange-coloured gelatinous precipitate of iodosulphate of cinchonidine may be formed in presence of a large proportion of that base (as in the alkaloids from Indian red-bark). If this occur, before adding more of the reagent the liquid must be heated till the precipitate disappears. Any large proportion of cinchonidine should by preference be previously separated by solution in ether (see page 452).

‡ Christensen recommends precipitation in the cold and filtration after one hour.—*Pharm Journ.* xii. 441.

the anhydrous, or by ·7409 the corresponding weight of crystallised sulphate of quinine.* It is probable that a volumetric modification of the foregoing process might be devised. Thus it might be found possible to titrate the precipitated herepathite with standard thiosulphate (hyposulphite), or to ascertain the excess of iodine in the filtrate by the same means.

Other methods for the separation of quinine from the remaining cinchona bases are given on pages 427, 430, 435, and 450, *et seq.*

The separation of quinine from strychnine becomes necessary in the analysis of "Easton's syrup" (phosphate of iron, quinine, and strychnine), and the "citrate of iron, quinine, and strychnine." In either case a known quantity of the sample (5 grammes if solid) is treated with ammonia and mixed chloroform and ether, as described on page 420. The chloroform is separated, evaporated, and the residue of mixed alkaloids dried at 120° C. After weighing, they are dissolved in 10 c.c. of water acidulated with a few drops of sulphuric acid. The solution is neutralised by ammonia and mixed with excess of ammonium oxalate. After standing twenty-four hours the precipitated oxalate of quinine is filtered off, the mother-liquor removed by gentle pressure, and the precipitate washed once with a little cold water. It is then dried at 100° and weighed.† Its weight, multiplied by ·878, gives the quinine in the quantity of the sample operated on. The filtrate and wash-water are then shaken with ammonia and chloroform and ether, and the dissolved alkaloid recovered in the usual way by evaporation of the solvent. The residue of alkaloid (consisting of strychnine, any amorphous alkaloid, and a mere trace of quinine) should be next twice treated with 3 c.c. of washed ether, which dissolves the amorphous

* By working in the manner already described there is little fear of the precipitate containing an indefinite proportion of iodine, whereas if solution of iodine were added directly there might be a tendency to the formation of one of the more-highly-iodised compounds which are known to exist.

† The mode of operating described in the text is due to B. W. Dwars. It would probably be better to wash the precipitate with ammonium oxalate, and then extract the quinine in the free state by agitating the precipitate with ammonia and ether.

alkaloid (and quinine) leaving the strychnine almost wholly undissolved.

QUININE SULPHATE. Diquinic sulphate. $(C_{20}H_{24}N_2O_2)_2H_2SO_4$. —This important salt, sometimes called "disulphate" or "basic sulphate" of quinine, is the ordinary medicinal sulphate of quinine of commerce.

Sulphate of quinine is usually met with in exceedingly light scales, or long, flexible, monoclinic needles, having a nacreous aspect.

The crystallised sulphate of quinine of commerce usually contains about 14·5 per cent. of water, a proportion which corresponds to a 7-atom hydrate. According to some authorities, however, the wholly uneffloresced crystals contain 8 Aqua, or at any rate $7\frac{1}{2}$ Aqua. On the whole, the evidence is in favour of the formula $Qu_2H_2SO_4+7H_2O$ being correct, and it certainly most accurately represents the commercial product. Occasionally, however, samples are met with containing a considerably higher percentage of water than corresponds to the above formula (=14·45 per cent. Aqua). In these cases the excess of water has probably been added as an adulterant.

Crystallised quinine sulphate is rendered perfectly anhydrous by exposure to a temperature of 100° C. If a higher temperature be employed for its dehydration, there is a danger of some of the alkaloid undergoing conversion into quinicine (see page 443). If the anhydrous sulphate of quinine be exposed to moist air, it rapidly absorbs from 4·8 to 5 per cent. of water, a proportion which corresponds to the formula $Qu_2H_2SO_4+2H_2O$. The same quantity of water is retained when the crystallised salt is dried over sulphuric acid, or crystallised from strong alcohol.

Quinine sulphate requires 750 parts of cold water for solution, but dissolves in about 30 parts of water at 100° C. It is far less soluble in water containing sulphate of magnesium, sodium, or ammonium than in pure water. In a strong solution of Rochelle salt, quinine sulphate is so little soluble that the alkaloid can scarcely be detected by the fluorescence or thalleioquin test. The solubility of sulphate of quinine in water is increased by the presence of ammonium chloride, or of potassium nitrate or chlorate.

In alcohol, quinine sulphate dissolves more readily than in water, requiring only seven or eight parts at a boiling temperature, but it is much less soluble in cold spirit (see "Tincture of Quinine," page 436). Quinine sulphate dissolves in about 24 parts of cold glycerin, the solution being precipitated by addition of water. Crystallised quinine sulphate is not soluble in fixed oils, ether, chloroform, or petroleum spirit. (It is said to dissolve in benzene.) In the anhydrous state one part of quinine sulphate is soluble in about 1000 parts of chloroform (see page 430).

In dilute sulphuric acid, quinine sulphate is readily soluble, owing to the formation of acid sulphate of quinine, $C_{20}H_{24}N_2O_2,H,HSO_4$. This salt is readily obtainable in crystals containing $7H_2O$. The crystallised salt loses 6 Aqua in the exsiccator, and becomes anhydrous at 100° C. When heated to about 135° C. it melts and is converted into the corresponding compound of quinicine (see page 442). Acid sulphate of quinine dissolves in eleven parts of cold water, and more readily in hot water or in alcohol.

From a solution of quinine in excess of dilute sulphuric acid, an acid sulphate may be obtained having the composition $C_{20}H_{24}N_2O_2,2H_2SO_4,+7H_2O(=C_{20}H_{24}N_2O_2,H,HSO_4+H_2SO_4+7H_2O)$.

Normal quinine sulphate has a specific rotation in alcoholic solution of $S_D=191{\cdot}5°$, calculated for the anhydrous salt. Excess of acid increases the rotatory power.

Sulphate of quinine is largely employed as a febrifuge and tonic. It has marked antiseptic properties.

The fluorescence of sulphate of quinine is considered on page 417; its reaction with iodine on page 421; and with the thalleioquin test on page 418.

EXAMINATION OF COMMERCIAL SULPHATE OF QUININE.—Commercial sulphate of quinine was formerly subject to adulteration of a very gross character. Among the bodies employed to sophisticate it are said to have been starch, gum, stearin, salicin, phloridzin, sugars, sulphate of magnesium, sulphate of sodium, chalk, asbestos, boric acid, &c.

Of such adulterants, the mineral additions would be readily recognised on igniting the sample. Starch, chalk, stearin

and boric acid would remain insoluble on treating the substance with cold dilute sulphuric acid, and gum would be precipitated on adding excess of alcohol to the solution thus obtained.

Soluble impurities generally may be detected and estimated by dissolving the sample in hot water and adding excess of baryta water. The alkaloid is then removed by agitation with ether. After removing the ethereal layer, a stream of carbonic acid is passed through the aqueous liquid to precipitate the excess of baryta, and the whole well boiled and filtered. Sulphate and carbonate of barium will be left insoluble, and the filtrate will contain any sugar or other soluble impurity present in the original sample, and the weight of the residue left on evaporation will allow of a determination of the amount. In presence of sugar the liquid will exert a dextro-rotatory action, and in presence of salicin a lævo-rotatory action of polarised light.

Treatment of the original solid sample with concentrated sulphuric acid, attended by gentle warming, will suffice for the qualitative detection of some impurities. Sugar and mannite become charred and salicin develops a striking red colour.

Similar general impurities may be rapidly tested for by treating 1 gramme of the sample of sulphate of quinine, previously well dried at 100° C., with 7 c.c. of a mixture of two volumes of chloroform and one of absolute alcohol. The contents of the tube should be shaken once round, the tube corked and set aside for ten minutes. Any inorganic adulterants, salts of ammonium, cane-sugar, milk-sugar, mannite and starch are left insoluble, but if the salt be pure it will be entirely dissolved. The residue may be filtered off, weighed, and further examined.

Salicin, if present in greater proportion than 1 per cent., may be detected by the last test. The residue insoluble in the chloroform-mixture will be coloured deep red by concentrated sulphuric acid, and will reduce Fehling's solution after boiling with dilute sulphuric acid. The reaction with strong sulphuric acid will be produced by the original sample if

the proportion of salicin be considerable. Smaller proportions of salicin may be detected in the filtrate from the precipitate produced by adding baryta to the aqueous solution of the sample. Another test for salicin is to dissolve ·25 grammes of the sample in 4 c.c. of water and four drops of concentrated hydrochloric acid. If salicin were present, on boiling the liquid for some minutes a white turbidity will be produced, due to the formation of saliretin.

Sulphate of quinine has occasionally been largely adulterated with or entirely substituted by the hydrochloride of cinchonine. This fraud is recognisable by testing for chlorides with nitric acid and nitrate of silver, and for cinchonine as described on page 429.

The most common impurity of commercial sulphate of quinine is an admixture of one or more of the sulphates of other cinchona alkaloids. This admixture is often accidental, owing to imperfect separation of the other alkaloids during manufacture, but occasionally an intentional admixture of other alkaloids occurs.

The detection and estimation of foreign alkaloids in commercial sulphate of quinine has received much attention, and considerable ingenuity has been exercised in the solution of this somewhat difficult problem.

The *British Pharmacopœia* prescribes the following method of testing the purity of commercial sulphate of quinine. The test is based on the relative solubility of quinine and the other cinchona alkaloids in ether. "Ten grains, with ten minims of diluted sulphuric acid and half a fluid ounce of water form a perfect solution, from which ammonia throws down a white precipitate. This redissolves on agitating the whole with half a fluid ounce of ether, without the production of any crystalline matter floating on the lower of the two strata, into which the agitated fluid separates on rest."

A test which is superior to the above is due to Kerner, and is the official method of the German Pharmacopœia. The following are the details of the method applied quantitatively, but for qualitative purposes, 1 gramme of the sample may be employed, and proportionately reduced quantities of water and ammonia added. 5 grammes' weight of the sample is

ground in a mortar with a little cold water, the mixture rinsed into a graduated cylinder or flask, and the volume of the liquid made up with water to 50 c.c. The whole is well agitated and left for some hours, when it is filtered through a dry filter. 40 c.c. of the filtrate is then mixed with 56 c.c. of ammonia of ·96 specific gravity, and the whole agitated. If the sample be free from more than traces of foreign alkaloids, the precipitate first formed will redissolve, but otherwise a permanent precipitate will be formed. This should be collected on a filter, washed with a little cold water, and, either dried and weighed, or redissolved in acidulated water and the liquid treated with ammonia and chloroform as described on page 419. The weight found will be the foreign alkaloid in 4 grammes of the sample, and when calculated into the corresponding amount of crystallised sulphate will show the proportion of admixture.

Dr Paul * has shown that the British Pharmacopœia test is not capable of recognising a moderate admixture of sulphate of cinchonidine in sulphate of quinine, owing to the property possessed by quinine of increasing the solubility of cinchonidine in ether, or at any rate of preventing the latter from separating in a crystalline state. Owing to this circumstance it becomes impossible to detect an admixture of 10 per cent. of cinchonidine sulphate in the commercial salt of quinine,—indeed, if the large volume of ether recommended in the Pharmacopœia be adhered to, it becomes difficult to detect even 20 per cent. of the cinchonidine salt. Hence, for the detection of cinchonidine in sulphate of quinine it is necessary first to separate the greater part of the latter salt. This may be done by utilising the fact that quinine sulphate requires 750 parts of cold water for solution, while cinchonidine sulphate is soluble in 100 parts. The test was originally proposed by Kerner (see above), but has been improved by Paul and Hesse. The following is the best mode of operating:—·5 gramme of the sample to be tested is treated in a test tube with 10 c.c. of boiling water. The tube is immersed in hot water till the greater part of the sample has dissolved, when it is allowed to cool, and is then passed

* *Pharm. Journ.* [3], vii. 653.

through a dry filter. 5 c.c. of the filtrate is then shaken in a narrow tube with 1·4 c.c. of ether and from 3 to 5 drops of ammonia.* If, on leaving the tube at rest and in a closed condition for two hours, the ethereal stratum be found free from crystals, the sample may be considered pure; but if it contain more than 0·25 per cent. of cinchonine sulphate, 0·5 of quinidine sulphate, or 1·0 per cent. of cinchonidine or homocinchonidine sulphate, a distinct separation of crystals will occur. The last two impurities appear granular, while crystals of cinchonine and quinidine form concentric groups of delicate needles. If the proportion of cinchonidine is as high as 3 per cent., the separation of crystals will occur immediately, or within three minutes; 2 per cent. will show in about ten minutes, while with less than 1 per cent. no separation will occur even after twelve hours. To detect smaller proportions of these alkaloids, the tube is opened and the ether allowed to evaporate spontaneously. On examining the residue with a lens it will appear distinctly crystalline if ½ per cent. of cinchonidine or homocinchonidine sulphate be present, and a mere trace will be recognisable by the presence of a few crystals in the amorphous mass of quinine. 0·5 per cent. of cinchonine sulphate, or 1·0 per cent. of quinidine sulphate will cause an almost immediate separation of crystals from the ether. Their presence is far more likely to be intentional than merely accidental or due to careless manufacture.

The above test is applicable to the examination of hydrochloride of quinine, if the ·5 gramme of the sample be mixed in the first place with ·25 gramme of crystallised sodium sulphate. The hydrochloride of quinine is more likely to be contaminated with the similar salts of cinchonine and quinidine than with the hydrochlorides of cinchonidine and homocinchonidine.

If it be desired to render the test more strictly quantitative as much as 5 grammes of the sample should be employed, and the solution and recrystallisation several times repeated. The deposit from the ether must be passed through a small filter and weighed. The details of the process are given on last page.

* It is perhaps safer to add first a few drops of dilute acid and then sufficient ammonia to constitute a moderate excess.

Operating in this manner, Dr Paul found in commercial sulphate of quinine amounts of cinchonidine representing from 1 to 10 per. cent. of the crystallised sulphate, and Fletcher states that, while English quinine is usually free from this impurity, certain foreign brands always contain from 10 to 15 per cent. In one instance the proportion exceeded 25 per cent.

For the detection of cinchonine or quinidine in quinine sulphate, Hesse proposes to dry the sample at 100° C., and agitate 1 gramme with 15 c.c. of chloroform free from alcohol. The liquid is passed through a small filter. If 10 c.c., on evaporation at a gentle heat, leave an amorphous residue weighing more than ·035 gramme, cinchonine or quinidine sulphate is certainly present. If the residue be crystalline and less than the above weight, it may be tested for the foreign alkaloids by heating it with 5 c.c. of water, adding ½ gramme of potassium-sodium tartrate, cooling, filtering from the precipitated quinine and cinchonidine tartrates, and mixing the filtrate with an equal volume of ammonia. If quinidine or or cinchonine be present, a precipitate will be formed, and may be further examined by agitation with ether (see page 419), or by treatment with iodide of potassium (see page 441).

Sulphate of cinchonidine, if present, will remain undisolved by the chloroform, but will swell up into very bulky needles, which suck up the chloroform like a sponge and do not yield it again without pressure.

For the detection of amorphous alkaloid in commercial quinine sulphate, De Vrij recommends the following method:—The sample is dissolved in dilute acid, and shaken with ammonia and ether for estimation of total alkaloid. Sufficient decinormal oxalic acid is added to the ether-residue to convert the alkaloid into neutral oxalate, and the liquid is evaporated at a steam-heat and the residue thoroughly dried in the water-bath. It is then dissolved in chloroform, and the liquid filtered if necessary. The clear solution is next treated in a test tube with a few drops of water, when crystals of oxalate of quinine will appear in the chloroform. If the sample were pure the aqueous layer will remain clear and uncoloured, but if amorphous alkaloid be present it will be dissolved by the water and colour it yellow.

QUININE HYDROCHLORIDE. Hydrochlorate of quinine.—$C_{20}H_{24}N_2O_2,HCl+2H_2O$. This salt forms long asbestos-like prisms, which become anhydrous at 120° C. It is soluble in about 40 parts of cold water.

It has been recently proposed to substitute for medicinal purposes the hydrochloride for the sparingly soluble sulphate of quinine. The former salt is the more expensive, owing to the increased difficulty of crystallising, and the high percentage of quinine contained in it (84·2 per cent., against 73·5 in the crystallised sulphate).

Quinine hydrochloride is prepared by reacting on the sulphate with chloride of barium. Hence it is apt to contain either undecomposed sulphate of quinine, or else barium chloride. The latter impurity is, of course, very objectionable.

Quinine hydrochloride may be assayed in much the same manner as the sulphate (see page 426, *et seq.*).

Quinine hydrochloride has on several occasions been accidentally mixed with or replaced by the corresponding salt of morphine. The impurity may be detected by warming the salt with dilute nitric acid, which acquires a yellow or red colour if morphine be present, or the salt may be placed in a porcelain crucible and moistened with very neutral ferric chloride, which will produce a green colour if morphia be present. Lastly, the aqueous solution of the salt may be treated with ammonia and agitated with a small quantity of ether, when any morphine (or cinchonine) will remain undissolved.

QUININE TANNATES.—Quinine tannate forms a yellowish amorphous powder, very sparingly soluble in cold water, pretty readily in hot. It is also soluble in alcohol. Its solution gives the reactions of tannic acid. A tannate of quinine has come into use of late on account of its nearly tasteless character. The commercial product varies greatly in composition, the bitter taste decreasing with the amount of alkaloid contained in the specimen. In some cases the quinine is largely replaced by other cinchona bases. The following analyses by Jobst,* illustrate the composition of commercial "tannate of quinine":—

* *Arch. Pharm.* [3], xii. 331; and *Journ. Chem. Soc.* xxxiv. 678.

	1	2	3	4	5	6	7
Water lost at 120° C.	7·2	9·7	9·1	9·8	10·2	10·7	11·4
Quinine . . .	31·37	22·72	4·46	4·93	6·23	10·00	7·40
Quinidine . .	...	...	11·97	2·43	Trace.	...	...
Cinchonidine .	...	...	7·33	13·10	23·80	...	...
Cinchonine . .	...	...	...	3·35	Trace.	...	...
Total Alkaloid	31·37	22·72	23·76	23·82	27·03	10·00	7·40

To ascertain the total alkaloid in quinine tannate, Jobst powders 1 gramme of the sample, and mixes it with milk of lime. The mixture is dried on the water-bath, and the resulting powder exhausted with chloroform. The chloroform is filtered, evaporated at a steam heat, and the residue weighed after drying at 120° C. The alkaloid thus separated can be further examined as described on page 452. There seems no reason why the mixture of the sample with milk of lime should not be agitated directly with chloroform, thus avoiding the evaporation to dryness of the aqueous liquid.

QUININE VALERATE forms colourless rhomboidal plates, having a pearly lustre and a faint odour of valeric acid. It is not deliquescent, and fuses at a low temperature. Quinine valerate requires 110 parts of cold or forty of boiling water for solution. It is easily soluble in alcohol. Valerate of quinine is liable to contain much the same impurities as the sulphate (see page 425). Sulphate and hydrochloride of quinine, and valerate and acetate of zinc, are also probable adulterants.

QUININE CITRATE.—This body, in combination with ferric citrate, forms the "citrate of iron and quinine" of the *British Pharmacopœia*. This preparation is made by dissolving precipitated ferric hydrate in citric acid, and adding a proper proportion of quinine.*

* The compilers of the *Pharmacopœia* appear to have assumed that, when prepared according to their directions, the product would equal four times the weight of crystallised sulphate of quinine used for preparing the quinine introduced. As a matter of fact the yield is 4·45 to 4·50 times the weight. The *Pharmacopœia* gives a very unsatisfactory mode of assay, according to which the preparation is to contain 16 per cent. of quinine.

CITRATE OF IRON AND QUININE occurs in commerce in the form of thin transparent scales, varying in colour from a delicate golden green to reddish-brown, according to the proportion of ammonium citrate present. The preparation should be somewhat slowly, but freely and completely soluble in water. It is insoluble in alcohol or ether. The aqueous solution is rather strongly acid, and has a very bitter and chalybeate taste. On adding ammonia to the cold solution white hydrate of quinine is thrown down, and the liquid assumes a darker colour. No ferric hydrate is precipitated unless the liquid be heated, or a fixed alkali substituted for the ammonia.

Citrate of iron and quinine is an expensive preparation, and hence is liable to several sophistications.

Adulteration with potassio-citrate or potassio-tartrate of iron will be detected by the strongly alkaline reaction of the residue left on igniting the substance. The substitution of tartaric acid for the citric acid of the sample may be detected as described in Volume I. page 275.

The proportion of water in the sample may be ascertained by drying a weighed quantity in the water-oven. It should not exceed 10 to 12 per cent.

Excess of citric acid is indicated by the extra acidity of the sample, but the commercial substance always contains a much larger proportion of acid than is prescribed in the *British Pharmacopœia*, the mode of preparation there laid down being very imperfect.

The proportion of oxide of iron can be estimated in the pure preparation with sufficient accuracy by igniting a known weight of the sample. After testing the ash for fixed alkali, a few drops of nitric acid should be added and the residue again ignited. This treatment ensures the complete combustion of the carbon. Citrate of iron and quinine ought to yield from 18 to 20 per cent. of ferric oxide on ignition. A more accurate estimation of the iron can be made in the ash, if desired.

Sulphates are almost invariably present in citrate of iron and quinine, owing to imperfect washing of the ferric hydrate employed, or to the introduction of the quinine as sulphate instead of precipitated hydrate. The employment of sulphate of quinine is rather desirable than otherwise, as the

proportion of sulphuric acid thus introduced is not large, and the preparation is more likely to contain the intended proportion of quinine.*

For the estimation of the alkaloid in the citrate of iron and quinine the *British Pharmacopœia* directs the weighing of the precipitate produced by ammonia. The process is admittedly unsatisfactory, and in practice has been already replaced by a method suggested by the author. This is simply agitation with ether to dissolve the precipitate produced by ammonia. The ethereal layer is subsequently evaporated, and the residue weighed. The details of the process are described on page 419. The following are the special precautions desirable:—1. The *cold* solution of the sample must be treated with a considerable *excess* of ammonia. 2. If a fixed alkali be substituted for the ammonia, sufficient citric acid must first be added to prevent any precipitation of ferric hydrate. 3. The volume of ether used should equal that of the ammoniacal liquid, and the agitation should be conducted immediately. After withdrawing the ethereal layer the aqueous liquid must be shaken with more ether.† 4. Care must be taken that the whole of the precipitated alkaloid is dissolved by the ether. This occurs instantaneously with pure quinine, but if cinchonine has been substituted it will remain undissolved. In such samples the treatment with ether should be followed by agitation with a mixture of 4 parts of chloroform and 1 of amylic alcohol (see page 437).

The proportion of dry ether-residue obtainable from samples

* Mr F. W. Fletcher informs me that a preparation made with sulphate of quinine contains even less sulphate than when the hydrate of quinine is used, as the lime salts introduced in the water employed for washing the alkaline ferric hydrate are retained by the latter, and are subsequently precipitated as calcium sulphate, instead of remaining in the finished product.

† Mr A. N. Palmer has stated that chloroform may be advantageously substituted for ether in the above process, owing to incomplete removal of the alkaloid by the latter solvent. In a subsequent note, which appears to have escaped attention, he withdrew this statement (*Pharm. Journ.* [3], viii. 89 and 127), and appears to have shaken once with ether but twice with chloroform. Chloroform yields equally accurate results with ether, but separates very slowly from the aqueous liquid, while with ether a perfect separation occurs in a few seconds. A mixture of chloroform and ether may be advantageously used (see page 420).

of citrate of iron and quinine which answer the *Pharmacopœia* test is *fully* 14 per cent. The percentage ought not to fall below 13·8 as a minimum. The proportion actually obtained from commercial specimens is sometimes as low as 5 to 6 per cent. From a sample of Howard's citrate the author obtained 16·4 per cent. of ether-residue.

The adulteration of citrate of iron and quinine is not limited to deficiency of alkaloid, the quinine being sometimes replaced by other cinchona bases. Any considerable proportion of cinchonine (or quinidine) will be detected on treatment with ether as described above, but the amorphous alkaloids and cinchonidine (in moderation) will show no sign. They may, however, be recognised by the following method described by Fletcher.* Although the quantity of the sample operated on is considerable, the quinine is nearly all recovered as sulphate. 25 grammes of the sample are dissolved in 50 c.c. of cold water, and excess of ammonia added with constant agitation. The separated alkaloid is removed by shaking with three successive portions of ether, using 25 c.c. each time. The ethereal solution is evaporated to dryness, and the residue heated to 120° C. for fifteen minutes. The weight of residue thus obtained represents the anhydrous total alkaloid in 20 grammes of the sample. Enough sulphuric acid is next added to effect the conversion of the alkaloid into neutral sulphate. This will be done if the weight of the residue in grammes be multiplied by the factor 30·86, and a number of cubic centimetres of decinormal sulphuric acid equal to the product run in from a burette. On heating the liquid and stirring, complete solution of the alkaloid takes place. The liquid is then allowed to cool, and the crystalline mass obtained is thrown on a calico-filter 3 inches in diameter, stretched over a small beaker, and, when drained, the filter is tightly squeezed to remove the remainder of the liquid. The pressed mass is detached from the filter, dried at 100° C., and weighed. The residue consists of pure anhydrous sulphate of quinine, and its weight multiplied by 1·18 represents the corresponding quantity of crystallised sulphate. To the amount thus found must be added 1·33 milligrammes for each 1 c.c. of

* *Year-Book of Pharmacy*, 1875, p. 485.

mother-liquor, a correction which corresponds to a solubility of 1 part of crystallised sulphate of quinine in 750 of cold water. By multiplying the crystallised sulphate by the factor ·735, the amount of anhydrous quinine in 20 grammes of the sample is arrived at. The mother-liquor is filtered through paper into a graduated tube, and the volume noted. 20 c.c. of washed ether and an excess of ammonia are then added, the tube closed and well agitated, and then set aside for six hours. At the end of this time any cinchonidine or quinidine present will be found to have crystallised out at the junction of the two liquids. The stratum of ether is removed by a pipette, the crystals washed with two successive quantities of 10 c.c. of ether, the last drops of which may be absorbed by a little roll of filter-paper. The crystals are then thrown on a double tared filter (previously dried at 120°), dried at 120° C., and weighed, the other filter being used as a counterpoise. In practice it is found that the weight so obtained represents about two-thirds of the total cinchonidine and quinidine present. Should the amount obtained exceed 0·1 gramme, the process should be repeated on the sulphate of quinine, by dissolving it again in 100 c.c. of boiling water and proceeding as before.

Amorphous alkaloids, which are not unfrequently present in considerable proportion, will remain dissolved in the ether from which the crystals of cinchonidine and quinidine are deposited, and may be recovered by evaporating the liquid.

TINCTURE OF QUININE (*British Pharmacopœia*) is directed to be made by dissolving 160 grains of crystallised sulphate of quinine in 20 fluid ounces of tincture of orange-peel, by the aid of a gentle heat, the solution being filtered after three days. This is a somewhat unsatisfactory preparation, as in cold weather it is apt to deposit crystals of sulphate of quinine, and so alter in strength. According to some observers, separation does not occur if the spirit employed for preparing the tincture of orange-peel be of full strength (·920 sp. gravity). In some cases, at least, the deposit consists largely of calcium sulphate. To determine the proportion of quinine in the tincture, 1 fluid ounce should be concentrated, and shaken with ether to remove the essential oil of orange-peel. After removing the ether, the aqueous liquid should be

cooled, an excess of ammonia added, and then the whole shaken with ether in the usual way (see page 419). The residue obtained on removing and evaporating the ether ought to weigh 5·88 grains, an amount equivalent to 8 grains of the crystallised sulphate.

QUININE WINE (*British Pharmacopœia*) contains 1 grain of crystallised sulphate of quinine and 1½ grains of citric acid in each fluid ounce of orange wine. It is extensively adulterated by partial omission of the quinine or its replacement by other cinchona alkaloids. For its assay, 2 fluid ounces may be concentrated to ½ ounce, and then treated like the tincture of quinine (see above). If the alkaloid prove insoluble in ether, a mixture of chloroform and amylic alcohol must be substituted for the ether.

Cinchonine. Cinchonia. $C_{20}H_{24}N_2O$.—This important base is almost invariably present in cinchona barks. It crystallises from alcohol in anhydrous shining prisms or needles. It melts at 165° C. to a colourless liquid, and partially sublimes at a higher temperature. According to Hlasiwetz it may be readily sublimed in a current of hydrogen or ammonia.

Cinchonine is almost insoluble in cold water, and requires 2500 parts of boiling water for solution.

One part of cinchonine dissolves in 120 parts by weight of rectified spirit, in 102 parts of chloroform, and in 109 parts of amylic alcohol. It requires only about 13 parts of a mixture of 6 grammes of chloroform with 1 of alcohol of the above strength, and is soluble in 23 parts of a mixture of 4 of chloroform and 1 of amylic alcohol.

Prescott found the following to be the solubility of cinchonine in different physical conditions, and at the boiling-point of the solvent:—

Condition of alkaloid.	Parts by weight of washed solvent required.			
	Ether.	Chloroform.	Amylic alcohol.	Benzene.
Crystallised .	719	828	...	...
Amorphous .	563	...	...	..
Nascent . .	526	178	22	376

To obtain the alkaloid in the "nascent" state the solvent was added to its sulphuric acid solution, which was then warmed to the boiling-point of the former. The liquid was next made slightly alkaline with ammonia, shaken, kept warm for five minutes, and filtered.

It will be seen from these results that amylic alcohol is by far the best solvent for cinchonine, except a mixture of amylic alcohol and chloroform. On the other hand, ether is the best solvent for effecting an approximate separation of cinchonine from quinine.

When heated to a high temperature with an alkali, cinchonine yields a volatile base called quinoline, or chinoline, C_9H_7N, boiling at 243° C., together with other products. Quinine on similar treatment yields a base boiling at about 283°, which forms a readily crystallisable non-deliquescent hydrochloride, while quinoline hydrochloride crystallises with difficulty and liquefies on exposure to the air.

Cinchonine is not precipitated in the cold from a solution containing tartaric acid by adding sodium hydrogen carbonate. On heating the liquid, however, carbonic acid escapes and cinchonine is separated.

The precipitate formed by ammonia in solutions of cinchonine is not soluble in excess of the reagent.

Cinchonine is sharply distinguished from quinine by the very limited solubility of the free base in ether, by the solubility of the anhydrous neutral sulphate in chloroform, by its failure to give the thalleioquin reaction, by its dextro-rotatory power, and by the non-fluorescence of its solution in excess of dilute sulphuric acid. Methods of detection and separation based on these facts are given on pages 427 and 430.

