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ELEMENTS OF CHEMISTRY:

THEORETICAL AND PRACTICAL.



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PREFACE TO THE FOURTH EDITION.

THE principal objects which the author proposed to himself in the present Treatise will probably be best explained by the following extracts from the Preface to the first edition :—

‘ In the work of which the present volume forms the third and concluding portion, it has been the aim of the author to give the leading facts and doctrines of chemical science, in as concise a form as possible, without sacrificing clearness and accuracy to brevity. But in order that the reader may be enabled to refer to original sources when further information is needed, references have been given to the papers from which the more important details have been obtained, particularly to the recent memoirs on organic chemistry.

‘ It will be observed that in the arrangement of the present volume, free use has been made of the system of classification in homologous series, which was employed with such admirable results by the late highly gifted M. Gerhardt.

‘ The general method of classification adopted by that eminent chemist in his *Traité de Chimie Organique*, excellent as it is in many respects for the advanced cultivator of the science, is not, however, well adapted to the plan of a didactic work like the present; and it was judged preferable, after a preliminary sketch of the methods of investigation and classification employed, to commence the detailed description of the products of organic chemistry with that of a few of the best known and most familiar compounds derived from the vegetable kingdom, although their composition is less simple than that of many other organic substances: for this reason sugar, starch, and vegetable fibre were made the starting point; and from them the transition was easy

to the processes of fermentation, and the comprehensive group of alcohols, and their derivatives, the ethers and allied compounds.

‘In treating these various classes of compounds, the author preferred to examine successively the different members of each homologous group, before passing to the consideration of the derivatives from the typical or leading member of each group. For instance, in the case of ordinary alcohol, instead of describing ether, aldehyd, and acetic acid in succession,—the different varieties of alcohol, such as wood spirit, fusel oil, &c., are first described; then the series of the vinic acids, and then that of the ethers. By thus presenting the different members of the same homologous series in succession to the student (see p. 38) he is enabled to trace more readily their similarities and their differences, and to note the general method adopted in their preparation, than if his attention were distracted by passing to other bodies of totally different character and properties. This plan conduces to brevity as well as to clearness, and facilitates the description of the various series from a more general point of view, than would be readily practicable, if the arrangement followed by most writers since the appearance of Liebig’s classical work on organic chemistry were adopted.’

The most important changes in the present edition consist in the introduction of the metrical system of weights and measures concurrently with our own, in the statement of the temperatures on the Centigrade scale as well as on that of Fahrenheit, and in the uniform adoption of the new form of notation, together with the system of nomenclature originally introduced by Berzelius.

The substitution of such terms as potassic nitrate for nitrate of potash