CINCHONINE SULPHATE. $(C_{20}H_{24}N_2O)_2H_2SO_4+2H_2O$.—This salt is obtained by exactly neutralising the free alkaloid by dilute sulphuric acid. It forms short, shining, rhombic prisms, with dihedral summits. The salt becomes anhydrous at 100° C. Cinchonine sulphate dissolves in 54 parts of cold water, and is readily soluble in alcohol. It is insoluble in ether. The *anhydrous* salt is soluble in 60 parts of cold or 22 of boiling chloroform, a fact which distinguishes it from the sulphates of cinchonidine and quinine.

A solution of cinchonine sulphate does not give the thalleioquin reaction, and is not rendered fluorescent by dilution with very weak sulphuric acid.

The mode of assaying of cinchonine sulphate is sufficiently indicated under the head of "Quinine Sulphate" (page 425).

CINCHONINE HYDROCHLORIDE. Muriate of cinchonine. $C_{20}H_{24}N_2O,HCl+2H_2O$.—This salt is readily soluble in water and alcohol, and somewhat so in ether and chloroform. It is not unfrequently employed to adulterate sulphate of quinine. In such case the solution of the sample in very dilute sulphuric or nitric acid will give a white, curdy precipitate of silver chloride on adding silver nitrate. Cinchonine will be detected by the tests for that alkaloid.

When heated in a dry test-tube, cinchonine hydrochloride gives purple fumes much resembling the vapour of iodine. The *sulphates* of the cinchona bases do not give this reaction.

Cinchonidine. $C_{20}H_{24}N_2O$.
Quinidine. Conchinine. $C_{20}H_{24}N_2O_2$. } These two alkaloids occur in greater or less quantity in cinchona barks in association with cinchonine and quinine. Their physical and chemical characters are sufficiently described on pages 412 and 415.

QUINIDINE resembles quinine in being deposited in hydrated crystals from alcohol, in its tolerably ready-solubility in ether, in giving the thalleioquin reaction, and in the fluorescence of its solution in dilute sulphuric acid.

CINCHONIDINE resembles quinine in its lævo-rotatory action on polarised light, and in the insolubility of the anhydrous neutral sulphate in chloroform, and the sparing solubility of the tartrate in water.

Quinidine is distinguished from quinine by the permanent bulky precipitate its solutions yield on successive treatment with chlorine water, potassium ferricyanide, and ammonia. Also in being precipitated by potassium iodide.

Cinchonidine is distinguished from cinchonine by the insolubility of the anhydrous sulphate in chloroform and by the precipitation of its solutions by Rochelle salt. Also by the

formula of the crystallised sulphate, and its lævo-rotatory action on polarised light.

Both cinchonidine and quinidine possessed well-marked febrifuge properties.

Quinidine is present in all samples of commercial quinoïdine.*

CINCHONIDINE SULPHATE. $(C_{20}H_{24}N_2O)_2H_2SO_4+6Aq.$—This salt requires about 100 parts of cold water for solution. It is readily soluble in alcohol.

Cinchonidine sulphate is sometimes contaminated with an admixture of the corresponding salts of cinchonine and quinidine. To detect these Hesse† dissolves ·5 grammes of the salt in 20 c.c. of water at 60° C., and adds 1·5 grammes of Rochelle salt. A crystalline precipitate of the sparingly soluble cinchonidine tartrate is produced. After standing one hour the liquid is filtered, and the filtrate tested with a drop of ammonia. Any turbidity or precipitate is due to the presence of quinidine or cinchonine. They may be distinguished by treating the filtrate with potassium iodide as described on pages 441 and 454.

Hager recommends the use of 0·1 gramme of cinchonidine sulphate, 0·3 of Rochelle salt, and 20 c.c. of cold water. The liquid is frequently agitated, filtered after one hour, and tested with a few drops of ammonia. As thus performed, the test is less strict than that of Hesse, but perhaps, on that account, is better suited for medicinal purposes.

The precipitate of cinchonidine tartrate obtained in the above tests is soluble in 1200 parts of cold water. After drying at 100° C., it contains 80·84 per cent. of cinchonidine. It will contain quinine if any of that base were present in the sample. In such case the solution of the precipitate in excess of dilute sulphuric acid will be notably fluorescent.

Hesse has also proposed to distinguish the sulphates of the cinchona bases by their behaviour with chloroform. The *anhydrous* neutral sulphates of quinine and cinchonidine are almost insoluble in alcohol-free chloroform, while the corre-

* For its extraction from quinoïdine, see De Vrij, *Jahresb.* 1866, p. 473.

† *Zeitsch. f. Anal. Chem.* xv. 464.

sponding salts of cinchonine and quinidine dissolve readily. As the test is also applicable for ascertaining the purity of quinine sulphate, the details are described in the section on that salt (see page 430).

QUINIDINE SULPHATE; $(C_{20}H_{24}N_2O_2)_2H_2SO_4+2H_2O$, requires about 350 parts of cold water for solution. The salt differs from the sulphates of the other cinchona alkaloids in requiring a temperature of 120° to render it anhydrous, and in readily taking up the water again in moist air.

For the detection of inorganic impurities (*e.g.*, calcium or sodium compounds) in the commercial salt, Hesse treats 1 gramme of the sample with 7 c.c. of a mixture of 2 volumes of chloroform with 1 of alcohol of 95 per cent. Complete solution will take place in the absence of impurities.

The presence of cinchonidine sulphate in the quinidine salt may be detected by treating the sample with pure chloroform. Unless only a very small proportion of the impurity be present part of it will remain undissolved. Smaller quantities may be detected by shaking the chloroform solution with cold water, in which the whole of the cinchonidine and part only of the quinidine salt will dissolve, and the former will be precipitated on addition of Rochelle salt.

A solution of quinidine sulphate in chloroform is at first colourless, but on keeping becomes yellow with a slight green reflection.

De Vrij* utilises the fact that quinidine hydriodide requires 1200 parts of water for solution to test the purity of the commercial sulphate of quinidine. He dissolves 1 gramme of the sample in 50 c.c. of hot water, and adds 0·5 gramme of iodide of potassium free from any alkaline reaction. If the sample be pure a heavy sandy powder of hydriodide of quinidine is precipitated, and if the liquid be allowed to stand twelve hours and is then filtered, addition of a few drops of ammonia will cause no turbidity in the clear filtrate. A slight turbidity indicates a trifling admixture of other alkaloids, but if a decided precipitate occur the alkaline liquid should be shaken with a mixture of amylic alcohol and chloroform (see page 438), or chloroform only, and the solvent evaporated to ascertain

* *Pharm. Journ.* [3], viii. 745.

the proportion and nature of the admixture, which may be cinchonidine or quinine, but is usually cinchonine. The appearance of the precipitated hydriodide is sufficient indication of the presence of impurity, as in the presence of cinchonine or cinchonidine it is resinous instead of being sandy.

Quinidine sulphate in alcoholic solution has a specific rotation of $S_D = +216{\cdot}7°$ for the crystallised salt, which corresponds to a value of 261·2 for the alkaloid itself. The rotation is increased by addition of sulphuric acid.

Quinamine. $C_{19}H_{24}N_2O_2$.—This alkaloid was first discovered by Hesse in the bark of *Cinchona succirubra*, and has since been detected in *Calisaya, rosulenta*, and other barks.

Quinamine crystallises in delicate hair-like anhydrous needles, which melt at 172° C. Its rotatory power in alcoholic solution is +104·5 for the D line.

Quinamine is nearly insoluble in cold water, more readily in boiling. Hot alcohol dissolves it freely. It also dissolves in boiling ether, petroleum spirit, and benzene.

Quinamine itself is almost tasteless, but its solutions in acids are very bitter. The solution in excess of dilute sulphuric acid exhibits no fluorescence. Acid solutions of quinamine are very prone to decomposition with formation of amorphous alkaloid. When tested with chlorine or bromine water and ammonia, solutions of quinamine yield a yellowish amorphous precipitate, but no green colour. The solid alkaloid, when moistened with strong nitric acid, gives a yellow coloration.

Amorphous Alkaloids.—Certain uncrystallisable alkaloids exist ready-formed in cinchona barks, the proportion present being probably affected by sunlight and the presence of any free acid in the bark.

In the preparation of the salts of the alkaloids from cinchona bark, a further portion of the bases undergoes conversion into a resinoid substance known in commerce as "quinoïdine" or "amorphous quinine." It is a dark brown, brittle, "extractiform" mass, softening below 100° C., and having usually a slight alkaline reaction. It is obtained in quinine factories by precipitating the brown mother-liquors with ammonia, and consists largely of two

alkaloids, quinicine and cinchonicine, which are isomeric with and appear to be due to the action of heat on quinine or quinidine, and cinchonine or cinchonidine respectively. These amorphous products may also be obtained by heating the crystallised bases in glycerin to a temperature of 200° C., a red substance being formed at the same time.

To prepare the pure amorphous alkaloid, the acid sulphate of quinine or cinchonidine, according to the product required, is first rendered anhydrous by careful drying at 100° C., and is then raised for a few minutes to a temperature of 130 to 135° C., when it melts and is wholly converted into the acid sulphate of the new alkaloid.

QUINICINE, $C_{20}H_{24}N_2O_2$, is a yellowish amorphous anhydrous body, which melts at about 60° C., assuming a reddish-brown colour which becomes darker at 100°. It is nearly insoluble in water, but has a bitter taste. The alcoholic solution has a strong alkaline reaction and absorbs carbonic acid from the air. The alkaloid is readily soluble in chloroform or ether. Quinicine gives a green coloration when treated in solution with chlorine or bromine water and ammonia, but is distinguished from quinine and quinidine by producing a white amorphous precipitate with sodium hypochlorite or solution of bleaching powder. In applying this test the liquid should be slightly, but not strongly, acidulated with hydrochloric acid. Quinicine may be separated from the accompanying alkaloids by adding ammonia, when the ammonium salt formed dissolves the separated alkaloid, which may be recovered by agitation with ether. If soda be employed instead of ammonia the alkaloid is thrown down as an oily mass.

A solution of quinicine in excess of dilute sulphuric acid has a yellow colour but exhibits no fluorescence.

Quinicine forms crystallisable compounds with acids, and double salts with the chlorides of platinum and gold. Neutral oxalate of quinicine dissolves readily in hot chloroform, alcohol, or water. In solution in a mixture of alcohol and chloroform the oxalate exhibits a right-handed rotation corresponding to a value of $S_D = +25{\cdot}8°$ for the alkaloid.

Quinicine solutions are not precipitated by Rochelle salt. They are completely precipitated by adding excess of potas-

sium thiocyanate, which throws down quinicine thiocyanate as an oil which subsequently solidifies. It is soluble in pure water, but insoluble in solutions of alkaline thiocyanates.

CINCHONICINE, $C_{20}H_{24}N_2O$, when precipitated by soda from the solution of one of its salts, forms a yellow viscous mass readily drawn out into colourless strings. It liquefies at about 50° C., and at 80° turns brown. At higher temperatures (*e.g.*, 100° C.) it becomes dark brown, and is converted into a substance resembling "quinoïdine." Upon cooling it remains soft. As deduced from the rotatory power of the oxalate, in alcoholic, aqueous, or chloroformic solution, the value of S_p for cinchonicine is $+20{\cdot}1°$.

In most reactions, including its behaviour with ammoniacal salts and with hypochlorites, cinchonicine closely resembles quinicine, and hence is distinguished from cinchonine and cinchonidine. It is distinguished from quinicine by giving no green colour with chlorine or bromine water and ammonia.

Cinchonicine is bitter, and in the free state has a strongly alkaline reaction. It neutralises acids perfectly, and many of the resultant salts are crystallisable.

APODIQUINICINE, $C_{40}H_{46}N_4O_3 = 2C_{20}H_{24}N_2O_4 - H_2O$. — This base constitutes the greater part of the amorphous alkaloid contained in commercial quinoïdine. It is wholly amorphous, as also are all its salts. Its solution in excess of dilute sulphuric acid is fluorescent. It gives the thalleioquin reaction, and is dextro-rotatory.

De Vrij has pointed out a distinction between quinicine, cinchonicine, and the true amorphous alkaloid (apodiquinicine?). If the neutral oxalates of the bases be rendered anhydrous by heating at 100° C., and the dry salts treated with chloroform, they behave in a characteristic manner.

Oxalate of quinicine dissolves sparingly in chloroform at the ordinary temperature, but freely in the boiling liquid. On cooling, the solution deposits the greater part of the oxalate in crystals.

Anhydrous oxalate of cinchonicine dissolves freely in cold chloroform. By adding a few drops of water on the surface, the solution is transformed in a few minutes into a solid mass.

The oxalate of the amorphous alkaloid is very soluble in chloroform. The solution remains clear on adding a few drops of water, but the water dissolves out some of the oxalate from its chloroformic solution. The amorphous oxalate is highly deliquescent, but the oxalates of quinicine and cinchonicine remain unchanged in the air.

COMMERCIAL QUINOÏDINE is said to be liable to certain adulterations, such as mineral matters, resins, liquorice, glucose, &c. To examine it, 1 gramme of the powdered sample should be heated to boiling, with constant agitation, with 25 c.c. of water. When cool the water should be nearly colourless, and should remain so when 1 gramme of caustic soda is added to the decanted liquid, and the whole again boiled. A brown coloration would be caused by liquorice, glucose, dextrin, aloes, &c. These bodies are also indicated by their insolubility in ether, in which quinoïdine itself readily dissolves with brown colour.*

Cinchona Barks.—The bark from which the various cinchona alkaloids are obtained is the product of a number of trees of the genus *Cinchonæ* or *Cinchonaceæ*, belonging to the class *Rubiaceæ*. The species yielding the alkaloidal bark are very considerable in number, and can be discriminated only with great difficulty. The three principal species are *C. officinalis*, *C. Calisaya*, and *C. succirubra*. In pharmacy, however, it is usual to classify the barks as pale or crown bark, calisaya or yellow bark, and red bark.

A specimen supposed to be one of cinchona bark, can be readily identified as such by heating a small quantity in a test tube, when a carmine-red tar will be produced if the sample contain any of the cinchona alkaloids.

Cinchona barks contain, in addition to woody fibre and the characteristic alkaloids, several well-defined acid principles, colouring matters, traces of volatile oil, and indifferent bodies.

KINIC ACID, or quinic acid, $C_7H_{12}O_6$, crystallises in well-defined hexagonal plates, fusing at 161° C. It has a

* A method of effecting the transformation of the comparatively valuable alkaloids of commercial quinoïdine into crystallisable quinine is a great desideratum.

strong and purely-acid taste, and is soluble in two parts of water. It is less soluble in alcohol and almost insoluble in ether. Its solutions are lævo-rotatory. When distilled with manganese dioxide and sulphuric acid, kinic acid yields quinone, $C_6H_4O_2$, which is deposited in deep yellow prisms on the cooler part of the apparatus.

QUINOVIC ACID, $C_{24}H_{38}O_4$, is a body crystallising in tasteless scales, which are insoluble in water, ether, or chloroform. It is sparingly soluble in cold, but readily in boiling alcohol, the solution being dextro-rotatory. Quinovic acid in small proportion is constantly present in cinchona barks.

CINCHO-TANNIC ACID is a glucoside which is an important constituent of cinchona barks. It may be precipitated as a lead salt from a decoction of bark—previously treated with magnesia to separate colouring-matter—by addition of lead acetate. The precipitate when decomposed by sulphuretted hydrogen yields a solution of cincho-tannic acid. It is an amorphous, hygroscopic substance, very soluble in water, alcohol, and ether; gives a green colour with ferric chloride; is precipitated by gelatin and tartar-emetic; yields pyrocatechin by dry distillation; and is readily decomposed in presence of excess of alkalies, with formation of

CINCHONA-RED, or cinchofulvic acid, $C_{12}H_{14}O_7$.—This is the natural colouring matters of (red) cinchona-barks, from which it may be extracted by treatment with alkalies. It is re-precipitated from its red ammoniacal solution on addition of hydrochloric acid. Cinchona-red is also produced by boiling cincho-tannic acid with dilute sulphuric acid, glucose being simultaneously formed. On fusing cinchona-red with potash, proto-catechuic acid, $C_7H_6O_4$, is produced. Cinchona-red is insoluble in water or ether, but sparingly soluble in alcohol. It is sometimes present in red bark to the extent of 10 per cent.

QUINOVIN, or chinovin, $C_{30}H_{48}O_8$, is an amorphous, indifferent body, which appears to be a constant constituent of every part of the cinchonas, though seldom exceeding 2 per cent. It is dissolved on treating the bark with weak soda, and on adding hydrochloric acid to the solution is precipitated in admixture with quinovic acid and cinchona-red. Treat-

ment with milk of lime dissolves the two former bodies, which are re-precipitated by an acid, and separated by chloroform, which dissolves only the quinovin. Quinovin dissolves in boiling water, and more readily in alcohol. The solutions are dextro-rotatory. On treatment in alcoholic solution with hydrochloric acid gas, quinovin is converted into quinovic acid and a sugar-like body called mannitan.

ALKALOIDS.—These are the most important of the constituents of cinchona-bark. The chief have already been fully considered (see also the tables on page 412, *et seq.*).

Some kinds of cinchona bark are occasionally wholly destitute of alkaloids. Such specimens do not give a carmine-red tar when heated in a dry tube, this reaction being produced only when a cinchona base is heated with woody fibre.

The proportions of total alkaloids, as also the percentage of quinine, are extremely variable, and chemical analysis is the only means of forming an opinion as to the richness of a specimen of bark. De Vrij found the *C. officinalis* grown at Ootacamund contained a proportion of total alkaloids varying from 11·96 per cent. (of which 9·1 per cent. was quinine) down to less than 1 per cent. Quinine is not seldom absent from barks containing some other of the cinchona alkaloids. The highest yield of total alkaloid known was from an Ootacamund bark, which contained 13½ per cent., the greater part being quinine.

Of the cinchona alkaloids, quinine and cinchonine are of the most frequent occurrence. Cinchonidine is perhaps less common, though it occurs very largely in Indian red bark. Quinidine is not very frequent, and is never present in large amount. The external conditions under which the trees are grown largely affect the relative and absolute proportions of the alkaloids in the bark.

According to the *British Pharmacopœia* yellow cinchona bark should yield not less than 2 per cent. quinine and other alkaloids soluble in ether; pale bark not less than 0·5, and red bark not less than 1·5 per cent of total alkaloids.

Assay of Cinchona Barks.—The complete assay of the various species of cinchona bark, with the view of ascertaining the proportion of the different alkaloids contained in

them, is a process at once important and difficult. A great many methods have been proposed, but very few can be trusted to yield accurate results when employed by chemists unused to them. Again, a process which is suitable when quinine is the chief alkaloid present becomes difficult of application when the cinchonine is in excess. Unfortunately, also, certain processes which are extensively employed by professed quinologists are kept strictly to themselves.

In choosing a process of assaying cinchona bark, due consideration should be given to the kind of information required. Thus, a pharmacist desiring to know the alkaloidal strength of his bark will require a less accurate and elaborate process than a manufacturer buying bark for the extraction of quinine. Again, in some cases it is sufficient to determine the percentage of total alkaloids, while in others it is very important to ascertain the proportion of crystallised sulphate of quinine which the bark is capable of yielding. On this account, it is desirable to discuss the determination of the total alkaloids and of the actual quinine separately.

Determination of the Total Alkaloids of Cinchona Bark.—1. The following process is that of De Vrij, with certain modifications suggested by Prescott and Muter. It is applicable to all varieties of bark. 20 grammes of the finely powdered bark, weighed after drying at 100° C., is thoroughly mixed with 5 grammes of quicklime and 50 c.c. of water. The mixture is then dried at a very gentle heat. When dry, it is transferred to a flask fitted with an inverted condenser, and boiled with 200 c.c. of the strongest rectified spirit.* The liquid is allowed to cool, and is then passed through a filter 6 inches in diameter, and the residue is again boiled with 100 c.c. of alcohol, and then washed twice with alcohol, using 50 c.c. each time. The filtrate is next rendered slightly acid by dilute sulphuric acid, and, after allowing any precipitate of calcium sulphate to subside, the liquid is passed through a very small filter, which is washed with a little

* The spirit may be methylated, but should be previously dehydrated to about 93 per cent. by being kept in contact with freshly-ignited potassium carbonate. Xoxheth's extracting apparatus, shown on page 127, might doubtless be advantageously employed for the alcoholic treatment described in the text.

alcohol. The filtrate is evaporated or distilled till the alcohol is expelled, cooled, and again passed through a small filter, the precipitate, consisting of quinovic acid and fatty matter, being washed with water slightly acidulated with sulphuric acid. The filtrate, which contains the alkaloids in the form of acid sulphates, is then concentrated to about 50 c.c. or less, and transferred to a separator (see page 165) of 100 to 150 c.c. capacity. Soda is next added in decided excess, and the liquid containing the separated alkaloids then shaken without delay with 30 to 40 c.c. of previously washed chloroform. After a few minutes' agitation, the liquid is left at rest till the chloroform has completely separated from the aqueous layer. The lower stratum is then tapped off, and the watery liquid agitated three times more with chloroform, using from 25 to 30 c.c. on each occasion. The mixed chloroformic solutions are then distilled to a small bulk, the residual liquid evaporated to dryness, and the residue dried in the water-oven till constant in weight. The amount so found represents the total alkaloids in the 20 grammes of the bark taken. Cinchonine and cinchonidine readily become anhydrous at 100°, and quinine may be trusted to do the same. Quinidine retains 2 Aqua in the water-oven, but the proportion in which this base occurs is too small appreciably to affect the accuracy of the assumption that the alkaloids are weighed in the anhydrous state. If preferred, however, the temperature may be raised to 115° C.*

For the assay of *yellow* cinchona bark, ether may be substituted for the chloroform employed in the above process.

* With a few modifications of minor importance, the method described in the text is that used by our best quinologists. Dr Paul prefers to work on a very large quantity of the bark (about 2 lbs.). Having treated with lime, alcohol, and acid in the manner described in the test, he precipitates the aqueous solution of the sulphates with soda, filters, washes slightly, dissolves the precipitate in acetic acid, and filters from any undissolved colouring matter. The filtrate is divided into two equal parts, A and B. A is precipitated by ammonia, filtered, and the filtrate shaken with chloroform, which is then used to dissolve off the alkaloids from the filter. The solution is evaporated, and the total alkaloids weighed, after drying at 115° C. B is treated in a manner similar to A, but the chloroform is replaced by ether. The alkaloid thus dissolved is called "quinine," the difference between that and the total alkaloids being the "other alkaloids."

2. The foregoing method being thoroughly satisfactory for the extraction of the total alkaloids of cinchona bark, it is only necessary to describe in detail one other, which is that of Hager. The accuracy of the method has been confirmed by O. Medin.*

Ten grammes of the dried and finely-powdered bark are treated for a short time with 100 c.c. of water and 10 grammes of caustic potash solution of 1·35 specific gravity. The mixture is then heated and kept at the boiling point for a quarter of an hour. 15 grammes' weight of diluted sulphuric acid (sp. gr. 1·115) is next added, and the whole boiled for twenty minutes. After cooling, both liquid and residue are transferred to a measuring cylinder, and diluted with water till the whole has a volume of 110 c.c.† The liquid is then passed through a dry filter, and 60 c.c. of the filtrate (=6 grammes of bark), are mixed with 50 c.c. of a cold, saturated, aqueous solution of picric acid. After standing for half an hour the precipitated picrates are filtered off, washed with a little cold water, dried at 100°, and weighed. The product contains 42·5 per cent. of its weight of alkaloids, calculated as quinine. A preferable plan is to suspend the washed precipitate in cold water, add excess of caustic soda, and agitate with chloroform. The chloroformic solution of the alkaloids is then treated as in process 1. The picric acid method of assaying cinchona barks is said to be accurate, easy, and expeditious.

Probably a very perfect and expeditious method of obtaining the total alkaloids from cinchona barks would be to extract the dried mixture of the powdered sample with lime, obtained as described in process 1, in a Xoxheth's apparatus, with chloroform. Very little of the solvent would be required, and by avoiding the evaporation of dilute alcoholic or aqueous solutions, there would be no danger of producing amorphous alkaloids.

Separation of the Alkaloids of Cinchona Barks.—The separation of the various alkaloids of cinchona bark is a far

* *Zeitsch. Anal. Chem.* viii. 477; and ix. 447.

† This is allowing 100 c.c. for the liquid, and 10 c.c. for the bulk of the residual woody fibre, &c.

more difficult problem than the determination of the total amount present. In some cases it is sufficient to determine the proportion of crystallisable quinine, which may be effected as described on page 453, but in other cases it is necessary to determine also the cinchonine, cinchonidine, and occasionally the quinidine, quinamine, and amorphous alkaloids. Such an analysis is very difficult, and its accurate performance presents special obstacles to an inexperienced analyst. For the separation of quinine from the admixed alkaloids, ether is usually employed, but it must be remembered that the separation effected by this solvent is not an absolute one, all the free cinchona bases being more or less soluble in ether, especially in the presence of quinine. The anhydrous sulphates of quinine and cinchonidine are almost insoluble in chloroform free from alcohol (see page 430), but in presence of sulphate of cinchonine or quinidine, sensible quantities pass into solution. Crystallisation of the quinine sulphate from water affords a simple and fairly accurate mode of separation, which has the advantage that it is similar to the process employed by the manufacturer.

The tabulated scheme for the separation of the principal cinchona bases on next page is founded on a method described by De Vrij.* The process requires a considerable weight of alkaloids, and does not yield strictly accurate results. Traces of quinidine and cinchonidine are dissolved by the ether, and are only recovered on treatment of the amorphous alkaloids with a limited quantity of ether as directed. In presence of much quinine the solubility of cinchonidine in ether is notably increased. The best part of the process is the accurate estimation of the crystallisable quinine, and this determination may be still further improved by substituting iodosulphate of quinoïdine for the tincture of iodine, as described on page 421;† but this mode of operating sacrifices the possibility of investigating the nature of the amorphous alkaloids.

* *Pharm. Journ.* [3], ii. 642.

† If desired, the herepathite may be converted into crystallised quinine sulphate by heating it with alcohol and sulphurous acid till colourless, and then neutralising with soda and proceeding as described on page 453.

A weight of not less than 2, and preferably 5, grammes of the mixed alkaloids in a free state is finely powdered, and treated in a closed tube with ten times its weight of ether (free from alcohol). The mixture is well shaken and left at rest for twelve hours, when it is filtered, and the residue washed with a small quantity of ether.

A. The Residue is dried and weighed. It may contain *cinchonine*, *cinchonidine*, and *quinidine*. It is dissolved in a slight excess of dilute hydrochloric acid, and the solution rendered neutral by cautious addition of soda. The cinchonidine is then precipitated as tartrate, the quinidine as hydriodide, and the cinchonine as hydrate, the operations being conducted exactly as described on page 454, with the exception that quinine and amorphous alkaloids having been previously removed, the processes and calculations necessitated by their presence may be omitted.

B. The Ethereal Solution is evaporated to dryness, and the residue weighed. It consists of *quinine*, *amorphous alkaloids*, and *quinamine*, with traces of *quinidine* and *cinchonidine*. It is dissolved in 10 parts of proof spirit, acidulated with $\frac{1}{20}$ of sulphuric acid. To this solution an alcoholic solution of iodine is gradually added as long as a precipitate is produced. Excess of iodine must be carefully avoided. In presence of much quinine, a black precipitate of herepathite is immediately produced, but, if the quantity is small, some time is required for its appearance. In such a case only a small quantity of iodine solution must be added, and the liquid well stirred, and left twelve hours. The precipitate is filtered off, and washed with strong alcohol.

The Precipitate consists of herepathite. It is dried at 100° C., weighed. The weight, multiplied by ·55055, gives the quantity of *quinine* in the mixed alkaloids operated upon. The precipitate may also be treated as suggested in the note on page 451.

The Solution is treated with sulphurous acid till colourless, and then carefully neutralised with caustic soda. The alcohol is evaporated off, and the liquid treated with excess of soda or ammonia, and agitated with chloroform. The residue left on evaporating the chloroform consists of *amorphous alkaloids*, with traces of *quinidine* and *cinchonidine*. The two latter will remain undissolved on treatment with a limited quantity of ether, and the amorphous alkaloids may be distinguished as described on page 444.

In some cases it is desirable to separate the quinine in the actual form of crystallised sulphate, this being regarded by many as the best proof of the proportion obtainable by the manufacturer. The following method described by Muter is the most accurate mode of proceeding:—

Treat the total alkaloids or the ether-residue from 20 grammes of bark with warm distilled water slightly acidulated with dilute sulphuric acid, till the mixture is perceptibly acid. Add water to make 70 c.c. for each 1 gramme of alkaloids taken, and then very dilute soda with constant stirring till the liquid is exactly neutral, with a faint tendency to acidity. Digest the liquid at 85° C. for five minutes; then cool, and leave at 15° C. for one hour. Filter the liquid through a small double filter (2¾ inches diameter), the two filters being previously trimmed to equal weight, and receive the filtrate in a graduated cylinder. Wash carefully with water at 15° C. till the filtrate and washings measure 90 c.c. for each 1 gramme of the mixed alkaloids. The filter and contents are now completely dried at 100° C., and weighed, the second filter being used as a counterpoise. To the weight in grammes add ·000817 gramme for each c.c. of filtrate and washings. The sum divided by 0·855 gives the corresponding amount of crystallised sulphate, and this number multiplied by 5 gives the crystallised quinine sulphate obtainable from 100 grammes of dried bark.

The quinine sulphate so obtained is apt to contain cinchonidine sulphate (see page 435).

The foregoing method may be applied with advantage to the residue obtained by evaporating to dryness the ethereal solution B. of De Vrij's process (page 452), and for many practical purposes is even preferable to precipitation as herepathite.

The remaining alkaloids may be recovered from the filtrate from the quinine sulphate by concentrating the liquid somewhat, adding soda in excess, and agitating with chloroform. On evaporating the chloroform, the bases will be obtained in a solid state, and may be separated in the following manner. The method may also be applied to the total mixed alkaloids extracted from a sample of bark, in which case it may be carried on simultaneously with the treatment for crystallised quinine sulphate described above.

Analysis of Cinchona Bases. Separation of Cinchonine, Cinchonidine, and Quinidine.

The mixed alkaloids extracted from the bark or the filtrate from quinine sulphate by treatment with soda and chloroform, or the residual alkaloids left on treating the total alkaloids with ether (see page 452), are dissolved in strong alcohol. The solution is rendered faintly acid by hydrochloric acid, and evaporated to dryness at 100° C. The residue is dissolved in the least possible bulk of water at 40° C., and the trace of free acid neutralised by soda. A saturated solution of Rochelle salt is next added in excess, the liquid cooled to 15° C., and repeatedly stirred during one hour. Crystalline streaks in the track of the glass rod consist of tartrate of cinchonidine (or quinine). The precipitate is collected on a double tared filter, and washed cautiously with cold water, the filtrate and washings being collected in a graduated cylinder.

The Precipitate is dried at 100° to 105° C. and weighed, the outer filter being used as a counterpoise. The amount found is corrected by adding ·00083 gramme for each 1 c.c. measured by the filtrate and wash-water. The sum multiplied by ·804 gives the weight of *cinchonidine*. If quinine has not previously been separated, the amount of crystallised sulphate found must be multiplied by ·915, and the product subtracted from the weight of the tartrate before calculating it to cinchonidine.

A. The Filtrate is concentrated to its original bulk, cooled, a drop of dilute acetic acid added, and then excess of a saturated solution of potassium iodide (free from any alkaline reaction). The liquid is left for two hours at 15° C., being frequently stirred. Any streaks in the track of the glass rod are produced by quinidine hydriodide. The liquid is filtered on a double counterpoised filter, and the precipitate cautiously washed with cold water.

The Precipitate is dried at 100° and weighed. Its weight is corrected by the addition of ·00077 gramme for each 1 c.c. of filtrate and washings (B). The sum, multiplied by ·7168, gives the *quinidine*.

B. Filtrate is measured and made distinct by alkaline with caustic soda. The precipitated *cinchonine* is filtered off, washed, dried, and weighed, or else extracted by agitation with chloroform. The weight found is corrected by deducting ·00052 for each 1 c.c. measured by filtrate A., and ·00066 for each c.c. of filtrate B. Any *amorphous alkaloid* may be dissolved out by spirit of ·94 sp. gravity.

The foregoing process, with experience, gives very good results the sum of the separated alkaloids frequently amounting to 99 per cent. of the mixed bases operated on. It is well suited for Indian barks. The most defective part of the process is the separation of the cinchonine from the amorphous bases by dilute spirit. A cautious employment of ether is perhaps preferable. If the process of separation be conducted simultaneously with the determination of the crystallised quinine sulphate in another portion, the whole analysis can be completed in about six hours.

The mixed alkaloids of yellow cinchona bark consist almost wholly of quinine, and hence the portion soluble in ether represents the whole useful constituents of the bark. Pale- and red-barks, on the other hand, contain a considerable proportion of alkaloids insoluble or sparingly soluble in ether. Hence the use of chloroform in the general process for assaying cinchona barks (see page 448).

In some cases the alkaloids soluble in ether are contaminated to a considerable extent with colouring matter. In this event, the following is a good method of obtaining colourless quinine sulphate :—The ether-residue is dried thoroughly and weighed. It is then dissolved in 30 c.c. of absolute alcohol, and decinormal sulphuric acid cautiously added from a burette, using litmus paper as an indicator, till the liquid is neutral or *very* faintly acid. The measure of acid used is noted. Each c.c. is equivalent to ·324 grammes of anhydrous alkaloids. The liquid is next evaporated nearly to dryness, and a measure of decinormal sulphuric acid added equal to that previously required for neutralisation. 30 c.c. of hot water are added, and the liquid boiled till complete solution results. Purified animal charcoal (prepared as described on page 227) is added, in quantity equal to the weight of the ether-residue. Heat the liquid on the water-bath for 20 minutes, filter, and wash the residue twice with boiling water acidulated with sulphuric acid. The filtrate is brought to a concentration of 70 c.c. for each 1 gramme of ether-residue taken, and then cautiously neutralised with caustic soda, and further treated as described on page 453.

Special processes for separating certain of the cinchona

bases will be found on pages 435, 441, and 445, as also methods for testing the purity of the various commercial salts of the alkaloids.

OPIUM ALKALOIDS.

Opium is remarkable for the large number of nitrogenised organic bases contained in it. At least fifteen alkaloids have been isolated from it, and the list appears to be still incomplete. Most of these bodies have well-defined basic properties, and the majority are poisonous. Some of them, as morphia and narcotine, occur in opium in considerable quantity, but the greater number are present in very small proportion, and are entirely absent from some samples.

The free opium alkaloids are generally but slightly soluble in water, but dissolve more readily in alcohol. In many instances the solutions of the free alkaloids are strongly alkaline to litmus. Their different behaviour to solvents affords a valuable means of distinguishing and separating them. They are precipitated from concentrated solutions of their salts by caustic alkalies and alkaline carbonates, some of the precipitates dissolving in excess of the reagent. Most of the opium alkaloids (except papaverine) have a powerfully lævo-rotatory action on polarised light, but the specific rotatory power varies so erratically with the solvent and the concentration of the solution that the fact has little practical value. Many of the opium alkaloids furnish characteristic colour-reactions when treated with strong acids and oxidising agents.

The table on next page gives the names and formulæ of the more important opium alkaloids, and shows their behaviour with various solvents. Apomorphine and apocodeine are not natural constituents of opium, but are formed by the dehydration of morphine and codeine respectively. They are introduced into the table for convenience of comparison.

Morphine, codeine, and thebaine are powerful bases; narceine, narcotine, and papaverine weak ones. The last three are even extracted by chloroform from their acid solutions. Morphine, narcotine, codeine, and thebaine are also powerfully poisonous, the last being the most active. Papaverine does not appear to be poisonous.

TABLE OF OPIUM ALKALOIDS.

Alkaloid.	Formula.	Parts of solvent required to dissolve 1 part of alkaloid.								
		Water.	Water with		Alcohol.	Amylic Alcohol.	Ether.	Chloroform.	Benzene.	Petroleum Spirit.
			Caustic Soda.	Ammonia.						
Morphine . .	$C_{17}H_{19}NO_3$	nearly insoluble, cold; 500, hot	readily soluble	slightly soluble	50, cold 30, hot	400, cold, more readily hot	slightly soluble	90	insoluble	insoluble.
Apomorphine .	$C_{17}H_{17}NO_2$	slightly soluble	soluble, turning black	soluble, quickly turning black	very soluble with green colour	...	very soluble	very soluble	...	...
Codeine . . .	$C_{18}H_{21}NO_3$	75, cold 17, hot	very slightly soluble	same as with water	readily soluble	7	readily soluble	readily soluble	12	nearly insoluble.
Apocodeine . .	$C_{18}H_{19}NO_2$	insoluble	...	...	soluble	...	soluble	soluble	...	...
Narcotine . .	$C_{22}H_{23}NO_7$	25,000, cold 7,000, hot	insoluble	insoluble	100, cold 20, hot	300	50, cold 20, hot	3	25	nearly insoluble.
Narceine . .	$C_{23}H_{29}NO_9$	375, cold 200, hot	soluble	slightly soluble	945, cold easily, hot	nearly insoluble	insoluble	sparingly soluble	insoluble	insoluble.
Thebaine(paramorphine)	$C_{19}H_{21}NO_3$	insoluble	insoluble	insoluble	10	60	soluble	18	19	insoluble.
Papaverine . .	$C_{21}H_{21}NO_4$	insoluble	insoluble	insoluble	sparingly, cold readily, hot	70	slightly soluble	soluble	36	slightly soluble, cold. readily soluble, hot.
Pseudomorphine	$C_{17}H_{19}NO_4$	insoluble	soluble	insoluble	nearly insoluble	...	insoluble	insoluble	soluble	...

On treating a solution of the mixed alkaloids with an alkaline carbonate or ammonia, and agitating with benzene, morphine and narceine are left insoluble, the remainder passing into the benzene. Much the same separation occurs with chloroform, except that pseudomorphine is left with the insoluble alkaloids. By precipitating the hydrochlorides of the mixed alkaloids with excess of caustic soda, narcotine, codeine, thebaine, and papaverine are left insoluble, while the morphia, narceine, and pseudomorphine pass into solution. Narcotine and papaverine may be separated from thebaine and codeine by dissolving the free bases in dilute alcohol, rendering the liquid faintly acid with acetic acid, and adding three volumes of boiling water. Narcotine and papaverine are precipitated, as these alkaloids do not form acetates.*

The table on next page shows the leading colour-reactions of the opium alkaloids. The tests are supposed to be applied to the solid alkaloid in the manner prescribed for morphia on page 463, *et seq.* Some of the tints are liable to be modified by very slight changes in the conditions of experiment.

In addition to the alkaloids included in the table on next page, the following have also been proved to be occasionally present in opium, usually in very small amount:—

Alkaloid.	Formula.	Reaction on warming with concentrated H_2SO_4.	Reaction with Ferric Chloride.
Codamine . .	$C_{20}H_{25}NO_4$	Dirty red-violet colour turning dark violet, with trace of HNO_3,	Dark green.
Landanine . .	$C_{20}H_{25}NO_4$		
Landanosine .	$C_{21}H_{27}NO_4$		No colour.
Protapine . .	$C_{20}H_{19}NO_5$	Dirty green to brownish green.	No colour.
Cryptopine . .	$C_{21}H_{23}NO_5$		
Lanthopine . .	$C_{23}H_{25}NO_4$	Dark brown or black.	No colour.
Hydrocotarnine	$C_{12}H_{15}NO_3$	Dirty red-violet, not changed by trace of HNO_3.	...

Still other bases have been more or less satisfactorily identified, as opianine, $C_{21}H_{21}NO_7$; gnoscopine, $C_{34}H_{36}N_2O_{11}$; rhœadine, $C_{20}H_{21}NO_3$; and meconidine, $C_{21}H_{23}NO_4$; but the basic character of these is very doubtful.

* A detailed description of Hesse's method of separating the opium alkaloids will be found in Watt's *Dictionary of Chemistry*, vii. p. 875.

Alkaloid.	Nitric Acid. 1·42 sp. gr.	Colour-Reaction with Concentrated Sulphuric Acid			Fröhde's Reagent.	Other Reactions.
		Alone.	On adding $KClO_3$ or HNO_3.	With Sugar.		
Morphine . . .	Orange.	Cold, no colour; on heating, red-violet, then dirty green.	Violet blue, changing to dark-red.	Blue, violet, greenish, and dirty yellow.	Violet, changing to blue and dirty green.	Blue with $FeCl_3$. Brown with HIO_3.
Codeine	Yellowish* or light orange.	No colour; blue after long interval.	Blood-red.	Blue, violet, greenish, and dirty yellow.	Dirty green, changing to blue and yellow.	No reaction with $FeCl_3$.
Narcotine . . .	Red.	Colourless, quickly turning yellow; orange-red on warming, turning violet blue at higher temperature.	Carmine-red.	Not characteristic.	Yellowish green.	No reaction with $FeCl_3$. Yellowish red with Cl and ammonia.
Narceine . . .	Yellow.	Amber or brown, changing to dark-red.*	No colour.	Not characteristic.	Yellowish-brown, changing to yellow and colourless.	...
Thebaine . . .	Deep red.	Blood-red, turning yellow; olive-green on heating.	Same as with sulphuric acid.	...	Blood-red, turning yellow.	...
Papaverine . . .	No visible reaction.	Violet-blue, fading slowly (characteristic). Heating is sometimes necessary.	No colour.	...	Violet, becoming blue and colourless.	Solution in cold H_2SO_4 turns milky on dilution (characteristic).
Pseudomorphine	Orange-red, changing to yellow.	Cold, no colour, or olive-green; on heating, dingy green or purple, and finally red.	...	...	...	Blue with $FeCl_3$. Solution in cold H_2SO_4 gives crystalline ppte. on dilution.
Apomorphine . .	Blood-red or reddish violet.	...	...	...	Deep green, turning violet.	Pink with $FeCl_3$.

* Great discrepancies occur in the statements made respecting this reaction.

Morphine. Morphia. $C_{17}H_{19}NO_3$.—This alkaloid is the most important of the bases contained in *opium*, in which it exists in combination with meconic acid, and sometimes sulphuric or acetic acid.

Morphia crystallises in transparent colourless trimetric prisms, which are usually very short. The crystals melt when heated, and give off 1 atom of water, becoming carbonised at a higher temperature. Morphine is inodorous, has a persistent bitter taste, and is a powerful narcotic poison. It has a lævo-rotatory action on polarised light.

Morphine is nearly insoluble in cold water at 10° C., in traces at 20° C.; boiling water dissolves $\frac{1}{500}$. The solution has an alkaline reaction. It dissolves in 30 parts of boiling or 50 of cold absolute alcohol, and in a somewhat smaller quantity of rectified spirit. In ether it is almost insoluble when in a crystallised state, but dissolves sparingly when freshly-precipitated and amorphous. The same remark applies to its solubility in chloroform. A useful solvent for morphia is a mixture of equal volumes of ether and acetic ether (ethyl acetate); but even in this its solubility is limited, especially in the crystalline state. Amylic alcohol dissolves but little morphine ($\frac{1}{400}$) in the cold, but when heated is the best solvent for it.

In benzene and petroleum spirit morphia is insoluble, as also in volatile oils. On the other hand, solutions of caustic potash and soda dissolve morphia readily, as also does lime-water, and, to a limited extent, ammonia also (see page 461).

Morphia and its salts are very sensitive to the action of oxidising agents, a fact which is often utilised for their detection (see page 462). They reduce salts of gold and silver, permanganates, iodic and periodic acids, &c. The reactions of morphia with strong sulphuric and nitric acids are described on page 463.

Morphine dissolves easily even in dilute acids, forming salts of perfectly neutral reaction. Most morphia salts are crystallisable, bitter, and very poisonous. They are generally soluble in water and alcohol, but are insoluble in amylic alcohol, ether, chloroform, benzene, or petroleum spirit. Hence morphia is not removed from its acid or neutral solutions by agitation with either of the above solvents.

MORPHINE ACETATE, $C_{17}H_{19}NO_3,HC_2H_3O_2$, is a crystallisable salt, readily soluble in water and alcohol. It is partially decomposed by the evaporation of its aqueous solution at a boiling heat, crystals of morphine being deposited.

MORPHINE HYDROCHLORIDE, or Morphia Hydrochlorate, $C_7H_{19}NO_3,HCl$, crystallises with 3 Aq. in silky fibres, soluble in 20 parts of cold or 1 of boiling water, and still more readily in alcohol. It becomes anhydrous at 100° C. The commercial salt often has a buff or brownish tint from admixture of resinous matters, which are detected by the brown or black colour assumed by the salt when heated to 130° C.

MORPHINE MECONATE is interesting as being the form in which morphia exists in opium. It is readily soluble in water and alcohol. It does not crystallise.

MORPHINE TARTRATES.—These salts are readily soluble. Their solutions are not precipitated by caustic alkalies, alkaline carbonates, or chloride of calcium. The tartrate is best detected by precipitating the concentrated solution with acetic acid and potassium acetate in presence of alcohol (Vol. I. p. 265). The morphia can then be separated from the filtrate by an alkaline carbonate.

Analytical Reactions of Morphine.—Free morphia, when pure, or in the form of one of its ordinary salts, is readily detected.

REACTIONS OF SOLUTIONS OF MORPHIA.—The following reactions are produced by a *solution* of the hydrochloride or acetate of morphia:—1. On adding to a tolerably concentrated solution of a salt of morphia a fixed caustic alkali, an alkaline carbonate, ammonia, or lime-water, hydrated morphine, $C_{17}H_{19}NO_3+H_2O$, is thrown down as a white precipitate speedily becoming crystalline. The precipitate is almost insoluble in quite cold water, but dissolves in excess of ammonia or lime-water, and very readily in excess of caustic alkali. The alkaline carbonates, used in excess, redissolve the precipitate somewhat, but it is insoluble in excess of bicarbonates Excess of magnesia precipitates the alkaloid completely. The morphia precipitated by the foregoing reagents, and allowed time to become crystalline, presents a characteristic appearance under the microscope.

2. If morphia be liberated from the solution of a salt by one of the reagents mentioned above, and the liquid and suspended precipitate be at once shaken with hot amylic alcohol, cold acetic ether, or a mixture of equal measures of ether and acetic ether,* the morphia passes into solution, though with some difficulty, and may be obtained in a free state by separating the ethereal liquid, and evaporating it to dryness at a gentle heat. If the liberated morphia be allowed to crystallise before subjecting it to agitation with the solvent, its solution becomes almost impossible.

3. On adding to the solution of a salt of morphine a mixture of aqueous solutions of ferric chloride and potassium ferricyanide, slightly acidulated with hydrochloric acid, a blue coloration or precipitate of Prussian blue is produced. This reaction may be conveniently employed for detecting morphine in presence of the cinchona-bases.

4. On mixing a solution of morphine with one of iodine dissolved in hydriodic acid, a crystalline precipitate is formed even in extremely dilute solutions. Under the microscope the crystalline form is characteristic of morphine, which may thus be distinguished from papaverine and codeine, which bases also give crystalline precipitates with the reagent, while narcotine, narceine, and thebaine yield amorphous precipitates.

5. Addition of chlorine or bromine water, followed by ammonia, occasions in moderately concentrated solutions of morphine a red coloration, gradually changing to brown.

6. Morphine and its salts reduce iodic acid with liberation of iodine. This reaction is also produced by albuminoid and various other organic bodies, so that it is not absolute proof of the presence of morphia. The test becomes much improved and increased in delicacy by the following mode of operating:—

To the solution to be tested for morphia, as nearly neutral as possible, is added one of iodic acid in 15 parts of water. In presence of 1 part of morphia in 20,000 of liquid a yellow coloration is observed. In moderately strong solutions of morphia addition of starch-liquor changes the yellow-colour to blue, but not in solutions containing less than 1 per 1000. This is

* The acetic ether must be free from acid. This may be ensured by agitating it before use with some sodium bicarbonate.

important, as with other reducing agents the blue colour is well marked in far more dilute liquids. On adding excess of ammonia to the yellow liquid the colour is discharged if due to foreign matter, but distinctly deepened if due to morphia. If a solution of morphia which is too dilute to give a blue colour with iodic acid and starch, be mixed with these reagents, and some highly dilute ammonia allowed to flow from a pipette on to the surface of the liquid, two coloured rings make their appearance at the junction of the fluids. A blue ring is seen in the lower acid layer and a brown one in the upper alkaline portion. If a dilute solution of morphia be mixed with one of starch, and evaporated to dryness in a porcelain crucible at a gentle heat, and the residue, after cooling, be moistened with iodic acid, a blue colour will be produced in presence of 1–20,000 of a grain of morphia (Dupré).

In employing the iodic acid test it is essential that the reagent should not give free iodine on treatment with a drop of dilute sulphuric or acetic acid.

REACTIONS OF SOLID MORPHIA.—Morphia gives numerous other interesting and characteristic colour-reactions. They are best observed by operating on the solid alkaloid, which should be placed in a small porcelain basin or crucible. The residue of free morphia obtained by the evaporation of its solution in alcohol or acetic ether is well suited for the production of the following reactions :—

1. Solid morphia treated with a drop of *perfectly neutral* solution of ferric chloride or iron-alum, gives a very characteristic deep blue colour, changed to green by excess of the reagent. The colour is destroyed by free acid, by heat, or by contact with alcohol.

2. Nitric acid (1·42 sp. gr.) added to solid morphia turns it an orange colour, which is destroyed on adding sodium thiosulphate (hyposulphite). If a morphine salt be dissolved in a few drops of concentrated sulphuric acid, and a drop or two of water then added to heat the mixture, the subsequent addition of nitric acid will produce a rose-red coloration, changing to green, and finally to brown. The reaction is very delicate. Sodium hypochlorite, chlorine water, and potassium chlorate gives the same reactions as nitric acid.

3. Solid morphia, if pure, produces no coloration on treatment with concentrated sulphuric acid (narcotine turns yellow), but on adding potassium bichromate a green colour is produced owing to deoxidation of the salt. It is said that no colour-reaction is produced if for the bichromate be substituted the dioxide of lead or manganese. (Distinction from strychnine).

4. If morphia be heated to 100° C. with a few drops of concentrated sulphuric acid, and a minute fragment of potassium perchlorate (free from chlorate) added, a deep brown coloration is produced, which rapidly spreads throughout the liquid. No other alkaloid has been observed to produce this reaction. (Siebold.)

5. If solid morphia be mixed with 6 to 8 parts of powdered cane sugar, or solutions of the two bodies be mixed and evaporated to dryness, addition of a drop of concentrated sulphuric acid will produce a beautiful purple colour, changing gradually through blue and green to yellow. The test may be applied to a solution of morphia by saturating the liquid with sugar, and pouring it carefully on to some concentrated sulphuric acid, when a purple or rose-red coloration will be observed at the junction of the two fluids. Codeine gives a very similar reaction. (Schneider.) According to H. Weppen the delicacy of this test is much increased by adding a drop of bromine water after the sulphuric acid, this modification rendering the reaction equal if not superior to reaction 3 and 4, and less dependent on the purity of the morphia.

6. Solid morphia treated with about 1 c.c. of a freshly-prepared solution of 10 milligrammes of sodium molybdate in 10 c.c. of concentrated sulphuric acid, gives a fine violet coloration, changing to blue and dirty green, and finally almost vanishing. Papaverine and a few glucosides give a similar reaction.

DETERMINATION OF MORPHINE.—1. Tolerably accurate determinations of morphia, in the absence of interfering substances, may be made by precipitating the tolerably concentrated, cold aqueous solution with sodium bicarbonate, allowing time for the precipitate to become crystalline, filtering, washing moderately with very cold water, drying at 100° C., and weighing the hydrated morphia. Instead of weighing the alkaloid, the washed precipitate may be placed, together with the filter, in

a moderate excess of standard acid, and the excess employed ascertained by titration. 1 c.c. of decinormal acid neutralises 0·0285 gramme of anhydrous morphia.

2. Morphia may be extracted by adding sodium bicarbonate, and then agitating the solution with a mixture of ether and acetic ether or hot amylic alcohol. The solvent should be added before the liquid is made alkaline, the agitation conducted immediately, and the ethereal liquid separated without delay. On evaporation it leaves the morphia as hydrate.*

3. A volumetric determination of morphia may be made by the following method, due to Mayer:—A standard solution of potassio-iodide of mercury is prepared by dissolving 13·55 grammes of pure mercuric chloride and 49·84 grammes of pure dry potassium iodide in water, filtering, and diluting to 1 litre. 1 c.c. of this solution corresponds to ·020 grammes of morphia, or, more strictly, to ·0202 of the crystalised alkaloid, $C_{17}H_{19}NO_3,H_2O$. In using this method the morphia is dissolved in water acidulated with sulphuric acid, and the liquid so diluted that at the final reaction in titrating it shall measure about 200 c.c. for 1 gramme of the alkaloid. It is necessary to adhere approximately to this concentration to ensure accurate results, as the precipitate is by no means wholly insoluble in water. The mercury solution is added to that of the alkaloid as long as a white precipitate is produced. The final reaction is found by patiently waiting for the precipitate to subside after each addition liable to be final, then placing a drop of the liquid on a black surface and adding to it a drop of the mercury solution. In the event of a turbidity being produced the mixture is returned to the main quantity.† The process is not interfered with by the presence of extractive matters, but is rendered inaccurate by ammonia, alcohol, or acetic acid.

Further information on the determination of morphia will be found in the following section.

* If amylic alcohol be employed for the extraction its subsequent evaporation becomes difficult, and hence it is sometimes convenient to agitate the amylic alcohol with a known measure of standard acid, and thus estimate the extracted alkaloid volumetrically.

† A modification said to be accurate consists in adding a moderate excess of the mercurial solution, filtering through a dry filter, and titrating an aliquot part of the filtrate with standard nitrate of silver.

Opium is a gummy mass, consisting of the juice of the incised unripe fruit of *Papaver somniferum*, hardened in the air. It is remarkable for the large number of definite, highly complex, crystalline principles contained in it. The following list exhibits in a tabular form the names of the crystallisable principles normally or occasionally present in opium:—

Basic Bodies.	Indifferent Bodies.	Acid Bodies.
Morphine.	Meconin, $C_{10}H_{10}O_4$.	Meconic Acid, $C_7H_4O_7$.
Codeine.	Sugar, $C_{12}H_{22}O_{11}$.	Lactic Acid, $C_3H_6O_3$.
Narcotine, &c.		Acetic Acid, $C_2H_4O_2$.
(See page 458.)		

In addition to the inorganic constituents and the bodies in the above list, opium also contains gummy and pectous matters, albumin, wax, fat, caoutchouc, resin, and a humoïd acid. Woody-fibre and other extraneous matters are also frequently present.

The following may be taken as the *general* composition of opium:—

	Per Cent.		Per Cent.
Morphine	6 to 15	Fat	1 to 4
Narcotine	4 to 8	Gum and soluble humoïd acid matters	40 to 56
Other Alkaloids	0·5 to 2		
Meconin	under 1	Insoluble matters and mucus	18 to 20
Meconic Acid	3 to 8		
Peculiar resin and caoutchouc	5 to 10	Ash	4 to 8
		Water	8 to 30

MORPHINE is the most valuable of the constituents of opium. *Good* Smyrna opium deprived of water ought to contain 12 to 15 per cent. of morphine, and if the proportion be below 10 per cent. adulteration may be suspected. Egyptian opium is much poorer in morphine than that from Asia Minor, but it contains a large proportion of narcotine. Persian opium is extremely variable in quality, probably partly in consequence of the practice of mixing it with sugar and other adulterants. East Indian opium is remarkable for its low percentage of morphine, a peculiarity which is probably due partly to climate and partly to a defective method of collection. The variety known as "Patna garden opium" is prepared specially for medicinal use, and contains about 7 to 8 per cent. of morphine. In Chinese opium the proportion of morphine is generally low.

The morphine in opium usually exists in combination with

meconic acid, but in some cases it is apparently present as acetate, and occasionally as sulphate.

NARCOTINE exists in opium in widely different proportions and often in considerable abundance. Upwards of 10 per cent. has been occasionally met with. East Indian opium always contains more narcotine than morphine, whilst French opium sometimes affords neither narcotine, narceine, nor thebaine.

The narcotine in opium is generally assumed to be uncombined, as it is readily extracted by treating the original (dried) substance with ether or benzene.* Occasionally it resists the action of solvents unless the sample has been previously treated with ammonia.†

MECONIN, $C_{10}H_{10}O_4$, is an indifferent body crystallising in six-sided prisms which melt under water at 77° C., or alone at 110°, and distil at 155°. It may be readily crystallised from boiling water, in which it is pretty soluble. Meconin may be prepared by heating narcotine with nitric acid.

MECONIC ACID, $C_7H_4O_7$.—This peculiar acid is characteristic of opium, in which it exists chiefly in combination with the alkaloids, but sometimes a portion of it appears to be present

* From the acidulated solutions of most of its salts narcotine is readily removed by agitation with chloroform or benzene. Hence it is not proved that its extraction from opium is due to its presence in a free state.

† Twelve samples of opium analysed by Flückiger (*Pharm. Journ.* [3], v. 845) gave the following analytical results :—

Description of Opium.	Ethereal Extract, consisting of		Pure Narcotine.	Morphine.	
	Wax.	Crude Narcotine.		Crude.	Pure
1. Patna	14·2	10·0	4·0	11·2	8·6
2. Indian (1852–53)	12·7	9·0	6·1	11·2	4·3
3. Akbari	13·5	8·5	5·5	14·2	3·5
4. Behar	13·0	7·6	4·5	10·6	4·6
5. Malwa	6·5	7·6	4·7	14·4	6·1
6. Sind	9·4	8·0	3·1	...	3·8
7. Hyderabad	10·7	9·7	5·4	...	3·2
8. Candeish	...	...	7·7	...	6·1
9. Persian	14·8	10·2	6·4	...	7·1
10. Egyptian	11·5	12·2	8·7	...	5·8
11. Playford, Suffolk (1823)	8·8	9·3	6·0	...	4·3
12. English (1859)	12·0	11·6	8·1	...	8·3

in a free state. Its properties and reactions have already been fully described (see Vol. I. p. 276).

Determinations by Mr D. B. Dott* of the leading constituents of eighteen samples of opium, purchased from druggists of good standing in London, Dublin, and Edinburgh, showed that the water of undried opium averages 20 per cent., the insoluble matter 30, and the extractive 50 per cent., of which 8·88 is "morphia."† The proportion of "morphia" calculated on the dried opium averages 11·06 per cent. The proportion of morphia in the dry extract is 18·3 per cent.‡

According to Hanbury and Flückiger, *dried* opium from Asia Minor should yield from 55 to 66 per cent.—generally more

* The following were Mr Dott's results:*—The aqueous extract was determined by subtracting the sum of the water and insoluble matter from 100·00. The crude morphia contained on an average 7-10ths of its weight of the pure base.

Description of Opium.	Percentage Composition.			Percentage of Crude Morphia. (containing about 7-10ths of true morphine).
	Water.	Insol. Residue.	Aqueous Extract.	
1. Turkey	19·6	32·60	47·80	10·75
2. ,,	20·0	28·85	51·15	12·30
3. ,,	26·0	25·95	48·05	10·20
4. ,,	21·2	23·70	55·10	7·57
5. ,,	22·0	30·95	47·05	9·60
6. ,,	18·4	25·45	56·15	11·69
7. ,,	19·2	25·90	54·90	12·30
8. ,,	20·4	34·20	45·40	12·30
9. ,,	27·2	35·80	37·00	6·76
10. ,,	21·2	38·80	40·00	9·80
11. ,,	22·8	29·70	47·50	8·85
12. ,,	31·2	47·90	20·90	6·93
13. Persian	14·0	26·80	59·20	6·00
14. ,,	12·0	27·40	60·60	8·50
15. ,,	16·0	25·90	58·10	2·10
16. Malwa	15·2	24·10	60·70	7·30
17. ,,	13·6	25·20	61·20	5·88
18. Egyptian	14·8	28·30	56·90	7·00
Average	19·70	29·86	50·44	8·88

* *Year-Book of Pharmacy*, 1876, p. 498.

† The great variation in the quality of opium renders the composition of the tincture and other official preparations of opium very uncertain (see page 476).

‡ Mr Dott found in eleven samples of *Extractum Opii* of pharmacy proportions of morphia varying from 15·4 to 22·8 per cent., the mean being 19·7.

than 60—of extractive matter soluble in cold water, the proportion of the same obtainable from Indian opium being from 60 to 68 per cent.

From these results, it is evident that *dried* opium ought to yield the *minimum* amount of 55 per cent. to cold water, and this should contain at least 10 per cent of morphia, calculated on the dried drug.

ACTION OF SOLVENTS ON OPIUM.—The action of different solvents and reagents on opium is shortly as follows :—

Water dissolves meconic acid readily, as also meconate and acetate of morphia; free morphia very sparingly, and narcotine still less so (1 in 1000). Narceine is more soluble than morphine, while the resin, caoutchouc, &c., are insoluble, though certain gummy matters pass into solution.

Alcohol dissolves free morphia,as well as the acetate and meconate. The other alkaloids of opium, as also the resin and caoutchouc, are dissolved by alcohol.

Amylic alcohol dissolves all the alkaloids of opium, if in a free state. The resin also is slightly soluble in amylic alcohol.

Ether, benzene, and carbon disulphide dissolve about ·05 per cent. of free morphia, and the other free alkaloids of opium more readily. These solvents also dissolve the caoutchouc, but not the resin.

Acids dissolve all the alkaloids from opium, together with the resin.

Fixed alkalies, used in excess, dissolve morphine freely, while narcotine remains insoluble. Lime water dissolves morphine, but is a solvent for narcotine only in presence of morphine. The resin of opium is partly soluble in alkalies.

Ammonia dissolves morphia sparingly, narceine and codeine readily, while the other alkaloids and the resin of opium are insoluble.

From the foregoing statements, the arrangement of which is mostly due to Mr E. L. Cleaver,* it follows that an aqueous solution of opium will contain meconate of morphine and other alkaloids, calcium salts, meconic acid, extractives, and resinous matter dissolved by the free acid present.

* *Year-Book of Pharmacy*, 1876, p. 502.

An alcoholic solution will contain, in addition to the above, free narcotine, caoutchouc, fat, and resin.

Opium which has been exhausted with water still retains a bitter taste, but this is probably due to narcotine, as it is removed by carbon disulphide, benzene, or ether, in which morphia and its salts are insoluble. If the aqueous solution be distinctly acid, water may be trusted to dissolve the whole of the morphia from opium. In some processes of assaying opium, the sample is subjected to a preliminary treatment with benzene or ether to remove narcotine, caoutchouc, and colouring matter. By this means the subsequent exhaustion with water is much facilitated, and a purer solution of morphine is obtained.

In presence of much narcotine, morphine is soluble in benzene, but this is not true of the meconate or other *salts* of morphine. Hence there is no loss of morphine on extracting opium with benzene. Meconate of morphia is, however, freely soluble in a mixture of alcohol and chloroform, but the simultaneous presence of ether prevents its solution more or less completely.

Assay of Opium.—The assay of opium includes determinations of the morphia, water, and matter soluble in water. A search for the commoner adulterants should also be made.

W a t e r should be determined by taking a known weight of the opium in thin slices and noting the loss on drying at 100° C.

The e x t r a c t should next be determined by exhausting the dried sample with cold water, and collecting, drying, and weighing the residue; or evaporating the whole or an aliquot part of the solution to dryness and weighing the extractive matter left.

The a s h of opium is readily determined by igniting a weighed quantity of the sample. The residue should not exceed 8 per cent.

An aqueous solution of opium should give a red coloration with ferric chloride. The production of a black or blue-black coloration or precipitate will be due to t a n n i n, which is not a normal constituent of opium.

Genuine opium contains no s t a r c h, and hence, on boiling

with water the residue insoluble in cold water, the solution obtained should give no blue coloration with solution of iodine.

Sand, stones, bullets, and other make-weights are sometimes met with as adulterants of opium. Sugar, gum tragacanth, pulp of apricots and figs, pounded poppy capsules, &c., are also employed for the sophistication of opium.

DETERMINATION OF MORPHIA IN OPIUM.—The accurate estimation of morphia in opium is attended with peculiar difficulties, and hence but few of the numerous published processes for the assay of opium are really reliable. In addition to the method of assay prescribed in the *British Pharmacopœia*,* the following are very satisfactory processes.

1. The following method of assaying opium is due to Prollius.† It has the merit of exceptional simplicity, and is said to yield very good results. The sample of opium is exhausted with water, the solution evaporated on the water-bath, and the residue dissolved in alcohol of 34 per cent. in such quantity that each 10 c.c. represents 1 gramme of the sample. 100 measures of this tincture are shaken with 5 of ether and 2 of ammonia, and the liquid allowed to rest for twenty-four hours. The morphia collects in crystals at the junction of the two layers, and ultimately sinks to the bottom, all narcotine, colouring matter, &c., remaining in solution. The liquids are decanted, and the crystals collected, slightly washed with diluted alcohol, weighed, titrated.‡

* The following are the essential details of the *British Pharmacopœia* process of opium assay:—Soak 100 grains of the powdered sample in 1 ounce of water for twenty-four hours, with frequent stirring. Transfer to a percolator, and exhaust the insoluble matter by gradual addition of 3 ounces more of water. Boil the resultant solution for ten minutes with 100 grains of slaked lime and filter. Wash the residue with 1 ounce of boiling water, slightly acidulate the filtrate with hydrochloric acid, evaporate to ½ ounce, and allow to cool. Cautiously neutralise with dilute ammonia, carefully avoiding excess, filter from the brown matter which separates, wash with 1 ounce of water, again concentrate the filtrate to ½ ounce, and add a slight excess of ammonia. After twenty-four hours pass the liquid through a tared filter, wash the precipitated morphia with cold water, and dry at 100° C. "It ought to weigh at least from 6 to 8 grains."

† *Pharm. Centralhalle*, 1878, p. 20.

‡ A modification of the above process, due to Petit, consists in suspending 15 grammes of opium in 75 of water, and filtering. To 55 grammes of the filtrate (= 10 grammes of opium) add 3 c.c. of solution of ammonia and agitate,

2. The German Pharmacopœia Report gives the following process by Flückiger, who has had great experience in opium assays :—

15 grammes of opium are dried at 100° C. till constant in weight, the loss representing water. The dried opium is powdered, and 8 grammes' weight of the powder is repeatedly extracted with strong ether, to remove the narcotine, wax, and colouring matter. The residue is freed from ether by drawing air through the percolation-tube, or by simple exposure, and is then treated with 80 c.c. of water in a closed flask, the mixture being frequently agitated during twelve hours. The liquid is then placed through a dry ribbed filter of 5 inches diameter, and 42·5 grammes of the filtrate (=5 grammes dried sample) transferred to a small weighed flask. 22 grammes of ether-alcohol are then added.* Next, 1·5 grammes of ammonia of ·960 sp. gravity are added; and the flask is then closed, shaken, and set aside for twenty-four hours. After agitating so as to detach the crystals from the flask, the whole is filtered through a small ribbed filter, and, when the mother liquor has passed through, the precipitate is washed with 11 grammes (=8½ c.c.) of the ether-alcohol, and finally with 10 grammes of pure ether. Lastly, the crystals are transferred to the weighed flask, dried, and weighed. The weight found represents the crystallised morphia, $C_{17}H_{19}NO_3,H_2O$, in 5 grammes of the dried opium.

E. Mylius† has recently subjected the foregoing method of Flückiger to an experimental criticism. He finds that the determinations of morphia by this process are below the truth, owing to the solubility of the alkaloid in the ether-alcohol. The loss by this source was determined, and it was found that

when the morphia is rapidly deposited as a crystalline powder. The liquid is allowed to stand for a quarter of an hour, when 27 grammes of 95 per cent. alcohol should be added, the whole agitated several times, left at rest for half an hour, and then passed through a tared filter. The precipitate is washed with proof-spirit, dried at 100° C. and weighed.

* The "ether-alcohol" used is made by mixing 120 grammes of alcohol of ·815 sp. gr. with 100 grammes of ether. This means a mixture of nearly equal measures of the two liquids. The 22 grammes to be used will measure 17 c.c. A small graduated cylinder may be conveniently used as a wash-bottle.

† *Arch. Pharm.* [3], xv. 310.

by adding 0·088 grammes to the weight of morphia obtained the results became absolutely, and not merely relatively, correct. Mylius also suggests the weighing of the morphia on the filter instead of in the flask, in which the difficulty of complete dessication is considerable.* He prefers to remove the larger crystals to a filter, and detach the remainder with a glass rod, rinsing them on to the filter with a part of the filtrate. The crystals should then be washed with 10 grammes of ether-alcohol, and the filter gently pressed between blotting-paper till free from mother-liquor. It is then dried at 100° and weighed. Mylius then proposes to remove the morphia from the filter mechanically, and reweigh.

3. Professor A. B. Prescott† recently critically examined a number of the published methods of assaying opium for morphia, and after numerous experiments submitted the following method, which is essentially the Hager-Jacobsen process, to the Committee of Revision of the United States' Pharmacopœia:—The opium is dried at 100° C. till it ceases to lose weight. It is then powdered, and 6·5 grammes are placed on a paper filter of 4 inches diameter. Benzene is added in quantity sufficient to cover the powder and fill the funnel, and, when it begins to pass through, the neck of the funnel is closed, and the whole left to macerate for one hour. The funnel neck is then opened and the exhaustion continued with addition of more benzene, till a total volume of 50 c.c. has been used. The filter is then dried at a gentle heat till the odour of benzene has disappeared. The contents are next transferred (the filter being preserved) to a weighed stoppered flask of 100 to 120 c.c. capacity. Exactly 3 grammes' weight of freshly slaked lime is added, together with 20 to 30 c.c. of water. Agitate for several minutes, then close the flask and shake till a uniform mixture is obtained. Then add sufficient water to bring the contents of the flask to exactly 74·5 grammes. Digest, with occasional agitation, for one hour, at a temperature approaching 100° C. The flask is then cooled and the

* The difficulty might be avoided by titrating the morphia with decinormal acid, instead of weighing it.

† *Proceedings American Pharm. Association*, 1878, and *Pharm. Journ.* [3], x. 128 and 182.

weight of the contents made up again to 74·5 grammes. The liquid is next filtered through the paper previously used into a graduated cylinder, until a measure of exactly 50 c.c. has passed through, the filter being squeezed if necessary to make up the filtrate to this volume, which represents exactly 5 grammes of opium. To the filtrate, 8 drops of benzene and 3 c.c. of washed ether should be added, and the whole well agitated. Next add 4·5 grammes of powdered ammonium chloride, agitate again till the salt has completely dissolved, and set the tube aside in a cool place for three to three and a half hours. Then filter the liquid through a small filter, previously weighed and moistened, and wash the deposit several times with a few drops of water. The contents of the filter are next dried at about 50° C., washed with 3 c.c. of washed ether, redried, and weighed. The weight represents the morphia in 5 grammes of the dried opium. The foregoing process is based on the extraction of the wax and other impurities by benzene; the solubility of morphia in lime water; the decomposition of chloride of ammonium by lime, with formation of calcium chloride and ammonia; and the property possessed by benzene and ether of inducing the crystallisation of morphia, and preventing its deposition on the sides of the containing vessel.*

4. A process of opium-assay based in some respects on different principles from the above has been described by the late E. F. Teschemacher.† The following are the essential steps in the method, with certain recent modifications communicated to the author:—1000 grains of the opium are macerated for twelve hours, with about 4000 grains of cold water, and 300 grains of lead acetate, with occasional stirring. The meconic acid is converted into insoluble meconate of lead, while the morphia is dissolved as meconate. The narcotine is also left behind in an insoluble condition, as it does not form an acetate. The residue is ground to a paste with water, and the whole

* The employment of this curious weight is based on the assumption that benzene will extract 2·0 out of 6·5 grammes of opium, and, that consequently, the residue and lime together weigh 7·5 grammes, leaving 67 grammes for the water, 50 c.c. of which will represent 5 grammes of the sample.

† *Chem. News*, xxxv. 47.

diluted to a volume of 20,250 fluid grains.* The liquid is well mixed and passed through a dry filter. 15,000 fluid grains of the filtrate (=750 grains of opium) are evaporated to an extract on the water-bath, the residue treated with 3000 grains measure of methylated spirit, and the whole well stirred for ten minutes. The spirit precipitates the gummy matters of the opium, while the morphine acetate dissolves. The lead is next separated by addition of 20 grains (or as much as is necessary for its precipitation) of sulphuric acid diluted with 10 measures of water. After standing twelve hours the liquid is filtered, and the filtrate concentrated to about 1000 grains. While the liquid is still hot, 100 fluid grains of ammonia (sp. gr. ·880) are added, the whole being stirred rapidly and continuously for twenty minutes, to prevent the formation of large crystals, while the beaker is rapidly cooled by immersion in cold water. When cold, the liquid with the precipitate is rapidly and completely transferred to a filter large enough to hold the whole. The beaker is rinsed out, and the filter washed with "morphiated spirit" † till freed from mother-liquor. The precipitate is next washed off the filter with "morphiated water,"‡ and digested therein for a few minutes, to remove colouring matter, sulphate of ammonium, &c. It is again transferred to a filter, dried at 100° C., and then washed twice with benzene. This treatment completely frees the precipitate from narcotine, which is very readily soluble in benzene, in which liquid morphia is insoluble (as it is also said to be in benzene saturated with narcotine). The precipitate is next drained and again dried at 100° C., when the resultant alkaloid represents the morphia in 750 grains of the sample of opium.

* This instruction is based on the experience that the residue and lead meconate from 1000 grains of opium will measure from 200 to 300 grains, and hence may be safely assumed to be 250, leaving 20,000 fluid grains of liquid.

† The "morphiated spirit" is made by mixing 1 measure of ammonia (sp. gr. ·880) with 20 of methylated spirit, and digesting in the liquid a large excess of morphia for several days, with constant agitation. The filtered liquid contains ·33 per cent. of morphia.

‡ The "morphiated water" is made by agitating cold water with excess of morphia and filtering after twenty-four hours. The filtrate contains ·04 per cent. of alkaloid.

In this process, the most serious objection appears to be the tendency to decomposition of morphia by the evaporation of such large bulks of aqueous and alcoholic solutions. Also, there is no correction made for morphia dissolved in the morphia liquor, and no provision for its recovery. It is also questionable whether it is desirable to avoid the formation of large crystals of morphia, as a pulverulent or granular precipitate may look fairly colourless, and yet contain a notable amount of colouring matter. The use of spirit and water saturated with morphia is decidedly advantageous.

Very valuable hints on the assay of opium for morphia are contained in papers published by B. S. Proctor and E. L. Cleaver.*

Preparations of Morphine and Opium.—Opium is one of the most extensively employed drugs, and hence the number of official and other remedies of which it is an important constituent is very considerable. It is sometimes necessary to examine these preparations to detect the presence or to ascertain the proportion of opium or morphine present. The mode of effecting this is in many cases very similar to the methods employed for the assay of opium, and for the toxicological detection of morphine; but the following facts are serviceable in the analysis of such preparations, or in forming an opinion on their quality.

TINCTURE OF OPIUM, B.P.—This is the official name for the preparation commonly known as "laudanum." As the latter name is generally recognised as practically synonymous with the official designation, the proportions of opium and spirit employed in the preparation of the tincture ought to be those prescribed in the *British Pharmacopœia*. These are 1½ oz. or 656 grains of good opium in powder (elsewhere defined as yielding on assay at least 6 to 8 per cent. of morphia) and proof-spirit to the measure of 20 fluid ounces. It is a common practice to use a weaker spirit than the above (made from equal measures of water and rectified spirit), and to reduce the proportion of opium, or to employ an inferior quality. Hence commercial tincture of opium is of

* *Year-Book Pharm.* 1876, pp. 502, 511; 1877, p. 528; and 1878, p. 504.

very variable activity.* D. B. Dott found the specific gravity of twelve samples of the commercial tincture to range from ·922 to ·962, while the crude morphine contained in the same specimens and six others (the density of which was not observed) ranged from 4·37 to 0·55 grains per fluid ounce, the average being 2·66. As the specific gravity is dependent on the proportion of solid matter, as well as upon the strength of the alcohol present, in assaying tincture of opium it is desirable to determine the total extract, in addition to ascertaining the proportions of alcohol and morphine.

For the determination of the morphine in tincture of opium Prescott recommends the following process, somewhat modified from that of Hager:—25 grammes' weight of the tincture is evaporated at 100° C., and the residue mixed with 1 gramme of freshly-slaked lime. 24 c.c. of water should next be added, and the mixture heated on the water-bath for one hour. The liquid is filtered, and the filtrate and washings concentrated to 25 grammes, and mixed while warm with 1 c.c. of ether and three drops of benzene. 1·1 gramme of ammonium chloride is dissolved in the liquid, which is set aside for twenty-four hours. The liquid is then well shaken, the crystals collected on a weighed filter, washed with 8 c.c. of cold water, dried at 50° C., and weighed.

Compound Tincture of Camphor, B.P., is the present representative of the preparation formerly officially, and still commonly, called "Paregoric," or "Paregoric Elixir." Compound tincture of camphor is directed to be prepared with 40 grains each of opium and benzoic acid, 30 grains of camphor, and 30 minims of oil of anise; the whole being diluted with proof-spirit to 20 fluid ounces.

The proportion of alcohol in the compound tincture of camphor is indicated with sufficient accuracy by the specific gravity, which should not be greater than ·926.

The opium is the most important constituent of paregoric

* The difficulty caused by the natural variations in the quality of opium is well met by a process patented by Mr B. S. Proctor, who removes the greater part of the fatty and resinous matters and the worthless narcotine, and reduces the opium to a uniform rectified condition, in which it contains 10 per cent. of morphia.

elixir, and is apt to be deficient in amount or quality, besides being frequently wholly omitted. The last practice is due to the fact that preparations of opium cannot be legally sold except by registered pharmacists; hence a preparation destitute of opium is largely substituted by general shopkeepers for the genuine "paregoric" or "compound tincture of camphor" sold by the druggists. To recognise the presence of opium in paregoric the liquid should be diluted with proof-spirit till of a light yellow colour, and a drop or two of solution of ferric chloride added. If opium be present more or less red coloration will be produced, owing to the formation of meconate of iron. By comparing the depth of red colour with that given by a standard tincture, a rough approximation to the proportion of opium can be obtained. A determination of the actual morphine can be made, if desired, by the method employed for the assay of the tincture of opium, but a considerable measure of the paregoric is required.

The reaction with ferric chloride is valueless as an indication of the presence of opium if the preparation should have been coloured with cochineal, as is now frequently the case. A better method is to evaporate the tincture to a small bulk at 100° C., add a drop or two of hydrochloric acid, and agitate with ether to remove the camphor, oil of anise, and benzoic and meconic acids. The aqueous liquid is separated from the ethereal layer, rendered alkaline with potassium carbonate, and at once agitated with a mixture of ether and acetic ether, as described on page 462. The residue left on evaporation of the ethereal solution is examined for morphine by ferric chloride and other reagents (see page 463).

In an instance within the knowledge of the author, the opium of paregoric elixir was replaced by henbane.

Further information respecting the examination of compound tincture of camphor is given in Vol. I. page 114.

Various other preparations of morphia and opium are used in medicine, but the methods suitable for their examination are similar to those already described.

Toxicological Detection of Morphia and Opium.—In whatever form or manner it may be administered opium is found to act as a typical and powerful narcotic poison. Its

poisonous properties are essentially due to the morphia contained in it, and the symptoms produced by opium differ little from those consequent on the administration of pure morphia, except that in the latter case they are usually manifested more rapidly than in the former.

After poisoning by morphia or opium drowsiness and stupor are usually the first symptoms observed. At first the patient may be aroused without much difficulty, but as time goes on this becomes impossible, the drowsiness passing into complete coma, ending in death.* Poisoning by morphia or opium often closely simulates alcoholic drunkenness, and, in the absence of a smell of opium in the breath or vomit, it is often very difficult to distinguish between them.

Other diseases, notably uræmic poisoning due to rupture of the bladder, are apt to be mistaken for poisoning by morphia.

The dose of morphia necessary to destroy life is extremely variable. Death has been caused to infants by $\frac{1}{8}$th, $\frac{1}{10}$th, $\frac{1}{15}$th, and even $\frac{1}{19}$th of a grain of opium; as also by a few drops of tincture of opium. On the other hand, children have recovered after doses of 1 grain, 5 grains, and $7\frac{1}{2}$ grains of opium, and after two teaspoonfuls of laudanum. $\frac{1}{2}$ grain of morphia acetate has proved fatal to an adult; but, as a rule, the usual minimum fatal dose for an adult may be stated as 1 grain of a salt of morphia, or 5 grains of opium. Personal habit, as in the case of opium eaters, and idiosyncracy will of course largely modify the above conclusion.

The *post mortem* appearances of poisoning by morphia are by no means well-marked. The stomach and intestines usually appear healthy. If opium itself has been taken its peculiar and characteristic odour may often be recognised when the stomach is first opened.† Congestion of the lungs and brain are most commonly met with. The blood is usually very fluid.

* The *ante-mortem* symptoms of poisoning by morphia are a matter of observation for the medical attendant rather than the analyst, and hence they are not detailed here. Very valuable and complete information on this subject, and that of morphia poisoning generally, will be found in Woodman & Tidy's *Forensic Medicine and Toxicology.*

† I have observed an unmistakable smell of morphia in the contents of the bladder sixty hours after death by taking laudanum.

The detection of opium is based, in addition to the recognition of its smell, on the extraction of morphia and meconic acid in a sufficiently pure form to allow of the production of their characteristic reactions. The following is the most satisfactory mode of procedure :—

Notice if any smell of opium is apparent. If not, it may become evident on gently warming some of the contents of the stomach. Test a small quantity of the strained or filtered liquid with ferric chloride, and note if any red coloration is produced (see Vol. I. p. 277).

Next cut up the stomach and any solid contents into small pieces, and reduce the whole to pulp by beating in a mortar. Mix the product with the liquid contents of the stomach, and treat the whole with rectified spirit acidulated with acetic acid. Keep the mixture warm for some time, with occasional agitation. Then filter or strain from the solid matter.

The filtrate is treated with basic acetate of lead as long as a precipitate is produced, when the liquid is boiled and allowed to cool. When cold it is again filtered, and the precipitate washed with cold water.

The precipitate contains the meconic acid of any opium present. It should be washed off the filter with water, and completely decomposed by passing a rapid stream of sulphuretted hydrogen gas. The liquid is next filtered, and concentrated to a small bulk by evaporation at as low a temperature as possible. It should then be placed in a porcelain dish and tested with ferric chloride, which will produce a purplish-red coloration if meconic acid be present. The positive detection of meconic acid affords as perfect a proof of the presence of opium as does the recognition of morphia itself, but it is necessary to distinguish carefully between the coloration produced by meconic acid and the somewhat similar reactions given by thiocyanates and acetates. This may be effected with certainty, as described in Vol. I. page 277.

A very useful approximation to the amount of opium present may be obtained by comparing the depth of tint produced by ferric chloride with that obtained on treating a known quantity of opium in a similar way.

The filtrate from the lead precipitate contains any morphia which may have been present. Separate the excess of lead by passing sulphuretted hydrogen for some time, filter, evaporate cautiously nearly to dryness, add a little water and filter. The filtrate will probably have a bitter taste, if morphia (or other alkaloid) be present. Transfer the solution to a stoppered separator, and agitate with a mixture of ether and acetic ether, as described on page 465, after rendering the liquid alkaline with ammonia or (preferably) with an alkaline bicarbonate. The ethereal solution of the alkaloid is removed and evaporated to dryness at a steam-heat, portions of the residue being carefully examined by the colour-tests 1, 2, 4, described on page 464, *et seq.*, and by the iodic acid test given on page 462.

It not unfrequently happens, even in cases in which it is certain that opium was the cause of death, that no trace of morphia or meconic acid can be found on analysis of the stomach or its contents. In other cases the poison has been detected with moderate facility a considerable time after death. The cause of these discrepant results is very obscure, but they are probably mainly dependent on the opportunities which circumstances have given for the elimination or absorption of the poison before death has ensued. Hence the failure to find morphia does not prove that its administration was not the cause of death.

No morphine can be detected in the urine of patients who have taken large doses of the alkaloid into the stomach, but if hypodermically injected it readily passes into the urine.

PTOMAINES.—Recent researches have shown that during the progress of putrefaction bodies called ptomaines are produced under certain little-understood conditions. According to Casali they are acid or basic amidated compounds, but, whatever their constitution may be, in their chemical and physiological characters some of them present close resemblances to the vegetable alkaloids. Some of these cadaveric substances are narcotic like morphine, while others simulate the symptoms of strychnine or of atropine, compounds having different physiological actions being produced at different

stages of decay. The obscure poisonings produced by fish, cheese, mouldy bread, &c., are not improbably caused by one or other of these ptomaines.* According to Brouardel and Boutmy the presence of a cadaveric alkaloid can be detected by No. 3 test for morphine in solution (page 462), but morphine and atropine give a similar reaction.†

STRYCHNOS ALKALOIDS.

The various species of the genus of plants called *Strychnos* contain certain alkaloids remarkable for their intensely poisonous properties.

The alkaloids strychnine and brucine are found in the seeds of the *Strychnos nux-vomica* in combination with lactic and igasuric acids. The proportions of the bases vary considerably, but usually range from ·25 to ·50 per cent. of strychnine and from ·2 to 1·0 per cent. of brucine.

The seeds of *Strychnos Ignatiæ*, commonly called "St Ignatius' beans," contain about 1·5 per cent. of strychnine and 0·5 per cent. of brucine. They are employed for the manufacture of strychnine.

A third base, called igasurine, has been supposed to exist in nux-vomica; but the researches of Shenstone have proved the supposed alkaloid to be merely a mixture of strychnine and brucine.

The bark of *Strychnos nux-vomica* is also very poisonous, and has been termed "false angustura bark." The extreme bitterness of the strychnos bark, its twisted appearance, the impossibility of separating it into thin layers, and the blood-red coloration produced on applying nitric acid to the internal coat, are characters by which it is easy to distinguish it from true angustura bark.

The *Strychnos Tieuté* or "deadly upas tree" of Java is believed to owe its poisonous properties to the presence of strychnine.

The deadly effects of the *Woorara* or Indian arrow-poison have been attributed to strychnine, but are now proved to be due to a distinct base, curarine, which is described on page 496.

* *Journ. Chem. Soc.* xl. 57. † *Compt. Rendus.* xcii. 1056.

The proportion of total alkaloids contained in *nux-vomica*, St Ignatius' beans, false augustura bark, &c., may be determined by the method employed for the assay of cinchona bark (page 448). The strychnine and brucine may subsequently be separated by crystallisation from alcohol of ·942 specific gravity, which dissolves the brucine and mere traces of strychnine.

Strychnine. Strychnia. $C_{21}H_{22}N_2O_2$.—This is by far the most important of the strychnos alkaloids.

Strychnine occurs as a white powder, or in crystalline particles of variable appearance. The crystals are sometimes minute pearly scales, like mica; sometimes octahedra with a rhombic base; but more commonly large four-sided prisms. The crystals vary much according to the solvent from which they are deposited. For their production on a microscopic scale it is best to let the alkaloid deposit gradually by addition of an alkali to the solution of one of its salts (see also page 484).

Strychnine has no smell and is not deliquescent. On being heated it melts without decomposition, but is not volatile. Its solutions exert a lævo-rotatory action on polarised light, have a marked alkaline reaction, and are extremely bitter.

Strychnine is an exceedingly violent poison (see page 490).

Strychnine is very sparingly soluble in cold water, requiring from 6500 to 7000 parts for its solution, but it dissolves in 2500 parts of boiling water. It requires 100 parts of alcohol for solution, a fact which is utilised for its separation from brucine, which is readily soluble in the same liquid. Strychnine is soluble in about 10 parts of chloroform, but dissolves very sparingly in ether, the solubility being variously stated at 1 in 340 up to 1 in 1800. Doubtless the physical condition of the alkaloid largely affects its solubility. Strychnine dissolves with facility in a mixture of equal measures of chloroform and ether, a fact often utilised for its extraction. It is soluble also in 350 parts of petroleum spirit, and in 250 parts of benzene.

Strychnine is not removed from its acidulated solutions by agitation with any of the above immiscible solvents, but, on the contrary, may be extracted from its solutions in them by shaking the liquid with dilute sulphuric acid.

Strychnine is a strong base and completely neutralises acids, forming salts which are usually crystallisable and soluble in water, forming very bitter, exceedingly poisonous solutions. The salts of strychnine are mostly soluble in alcohol, but are insoluble in ether, chloroform, benzene, petroleum spirit, or amylic alcohol.

Analytical Reactions of Strychnine.—1. On adding to a not too dilute solution of a soluble salt of strychnine a fixed alkali, alkaline carbonate, ammonia, or lime water, strychnine is thrown down as a white precipitate insoluble in excess of the precipitant. The precipitate rapidly becomes crystalline. The crystals have a characteristic microscopic appearance, being usually well-defined, long, rectangular prisms. They are well developed if a drop of a dilute solution of a strychnine salt (*e.g.*, the acetate or sulphate) be placed on a slip of glass, and covered with a small beaker rinsed with strong ammonia. After half an hour the beaker may be removed, the drop of liquid covered with a circle of thin glass, and examined under the microscope. If the solution contain extraneous matter, it may be found difficult or impossible to obtain crystals from it.

2. If strychnine be liberated from the solution of one of its salts by one of the reagents mentioned above, and the liquid (with the suspended precipitate) be *at once* shaken with an equal measure of chloroform, the alkaloid is readily dissolved by the latter liquid, and may be obtained in a solid state by allowing the chloroform to separate completely from the aqueous layer, running it off by a tap and evaporating it to dryness at a steam heat. The agitation of the aqueous liquid with chloroform should be repeated if quantitative results are desired. From aqueous liquids containing little solid matter, chloroform separates tolerably readily, but if, as often happens in practice, there be much extractive matter present, the complete separation of the chloroform requires many hours or even days. This inconvenience may be wholly avoided by substituting for pure chloroform a mixture of equal volumes of ether and chloroform. This has a density of 1·11, and separates with facility from aqueous liquids (see page 492). Experiment has shown that the solubility of strychnine in a

mixture of equal volumes of ether and chloroform, is amply sufficient to ensure its complete extraction from the aqueous liquid.* Pure ether, on the other hand, though separating with extreme facility, has an extremely limited solvent power for strychnine, and cannot be trusted to effect its complete extraction.

3. As strychnine neutralises acids perfectly, it can be titrated with decinormal sulphuric acid in the same way as quinine (see page 420). 1 c.c. of decinormal acid neutralises ·0334 gramme of strychnine.

4. A very useful precipitant for strychnine in complex organic liquids is the nitric acid solution of sodium phosphomolybdate known as Sonnenschein's reagent, the preparation of which is described on page 408.†

On adding this to a neutral or slightly acid solution of the alkaloid, the strychnine is thrown down as a yellowish-white amorphous precipitate. The separation is complete even in very dilute liquids. Many alkaloids besides strychnine give similar precipitates, and hence the reagent is merely of service for concentrating the strychnine and purifying it from extraneous matters. The precipitate should be filtered off, washed with water containing the reagent, and the strychnine separated by suspending the precipitate in water, adding ammonia, and agitating with ether-chloroform, as in test 2. The precipitate can, however, be directly examined by the colour-reactions described on page 487.

5. Strychnine may also be separated from its tolerably concentrated neutral solutions by precipitation with chromate of potassium. The test is best applied to a chloroform-residue obtained as described in 2. This should be dissolved in dilute acetic acid, the liquid filtered, if necessary, and evaporated to dryness at 100° C. The resultant acetate of strychnine is dissolved in a little cold water, and neutral chromate of potassium is added to the solution. Chromate of strychnine, $(C_{21}H_{22}N_2O_2)_2,H_2CrO_4$, is thrown down as

* *Analyst*, vi. p. 141.

† According to Scheibler a still more delicate reagent for strychnine and other alkaloids can be made by adding phosphoric acid to a solution of sodium tungstate as long as a precipitate is formed and redissolved.

a yellowish-brown precipitate, soluble in boiling water and re-deposited on cooling in orange- or lemon-yellow needles and plates. The precipitate is very slightly soluble in cold water, a fact which enables strychnine to be separated from brucine, the chromate of which is more soluble. Chromate of strychnine gives the characteristic violet oxidation-product directly on treatment with strong sulphuric acid as described in paragraph 8; or the alkaloid may be obtained in a free state by suspending the precipitate in water, adding ammonia, and agitating with ether-chloroform, as in 2.

6. Strychnine forms a combination with iodine analogous to and having similar optical properties with herepathite (see page 421). The following is the best method of utilising the reaction for the detection of strychnine. On a microscope slide place a very small drop of an alcoholic solution of iodine, and allow it to evaporate. *Directly* it is dry add a drop of a solution of strychnine, made by dissolving the alkaloid in dilute acetic acid and adding a drop of sulphuric acid. Add also a drop of rectified spirit, and allow the mixture to evaporate spontaneously. On examining the residue under the microscope with a Nicol's prism and selenite, but using no analyser, characteristic crystalline structures will be observed. These may take the form of small circular tufts of very fine black needles; of minute dots of a more or less triangular form, exhibiting yellow, pink, and green tints; large triangular crystals of a yellow or green colour, composed of three parts radiating from a centre; numerous solid macled prisms, occasionally showing complementary tints; or solid rosettes of four, five, and six-sided prisms. In all cases it is desirable to compare the results with those obtained from a minute quantity of strychnine treated in precisely the same manner. The mode of operation may be varied considerably, provided that the essential conditions of simultaneous presence of alcohol, sulphuric acid, acetic acid, free iodine, and a trace of strychnia be duly observed. The test is said to be sensitive to 1-2500 of a grain of strychnine.

7. Strychnine is dissolved by cold concentrated sulphuric acid without charring or even change of colour. It also resists, with considerable energy, the action of sulphuric acid

at the temperature of boiling water. It is, however, not desirable to expose it too long to such extreme conditions.

8. On treating a *cold* solution of strychnine in concentrated sulphuric acid with an oxidising agent of almost any kind, a rich purple-blue coloration is developed. This changes more or less rapidly through purple and crimson to a bright cherry-red tint, which is somewhat persistent. The rapidity of the change of colour is largely dependent on the nature and quantity of the oxidising agent employed. Various substances have been recommended for the purpose. The following are the most notable :*—

(*a*) Potassium bichromate.—This is the most unreliable of reagents for the purpose, and ought on no account to be employed.

(*b*) Potassium permanganate.—This gives the reaction with great distinctness, but the rotation of tints is very rapid, and the reagent itself is apt to give a crimson colour with sulphuric acid.

(*c*) Potassium ferricyanide.—This reagent gives exceedingly good results. The change from blue to crimson and red is very rapid.

(*d*) Lead dioxide (PbO_2).—This oxidising agent acts remarkably well, but the puce colour natural to it is apt to distract the attention from the reaction to be looked for.

(*e*) Manganese dioxide (MnO_2).—This reagent, employed in moderate quantity and in the finely powdered state, is the one to which the author gives preference. The play of colours is remarkably well-developed, and the change of tint very gradual.

The oxidation-test for strychnine is usually performed in practice on the residues left by evaporating to dryness the ether-chloroform with which an alkaline solution of the alkaloid has been agitated. The test may, however, be directly applied to the chromate or phospho-molybdate of strychnine (see reactions 4 and 5). The following mode of operating is best calculated to ensure delicacy and accuracy:—

The solution of the strychnine in ether-chloroform should be evaporated in a porcelain dish or crucible. If the quantity

* For Lotheby's electrolytic test see page 489.

of strychnine to be sought for is likely to be very small, the dish should be immersed in hot water and the solution of the alkaloid allowed to fall slowly into it from a burette or pipette,* so that each drop may almost completely evaporate before another arrives. In this manner the strychnine-residue may readily be confined to a very small area, and the after-reactions thus rendered proportionately delicate. When quite dry and cold the residue should be treated with two or three drops of pure concentrated sulphuric acid, which should be thoroughly incorporated with it by means of a glass rod. The mixture should then be allowed to stand for five minutes in order to note if any colour is produced. Salicin and certain other bodies will cause a red coloration, while some may be more or less charred. If any marked coloration is produced, the dish should be heated on a water-bath for half an hour, the contents diluted with water, filtered, made alkaline with ammonia, agitated with a mixture of ether and chloroform (as in test 2), and the strychnine recovered by evaporating the solvent. The residue is then again treated with a drop or two of sulphuric acid.

The oxidising agent, which should be manganese or lead dioxide, is then added to the sulphuric acid by dipping a glass rod moistened with the latter into the powdered solid. A moderate quantity only should be used, so as not to obscure the reaction by excess of blackness. On stirring the drop of strychnine solution with the rod dipped in the oxide the blue coloration will become developed. In a minute or so it will be distinctly purple, passing in a few minutes to crimson, and ultimately to a cherry red, the last tint being very persistent. The test is exceedingly satisfactory, delicate, and characteristic. It is said to be capable of detecting $\frac{1}{20,000}$th of a grain of strychnine.

There are but very few substances which at all simulate the reaction of strychnine when treated with sulphuric acid and an oxidising agent, and few indeed of these that are dissolved together with strychnine on agitating the alkaline solution with ether-chloroform. Salicin, piperine, and certain resins give colours with sulphuric acid alone, but

* Or from the tap of the separating bulb.

they may be got rid of by heating the liquid on the water-bath, as already described. Aniline gives no colour with sulphuric acid alone, but coloured products are formed on treating the solution with an oxidising agent. These cannot be mistaken for the oxidation-products from strychnine, for the order of tints is entirely different, commencing, in the case of aniline, with a green, changing to a very persistent blue, and ultimately becoming black.

It is always *desirable* to purify the strychnine by extracting it from an alkaline liquid by agitation with ether-chloroform (see page 484), but the oxidation-reaction is readily obtained even in presence of considerable quantities of certain foreign matters. Thus oatmeal, tartar-emetic, and dextrin do not materially interfere with the reaction when the quantity of strychnine is considerable. Some extractive matters, however, wholly prevent the application of the colour-test, and the absence of strychnine must never be assumed till the test has been applied to an ether-chloroform residue.

Quinine, cinchonine, veratrine, and santonin may be found with strychnine in the ether-chloroform residue, but do not interfere with the application of the test. Morphia in small proportion does not interfere, and large quantities are excluded by its limited solubility in the ether-chloroform.

In small proportions brucine exercises no injurious influence on the oxidation-test for strychnine, but when much is present it is safest to separate the strychnine first of all as chromate, as described in reaction 5. Brucine can be sought for in the filtrate, as described on page 495. In toxicological investigations its presence together with strychnine points to an administration of one of the natural sources of the alkaloids, rather than to the use of a purified salt of strychnine.

Curarine, the active principle of the Indian arrow-poison, gives a series of coloured oxidation-products exactly like those of strychnine, but not being sensibly soluble in chloroform it is not liable to be found in the chloroform-residue (see page 496).

Many of the above sources of fallacy or confusion may be wholly avoided by performing the oxidation-test in a manner suggested by Letheby, which consists of employing electrolytic

oxygen instead of either of the oxidising agents mentioned on page 487. The solution of the ether-chloroform residue in a drop or two of strong sulphuric acid is placed in a cup-shaped depression in a piece of platinum foil. The foil is connected with the platinum plate of a single Grove's cell, and a platinum wire connected with the zinc plate of the battery. Immediately that the end of this platinum wire is dipped into the drop of acid, the violet colour of the oxidation-product will flash out, and on removing the wire from the liquid the tint will remain.*

8. An exceedingly delicate test for strychnine is the physiological one of Marshall Hall. A freshly-caught frog, the smaller the better, is the best subject for the experiment. The skin of the back should be raised with a pair of forceps, and a small slit made with a pair of scissors. Into the opening, the suspected liquid, as concentrated as possible, should be injected by means of a small pipette. The first symptom observed will be a difficulty in breathing, which gradually increases till the animal appears to gasp for breath. A slight tremor will be observed extending over the whole body, but specially noticeable in the hind legs. The frog sometimes remains perfectly quiet, but in other cases takes energetic and convulsive leaps. It should be placed under a beaker or bell-glass for easier observation. The characteristic tetanic convulsions next make their appearance. They are intermittent, the pupils being dilated during the spasms and contracted in the intervals. The convulsions may be induced by touching the frog, clapping the hands, or knocking on the table.

The physiological test is much reduced in practical value by the difficulty in obtaining young animals for experiment. On the whole it is decidedly less certain and characteristic than the chemical reactions, and in no case should be implicitly relied on unless confirmed by the results of the oxidation-test.

Toxicological Detection of Strychnine.—Owing to the violently poisonous character of strychnine, and the ease with which its preparations (under the disguise of "vermin

* The reaction may be rendered still more delicate by placing the drop of liquid at the bottom of a porcelain crucible, and momentarily immersing in the liquid two platinum wires connected respectively with the zinc and platinum plates of the battery.

killers," &c.), may be obtained by the public, it is very frequently the cause of death.*

The symptoms of poisoning by strychnine are more important to the medical man than to the chemist. They usually commence with a bitter taste, followed by a feeling of suffocation. The characteristic tetanic convulsions, often accompanied by opisthotonos, then come on, gradually becoming more frequent. Vomiting is not common. Lockjaw is a constant symptom. Consciousness, as a rule, is retained till the last, accompanied by a lively terror of the rapidly-recurring and agonising fits. Death usually ensues within a few hours.

From $\frac{1}{12}$ to $\frac{1}{40}$ of a grain is the usual medicinal dose of strychnine, but it may be increased in the case of a person accustomed to it. $\frac{1}{6}$ of a grain is usually distinctly dangerous. One grain may be regarded as the average fatal dose, and death has been known to occur from $\frac{1}{4}$ grain. Much larger doses have been recovered from.

The *post-mortem* appearances of poisoning by strychnine are not very striking or characteristic. Rigidity of the muscles is usually prolonged. The heart is usually, but not always, full of blood, especially on the right side. The stomach usually appears normal, but sometimes intensely congested. The most characteristic appearance is the intense congestion of the brain and spinal cord, often accompanied with considerable effusion of blood.

For the detection of strychnine in the dead body, the following method should be used, the portions of the body operated upon being chosen according to the manner in which the poison is likely to have been administered. Thus it is of no use to search in the stomach or intestines for strychnine injected hypodermically. If the poison has undergone absorption, it will most probably be met with in the liver, but all parts supplied with blood and most of the secretions may contain small quantities of the poison. In extreme cases it is desirable to operate on very considerable quantities of

* In my own experience of poisoned animals, extending over many years and to a great number of cases, strychnine has been found more frequently than all other kinds of poison taken together.

material, as death may be caused by so small a quantity of strychnine that the poison may be altogether missed if this precaution be not taken.

The portions of the body to be tested for strychnine should be cut into small fragments with a pair of scissors, and then further reduced by bruising in a mortar. The product is then treated with rectified spirit, mixed with about one part in twenty of acetic acid. This coagulates the albuminoïds, while allowing of the complete solution of the strychnine. After a few hours the liquid should be strained through muslin, and the clarified filtrate passed through a paper filter. The clear liquid is next evaporated nearly to dryness, diluted with water, and again filtered. The filtrate is once more evaporated to dryness, and the residue extracted with strong alcohol. The liquid is filtered, the alcohol removed by evaporation, and a small quantity of water added. The solution is placed in a tapped bulb or cylinder, diluted to about 20 c.c. with water, and a drop or two of hydrochloric acid added. An equal measure of ether is next added, and the whole well shaken. On standing a few minutes, the ether will separate on the surface, when the aqueous liquid should be withdrawn through the tap, and the ether then run off into a separate vessel.* The aqueous liquid is then returned to the separator, and about 30 c.c. of a mixture of equal volumes of ether and chloroform added. Enough ammonia to render the liquid distinctly alkaline is next added, and then the whole *immediately* shaken thoroughly for about a minute. On coming to rest the aqueous liquid will tend to separate from the mixed chloroform and ether, which has a density of about 1·1. If tolerably free from extractive matter, it will float on the surface of the ether-chloroform, but if largely charged with sugar or other soluble matter, it may be equally dense with the solvent, or even collect at the lower part of the separator. If, from the presence of extractive matters, the liquids do

* This preliminary treatment of the acidulated solution with ether is very advantageous. It effects a separation of glucosides, traces of fat, essential oils, and other matters, which otherwise would contaminate the strychnine. In some cases it is desirable to repeat the agitation with a mixture of equal measures of chloroform and ether.

not readily separate, water or ammonia should be added, so as to reduce the density of the aqueous liquid. An alternative, and perhaps preferable plan, is the gradual addition of ether, with cautious agitation, till the solvent separates readily at the surface of the aqueous liquid.*

When the division of the contents of the bulb into two layers is complete, the strata are separated from each other by means of the tap. If quantitative results are required, it may be desirable to agitate the aqueous liquid with a fresh quantity of ether-chloroform. The solution of the alkaloid in the ether-chloroform is passed through a small paper filter, if necessary, and then evaporated to dryness at a steam-heat in the manner described on page 488. The residue obtained may then be examined for strychnine by the tests given on page 484, *et seq.* If strychnine be present, the solution of the residue in alcohol will have a marked and persistent bitter taste, especially noticeable at the back of the tongue. The most delicate and characteristic chemical reaction of strychnine is the oxidation-test described on page 487. Reactions 4, 5, and 6, and the production of crystals of strychnine as described in 1, are also valuable as confirmatory tests, and should never be omitted if the material at disposal be sufficient for their performance. The bitter taste, however, in conjunction with a distinct reaction by the characteristic oxidation-test, may be regarded as ample proof of the presence of strychnine.

B l o o d should be examined for strychnine by diluting it with an equal bulk of water, adding a little acetic acid, boiling for a short time, filtering, and evaporating the filtrate nearly to dryness. The residue is taken up with alcohol, and the solution treated as already described.

From u r i n e strychnine may be directly extracted by agitating the fluid with ammonia and ether-chloroform.

Dialysis through parchment-paper is an efficient and

* This alternative is preferable to the addition of chloroform, which, if used in too large a proportion, will only separate from the dense aqueous liquid with extreme difficulty. The advantage of employing a mixture of ether and chloroform, rather than either solvent singly, for the isolation of strychnine was pointed out by me in a paper in the *Analyst*, vol. vi. p. 141.

occasionally a convenient means of separating strychnine from organic matters. The finely-divided tissue should be suspended in water, to which some alcohol and acetic acid have been added. Distilled water should be used on the other side of the membrane, and changed at intervals of twelve hours. After thirty-six to forty-eight hours the dialysate may be evaporated to dryness, and treated with alcohol, &c., as described on page 492.

It has not unfrequently happened that a *post-mortem* analysis has failed to detect strychnine in corpses almost certainly containing it. This result has probably been due in most cases to the use of defective methods of analysis, or to the search being restricted to too small quantities of material or to wrong parts of the body. Occasionally failure has probably been due to an elimination of the poison during life, especially in cases in which death has resulted from a minimum dose. Strychnine does not undergo decomposition in the dead body, and has been detected several years after death. Hence if elimination has not occurred prior to death, strychnine ought to be found by the toxicologist.

Brucine. Brucia. $C_{23}H_{26}N_2O_4$.—This alkaloid occurs in association with strychnine in *nux vomica*, St Ignatius' beans, and false angustura bark (see page 482). It presents a close general resemblance to strychnine, but is less powerfully poisonous, from 7 to 10 parts of brucine having the same physiological effect as 1 of strychnine.

Brucia occurs as a bitter, white, odourless, crystalline or amorphous powder, or in crystalline needles or four-sided prisms, containing 15·45 per cent. of water ($=C_{23}H_{26}N_2O_4+4H_2O$). It melts at 115°, and sublimes at 204° C.

Brucine is more soluble than strychnine in water, dissolving in 1050 parts of cold, and less than half that proportion of boiling water. In alcohol it dissolves very readily, a fact which is employed to separate it from strychnine. Brucine dissolves in 4 parts of chloroform, in 440 of ether, in 60 of benzene, and in 120 of petroleum spirit.

Brucine is a weaker base than strychnine, but resembles it closely in its general characters. Like strychnine, it is not acted on readily by cold sulphuric acid, or by caustic

alkalies. It dissolves without decomposition in hydrochloric acid.

ANALYTICAL CHARACTERS OF BRUCINE.—1. Brucine is precipitated in a free state on adding an alkali to the solution of one of its salts, and may then be taken up by agitating the alkaline liquid with ether-chloroform in the same way as strychnine (see page 484).

2. Brucine forms a soluble chromate, a fact which is occasionally used to separate it from strychnine. A better separation is effected by crystallising the free alkaloids from hot alcohol.

3. When treated with concentrated sulphuric acid* and an oxidising agent, brucine does not give the coloured products so characteristic of strychnine.

The most satisfactory reaction of brucine is that with nitric acid. On adding a drop or two of cold nitric acid of 1·42 sp. gr. to an ether-chloroform residue, or other solid product containing brucine, a scarlet or blood-red coloration is produced, which changes to yellowish-red, and finally to yellow.* If the mixture be now treated very cautiously with stannous chloride (or other reducing agent, such as sodium thiosulphate), a purple coloration is produced, which is destroyed by excess of either nitric acid or the tin salt.‡

The red coloration of brucine by nitric acid may also be developed by dissolving the alkaloid in strong sulphuric acid in a test-tube, and allowing nitric acid to run onto the surface of the heavier liquid. A red zone, passing to yellow, will be produced at the junction of the two liquids. If cold nitric acid be added to solid brucine, so as to develop the red colour, and the moisture be then largely diluted with water, a body called kakotelin, $C_{20}H_{22}N_4O_9$, separates in yellow flocks. The filtered liquid, after neutralisation by ammonia, gives a precipitate of calcium oxalate on being treated with calcium chloride. The precipitated kakotelin may be dissolved in

* According to some observers, strong sulphuric acid imparts to brucine a rose colour, turning first yellow and then yellowish-green.

† Strychnine, on the contrary, gives no coloration with cold nitric acid, but develops a yellow colour on warming.

‡ The orange colour produced by adding nitric acid to morphia remains unchanged on addition of stannous chloride.

dilute hydrochloric acid, and crystallised therefrom in orange-red or yellow scales.

The production of a red colour with nitric acid, accompanied by a formation of oxalic acid and yellow scales or crystals, insoluble in water but soluble in dilute acids, constitutes a combined reaction which is peculiar to brucine.

Curarine. $C_{18}H_{35}N$ (?).—This alkaloid is the active principle of the Indian arrow poison called *curari* or *woorara* (see page 482).

Curarine crystallises in four-sided prisms, which have a bitter taste, and are very hygroscopic. It is freely soluble in water and alcohol, but only slightly so in chloroform and amylic alcohol, and is insoluble in ether, benzene, turpentine, and carbon disulphide.

The aqueous and alcoholic solutions of curarine have a bitter taste and faintly alkaline reaction. The base forms crystallisable salts with hydrochloric, nitric, and acetic acids.

With strong nitric acid curarine gives a purple coloration.

If a filtered and highly concentrated solution of curarine be mixed with dilute glycerin, and a saturated solution of potassium bichromate added, amorphous curarine chromate is precipitated. Even after solution in boiling water it is again deposited in an amorphous state, a fact which distinguishes it from strychnine chromate, which forms well-defined crystals. Curarine chromate is more soluble in water than is strychnine chromate, and is never perfectly precipitated even by addition of glycerin or alcohol.

If the precipitate of curarine chromate be kept for some time it decomposes, but if treated without delay with concentrated sulphuric acid it develops a magnificent blue colour, which is often violet in the presence of impurities. The reaction simulates that obtained in a similar manner with strychnine, but curarine can be separated from strychnine by rendering the cold solution alkaline with ammonia, and then filtering. Strychnine will be found in the precipitate, whilst the curarine will remain in the liquid, owing to its solubility in water. The filtrate may be agitated with ether or benzene to remove any trace of strychnine, the aqueous liquid concen-

trated and the curarine converted into chromate and tested further, as already described.

Curarine is very unstable, and hence its solution should be subjected to as little manipulation as possible.

Curarine appears to owe its poisonous properties to its action on the nerves of motion, which it paralyses, so that an animal under its influence dies of suffocation from paralysis of the muscles of the chest. Hence its physiological effects closely resemble those produced by methyl-strychnine. Curarine appears not to act as a poison when taken into the stomach, but employed as a hypodermic injection, ·015 of a grain has been found fatal to a rabbit and ·004 to a frog. If, after administration of curarine, life be maintained by artificial respiration, symptoms of *diabetes mellitus* are observed, and the urine is found to contain sugar.

CURARI, curare, woorara, or urari is a poisonous extract, said to be prepared from the *Strychnos toxifera*, a native of Guiana,* but is probably a complicated mixture of vegetable extracts. It occurs in commerce as a black, shining, brittle, resinoid mass. About 83 per cent. is soluble in water, and 79 in diluted spirit. A mixture of glycerin and diluted spirit dissolves 85 per cent. Curari is exceedingly poisonous, and should be handled with the utmost care. It should never be allowed to come in contact with a cut or scratch, and, indeed, should never be touched with the naked fingers, or powdered or manipulated in the dry state. The symptoms produced by curari are similar to those occasioned by curarine itself. It has been proposed as a remedy for hydrophobia.

LESS IMPORTANT NON-VOLATILE BASES OF VEGETABLE ORIGIN.

The various bases of cinchona bark, opium, and the plants of the genus *Strychnos* are the most important of the natural non-volatile vegetable alkaloids, but the following also require some description. They are mostly but distantly related to each other, and are merely grouped together for convenience.

* The following information is largely taken from a valuable paper on curari by Mr John Moss (*Pharm. Journ.* [3], viii. 421).

The following table shows the names, formulæ, origin, and physiological effects of the alkaloids grouped together in this section :—

Name.	Chief Sources.	Formula.	Physiological Characters.
Aconitine.	Leaves and root of *Aconitum napellus* (monkshood), and allied species.	$C_{32}H_{43}NO_{12}$	A most violent poison. See page 499.
Atropine.	Leaves and root of *Atropa belladonna* (deadly nightshade).	$C_{17}H_{23}NO_3$	Poisonous; 1 grain usually fatal. Dilates the pupil of the eye.
Bebérine.	Bark of *Nectandria rodiæi*, *Pareira brava*, &c.	$C_{18}H_{21}NO_3$	Febrifuge. Used in intermittent fevers.
Berberine.	Calumba root, Barberry bark, and other plants of order *Berberideæ*.	$C_{20}H_{17}NO_4$	Tonic.
Caffeine or Theine.	In Coffee, ·5 to 2 per cent.; Tea, 1 to 4 per cent.; Maté or Paraguay tea, ·2 to 2 per cent.; Guarana, 5 per cent.; and Kola nuts.	$C_8H_{10}N_2O_4$	Somewhat doubtful; probably purely stimulant. In large doses distinctly poisonous.
Colchicine.	*Colchicum autumnale.*	$C_{17}H_{23}NO_6$ (?)	Very poisonous. Symptoms resemble those due to veratrine.
Cytisine.	*Cytisus laburnum* (laburnum).	$C_{20}H_{27}N_3O$	A narcotico-acid poison.
Daturine, Duboisine, or Hyoscyamine.	*Datura stramonium*, *Duboisia myoporoides*, and *Hyoscyamus* (henbane).	$C_{17}H_{23}NO_3$	Very similar to atropine, and either isomeric or homologous with it.
Emetine.	*Cephalis ipecacuanha.*	$C_{30}H_{44}N_2O_4$	Violently emetic. In large doses poisonous.
Physostigmine or Eserine.	*Physostigmatis faba* (Calabar bean); Esere.	$C_{15}H_{21}N_3O_2$	Very poisonous; powerfully contracts the pupil. Paralyses respiratory and voluntary muscles. Dilates the vessels of a frog's foot.
Pilocarpine.	*Pilocarpus pennatifolius* (jaborandi).	$C_{23}H_{24}N_4O_4$	Diaphoretic and sialogogue.
Piperine.	Various species of Pepper.	$C_{17}H_{19}NO_3$	
Theobromine.	The seeds and leaves of *Theobroma cacao* (cocoa)	$C_7H_8N_4O_2$	Similar to caffeine. Poisonous in large doses.
Veratrine.	*Veratrum officinale* (or sabadilla); *V. album* (or white hellebore); and probably in *V. viride* (or green hellebore).	$C_{32}H_{52}N_2O_8$ (?)	Produces vomiting and frothing at the mouth. The slightest trace applied to the nostrils causes violent sneezing

Many of the alkaloids of the above list have been but imperfectly examined, and their chemical reactions, especially, are only partly known. A character valuable for the recog-

nition of some of them consists in placing a drop of the solution on the eye of a rabbit, when, in a time varying from a few minutes to about an hour, a marked dilation or contraction of the pupil will often be observed. Thus:—

A. The pupil is *dilated* by
   1. Atropine and *belladonna.*
   2. Daturine and preparations of *stramonium*; nicotine and preparations of tobacco; hyoscyamine and preparations of henbane; and by extracts from solanaceous plants generally.
   3. Digitalin, and preparations of foxglove.
   4. Conine, and other preparations of the *umbelliferæ.*

B. The pupil is *dilated* by
   1. Morphia and other opium alkaloids.
   2. Aconitine, and preparations of aconite and other plants of the same order (*Ranunculaceæ*).
   3. Physostigmine, and preparations of the Calabar bean.
   4. Strychnine, and preparations of *nux vomica.*

A similar effect on the pupil is produced by the poisons when taken internally or hypodermically in sufficient quantity. Sometimes, as in the case of morphia and preparations of opium, the pupils are contracted during the earlier stages of the poisoning, but dilated subsequently, especially after death.

Aconitine, as met with in commerce, is of somewhat uncertain composition, several distinct bases having been confounded together under the same name. The alkaloids contained in *Aconitum napellus* appear to be distinct from those of *Aconitum ferox* and other species.

According to Wright, the root of *A. napellus* contains a highly active, crystallisable alkaloid of the formula $C_{33}H_{43}NO_{12}$. This he terms aconitine. Some roots contain, in addition, a nearly inert, bitter, crystallisable base termed picraconitine, $C_{31}H_{45}NO_{10}$, and a small quantity of an amorphous alkaloid. *A. ferox,* on the other hand, contains pseudaconitine, $C_{36}H_{49}NO_{12}$, and Japanese aconite, japaconitine, $C_{66}H_{88}N_2O_{21}$.

ACONITINE melts at 185° C., and on saponification with alcoholic potash yields a benzoate and a new alkaloid, aconi-

tine, according to the equation $C_{33}H_{43}NO_{12}+H_2O=C_7HO_2+C_{26}H_{39}NO_{11}$.* Aconitine yields a series of readily crystallisable salts.

PSEUDACONITINE melts at about 105° C., and on saponification yields pseudaconine, $C_{27}H_{41}NO_9$, and a salt of veratric acid, $C_9H_{10}O_4$. With the exception of the nitrate, the salts of pseudaconitine are mostly amorphous varnishes.

Both alkaloids possess similar physiological activity, and yield precipitates with picric acid, Mayer's reagent, Sonnenschein's reagent, &c.

COMMERCIAL ACONITINE is usually met with as an amorphous white powder, melting below 100° C., but is occasionally crystallised. It is unaltered in the air, is odourless, and has an acrid taste. It varies greatly in physiological activity, but must be handled with extreme caution, as it is probably the most violent poison known.

Aconitine is sparingly soluble in water, but dissolves readily in alcohol, ether, chloroform, or benzene, but not in petroleum spirit. It is not removed from its acidulated solutions by agitation with either of the above solvents, but is readily extracted by chloroform or benzene after adding excess of a fixed alkali or ammonia.

Aconitine gives no colour with nitric acid, even on warming. Cold concentrated sulphuric acid gives no immediate reaction, but very gradually, or more rapidly on warming, a deep brown coloration is produced, passing through various shades of reddish brown to violet. Sugar and sulphuric acid develop a red colour (see page 464), and on heating aconitine with phosphoric acid a violet colour is said to be produced.

With Sonnenschein's reagent aconitine yields a yellow precipitate, soluble in ammonia to a blue liquid. Mayer's reagent may be used for the precipitation and determination of aconitine (see page 408).

In toxicological inquiries, aconitine may be sought for in the same way as strychnine (see page 491), avoiding the use of mineral acids and fixed alkalies, and conducting all evaporations at as low a temperature as possible. Sonnenschein's reagent

* *Pharm. Journ.* [3], xi 2, 217.

affords a valuable means of concentrating the alkaloid without excessive evaporation. With care a chloroformic extract can be obtained to which the tests for the alkaloid can be applied. The chemical reactions of aconitine are not very delicate or characteristic except when the pure alkaloid is employed, and hence the following physiological tests should be carefully applied :—

(*a*) Rubbed inside the gums, an extract containing aconitine occasions a sensation of tingling and numbness, owing to the production of local anæsthesia.

(*b*) $\frac{1}{300}$ of a grain of aconitine hypodermically administered to a mouse will produce staggering and paralysis of the voluntary muscles.

As $\frac{1}{10}$ of a grain of aconitine acts as a fatal poison to a human being, there is usually but little chance of detecting the alkaloid after death. The symptoms during life and the results of the *post-mortem* examination are the best proofs of the administration of the poison.

ACONITE ROOT may be assayed for aconitine by Mayer's reagent (see page 407).

Atropine, $C_{17}H_{23}NO_3$, forms tufts or groups of needle-like prisms, having a persistent and unpleasantly bitter taste. It dissolves in about 300 parts of cold or 60 of boiling water, the solution having an alkaline reaction. It is also soluble in alcohol, amylic alcohol, ether, chloroform, and benzene, but is insoluble in petroleum spirit.

By the action of fuming hydrochloric acid, as also by heating with solutions of the caustic alkalies, atropine yields tropine, $C_8H_{15}NO$, and tropic acid, $C_9H_{10}O_3$. When atropine is evaporated to dryness with baryta-water and the residue strongly heated, an agreeable odour of hawthorn-blossom is developed.

Atropine is precipitated from the solutions of its salts by the fixed alkalies and ammonia, the precipitate being soluble in excess. From the alkaline liquid the atropine may be extracted by agitation with chloroform or ether.

A solution of hydrobromic acid saturated with free bromine gives with atropine a yellow precipitate, speedily becoming

crystalline, and insoluble in caustic alkalies, acetic acid, or dilute mineral acids.

Atropine is precipitated by Mayer's and Sonnenschein's reagents, and may be determined volumetrically by the former (see page 408).

In toxicological inquiries atropine may be isolated in the same manner as strychnine, but all treatment with strong acids or fixed alkalies should be avoided, and the evaporations conducted at as low a temperature as possible. By a judicious use of Sonnenschein's reagent, the evaporations can be in a great measure avoided.

When isolated in a condition of tolerable purity, atropine may be identified by its reactions with baryta-water and bromine. The most satisfactory test, however, is the dilation of the pupil of the eye of a young cat or rabbit when a drop of the concentrated extract or a particle of the alkaloidal residue is dropped into it. The effect may be produced in a time varying from a few minutes to half an hour.

If solid atropine be boiled for a few minutes with ten times its weight of strong nitric acid, the liquid then gently evaporated to dryness, and the cooled residue treated with a few drops of a freshly-prepared alcoholic solution of caustic potash, a magnificent violet colour is developed, gradually changing to wine-red and dirty red. The reaction is very delicate, and peculiar to atropine and its isomer daturine.

Bebérine, $C_{18}H_{21}NO_3$, is met with in commerce as the sulphate. This occurs in thin dark-brown translucent scales, forming a yellow, very bitter powder, which is soluble in water and alcohol.

On adding an alkali to the aqueous solution of the sulphate, the free base is separated as a pale yellow precipitate slightly soluble in water, but readily so in ether, chloroform, and benzene.

When boiled with concentrated nitric acid, bebérine yields a yellow resin, and gives a black resinous mass when heated with sulphuric acid and potassium bichromate.

Buxine, pelosine, and paricine are probably identical with bebérine.

Berberine, $C_{20}H_{17}NO_4$, occurs in a large number of plants

used in medicine, though the pure alkaloid is not official. Berberine forms beautiful, light yellow, silky needles or grouped prisms. It is pretty readily soluble in water, but only slightly in chloroform or benzene, and is insoluble in ether and petroleum spirit. It is extracted from its acidulated solutions by agitation with amylic alcohol.

A solution of a salt of berberine in hot alcohol deposits brilliant green crystalline scales on cautious addition of a dilute solution of iodine in potassium iodide. The iodo-compound resembles herepathite (see page 421) in its optical and general properties.

Caffeine or **Theine**, $C_8H_{10}N_4O_2$.—This alkaloid occurs in tea, coffee, and other vegetable products used as beverages in various parts of the world. Caffeine sublimes without decomposition when heated to about 130° C., but it volatilises in sensible amount even below 100° C. It has a slightly bitter taste, but is free from odour. Caffeine is sparingly soluble in cold water, but readily at the boiling point. In alcohol and ether it is sparingly soluble, the amount dissolved increasing with the temperature. In carbon disulphide and petroleum spirit caffeine is but slightly soluble. The best solvent for caffeine is chloroform, which dissolves 13 per cent. at the ordinary temperature and 19 per cent. at its boiling point. It is also soluble in benzene and amyl alcohol.

Caffeine is a very weak base, the solutions of its salts being decomposed by simple dilution. Agitation of its acidulated solutions with chloroform or benzene removes the alkaloid.

Concentrated nitric or sulphuric acid dissolves caffeine at at the ordinary temperature without change of colour. Under the action of oxidising agents, caffeine behaves like uric acid, $C_5H_4N_4O_3$, forming a coloured product analogous to alloxantin, and capable of conversion into a murexide-like substance by the action of ammonia. To utilise this reaction, the residue supposed to contain caffeine should be moistened with strong hydrochloric acid, a small crystal of potassium chlorate added, and the mixture subjected to a steam-heat for some minutes, after which it should be exposed to ammoniacal vapours, an excess being avoided. The production of a crimson or purple coloration proves the presence of

caffeine. An alternative method is to moisten the supposed alkaloid with strong nitric acid, evaporate gently to dryness, and then to expose the reddish-yellow residue to ammoniacal vapours.

For the estimation of caffeine in tea, the leaves should be finely powdered, and extracted in a Xoxheth's tube (see page 127) by means of water. The solution should be concentrated to a small bulk, mixed with magnesia, and at once shaken with chloroform, or the mixture evaporated to dryness at a low temperature, and exhausted with chloroform in a Xoxheth's tube. The caffeine left on evaporation of the chloroform may be purified by crystallisation from boiling water or alcohol.

Colchicine, $C_{17}H_{23}NO_6$ (?), usually occurs as yellowish-white resinous substance, of very doubtful basic character. It dissolves slowly but abundantly in water, forming a neutral solution, and is also readily soluble in alcohol. Colchicine is insoluble in petroleum spirit, but dissolves readily in ether, chloroform, benzene, and amylic alcohol, and is removed from either its acidulated or ammoniacal solutions by agitation with any of the last four solvents.

Colchicine dissolves in dilute acids and alkalies, the solution gradually becoming coloured intensely yellow. By boiling with dilute acid or baryta-water, it is converted into a new substance called colchicein, which crystallises in needles or glittering plates, has a less bitter taste than colchicine, but may be removed from its acidulated solution by agitation with chloroform. Ferric chloride gives a fine green coloration with a dilute acidulated solution of colchicein.

Colchicine is precipitated very perfectly by gallo-tannic acid and phospho-molybdic acid. The latter reagent is a useful one for separating it from solutions containing it. The precipitate gives the following reactions, but if preferred the free base may be obtained by agitating the precipitate with ammonia and chloroform, and evaporating the chloroformic solution to dryness.

Nitric acid of 1·42 sp. gravity colours colchicine and colchicein violet-blue, the tint changing to yellow and ultimately to green. If the violet solution be diluted with water it turns

yellow, and changes to a fine orange or red on adding excess of soda. Concentrated sulphuric acid dissolves colchicine with intense yellow colour, and on adding a drop of nitric acid a dark-brown spot is formed, passing gradually through violet and brown to yellow. Chlorine water occasions in an aqueous solution of colchicine a yellow precipitate which dissolves in ammonia with orange colour.

Daturine or **Hyoscyamine,** $C_{17}H_{23}NO_3$, is isomeric with atropine, and, like it, readily converted into tropine and tropic acid. In other reactions, hyoscyamine closely resembles atropine.

The symptoms of poisoning by *stramonium* set in somewhat earlier than those of *hyoscyamus* or *belladonna*, but are very similar, though more severe. Ringing in the ears, dryness of the throat, and flushed face, are early symptoms. Delirium of a violent kind, with spectral illusions, come on rapidly, while the pupils are widely dilated. There is often paralysis of the lower extremities. The only *post-mortem* appearance of importance is the congestion of the brain and its membranes.

Emetine, $C_{30}H_{44}N_2O_4$, is a yellowish-white powder, melting at 50° C. It is sparingly soluble in water, but dissolves in alcohol, ether, chloroform, benzene, petroleum spirit, and amylic alcohol. It is extracted by agitating its ammoniacal solutions with either of the four last solvents, but is not removed from its acidulated solutions.

Emetine forms a nitrate which is very sparingly soluble in cold water. On adding a drop of solution of bleaching powder to a fragment of solid emetine or one of its salts, followed by a drop of acetic acid, a very persistent bright orange or lemon-yellow coloration is produced.

IPECACUANHA may be assayed for emetine by the method employed for the estimation of the total alkaloids in cinchona bark (see page 448). It may also be examined by treating 15 grammes of the powder with 150 c.c. of rectified spirit, containing 15 drops of dilute sulphuric acid. After twenty-four hours the liquid is filtered, 100 c.c. evaporated to expel the alcohol, and the residual liquid titrated with Mayer's solution, as described on page 465. Each 1 c.c. of the standard

solution used corresponds to ·0189 gramme of emetine in the 10 grammes of ipecacuanha employed.

Physostigmine or **Eserine,** $C_{15}H_{21}N_3O_2$, as usually extracted from the Calabar bean is an amorphous, colourless, or brownish-yellow varnish. By operating at a low temperature, avoiding excess of light, it may be obtained crystallised.

Physostigmine is slightly soluble in water, but readily in ether, chloroform, and benzene, by which solvents it is extracted from its alkaline solutions.

On adding an alkali to the solution of a salt of physostigmine, the base is separated as a white precipitate, which becomes green or blue on exposure to the air.

A red coloration is produced on adding bromine water to a solution of a salt of physostigmine. 0·00006 of a gramme is said to be thus recognisable.

Concentrated nitric acid dissolves physostigmine with yellow colour. A similar coloration, changing to green, is produced by strong sulphuric acid.

Owing to the readiness with which physostigmine is decomposed by light or heat, its extraction from complex mixtures is very difficult. The chemical reactions are somewhat characteristic, but the most satisfactory test consists in applying a trace of the alkaloidal extract to the eye of a cat or rabbit, when strong contraction of the pupil will occur in about ten minutes.

A considerable dose of physostigmine or an extract of Calabar bean produces instantaneous paralysis of the lower extremities, while a smaller, but still fatal, dose causes gradual paralysis, with marked contraction of the pupil. Muscular twitchings, almost amounting to convulsions, sometimes occur. The physiological effects of physostigmine are exactly the reverse of those produced by strychnine.

Piperine, $C_{17}H_{19}NO_3$, is a weak base, crystallising in colourless four-sided prisms. It is nearly tasteless, and has no alkaline reaction. Piperine melts at about 100° C. It is nearly insoluble in water, but dissolves sparingly in ether, and with facility in chloroform, benzene, and petroleum spirit. It is extracted from its acidulated solutions by agitation with either of the last three solvents.

When boiled with strong potash or heated with soda-lime, piperine is converted into piperic acid, $C_{10}H_{12}O_4$, and piperidine, $C_5H_{11}N$. The latter is a powerful volatile alkaloid, soluble in all proportions of water and alcohol, and forming crystallisable salts with acids.

Concentrated nitric acid converts piperine into an orange-red resin, which is turned blood-red by caustic alkali, with formation of piperidine.

With concentrated sulphuric acid, piperine instantly gives an orange-red coloration, becoming brown on warming or standing.

Theobromine, $C_7H_8N_4O_2$, is the lower homologue of caffeine, $C_8H_{10}N_4O_2$, which alkaloid it closely resembles. Theobromine forms volatile trimetric crystals, sparingly soluble in water, alcohol, ether, chloroform, or benzene, and insoluble in petroleum spirit. Hot chloroform is its best solvent.

If theobromine be heated with dilute sulphuric acid and a little lead dioxide, carbon dioxide is evolved, and the filtered liquid evolves ammonia when heated with a fixed alkali, stains the skin purple-red, and gives an indigo-blue coloration on treatment with magnesia.

Veratrine, $C_{32}H_{52}N_2O_8$, is an alkaloid existing in several plants, probably in the form of a gallate. Veratrine is usually met with as a white amorphous powder, but may be obtained in crystals from its solution in alcohol. It has no smell, but if applied to the nostrils produces violent and uncontrollable sneezing. Veratrine is slightly bitter and acrid in taste, producing great heat and dryness in the fauces. An intense pricking sensation is produced when the alcoholic solution is applied to the skin.

Veratrine requires 9000 parts of cold or 1000 parts of boiling water for solution. It dissolves readily in alcohol, ether, chloroform, benzene, and amylic alcohol. The last four solvents extract it when agitated with an ammoniacal solution of the alkaloid, and amylic alcohol is said to remove it from its acidulated solutions also.

When solid veratrine is treated with concentrated sulphuric acid it slowly acquires a reddish-yellow colour, which changes after some minutes to a crimson red, and ultimately becomes violet. The reactions are hastened by warming the acid.

Cold hydrochloric acid dissolves veratrine without change of colour, but on warming the solution it becomes red. Nitric acid dissolves veratrine with light-red colour, changing to yellow.

JERVINE, $C_{26}H_{37}NO_3$; CEVADINE, $C_{32}H_{42}NO_9$; and CEVADILLINE, $C_{34}H_{53}NO_8$, occur in association with veratrine and other bases in various species of *Veratrum*.

VOLATILE ALKALOIDS OF VEGETABLE ORIGIN.

The alkaloids grouped under this section differ from all those previously described in being destitute of oxygen, liquid at the ordinary temperature, and volatile without decomposition.

The following table shows the names, chief sources, formulæ, and physiological action of the chief bases of this group. Only conine and nicotine require special description.

Name.	Chief sources.	Formula.	Physiological characters.
Conine, or Conicine.	*Conium maculatum* (hemlock).	$C_8H_{15}N$ $=(C_8H_{14})''HN$.	Odour of hemlock. Powerfully poisonous. Dilates the pupil. Causes convulsions, palsy, delirium.
Lobeline.	*Lobelia inflata* (lobelia; Indian tobacco).		Odour of lobelia. Contracts the pupil. Expectorant in small doses, an emetic in larger. In poisonous doses lobeline acts like nicotine.
Methylamine.	*Mercurialis annua* and *M. perennis*. Synthesis.	CH_5N $=(CH_3)H_2N$.	Odour of ammonia.
Nicotine.	*Nicotianum tabacum* (tobacco); Pituri.	$C_{10}H_{14}N_2$.	Odour of tobacco. Extremely poisonous. Powerfully sedative. One drop usually fatal.
Sparteine.	Broom-tops.	$C_{15}H_{26}N$.	Poisonous.
Trimethylamine.	With methylamine in *Mercurialis annua* and *M. perannis*. In ergot, herring pickle, &c. Dry distillation of *vinasse*. Synthesis.	C_3H_9N $=(CH_3)_3N$.	Odour of herrings.

Conine, Conia, or **Conicine,** $C_8H_{15}N$, is a liquid of peculiar and characteristic "mousy" odour, and acrid, bitter, and persistent taste.

Conine boils at 163° C., and burns with a yellow smoky flame. It may be distilled without decomposition in an atmosphere of hydrogen, but undergoes slight decomposition at high temperatures in presence of air. It distils readily with vapour of water or alcohol, and volatilises sensibly at ordinary temperatures.

Conine has a density of ·88, is soluble in about 90 parts of water, and is readily dissolved by alcohol, amyl-alcohol, ether, chloroform, and benzene. The alkaloid is removed from its aqueous or alkaline solutions by agitation with either of the last four solvents, and may be recovered therefrom by shaking the resultant solution with dilute acid.

Conine is colourless when freshly prepared, but becomes yellow and ultimately resinoid by keeping.* It is a strong base, the aqueous solution being powerfully alkaline in reaction, and neutralising acids perfectly. The salts are colourless and odourless, but the peculiar odour of the free base is immediately developed on adding a fixed alkali in excess.

Conine is a powerful poison, one drop being a distinctly poisonous dose, while ten drops may be fatal. In toxicological inquiries the viscera and contents of the stomach should be treated as described under strychnine, the purified extract being agitated with soda and ether instead of ammonia and chloroform. From the ether the alkaloid may be recovered by allowing the solvent to evaporate spontaneously in a cool place, or extracted as a salt by agitating the ether with dilute hydrochloric acid. From the purified salt of conine thus obtained the free base may be again liberated by adding soda, and recognised by the mousy odour of hemlock developed immediately or on warming the liquid.

If a beaker moistened with fuming hydrochloric acid be inverted over a watch-glass containing a drop of free conine, white fumes will be produced, and the alkaloid will be con-

* According to Schorm, pure conine does not undergo any change by exposure to light (*Pharm. Journ.* [3], xii. 863).

verted after a time into a *crystalline* hydrochloride. (Nicotine gives an amorphous hydrochloride.) On adding a large excess of strong hydrochloric acid to conine, a pale red tint is produced, which gradually deepens in colour. Nitric acid acts similarly.

Sulphuric acid produces no immediate change with conine, but the mixture gradually becomes purple-red, and then olive-green.

Mercuric chloride produces with conine a white amorphous precipitate, readily soluble in hydrochloric or acetic acid. (Nicotine gives a crystalline precipitate.) Silver nitrate gives a brown precipitate of argentic oxide with free conine, the colour afterwards changing to black. (Nicotine gives a white precipitate with silver nitrate, turning dark on exposure to light.)

Picric acid does not precipitate conine from solutions containing less than 1 per 1000 of the alkaloid, but nicotine is precipitated from solutions fifty times more dilute.

Conine develops an odour of butyric acid when heated with sulphuric acid and potassium bichromate.

Conine is often associated in hemlock with methyl-conine, $C_8H_{14}(CH_3)N$, and conhydrine, $C_8H_{17}NO$. Both these bases are nearly equally poisonous with conine.

Conine is said to coagulate albumin, thus differing from nicotine.

Nicotine, $C_{10}H_{14}N_2$, exists in the leaves of tobacco, in combination with citric and malic acids, the proportion present varying within very wide limits.

Pure nicotine is a colourless, oily fluid of 1·027 sp. gr. On prolonged exposure to air it becomes yellow, and eventually resinoid. It has a sharp, caustic taste, is intensely poisonous, and has a strong and unpleasant odour, recalling that of tobacco. Nicotine boils at about 240° C., with partial decomposition, but it distils readily with the vapour of water or alcohol, and volatilises to a notable extent at the ordinary temperature.

Nicotine has a lævo-rotatory action on polarised light, absorbs moisture from the air, and dissolves in water in all proportions, forming a liquid of powerfully alkaline reaction,

from which the nicotine is partially separated by addition of a fixed alkali.

Alcohol also dissolves nicotine in all proportions, and on evaporating or distilling the solution the alkaloid is found chiefly in the first fractions. It is extracted from its aqueous alkaline solutions by agitation with ether, chloroform, benzene, amylic alcohol, or petroleum spirit, and may be recovered from the solvent by separating and agitating with dilute acids. If oxalic acid be employed, the resultant solution may be evaporated to dryness and treated with alcohol, which dissolves the nicotine oxalate while leaving any ammonium oxalate undissolved. After again removing the alcohol by evaporation, the nicotine may be liberated from the warm liquid by adding excess of caustic soda, when the characteristic tobacco-like smell of nicotine will be observed, and the alkaloid can be obtained pure by distilling the liquid with water, or agitating it with ether and allowing the separated solvent to evaporate spontaneously in a cool place.

Treated with nitric acid, nicotine yields a thick reddish liquid. Sulphuric acid produces no change in the cold, but a brown colour is developed on heating.

On dissolving nicotine in dilute hydrochloric acid, and adding platinic chloride, nicotine chloroplatinate is thrown down as a sparingly soluble, yellowish, crystalline compound. The precipitate is soluble in hot water, especially in presence of free hydrochloric acid. Addition of alcohol increases the delicacy of the test. Ammonia gives a similar reaction, but conine yields no precipitate with platinic chloride.

On adding mercuric chloride to a solution of nicotine a white *crystalline* precipitate is produced, soluble in dilute hydrochloric or acetic acid. Strychnine produces a similar precipitate, nearly insoluble in acetic acid. Many other alkaloids are precipitated, but the compounds are almost invariably amorphous. This is the case with the precipitate produced by conine, which is almost the only alkaloid which will distil over with nicotine on boiling the solution with a slight excess of caustic soda. Ammonia, however, behaves like nicotine, and must, if necessary, be separated before applying the test. Ammonia is sharply

distinguished from nicotine, conine, and lobeline by adding a solution of iodine in iodide of potassium to the slightly *acidulated* solution of the base. Ammonia produces no change, but with either of the vegetable alkaloids a brown or brownish-red precipitate will result.

From conine, nicotine is distinguished by its odour, by being heavier instead of lighter than water, and by the reactions with hydrochloric acid gas, mercuric chloride, argentic nitrate, platinic chloride, and picric acid (see above, and page 510).

In toxicological investigations nicotine may be isolated in the same manner as conine (see page 509). An alternative method is to digest the suspected matters with water acidulated with acetic acid, and treat the filtered liquid with excess of lead acetate. The liquid is again filtered, the lead removed from the filtrate by passing sulphuretted hydrogen, and the clear solution treated with caustic soda, separated from any precipitate, and distilled; when a fluid having the odour and exhibiting the reactions of nicotine will be obtained. Any supposed nicotine which may be isolated should be tested by placing it on the tongue of a young rabbit or small bird, when tremors, paralysis, and convulsions will rapidly ensue. Nicotine appears to be unchanged by putrefaction, and hence may be detected in the tissues long after death.

Tobacco may be assayed for nicotine by mixing 25 grammes of the powdered leaves with 5 of slaked lime, and exhausting the mixture with hot water in a Xoxheth's tube (see page 127) furnished with an inverted condenser. The resultant solution is agitated with ether, and the ethereal stratum separated and shaken with a known measure of normal sulphuric acid, in quantity sufficient to produce a distinct acid reaction. The acid liquid is separated from the ether, and titrated back with standard alkali. Each 1 c.c. of normal sulphuric acid neutralised by the nicotine corresponds to ·162 gramme of the alkaloid.

The French tobacco-manufacturers introduce the tobacco into an apparatus allied to a Xoxheth's tube, and exhaust the sample with ammoniacal ether. The resultant solution is

allowed to evaporate spontaneously, and the residual crude nicotine is titrated with standard sulphuric acid.

If preferred, the solution of nicotine sulphate may be titrated by Mayer's reagent (see page 465). Each 1 c.c. of the mercuric solution corresponds to ·00405 gramme of nicotine. For the purpose of this titration it is sufficient to macerate the powdered tobacco for twenty-four hours in water acidulated with sulphuric acid, filter, and take for the titration a volume of the filtrate corresponding to ·5 gramme of original sample.

ANILINE AND ITS HOMOLOGUES. $C_nH_{2n-7}.H_2N$.

The term aniline or aniline oil is employed commercially to indicate a variable mixture of organic bases, consisting essentially of homologous bodies of which phenylamine, $C_6H_5.H_2N$, is the first member. All the true homologues of aniline or phenylamine are derived from the replacement of one or more atoms of hydrogen of the phenyl atom, C_6H_5, by a corresponding number of monad hydrocarbon radicals of the methyl series, in the same way that the homologues of benzene (see page 69) are derived by substitution.

Aniline and its homologues are found to a limited extent ready formed in coal-tar, but in practice they are always prepared by the reduction of nitrobenzene, $C_6H_5NO_2$, and its homologues, in the manner described on next page.

The more important general and physical characters of aniline are described below. Its homologues differ from aniline chiefly in their physical properties, their boiling points rising and densities decreasing with each increase in the number of atoms of carbon and hydrogen in the molecule. This is shown by the table on page 519 of the aniline bases constituting the main portion of commercial aniline oils.

Aniline and toluidine are the only members of the series which require consideration in separate sub-sections.

Aniline. Phenylamine. Amido-benzene. $C_6H_7N = C_6H_5NH_2$.—This substance has also, at the hands of various investigators, received the names of crystalline, kyanol, benzidam, and amido-benzol.

Aniline is produced by a variety of reactions, of which the following are the most important:—

1. By the action of nascent hydrogen or an equivalent reducing agent on nitrobenzene, $C_6H_5NO_2$, a body formed by the treatment of benzene, C_6H_6, by nitric acid. This is the only commercial method of producing aniline. The reducing agent now usually employed on a large scale is a mixture of iron filings and hydrochloric acid, which reacts as in the following equation:—$4C_6H_5NO_2 + 9Fe + 4H_2O = 3Fe_3O_4 + 4C_6H_5.NH_2$. Formerly, acetic acid and iron were commonly used. The presence of too large a proportion of iron may cause loss from a reproduction of benzene. Too much acetic acid, on the other hand, resulted in the formation of acetanilide, while deficiency of both iron and acid favours the production of azobenzene (see page 520).

2. By passing ammonia and benzene vapour through tubes heated to redness:—$C_6H_6 + NH_3 = H_2 + C_6H_7N$.

3. By the prolonged reaction of phenol and ammonia when heated together under pressure—

$$C_6H_5.OH + NH_3 = C_6H_5.NH_2 + OH_2.$$

4. By distilling indigo with caustic potash.

5. By the destructive distillation of coal, turf, &c.

Pure aniline is a colourless oily liquid, but most specimens have a sherry-yellow colour, and rapidly darken on exposure to air and light. It has a faintly vinous odour and aromatic burning taste. It refracts light strongly, but has no rotatory action. Aniline, when very pure, freezes at $-8°$ C., but a slight admixture greatly reduces its solidifying point. It boils at 182° C., and distils unchanged. The density of aniline is 1·02 at 16° C.

Aniline is only slightly soluble in water, but it dissolves readily in alcohol, ether, wood-spirit, acetone, chloroform, carbon disulphide, and volatile hydrocarbons.

Aniline is itself a solvent for sulphur, phosphorus, indigotin, camphor, and colophony, but does not dissolve caoutchouc or copal.

Aniline is a powerful poison, producing symptoms similar to those caused by nitrobenzene (see page 91). According to

Wöhler and Frerichs, aniline does not exert any poisonous action on dogs. Runge found the aqueous solution to kill leeches and the parts of plants immersed in it.

Aniline becomes brown by exposure to air and light from formation of a resinous body, the change progressing rapidly at high temperatures.

Aniline, in presence of an excess of acid, imparts a deep yellow colour to pine wood and elder pith.

Under the influence of oxidising agents aniline gives products and reactions which vary considerably according to the oxidiser employed; thus,—

(*a*) When treated with excess of nitric acid and the mixture evaporated at 100° C., aniline is decomposed with formation of a brown substance. With smaller proportions of nitric acid various coloured products are formed.

(*b*) When treated with dilute sulphuric acid and manganese dioxide aniline yields ammonia and quinone, $C_6H_4O_2$, but the greater part of the product undergoes still further change.

(*c*) When a solution of aniline is treated with a dilute solution of bleaching powder, avoiding excess, a fine purple coloration results, which gradually changes to brown. When carefully applied, the reaction is delicate and characteristic.

(*d*) On treating aniline or one of its salts in a solid state with strong sulphuric acid and then adding a minute fragment of manganese dioxide or other oxidising agent (in the manner described under "strychnine"), a fine purple coloration is produced. A better result is obtainable by employing electrolytic oxygen in the manner described on page 489, and in this form the test is the most delicate and satisfactory which can be applied.

Aniline has marked basic properties, a long series of well-defined and crystallisable salts being obtainable from it. It has, however, no action on litmus or turmeric, though it affects a few of the more delicate vegetable colours. It expels ammonia from its salts at a boiling temperature, but is itself displaced in the cold. Aniline decomposes the solutions of many metallic salts with precipitation of the corresponding hydrates.

The following are the more important salts of aniline :—

ANILINE ACETATE, $C_6H_7N,C_2H_4O_2$, does not crystallise. When heated, it loses the elements of water and forms acetanilide (see page 520).

ANILINE HYDROCHLORIDE; or Aniline Hydrochlorate, C_6H_7N,HCl.—This salt crystallises with great facility in colourless needles which are very soluble in water and alcohol. It may be sublimed without decomposition, and yields double salts with platinic and auric chlorides.

ANILINE SULPHATE. $(C_6H_7N)_2,H_2SO_4$.—Obtained by saturating sulphuric acid with aniline. The salt crystallises in brilliant needles, which are readily soluble in water, less readily in alcohol, and insoluble in ether. A solution in boiling alcohol solidifies on cooling. Aniline sulphate may be dried at 100° C. without alteration. No acid sulphate of aniline has hitherto been prepared.

DETECTION AND SEPARATION OF ANILINE.—The colour-reactions of aniline (see last page) are amply sufficient for its recognition, provided that a proper process of separation be previously applied.

Aniline may be liberated from the aqueous solutions of its salts by addition of caustic soda, and may then be extracted by agitating the liquid with ether. On separating the ethereal layer, and agitating it with dilute hydrochloric acid, the aniline passes into the aqueous liquid, which may then be concentrated or evaporated to dryness, and examined by the colour-reactions already described. From strychnine, which is the only substance with which aniline is at all apt to be confounded, it may be separated by adding caustic soda to the concentrated solution, and distilling over the aniline by driving in a current of steam. The strychnine remains in the flask, while the aniline will be found in the distillate if it be acidulated with hydrochloric acid and concentrated to a small bulk at 100° C. The same plan may be employed for detecting aniline in toxicological inquiries, or the process used for isolating strychnine may be used (page 492), but instead of evaporating the ether-chloroform it should be separated and agitated with dilute hydrochloric acid in the manner above described.

Toluidine. Toluylamine. Amido-toluene.

$$C_7H_9N = \left.\begin{matrix}(C_7H_7)\\H_2\end{matrix}\right\}N = \left.\begin{matrix}C_6H_4(CH_3)\\H_2\end{matrix}\right\}N.$$

—Toluidine exists together with aniline in coal-tar. It is produced by processes exactly analogous to those which result in the formation of aniline, and together with that base constitutes the larger portion of the aniline oils of commerce (see page 519). Toluidine has also been obtained in a very interesting manner by heating the hydrochloride of methyl-aniline to 350° C. in a sealed tube, when change of position of the atoms within the molecule takes place, thus :—

$$\left.\begin{matrix}C_6H_5\\CH_3\\H\end{matrix}\right\}N = \left.\begin{matrix}C_6H_4(CH_3)\\H\\H\end{matrix}\right\}N.$$

In its general chemical relationships toluidine presents the closest resemblance to aniline, and yields a series of substitution-products scarcely distinguishable from those of its homologue.

Three distinct isomeric varieties of toluidine are known, closely resembling each other in most characters, but still presenting certain well-marked differences.

ORTHOTOLUIDINE has only been obtained by a very circuitous synthetical process.

PARATOLUIDINE is obtained by the reduction of the nitrotoluene derived from the toluene produced by the dry distillation of tolu-balsam; also by heating hydrochloride of methyl-aniline, as above described.

METATOLUIDINE occurs in the mixture of aniline bases obtained by heating indigo with caustic potash; also by passing over heated soda-lime the vapour of the amidotoluic acid formed by acting with nitric acid on xylene; and in other ways. If a solution of a salt of metatoluidine be treated with solution of chloride of lime, the mixture then shaken with ether, and the ether separated and agitated with acidulated water, a magnificent purple tint, similar to the colour of a solution of permanganate, is developed. Orthotoluidine, when similarly treated, gives the same reaction, but paratoluidine and aniline give no colour.

The following table illustrates the differences between aniline and the three isomeric toluidines:—

	Aniline.	Orthotoluidine.	Paratoluidine.	Metatoluidine.
Sp. gravity	1·025 to 1·028	...	...	·998 to 1·002
Melting point	Liquid; solidifies at −8° C.	Liquid; does not solidify at −13° C.	Solid; melts at +45° C.	Liquid; does not solidify at −20° C.
Boiling point	182°	197°	200°	199°
Reaction with bleaching powder and ether, &c.	No coloration.	Purple coloration	No coloration.	Purple coloration
Properties of the acetyl-derivative—				
Melting point	101 to 112°	65 to 66°	147°	102°
Boiling point	295°	302 to 304°	300 to 307°	295°
1000 parts of water dissolve	...	4·3 parts at 13°	·89 parts at 22°	8·5 parts at 19°

The smell of pure aniline is very different from that of the toluidines. The existence of orthotoluidine in commercial aniline oils has not been definitely proved. Rosenstiehl found commercial toluidine, boiling constantly at 198° C. to contain 62 per cent. of paratoluidine, 36 per cent. of metatoluidine, and 2 per cent. of aniline, but the relative proportions of the isomers is probably liable to great variation (see also page 522). The presence of toluidine in commercial aniline is indicated by the density of the sample, its diminished solubility in dilute alcohol, and by the results of the fractional distillation (see page 522). In addition to these characters, the following tests are sometimes of service:—

Pure aniline affords no rosaniline on treatment with oxidising agents, but if toluidine be present fuchsine is readily formed. The test is best made by mixing 5 c.c. of the sample of aniline with an equal measure of a concentrated solution of arsenic acid, containing about 75 per cent. of As_2O_5 and having a density of 2·04. The mixture, contained in a small flask or long test-tube, is immersed in a paraffin-bath, heated to 180° C. The mixture rapidly changes in colour, and swells considerably. When the action is complete, the contents of the tube acquire a metallic bronze appearance and no longer intumesce. The product is treated with boiling water, when, if the sample contained toluidine, arseniate of rosaniline dissolves and communicates an intense crimson colour to the

liquid. Neither pure aniline nor toluidine alone gives this reaction.

If a sample of commercial aniline be mixed with some solid fuchsine and a few drops of glacial acetic acid, and the whole heated to 180° C., as described above, ammonia is abundantly evolved, and in a short time the mixture becomes intensely blue from the formation of triphenyl-rosaniline. With pure aniline the blue is very pure in shade, but when toluidine or xylidine is treated in a similar manner the product is intensely purple, and a mixture of the bases gives proportionately intermediate shades of colour. If a little of the "melt" be withdrawn from the tube, diluted considerably with alcohol, a few drops of acetic acid added, and then streaked on white filter-paper by means of a glass rod, the purple tint is readily observed, especially if the paper be held up before a gas-flame. (See also page 530).

Commercial Aniline; Aniline Oils.—The composition of the products known in commerce under the name of "aniline" varies through wide limits. The boiling point may range from 180 to 200°, and even up to 210° C., and the chemical composition will depend on that of the benzol from which the aniline is derived (see page 77).

The following table contains a list of the aniline bases the presence of which has been definitely recognised in aniline oils.

Empirical Formula.	Name of Base.	Dissected Formula.	Boiling Point, &c.	Melting Point.
C_6H_7N.	Aniline.	$C_6H_5.NH_2$	182	− 8
C_7H_9N.	Para-toluidine.	$C_6H_4\{(CH_3)\ p.\ NH_2.$	200	+ 45
	Meta-toluidine.	$C_6H_4\{(C_6H_3)\ m.\ NH_2$	199	liquid at − 20.
$C_8H_{11}N$.	Xylidine; various isomers.	$C_6H_3\{CH_3\ CH_3\ NH_2$	212 to 216	
$C_9H_{13}N$.	Cumidine; various isomers.	$C_6H_2\{CH_3\ CH_3\ CH_3\ NH_2$	225 about.	Various; one melts at 60°.

In addition to the bases classified in the foregoing table,

commercial aniline oils contain larger or smaller quantities of various other bodies as bye-products of the manufacture. These substances constitute the essential portion of aniline tailings. The following are the most important and best known of these bodies :—

ACETANILIDE, $C_8H_9NO = C_6H_5.NH.C_2H_3O$, is a product of the dehydration of aniline acetate by heat, and was often a cause of considerable loss in the manufacture of aniline by reducing nitrobenzene with acetic acid and iron. Dilute alkalies have little action on it, but by fusion with caustic potash it is readily converted into potassium acetate and aniline. The physical characters of acetanilide are given on page 518, as also are those of para- and meta- acetoluide, which also occur in some kinds of aniline "tailings."

AZO-BENZENE, $C_{12}H_{10}N_2$, melts at 65° and distils unchanged at 293° C. It is a product of the incomplete reduction of nitrobenzene, and by treatment with nascent hydrogen yields aniline, C_6H_7N, and a body called benzidine $C_{12}H_8:(NH_2)_2$, which melts at 218°, and is partly decomposed by distillation. Azo-toluene resembles azobenzene.

NITRANILINE, $C_6H_6N_2O_2 = C_6H_4(NO_2).NH_2$, is a product of the reduction of dinitrobenzene. It forms long yellow needles, melting at 141°, and volatile without decomposition. It is but slightly soluble in water, but dissolves readily in alcohol and ether. Nitrotoluidine presents similar characters.

PARA-PHENYLENE-DIAMINE. $C_6H_8N_2 = C_6H_4 : (NH_2)_2$.—This is the only one of the three diamido-benzenes which is known to occur in aniline oils. It results from the complete reduction of dinitrobenzene, and is important as the source of phenylene brown. It melts at 63°, and boils at 287°. Homologues of phenylene-diamine are probably present in aniline tailings.

PARANILINE, $C_{12}H_{14}N_2$, is a body present in aniline tailings. It melts at 192° and boils above 330.°

XENYLAMINE, $C_{12}H_9NH_2$, melts at 45° and boils at 322° C.

At present nothing is known as to the influence of these constituents of aniline oils, *i.e.*, other than aniline and its homologues, upon the tinctorial value of the colouring matters

produced. For the most part they are got rid of by fractional distillation of the aniline oil before it is used for fuchsine-making, and especially if intended for production of methyl-aniline violet. Still it is probable that the presence of some of these bodies even in traces may have a notable influence on the reactions which occur, and in the yield and shade of colouring-matter produced.

THE ASSAY OF ANILINE OILS, as commonly practised, is limited to observations of the colour, odour, and specific gravity of the sample, together with a careful fractional distillation, and tests for water, benzol, and nitrobenzol.

A very useful indication of the general composition of the aniline is obtained by submitting the sample to fractional distillation, and noting the proportions of distillate obtained at various temperatures. The method may be employed in two ways. Either the distillate may be measured after each rise of 5 degrees in the boiling point of the sample, or the temperature may be observed when each consecutive 5 or 10 per cent. fraction has passed over. The latter is the plan now commonly adopted, 100 c.c. of the sample being employed, and the arrangement of the apparatus being exactly the same as in the fractional distillation of benzols described on page 83.

The heat is applied cautiously at first, in order to dissipate any water. When this is effected, which will be known by the rapid rise of the thermometer, the heat is so regulated that the distillate shall fall in distinct drops, about sixty per minute. With each increase of 10 c.c. in the volume of the distillate the temperature indicated by the thermometer is observed and recorded, the process being continued till 90 or 95 c.c. have passed over.

A very simple test for aniline oils has been communicated to the author by Mr B. Nickels, in whose hands it has given useful results, and has indicated differences between samples not readily distinguishable by the ordinary fractional distillation process. The test is based on the greater solubility in dilute alcohol of aniline as compared with toluidine and xylidine, and is thus performed :—5 c.c. measure of the sample is taken with a pipette and diluted to 40 c.c. with methylated

spirit. Distilled water is then gradually added from a burette, with constant shaking, till a permanent turbidity is produced, when the volume of water employed is noted. Operating in this way, a sample of very pure aniline required 126 c.c. of water to induce permanent turbidity. The following figures, communicated by Mr Nickels, show the results yielded by three typical specimens of commercial aniline :—

	A. Pure Aniline.	B. Heavy Aniline.	C. Toluidine.
Colour	Pale Amber.	Amber.	Deep Brown.
Sp. Gravity at 15·5° C. . .	1·025	1·011	1·002
Water required for precipitation	106·4 c.c.	73·7 c.c.	63·2 c.c.
10 per cent. distilled over at .	183½° C.	189° C.	195° C.
20 ,, ,, ,, . .	183⅛	189⅝	195¾
30 ,, ,, ,, . .	183¾	190	196
40 ,, ,, ,, . .	184	191	196½
50 ,, ,, ,, . .	184¼	191½	197
60 ,, ,, ,, . .	184	192¼	197½
70 ,, ,, ,, . .	184	193	198
80 ,, ,, ,, . .	184	194⅛	198½
90 ,, ,, ,, . .	184½	197	199¾
95 ,, ,, ,, . .	184¾	201	

The sample marked A was a fair commercial specimen of the quality known as "pure aniline." This quality actually contains some 95 per cent. of real aniline, and it is made from high-class benzols. An article of this high quality is required for the manufacture of aniline blue, triphenylrosaniline (see page 527), any notable admixture of toluidine resulting in a product dyeing with reddish tinge.*

The quality known as "heavy aniline," exemplified by sample B, is employed for the manufacture of aniline red or fuchsine (see page 533). This class of aniline is produced from benzols containing a considerable proportion of toluene, and the aniline oil itself is a mixture of aniline and toluidine, the latter body being present in larger proportion than the former.

* In good samples the boiling points hold closely together, differing by one or two degrees only. Inequalities or jumps in the boiling point, especially at the beginning and end of the distillation, indicate badly-made samples or mixtures.

Sample C is a specimen of commercial "toluidine," and really consists chiefly of that base. This class of oil is principally employed for mixing with low-boiling aniline oils, in order to adjust the proportions of aniline and toluidine to produce the largest yield of fuchsine or rosaniline.

ANILINE TAILINGS is the name applied to the least volatile portion of aniline oils. Tailings contain little or no aniline; some toluidine, xylidine, and cumidine; nitrobenzene and its homologues, and various bye-products, the more important of which are described on page 520.

Reimann distinguishes aniline oils as kuphanilines and baranilines, according as they are light or heavy. The former distil chiefly below, and the latter largely above 200° C. According to Reimann, the following is the usual composition of light and heavy aniline oils:—

	Light Aniline Oil. Kuphaniline.	Heavy Aniline Oil. Baraniline.
	Per Cent.	Per Cent.
Water, odorine, &c.	5	...
Aniline	90	...
Para- and meta-toluidine . . .	5	70
Higher homologues, &c., "tailings" .	...	30
	100	100

According to Reimann, the oil most suitable for making fuchsine is one containing 75 per cent. of kuphaniline and 25 of baraniline, or, in other words, an oil of which 68 per cent. distils below 190° C., and 92 per cent. below 200°.

Water will, if present, be found in the very first portions which come over when the sample is submitted to distillation. Water may exist in quantities varying from a trace to 3 or 4 per cent.; it takes the form of globules which are not miscible with the rest of the distillate, or with petroleum spirit.

On saturating the first 10 c.c. of the distillate with a slight excess of hydrochloric acid, any benzol which may be present will be separated in oily globules which float even on diluting the liquid with water.

On saturating 10 c.c. of the original sample with hydro-

chloric acid, a mere trace of nitrobenzol will be apparent by the milky appearance assumed by the liquid. On diluting the liquid with water, and leaving it at rest for some hours, any considerable quantity of nitrobenzene will collect at the bottom in the form of oily globules, which, after separating the acid liquid, may be identified by the smell and other characters. (See page 89.) Still smaller quantities of nitrobenzene may be recognised if the "tailings" be operated upon, instead of the original sample. Nitrobenzene occurs more frequently in magenta-aniline and toluidine than in the oils of lower boiling point.

The foregoing tests, if carefully applied, afford very accurate indications as to the quality and probable value of ordinary aniline oils.

In the case, however, of the qualities known as recovered anilines, less reliable results are obtained. In the production of triphenyl-rosaniline or aniline-blue, in which a rosaniline salt is heated together with aniline, a certain quantity of aniline distils off, and is, of course, condensed and recovered. The same thing happens when arsenic acid and aniline oil are heated together for the manufacture of magenta or aniline-red, except that in this case the recovered base contains a much larger proportion of true aniline than the original oil. Recovered anilines are deeper in colour and of greater body than unused oils, and they have a strong and somewhat characteristic odour. They are rarely met with outside the colour-works in which they have their origin.

Luxor has proposed to ascertain the relative value of commercial anilines by estimating the respective amounts of red colour yielded by them on oxidation with arsenic acid. The results are somewhat fallacious, as it is difficult to obtain constant conditions on a small scale, and the produce of colouring matter is largely dependent on the relative proportions of aniline and paratoluidine present in the sample. By varying the process so as to produce a colouring matter such as the sample of aniline would be practically used for, better results are obtainable, and, with care and attention to details, the method is capable of yielding valuable indications in experienced hands.

Methods for detecting small quantities of toluidine and xylidine in aniline are described on page 518.

BASIC ANILINE DERIVATIVES.

By the action of chemical reagents on aniline and its homologues, and by the substitution of basylous organic radicals for one or more atoms of hydrogen in the products thus obtained, chemists have effected the synthesis of a large number of basic and other bodies, very many of which are remarkable for their brilliant colours and have received an enormous application in dyeing and printing.* Many of them dye wool and silk without requiring the use of a mordant; and by the employment of suitable means, they can also be fixed on vegetable fibres.

The detailed consideration of the numerous basic derivatives of aniline would require more space than can be devoted to the subject, and hence this article will be limited to a description of the more important members of the group, and to the modes of assaying them. The following outline will sufficiently indicate the chemical constitution and methods of producing the complex bases in question:—

1. When aniline is heated with the salt (hydrochloride) of a primary monamine, one of the atoms of hydrogen is replaced by the organic radical of the amine, as in the following examples:—

(*a*) $C_6H_5.H_2N + C_6H_5.H_2N,HCl = (C_6H_5)_2HN + H_3N,HCl$.
Aniline hydrochloride. Diphenylamine.

(*b*) $C_6H_5.H_2N + CH_3.NO_3 = C_6H_5,CH_3.HN,HNO_3$.
Methyl nitrate. Methylaniline nitrate.

* The basic colouring matters attainable from coal-tar may be divided into two main classes, namely:—

a. Bases in which the nitrogen is wholly amidic. Of these rosaniline and its numerous derivatives, malachite-green, chrysotoluidine, and magdala-red are examples.

b. Bases in which the nitrogen exists partly in replacement of hydrogen, atom for atom. These are the so-called "azo-dyes," and include chrysoïdine, saffranine, biebrich scarlet, bismarck brown, &c.

The bases of these two groups may be distinguished by the action of zinc and acetic acid, as described on page 533.

In addition to the above-mentioned basic colouring matters, there are also obtained from coal-tar various acid nitro-derivatives (*e.g.* picric acid), and numerous non-nitrogenised acid or indifferent bodies, as aurin, alizarin, eosin, &c.

Diphenylamine is a crystalline solid, melting at 45° and distilling without change at 310° C. It is remarkable for its power of yielding deep blue products of high tinctorial power when treated with certain oxidising agents.

Methylaniline is an oily liquid boiling at 192° C., and when pure yields little or no colouring matter by oxidation. In presence of methyltoluidine, C_7H_7,CH_3,HN, the yield is much greater.

2. By treating methylaniline with a methylic ether, dimethyl-aniline, or dimethyl-phenyl-amine, $C_6H_5(CH_3)_2N$ is obtained.

3. If a cold saturated solution of aniline sulphate be mixed with an equal measure of a cold solution of potassium bichromate and allowed to stand, a precipitate is gradually formed, which, when washed with acidulated water, consists of impure sulphate of mauveine. This, when dissolved in boiling water, and the solution precipitated by an alkali, yields the free base mauveine, $C_{27}H_{24}N_4$.

4. On heating a mixture of aniline and toluidine with an oxidising agent of moderate power, such as arsenic acid or mercuric chloride or nitrate, a coalescence of the molecules occurs with simultaneous oxidation of hydrogen, the result being the formation of a base called rosaniline or fuchsine, remarkable for the intense crimson-red colour of the solutions of its salts:—$C_6H_7N + 2C_7H_9N + O_3 = C_{20}H_{19}N_3 + 3H_2O$.

According to Fischer, rosaniline is a carbinol of the formula $C_{20}H_{21}N_3O$, the elements of water being assimilated.

5. From the residues of the manufacture of rosaniline, the less-hydrogenised bases chrysaniline, $C_{20}H_{17}N_3$, and chrysotoluidine, $C_{21}H_{19}N_3$, are obtainable. They are remarkable for forming almost insoluble nitrates, and the latter is extensively employed under the name of "aniline yellow."

6. The residues of the manufacture of rosaniline also contain a base called mauvaniline, $C_{19}H_{17}N_3$, which is a lower homologue of rosaniline, and appears to result from the coalescence and oxidation of *two* atoms of aniline and *one* of toluidine. Mauvaniline salts are soluble in water, and dye fine purple-red tints.

7. By the action of certain reducing-agents on rosaniline, the colourless base leucaniline, $C_{20}H_{21}N_3$, is produced, but by heating rosaniline with hydriodic acid aniline and toluidine are regenerated.

8. By heating a salt of rosaniline with aniline, one, two, or three atoms of hydrogen in the original base may be replaced by the phenyl radical, with the formation of mono-, di-, or lastly, tri-phenylrosaniline, $C_{20}H_{16}(C_6H_5)_3N_3$. These substituted products become more intensely blue with each replacement of the hydrogen atoms, so that the mono-derivative is reddish-violet, diphenyl-rosaniline bluish-violet, while the triphenylated base is a nearly pure blue (*Bleu de Paris*).

9. Triphenylrosaniline is insoluble in water, a property which renders its use in dyeing very difficult. Hence it is commonly converted into a soluble sulphonic acid by heating the base with sulphuric acid. According to the strength of acid and the temperature employed, one, two, three, or four atoms of hydrogen in the base can be replaced by the group HSO_3. Formerly, the higher substitution-products were obtained, but now triphenylrosaniline-monosulphonic acid, $C_{20}H_{16}(C_6H_5)_2(C_6H_4SO_3H)N_3$, is produced. This is insoluble in water, and hence is employed in the form of a sodium salt, which is known as "Nicholson's blue."

10. Just as several of the atoms of rosaniline may be replaced by phenyl or toluyl, so may the radicals ethyl or methyl be substituted for one, two, or three atoms of the hydrogen in rosaniline. The replacement is effected by heating magenta or free rosaniline with alcoholic potash or soda and chloride or iodide of methyl. The "Hofmann's violets" so obtained vary from RRR, the very red, which is chiefly a salt of monomethyl-rosaniline, $C_{20}H_{18}(CH_3)N_3$, to BBB, the bluest shade, consisting of the highest substitution products.* Similar, but not identical, dyes may be obtained by introducing the methyl or ethyl radical into aniline (see paragraph 1) before submitting the latter to the action of

* It is a curious fact that while the substituted rosanilines become bluer with each replacement of the hydrogen atoms by phenyl, toluyl, methyl, or ethyl, the colour of the substituted *mauveines* follows the reverse rule.

oxidising agents. "Methyl-auiline violet" or "Paris violet" is thus produced.

11. By employing an excess of methyl iodide above that necessary to produce the tri-methylated derivative, two molecules of methyl iodide become attached to the triamine base, with formation of dimethyliodide of trimethylrosaniline, $C_{20}H_{16}(CH_3)_3N_3(CH_3I)_2$.* The solution of this body treated with picric acid yields a sparingly soluble picrate of similar constitution, known in commerce as iodine-green. Methyl-green is a similar substance obtained by heating Paris or methyl-aniline violet with methyl chloride or nitrate. It is not used as a picrate, but as a soluble double compound of zinc chloride and methyl green of the formula—

$$C_{20}H_{16}(CH_3)_3N_3(CH_3Cl)_2,H_2O+ZnCl_2.$$

12. By heating chrysotoluidine with methyl iodide, the hydriodide of the substitution-product trimethyl-chrysotoluidine, $C_{21}H_{18}(CH_3)_3N_3$, is obtained in brilliant crimson needles, the solution of which dyes silk and wool orange-red.

13. By heating aniline with chlorate of potassium and hydrochloric acid "aniline black" is produced. The nature of this remarkable colouring matter is still imperfectly understood.†

14. When nitrobenzene is reduced in an alkaline solution it yields azobenzene, $(C_6H_5)_2N_2$, instead of aniline. One of the phenyl atoms of azobenzene is replaceable by salt radicals, with production of a series of well-defined salts. These may also be obtained by the action of nitrous acid or a nitrite on cold aqueous solutions of aniline salts—

$$C_6H_7N,HNO_3+HNO_2=C_6H_5N_2,NO_3+2H_2O.$$

On treating the diazobenzene nitrate thus obtained with aniline two isomeric bodies are obtained. One of these, diazo-amidobenzene, is an indifferent substance, while the other, amid-azobenzene, $C_6H_5N_2,C_6H_4(NH_2)$, is a base. The similar product, diamido-azobenzene, $C_6H_5N_2,C_6H_3(NH_2)_2$, forms a hydrochloride which constitutes the important dye called chrysoïdine. Bismarck-

* Or di-iodide of pentamethyl-rosaniline.

† See, however, a valuable paper by J. Wolff, *Chem. News*, xxxix. 273, xl. 3.

brown, saffranine, and Biebrich scarlet are other azo-dyes of a still more complex constitution. The tropæolines are obtained by the reaction of amidobenzene or a sulphonic acid of a phenol on a salt of diazobenzene.

Analysis of Aniline Dyes.—The analytical examination of coal-tar dyes is of two kinds. In the one case the general nature of the dye is known, and it is merely required to test it for probable adulterants, and to ascertain its dyeing properties. In the other case the very nature of the dye is unknown, and it is desired to identify it.

The *general* methods of examining coal-tar dyes for adulterants are given below. Special tests for particular dyes, and methods for recognising them on tissues are described in the sections commencing on page 533.

ASSAY OF ANILINE DYES.—Coal-tar dyes are frequently adulterated with cheaper colouring matters, and with diluents, such as sugar. Crystallised magenta is often thus sophisticated. On spreading out such a sample on a piece of white paper placed in a strong light, the large fragments may be recognised by their edges being less deeply tinted than the genuine crystals of the dye. When removed and cautiously washed with strong alcohol, the sugar fragments become nearly colourless, and may be identified by the odour of caramel produced on heating. The amount of sugar present may be ascertained with approximate accuracy by treating a known weight of the sample with absolute alcohol saturated with sugar, in a manner somewhat similar to that described on page 320. A better method consists in precipitating the hot aqueous solution by picric acid. The filtered liquid is treated with basic acetate of lead, again filtered, the lead in the filtrate removed by sulphuretted hydrogen or sulphurous acid, and the sugar estimated polarimetrically, or inverted and determined by Fehling's solution (page 284).

Starch is left insoluble on treating the sample with cold water or alcohol, and may readily be recognised in the residue by its microscopical characters and the reaction with iodine (see page 370).

Mineral matters may be detected and estimated by igniting the sample. In some instances they may be perfectly

normal constituents of the dye, as the base of Manchester-yellow and the zinc chloride of malachite-green. Sulphate of sodium, chloride of sodium, &c., are not unfrequently added as actual adulterants; but small proportions may be present as accidental impurities.

Arsenic is a common impurity in fuchsine and other aniline dyes. It may be detected by Marsh's test; or the acidulated solution may be treated with bromine water, excess of ammonia added, the liquid filtered if necessary, and magnesia mixture then added. A gradual precipitate of the ammonio-magnesium arseniate, deposited in streaks in the track of the glass rod used for stirring, will be formed if arsenic be present. The arseniate may be distinguished from the similar phosphate by washing the precipitate or streaks with water, and adding silver nitrate, when the arseniate will be turned brown, or the phosphate yellow.

Bronze powder has been employed for adulterating aniline dyes.

Foreign colouring matters may often be recognised by a judicious treatment with solvents, or more systematically as described on page 532. Magenta may be conveniently examined for violaniline, mauvaniline, or chrysotoluidine by dissolving the sample in the smallest possible quantity of alcohol, diluting the solution with rather more than its own bulk of water, and placing the liquid on a piece of filter paper. If the magenta be impure, concentric circles of different tones of colour will be produced. A similar plan may be employed for the examination of blues and violets.

A valuable mode of ascertaining the actual percentage of colouring matter in a specimen of fuchsine or other aniline dye consists in comparing its oxidising power with that of an equally concentrated solution of some pure dye of the same nature, used under precisely similar conditions. For this purpose two equal quantities of solution of sodium hyposulphite (Schützenberger's "hydrosulphite") should be introduced into small flasks containing a little heavy petroleum oil (Kerosene). A solution of rosaniline of known strength is then run in from a burette, while the flask is immersed in boiling water. The decolorisation is instantaneous, and the process is at an end

when a permanent pink tint is obtained. An equal volume of the hyposulphite is then treated in an exactly similar manner with the solution of the fuchsine to be tested, when the volume run in from the burette, compared with the measure of pure rosaniline solution previously employed, gives the requisite data for calculating the purity of the sample. When it is merely desired to compare the *relative* purity of two dyes, one of them is employed instead of the standard sample.

According to Stamm,* 1 molecule of any aniline dye reduces the same volume of hyposulphite as 2 molecules of ammoniocupric sulphate, and hence the method may be employed for ascertaining the molecular weights of aniline-derivatives. Hofmann's violet and Paris violet give absolutely identical results, and Paris green requires a volume of hyposulphite closely corresponding with the formula $C_{20}H_{17}(CH_3)_5N_3Cl_2+H_2O$.

One of the best methods of assaying aniline dyes, both for purity of tone and amount of colouring matter, is to compare the dyeing powers of the sample with those of a specimen of known purity. As a rule from 1 to 3 grammes of each specimen should be dissolved in a litre of distilled water. Equal weights of unstoved white woollen yarn are suspended in each solution. The liquids are immersed in the same water-bath, which is heated gradually to 80° C. After an interval of one hour from the commencement, the temperature may be increased till the water boils, and after another half hour the swatches of wool may be removed, rinsed with water, and their tints compared. When the wool is not dyed to an extent approaching saturation it is easy to compare the relative depths of the tints. By employing 1 gramme of the standard, and several quantities, varying from 1 to 2 grammes, of the sample to be compared, it is easy to arrive at their relative dyeing powers. As a rule water only is necessary, but some dyes are best tested in a slightly acid solution. In testing soluble-blues, the wool should be heated to boiling in a dilute solution of the dye to which borax has been added, and the swatches then removed, rinsed with water, and the colour developed by immersion in dilute acid.

Another method of operating is to dissolve 0·5 gramme of

* *Bull. Soc. Chem.* [2], xix. 124 ; *Journ. Chem. Soc.* xxvi. 1263.

the colouring matter in warm alcohol, and dilute the solution to 50 c.c., so as to obtain a 1 per cent. solution of the dye. Heat some water nearly to boiling in a porcelain basin, and add 1 gramme of fine white wool, and let it get thoroughly wetted, then remove it, and add 1 or 2 c.c. of the dye solution, after which the wool should be returned and the liquid heated for ten minutes. If the whole of the colour is taken up, the wool is removed, another addition of the colouring matter made, the dyeing repeated, and so on until the wool is saturated. The volume of dye solution decolorised by the wool will be inversely as the purity of the samples.

IDENTIFICATION OF ANILINE DYES.—The identification of a coal-tar dye is often very troublesome, but is much facilitated by a judicious employment of certain general reagents, which will suffice to define the substance as belonging to a certain class. The colour or absorption-spectrum of an aqueous or alcoholic solution of the dye is also a valuable indication, and water and alcohol may often be advantageously employed to effect a separation of mixed colours.

The great point of resemblance in the generality of coal-tar dyes is that they are "substantive colours," or, in other words, will dye silk and wool without a mordant. To ascertain whether the dye is of this character it is usually only necessary to heat a fragment of white wool or a skein of white silk in a solution of the dye; usually a neutral or faintly acid solution is the best, but with Nicholson's blue and a few other dyes the stuff should be heated in the alkaline solution, and then removed and immersed in dilute acid, when the blue colour becomes fixed. Alizarin and purpurin are not substantive colours, and hence cannot be fixed on wool or silk without a mordant.

The following general methods of examination are of service in classifying the coal-tar colours:—

1. Agitate a small quantity of the dye with dilute sulphuric acid and ether. On separating the ether and evaporating it to dryness, a sensible residue will be left if the dye contained picric acid (or a picrate), a nitrocresylate (victoria yellow), a nitronaphthylate (manchester yellow), rosolic acid, aurin,

eosin, &c. The basic dyes are not removed from an acidulated solution by agitation with ether, and hence a complete separation of the above-named substances may be effected by a judicious employment of this method.

2. By heating with acetic acid and zinc-dust most basic aniline-derivatives are reduced with formation of colourless leuco-compounds, from which the colouring matters are reproducible only by the employment of moderately-strong oxidising agents. The azo-compounds similarly yield colourless hydroazo-compounds, but these differ from the leuco-derivatives by degenerating the original colouring matters on mere exposure to air. The yellow dye amid-azobenzene, chrysoïdine, saffranine, biebrich-scarlet, and bismarck-brown are dyes of this character.

3. Spiller has shown * that treatment of the sample with concentrated sulphuric acid affords a valuable means of recognising coal-tar dyes, which are none of them charred by its action, except under very severe conditions. To apply the test it is merely necessary to heat a few grains of the solid substance in a test-tube with concentrated sulphuric acid. Very frequently, useful information can be gained by observing the absorption-spectrum of the coloured liquid obtained. The reactions of the various coal-tar dyes with sulphuric acid are given under the individual dyes.

A careful application of the foregoing principles, together with the results of the special tests for the dyes suspected to be present, will usually lead to an identification of the colouring matter.

Methods for the recognition of colouring matters on tissues will be given in the sequel.

Rosaniline. $C_{20}H_{19}N_3$.—Rosaniline is the artificial organic base which exists as one or other of its salts in the magnificent dyeing materials known as aniline-red, magenta, fuchsine, roseine, azaleine, rubine, and by other more fanciful names. The colouring matter is produced whenever a mixture of aniline and toluidine is heated to about 180° C. with an oxidising agent of moderate power. Hofmann showed that the persence of both aniline and toluidine was

* *Chem. News*, xlii. 191.

necessary for the production of the colour, the reaction being as follows :—$C_6H_7N + 2C_7H_9N + O_3 = C_{20}H_{19}N_3 + 3H_2O$.*

A great number of oxidising agents have been employed and patented, but the one by far most commonly used is arsenic acid, though mercuric nitrate and other bodies are still employed to a less extent. According to the oxidising agent employed, and the subsequent treatment, the product is either the hydrochloride, nitrate, acetate, or other salt.

Free rosaniline can be obtained by precipitating a solution of either of the commercial salts of rosaniline by excess of ammonia. If a boiling solution of the hydrochloride be employed, a reddish crystalline precipitate is produced, and the colourless liquid deposits on cooling a further crop of crystals of the pure base in colourless needles and plates, and having the composition $C_{20}H_{19}N_3,H_2O$.

Rosaniline is a non-volatile, colourless, bitter substance. Heated in boiling water it melts, and dissolves to the extent of 0·3 per cent., a portion being deposited on cooling. In alcohol it dissolves in the proportion of about 1 per cent. In ether and benzene it is said to be insoluble, but is very soluble in aniline.

When heated alone to about 220° C. rosaniline is decomposed. If the free base or one of its salts be heated with water under pressure to about 240° C., carbolic acid and ammonia are produced, with other products; but if the water be acidulated with hydrochloric acid, or if the rosaniline be heated with concentrated hydriodic acid, it is completely resolved into aniline and toluidine.

Rosaniline is a powerful triamine-base, capable of combining with either one, two, or three equivalents of an acid. The mono-acid salts correspond to ordinary magenta, and are stable crystalline bodies, having a beetle-green metallic lustre. They are mostly soluble in water and alcohol, forming crimson-red solutions of a high tinctorial power. The tri-acid salts are brownish-yellow, both in the solid state and in solution, and are readily soluble in water and alcohol. The di-acid salts

* Fischer has recently advanced strong reasons for believing that the true formula for free rosaniline is $C_{20}H_{21}N_3O$, the elements of water being assimilated.

are little known and difficult to prepare. The mono-acid salts are the most interesting and important. Their solutions dye silk and wool a magnificent crimson colour, without the use of a mordant, and by proper means the colouring matter may be fixed on vegetable fibres.

ROSANILINE ACETATE. "Magenta." $C_{20}H_{19}N_3,C_2H_4O_2$.—This salt forms magnificent crystals of a green hue and metallic lustre. It is readily soluble in water and alcohol, forming splendid crimson-red solutions which readily dye animal fibres.

ROSANILINE HYDROCHLORIDE, or Rosaniline Hydrochlorate. $C_{20}H_{19}N_3,HCl$. "Roseine" crystallises in very small, sparingly soluble rhombic plates. It is readily soluble in alcohol, but insoluble in ether. The double salt formed with platinic chloride is uncrystallisable. The tri-acid hydrochloride of rosaniline is reddish-brown, very soluble, and readily decomposed into free acid and the mono-acid salt.

ROSANILINE NITRATE constitutes the commercial products known as "Azaleine" and "Rubine." The picrate forms magnificent reddish needles nearly insoluble in water. The sulphate resembles the hydrochloride.

ROSANILINE TANNATE is important in dyeing owing to its insolubity in water affording a means of fixing the colouring matter on vegetable fibres, and of recovering rosaniline from spent dye-liquors. It dissolves in alcohol, wood-spirit, and acetic acid.

THE ASSAY OF ROSANILINE SALTS is fully described on page 529. The usual adulterants are sugar, starch, gum, and occasionally bronze-powder and other inorganic matters. Arsenic is a common contamination, the proportion occasionally reaching 6 or 7 per cent. According to Springmühl, the arsenic is not absorbed by the wool which the fuchsine may be used to dye.

Besides the salts of rosaniline, various other red dyes are obtainable from coal-tar products, and several are true aniline-derivatives. The following are the chief red colouring matters which are at all apt to be confounded with the salts of rosaniline.

SAFFRANINE, $C_{21}H_{20}N_4,HCl$, forms a brown powder or crystals, soluble in water or alcohol to a fine orange-red solution.

Hydrochloric acid turns the solution rather more blue, and produces a distinct violet-blue coloration if used in large excess or added to the solid substance. (Distinction from rosaniline salts, which turn yellow or brownish.) Addition of caustic soda heightens the colour of the solution, and produces a red precipitate, redissolving on boiling. Stannous chloride occasions a red precipitate, the liquid also remaining red. (Fuchsine gives a violet precipitate). Solid saffranine yields with concentrated sulphuric acid a splendid green solution, changing successively to greenish blue, blue, purple, violet, and finally to red, by the gradual addition of water.

BIEBRICH SCARLET.—By acting on β-naphthol with diazoazobenzene, β-naphthol-tetrazobenzene is formed as a brick-red powder. The sodium mono-, di-, (and tri-) sulphonates of this body crystallise in deep-red needles, and constitute the dye of commerce. Heated with strong sulphuric acid it yields a bluish-green, deep purple, or bluish-black solution. (Distinction from fuchsine and saffranine.)

MAGDALA RED is the hydrochloride of rosanaphthylamine, $C_{30}H_{21}N_3$,HCl. It is a reddish-brown substance, only slightly soluble in cold water, but dissolving in alcohol to a red solution exhibiting a fine fluorescence which is destroyed by treatment with strong nitric acid. Hydrochloric acid occasions no change, and the same is true of stannous chloride and cyanide of potassium. The colour of the solution is somewhat intensified by addition of ammonia. Solid magdala-red dissolves in strong sulphuric acid to a deep blue-black liquid.

RED CORALLIN or PEONIN is prepared by heating aurin with alcoholic ammonia. It occurs as a violet powder or brown needles, soluble in water to a red solution having an alkaline reaction. Addition of hydrochloric acid occasions an orange-yellow precipitate, dissolving on boiling and again separating on cooling. Ammonia and soda slightly deepen the colour of the aqueous solution. The colouring matter is extracted by agitating the acidulated solution with ether. On separating the ether and agitating it with ammonia, the latter is coloured red.

AURIN. ROSOLIC ACID.—Several analogous bodies appear

to have been confounded together under these names. Commercial aurin forms a reddish powder or crystalline fragments having a feeble metallic reflection. It is nearly insoluble in water, but dissolves in alcohol to a yellow or brownish liquid which turns red on addition of an alkali. In presence of soda or ammonia, aurin is readily dissolved by water. The alkaline liquid does not dye, but the colouring matter becomes fixed on neutralisation. If the solution be acidulated and agitated with ether the aurin is extracted, and may be obtained by separation and evaporation of the solvent; or on shaking the ether with ammonia the latter liquid is coloured magenta-red. (Distinction from rosaniline and other basic dyes, these not being extracted from their acidulated solutions by agitation with ether.)

EOSIN is the potassium compound of tetrabromfluorescein, $C_{20}H_6Br_4O_5K_2$. It forms a bronze-coloured crystalline powder having a strong green reflection. It is soluble in water to a red liquid having a fine green fluorescence. The dilute solution is pink with a yellow fluorescence. On addition of hydrochloric acid the fluorescence is destroyed, the liquid becomes yellow, and on heating gives a yellow precipitate. Ammonia and soda occasion no change. Solid eosin dissolves in strong sulphuric acid with yellow colour. The lead-salt of eosin is obtained as a fine red precipitate ("vermillionette") by adding lead acetate to an aqueous solution of eosin. On agitating an acidulated solution of eosin with ether, tetrabromfluorescein is extracted and may be recovered from the ether by agitation with an alkali.

ARTIFICIAL MUREXIDE or ammonium isopurpurate, $NH_4,C_4H_4N_5O_6$, forms small brown needles with green reflections. It is soluble in water to a violet-red liquid, turned red and subsequently decolorised by hydrochloric acid. Soda turns the solution violet-blue, the liquid becoming redder on heating, and being nearly decolorised on boiling. Ammonia gives a yellow colour on boiling, and potassium cyanide a violet-red (fuchsine is decolorised on heating with potassium cyanide). Murexide is now rarely used.

THE RECOGNITION OF RED DYES ON TISSUES may be effected by a careful application of the following principles:—

1. Boiling alcohol removes fuchsine, saffranine, corallin, aurin, eosin, archil, and santal, but does not sensibly affect tissues dyed with alizarin and madder-dyes, cochineal, safflower, brazil-wood, lac-dye, or kermes. Fuchsine, saffranine, and archil colour the alcohol red, and santal wood yellowish-red, but the others form yellowish, brownish, or nearly colourless solutions. On evaporating the alcoholic solution to dryness, and treating the residue with strong sulphuric acid, fuchsine yields a yellow or brown solution, but saffranine produces a fine green colour, changing through various tints by gradual addition of water (see page 536)

2. Ether removes corallin, aurin, and eosin, more or less perfectly. Tissues dyed with turkey-red acquire a dull cherry-red colour, and the ether leaves a brilliant scarlet fat on evaporation. This, when boiled with caustic soda yields a purplish blue solution, from which acids precipitate orange-coloured flakes of alizarin.

3. By boiling with ammonia, corallin, aurin, and eosin are usually dissolved from the tissue, the liquid being coloured red. On removing the tissue, and agitating the liquid with ether and an acid, the colouring matters are extracted from the aqueous liquid, and may be detected in the ethereal solution by separating it and evaporating to dryness, or agitating with ammonia. Safflower colours ammonia reddish-yellow.

4. On moistening the fabric with a dilute solution of caustic soda, the colour due to rosaniline is very gradually destroyed. Saffranine remains unchanged, but safflower is turned yellow, the original tint being restored by an acid. Cochineal is turned purple. Aurin, corallin, and eosin behave as with ammonia.

5. On treating the tissue with dilute hydrochloric acid, rosaniline is usually turned yellow, but the colour is restored by washing with water. Saffranine is unchanged unless the acid be concentrated, when a blue colour is produced, restored to red by washing with water. The sky-red is unchanged. Madder-red and pink become yellow, and after washing with water the dye dissolves in dilute caustic alkali with purplish-blue colour. Tissue dyed with brazil-wood is turned

bright orange by dilute acid, and corallin and cochineal yellow. Ammoniacal cochineal, however, is unchanged by dilute acid.

6. On boiling the tissue in an aqueous solution of aluminium sulphate the liquid will become reddish with most dyes, and in the case of madder-red show a green fluorescence. On adding an equal measure of acid sodium sulphite to the red liquid, the solution will be bleached if the dye be fuchsine, saffranine, corallin, safflower, brazil-wood, or santal-wood, but not bleached if the colour be due to cochineal, lac-dye, archil, or kermes.

7. On igniting the tissue, the red coal-tar dyes usually leave very little ash, as they require no mordant on silk and wool, and on cotton are usually fixed by means of tannin. On the other hand, madder-red and -pink leave an ash containing a notable quantity of alumina, and the ash of tissues dyed with cochineal or brazil-wood, or other dye-woods, will be found to contain either alumina or oxide of tin. Murexide, which is now rarely used, is fixed by compounds of lead or mercury. Of course the latter metal must not be sought for in the ash.

Aniline Violets.—The violet and purple colouring matters derived from aniline are very numerous, but those practically valuable may be arranged in one of the two following classes:—

1. ANILINE VIOLETS PROPER are salts of methylated, ethylated, or phenylated rosanilines or violanilines. The less highly substituted products have the redder shades (see page 527). "Hofmann's violet," "Imperial violet," and "Paris violet," are the three principal varieties. The violets of this class are usually yellowish-green masses or powders, soluble in water to fine violet solutions. Methylaniline violet presents the peculiarity of being soluble in chloroform. Aniline violets are decolorised on boiling with potassium cyanide, a turbid solution being produced. (Distinction from mauve.) With concentrated sulphuric acid they yield yellow or brownish-yellow solutions.

2. MAUVE, ANILINE PURPLE, or PERKINS' PURPLE, is the salt of the base mauveine, $C_{27}H_{24}N_4$, produced by the

action of chromic acid or hypochlorous acid on aniline. Mauve occurs in commerce in sub-crystalline masses, as a paste, and in solution. It is readily soluble in water to a fine reddish-purple liquid. Addition of hydrochloric acid occasions a red precipitate, re-dissolving on boiling but again appearing as the solution cools. Soda precipitates violet-blue mauveine, which is not decolorised by ebullition. Cyanide of potassium gives a clear violet-red solution on boiling (distinction from Hofmann's and similar violets).

THE ASSAY OF ANILINE VIOLETS is described on page 529.

The following method may be employed for the identification of coal-tar violets and similar colouring matters on fabrics.

1. Heat the tissue for a few minutes with ammonium sulphide, and note any change of colour. The tissue is—

Bleached, if the dye was *alkanet*.	Coloured brownish-red. Remove the tissue and moisten it with cold dilute HCl. If coloured 1. Purple; the dye was *mauve*. 2. Yellowish; *Hofmann's violet*	Bleached. Boil a fresh portion of the tissue with strong alcohol. The solution is— 1. Violet; the dye was *soluble violet*. 2. Crimson red; the dye was *magenta*. 3. Colourless, the tissue remaining violet; *indigo-carmine*.	Almost unchanged. Boil a fresh portion of the tissue with alcohol. The liquid is—	
			Pink or brown, changed to violet by ammonia, and to red by acids. The dye is *archil*, with or without *indigo*.*	Almost colourless. Heat fresh portion of tissue with dilute HCl which is coloured 1. Red; *logwood*, with or without *indigo*.* The ash will contain alumina. 2. Yellow or colourless; logwood, or *alizarin* and *madder dyes*.† The ash will contain iron.

2. Moisten the tissue with dilute hydrochloric acid. The colour will be unchanged if the dye be mauve or phenyl-violet. *Mauve* is turned blue by strong hydrochloric acid,

* If indigo be present the tissue, previously exhausted by alcohol, will impart a blue colour to boiling chloroform.

† *Alizarin* and *purpurin* are now coal-tar products, but are neither bases nor derivatives of aniline. They differ from the aniline violets by being nearly insoluble in water; by being precipitated by acids but not by alkalies; by being removed from their acidulated solution by agitation with ether; and by not dyeing silk or wool without the use of a mordant.

but is unaffected by dilute caustic soda, whereas the colour due to *phenyl violet* is quickly discharged by the latter reagent, and restored on acidifying. Dilute hydrochloric acid turns tissues dyed with *Hofmann's or Paris violet* yellow, the original tint being restored by washing with water. Dilute acid turns *logwood violet* yellow or red, the ash containing alumina. On boiling the tissue in dilute solution of bichromate of potassium it is turned brown or black. *Archil* is turned red by dilute acid, becoming blue on adding excess of ammonia.

Aniline Blues.—The blue colouring matters derived from aniline are very numerous, the exact tints varying with the degree of substitution, as already explained (see page 527). They may all be arranged in one of the three following classes:—

1. Salts of mono-, di-, or tri-phenylated rosanilines or allied bases. Triphenyl-rosaniline, $C_{20}H_{16}(C_6H_5)_3N_3$, is by far the most usual. These blues are but slightly soluble in water, more readily in glycerin, and in alcohol they dissolve to intensely blue solutions, which are precipitated on dilution with water and decolorised by bleaching powder or sodium hyposulphite (see page 530). They dissolve in concentrated sulphuric acid to dark-brown solutions.

2. Conjugated sulpho-acids of the bases of the last class, or salts of these sulphonic acids. Thus, "Nicholson's blue" or "soluble blue" is the sodium salt of triphenyl-rosaniline-monosulphonic acid, $C_{20}H_{16}(C_6H_5)_2(C_6H_4.SO_3H)N_3$. This salt occurs in commerce as a greyish-black amorphous mass, which is readily soluble in hot water. Addition of an acid produces a blue precipitate, soluble in excess of soda. If wool be heated in a solution of Nicholson's blue to which borax has been added, the colourless salt is taken up by the fibre and cannot be removed by washing with water, but on immersing the wool in dilute sulphuric acid the blue colour is developed.

3. AZO-DIPHENYL BLUE is the hydrochloride of a base of the formula $C_{18}H_{15}N_3$, produced by reacting with aniline on diazo-amido-benzene, $C_{12}H_{11}N_3$. The blue is insoluble in water but dissolves readily in warm alcohol, and dyes wool

and silk a deep violet-blue. Azo-diphenyl blue may be distinguished from blues of the first two classes by its behaviour on reduction (see page 533).

ADULTERATIONS OF ANILINE BLUES. The substances met with as impurities and adulterants of aniline blues are those named on page 529. Sugar, starch and gum are sometimes used, and Nicholson's blue often contains a considerable percentage of sodium carbonate or sulphate. In testing for the last admixture it must not be forgotten that the pure dye should leave a considerable proportion of sulphate of sodium on ignition, and that it is only the excess over this amount which is objectionable. Arsenic is not an unusual contamination.

Aniline blues may be assayed by the general processes described on page 530.

Aniline blues are frequently employed in admixture with Prussian blue and preparations of indigo. The nature of such mixed dyes when occurring on a fabric may be recognised as follows:—

<table>
<tr><td colspan="3">Boil the fabric in strong alcohol. If the liquid be blue, decant and repeat the treatment till no more colouring matter is extracted.</td></tr>
<tr><td>If the alcohol was coloured blue the dye contained an aniline blue.</td><td colspan="2">Fabric; if colourless was dyed solely by an aniline blue. If blue after repeated treatment with fresh quantities of alcohol, boil the same portion of fabric with an aqueous solution of aluminium sulphate.</td></tr>
<tr><td></td><td>A blue solution indicates the presence of indigo-sulphuric acid, in which case the cold liquid will be coloured yellow or brown on adding ammonium sulphide.</td><td>Fabric if still blue is dyed with indigo or Prussian blue. The former is bleached by dilute bromine water, while the latter is unaffected. Indigo is unchanged by boiling with sodium carbonate, but prussian blue is turned brown and a ferrocyanide is found in the solution.</td></tr>
</table>

Logwood will yield a red solution when the fabric is boiled with dilute hydrochloric acid. On ignition, the tissue will leave an ash containing alumina.

Aniline Greens.—The colouring matters best entitled to the name of aniline greens are those produced by the action of methyl iodide or bromide on methyl-aniline-violet. In this manner there is obtained the dimethyl-iodide of trimethyl-rosaniline, $C_{20}H_{16}(CH_3)_3N_3,2CH_3I$, or it may be prepared by the direct treatment of an alcoholic solution of a salt of rosaniline with a large excess of methylic or ethylic chloride, bromide or iodide.

"IODINE GREEN,"* obtained in the above manner, is soluble in water and alcohol, forming a blue or greenish blue solution. In ether and benzene it is insoluble, and may be precipitated from its alcoholic solution by addition of ether.

The corresponding acetate crystallises in slender needles, and the nitrate in prisms.

The picrate of "verdaniline" is largely met with in commerce, and is obtained by precipitating a cold solution of the crude green by picric acid. It is very slightly soluble in water, and hence requires a large addition of alcohol when used as a dye. In commerce, it is usually met with as a greenish paste.

Owing to the sparingly solubility of the picrate, and the difficulty of obtaining the iodide in a state of purity, the solution of the latter is often treated with a salt of zinc and common salt added, when a precipitate is formed of the composition $C_{20}H_{16}(CH_3)_3N_3,2CH_3Cl,H_2O + ZnCl_2$. This is known as "soluble green." It is readily soluble in water, and dyes a shade less yellow than the picrate.

On treatment with caustic alkalies the solutions of salts of verdaniline yield a colourless base. They are not, like the salts of aniline-violet, precipitated by sodium carbonate. Oxidising and reducing agents all destroy the green. Hydrochloric acid produces a yellowish-green colour, turning bluish or becoming decolorised by heat or excess of acid. Concentrated sulphuric acid yields with aniline-green a bright yellow solution; and on heating, the iodide gives violet vapours of iodine, and the chloride or zinco-chloride fumes of hydrochloric acid. The alcoholic solution of the picrate yields the sparingly soluble potassium picrate on addition of potassium

* Crystallised iodine green is known as "crystallised green."

acetate, and picric acid may be extracted by agitating the dye with dilute sulphuric acid and ether.

Perkin's Green resembles iodine-green, but is precipitated by sodium carbonate. It yields a sparingly soluble picrate, closely resembling that of verdaniline.

Methyl-green or *methyl-aniline green* is similar in constitution and properties to the double chloride of zinc and iodine-green already described as soluble green. Sodium carbonate gives no precipitate in the cold.

ALDEHYDE GREEN is the salt of an organic base supposed to contain $C_{27}H_{27}N_3S_2O$. It is produced by the action of sodium thiosulphate on the product obtained by treating magenta with aldehyde. Aldehyde-green is an unstable green powder, only slightly soluble in water, and is now little used.

ALKALI GREEN is the sulphonate of a body obtained by the oxidation of a diphenylamine-derivative. In its characters and mode of use it resembles "soluble blue." (See page 541).

MALACHITE GREEN is the double zinc salt of a base of the formula $C_{23}H_{24}N_2$, produced by heating dimethylaniline with zinc chloride and benzoyl trichloride. It is a deep green body, soluble in water and alcohol. On adding soda to the solution the free base is separated as a reddish oil, soluble in ether. Malachite green is turned yellow by strong hydrochloric acid, and yields a colourless leuco-compound when treated with zinc and dilute acid. In strong sulphuric acid malachite green dissolves to a bright yellow liquid. Malachite green is less affected by soap, acids, or heat than the other coal-tar greens.

ADULTERATIONS OF ANILINE GREENS.—Iodine-green varies much in price and quality, the commercial value not always following the dyeing properties, which in samples of the same price may vary as much as 50 per cent. Crystallised green is usually purer than the amorphous kinds, but not always. Aniline greens vary much in tint, yellow shades being due to picric acid or other yellow dye, and green ones to soluble aniline blue. The latter, when present in small proportion, is best recognised by yellow light. Large amounts may be detected by treating the dye with picric acid and glycerin, when the verdaniline remains insoluble, and any blue admixture may be recognised by the colour and characters of the

filtered liquid. If the dye be the picrate of verdaniline mixed with soluble blue, mere treatment with water is sufficient to detect the admixture. Free picric acid may be detected by agitating with water and ether, and a picrate in the manner already described.

Some greens contain accidental admixtures of sodium acetate and black insoluble bodies, besides some aniline violet.

Intentional additions of sugar are occasionally made, and compounds of magnesium, lead, and chromium have been met with. Arsenic is found in some samples. Zinc chloride is a normal constituent of soluble and malachite greens.

Comparative tinctorial and dyeing tests of aniline greens can be made in the manner described on page 531.

Mixed Greens are made by blending yellow and blue colouring matters. Such products, or the tissues dyed with them, may be examined as follows:—Boil with strong alcohol. Aniline greens are completely dissolved, as also are picrates. Any blue residue will consist of *indigo* or *prussian blue*, which may be distinguished by adding dilute bromine water. The indigo will be bleached, but the prussian blue remains unaffected. On the other hand, prussian blue is turned brown by soda, while indigo remains unchanged. If the alcohol acquire a green colour, aniline blue is present, in which case the original substance or fabric should be boiled with dilute hydrochloric acid, when a blue residue will be left, and the solution can be examined for picric acid and other yellows.

Aldehyde green and some other aniline greens are decolorised by heating with potassium cyanide solution, but the picrate of verdaniline is turned brown.

Aniline Yellows.—A great number of yellow or orange colours are obtainable from coal-tar, but only a few of them are of basic character or much importance.

CHRYSANILINE YELLOW OR ORANGE is a salt of chrysotoluidine, $C_{21}H_{21}N_3$. It forms a reddish or orange powder, soluble in water to an orange solution. Hydrochloric acid somewhat deepens the colour of the liquid, but occasions no precipitate. Caustic soda gives a yellow precipitate, which melts on boiling, the liquid being coloured pale yellow. With strong

sulphuric acid the solid dye gives a yellow or brown solution which is strongly fluorescent. Cyanide of potassium gives a yellow precipitate, and the liquid acquires a yellow colour on boiling. A tolerably concentrated solution of chrysotoluidine (or of chrysaniline) gives a yellow crystalline precipitate on adding a solution of sodium nitrate, owing to the formation of a very sparingly soluble nitrate of chrysotoluidine. This reaction distinguishes the dye from picric acid and allied bodies, these forming soluble sodium salts, though their potassium compounds are nearly insoluble. They are also distinguished by the red or brownish colour developed on boiling with potassium cyanide, and by being extracted from their acidulated solutions by agitation with ether, whereas chrysotoluidine is only dissolved by ether or benzene in presence of an alkali.

PHOSPHINE is a salt of chrysaniline, and in its characters resembles the last colouring matter.

AMID-AZOBENZENE, $C_{12}H_{11}N_2 = C_6H_5.N_2.C_6H_4(NH_2)$, has been employed to a considerable extent under the vague name of "aniline yellow." It is volatile, and may be removed from the tissue dyed with it by cautious application of heat. Hence it is now nearly discarded.

CHRYSOÏDINE, or diamido-azobenzene, $C_{12}H_{12}N_4 = C_6H_5.N_2.C_6H_3(NH_2)_2$, forms a hydrochloride which crystallises in fine yellow needles, only slightly soluble even in boiling water, but readily soluble in alcohol, ether, chloroform, benzene, and aniline. On adding excess of hydrochloric acid to a solution of chrysoïdine a fine red colour is produced. Solid chrysoïdine yields with concentrated sulphuric acid a deep orange solution, which turns almost scarlet on heating. (Distinction from chrysaniline yellow.) By treatment with zinc-dust and acetic acid both chrysoidine and the last base are converted into hydrazo-compounds, the solutions of which have a light yellow colour, and greedily absorb oxygen with reproduction of the original bases.

YELLOW CORALLIN is a variety of rosolic acid which dyes a more yellow tint than red corallin. Its characters are practically identical with those of aurin (see page 536). It is not an aniline-derivative.

PICRIC ACID, VICTORIA YELLOW, and MANCHESTER or NAPH-

THALENE YELLOW were described in Vol. I. (p. 327, *et seq.*). They are not aniline-derivatives, and have well-marked acid characters. They may be removed from their acidulated solutions by agitation with ether or benzene, but the metallic salts are insoluble in these solvents and in alcohol.

ADULTERATIONS OF ANILINE YELLOWS. The colours which are sold commercially as aniline yellow and aniline orange are mostly instances of yellow and red colouring matters. Naphthalene yellow and picric acid are frequently sold as aniline yellow, and are employed for sophisticating the basic dyes. Picric acid may be readily recognised by heating the substance with solution of potassium cyanide, when a dark red coloration will be produced. The presence of picric acid, whether in the free state or as a picrate, is objectionable, as it diminishes the brilliancy of the yellow colour, and acts prejudicially in other ways. Picric acid may be estimated by precipitating an alcoholic solution of the dye with an alcoholic solution of potassium acetate. The precipitate of potassium picrate may be dried at 100° C. and weighed. Chrysaniline often contains arsenic, the proportion sometimes reaching upwards of 5 per cent.

Examination under the microscope, and treatment with cold water will be found of service in the detection of adulterations of aniline yellows.

Yellow dyes on fabrics may be recognised by the application of the following tests:—

1. Heat the tissue in a dilute neutral solution of ferric chloride. Annatto, turmeric, and the coal-tar yellows will be little altered, but if the dye be madder-yellow, fustic, quercitron, flavin, weld, &c., the tissue will be coloured more or less yellowish-green, olive-green, brown, or nearly black.

2. Boil the tissue with alcohol, and test portions of the solution in the following manner:—

(*a*) Add excess of hydrochloric acid. A red colour indicates *chrysoïdine.*

(*b*) Add an alcoholic solution of potassium acetate and stir well. A pale-yellow crystalline precipitate is produced by a coal-tar acid. Heat the tissue with ammonio-sulphate of copper, and then wash with water. The colour of *naphthalene*

yellow is changed to olive-green, and that of *picric acid* to bluish-green. If the alcohol be evaporated off and the residue boiled with solution of potassium cyanide, picric acid gives a blood-red or purple-red coloration, but with naphthalene yellow the coloration is less distinct.

(*c*) Add solution of soda. *Aurin* yields a crimson-red solution, and the vegetable yellows are mostly coloured reddish-brown.

(*d*) Add sodium nitrate and stir well. *Chrysaniline* gives a yellow crystalline precipitate.

(*e*) Evaporate the alcoholic solution to dryness, and treat the residue cautiously with concentrated sulphuric acid. *Annatto* gives a bluish-green colour; *chrysoïdine* a deep orange, turning almost scarlet on heating; *naphthalene yellow*, a yellow solution, becoming colourless on heating; *chrysaniline*, a yellow or brown strongly fluorescent solution; and *aurin*, a yellow-brown colour, without fluorescence.

3. Moisten the tissue with dilute soda. *Aurin* colours crimson-red, and most of the *vegetable yellows* (except annatto) reddish-brown. *Turmeric* is distinguished from all other yellows by evaporating the tissue to dryness with a solution of borax, acidulated with hydrochloric acid. A fine brownish-red colour is obtained, which turns blue-violet on moistening the tissue with soda.

4. Boil the tissue with aluminium sulphate solution, and then add an equal measure of water. *Madder yellow* gives a red liquid with green fluoresence; *fustic*, a yellow solution, with bluish-green fluoresence; while the other vegetable yellows (except turmeric) give yellow non-fluorescent liquids.

5. Ignite the tissue, and examine the ash for chromium, lead, iron, tin, and aluminium. *Chrome yellow* will leave an ash containing the first two metals. Most of the vegetable yellows are mordanted with alumina. *Madder yellow* contains tin as a mordant. Turmeric, annatto, and the coal-tar yellows are usually employed without mordants, at least on silk and wool.

Aniline Browns and Black.—These colouring matters do not commonly require assay, and hence need not be described in full.

PHENYLENE BROWN, called also Manchester Brown and Bismarck Brown, is the hydrochloride of triamido-azobenzene, $C_6H_5.N_2.C_3H_2(NH_2)_3$. It is obtained by reacting with sodium nitrite on the hydrochloride of diamido-benzene (phenylene-diamine), $C_6H_4(NH_2)_2$, produced by the reduction of meta-dinitrobenzene. Bismarck-brown is one of the fastest and most stable of the aniline colours.

ANILINE BLACK differs remarkably from all other aniline colours in that it is wholly insoluble in water, alcohol, soap-lye, or acid or alkaline solutions. Hence it has to be formed on the tissue itself. It gives a deep velvety shade on cotton, changed to dull green by the action of acids, and restored to its original colour by neutralisation. Dilute solution of potassium bichromate intensify the colour. Hypochlorites slowly destroy the colour, but if the action be arrested when the colouring matter has a red shade, and the tissue is then washed and exposed to the air, it slowly becomes black again.

The nature of aniline black is very imperfectly understood, but it seems certain that there are two distinct kinds, of which one is apt to turn greenish by the action of sulphur dioxide.

The presence of copper was formerly considered essential to the production of aniline black, but vanadium, uranium, and iron can be substituted for copper with more or less success.

Aniline black on tissues is readily recognised by its resistance to reagents. *Logwood black* leaves an ash containing iron or chromium, as also do *madder and tannin blacks.* Logwood, madder, and tannin blacks are turned red by dilute acid, and are readily bleached by bromine water or hypochlorites.

ERRATA IN VOLUME II.

Page 3, line 5 of foot-note, *for* "page 9" *read* "page 105."

Page 86, line 15, *for* "90·5°" *read* "99·5°."

Page 119, in formula showing decomposition of fats by steam, *for* "O_2" *read* "O_3."

Page 194, line 10, *for* "·946" *read* "·9146."

Page 220, line 7 from bottom, *for* "dissolved" *read* "dissolve."

Page 233, line 19, *after the word* "filter" *insert the words* "or piece of fine cambric."

Page 234, line 23, *after the words* "piece of cambric" *insert the words* "or filter."

Page 255, in column headed "Total," *for* "99·62" *read* "99·82"; and *for* "100·12" *read* "100·21." In column headed "Sodium Chloride and Sulphate," *for* "·50" *read* "2·50."

Page 412, last column, *for* "page 316" *read* "page 416."

Page 499, line 13, *for* "dilated" *read* "contracted."

Page 501, line 8, *after the word* "gums" *read* "or placed on the tongue.

ADDITIONAL ERRATA IN VOLUME I.

Page 21, line 12, *for* "hydrogen" *read* "nitrogen."

Page 36, line 9, *for* "110·2" *read* "130·2."

Page 64, line 2, *for* "wine or unfermented liquids" *read* "wine and other fermented liquids."

Page 74, line 11, *for* "each" *read* "the second."

Page 109, line 7, *for* "gin" *read* "whisky."

Page 152, line 9 from bottom, *for* "nitroci" *read* "nitrosi."

Page 204, line 20, *for* "acetic" *read* "oxalic."

Page 254, line 7, *for* "1½ to 6 per cent." *read* "2 to 9 per cent."

Page 255, line 13, *for* "·104" *read* "·094;" and *for* "·750" *read* "·075."

Page 293, lines 2 and 7, *for* "25 c.c." *read* "20 c.c."; and line 8, *for* "4" *read* "·5."

Page 324, formula of picric acid should be:—$C_6H_3\left.\begin{matrix}(NO_2)_3\\H\end{matrix}\right\}O$.

Page 326, lines 15 and 26, *after* "phenyl-sulphuric" *insert the word* "acid."

INDEX.

NEILL AND COMPANY, EDINBURGH,
GOVERNMENT BOOK AND LAW PRINTERS FOR SCOTLAND.

Catalogue D.]

LONDON, NEW BURLINGTON STREET,

FEBRUARY, 1882.

A LIST

OF

J. & A. CHURCHILL'S

WORKS

ON

CHEMISTRY, MATERIA MEDICA,

PHARMACY, BOTANY,

THE MICROSCOPE,

AND

OTHER BRANCHES OF SCIENCE

INDEX

**** *The Works advertised in this Catalogue may be obtained through any Bookseller in the United Kingdom, or direct from the Publishers, on Remittance of their cost.*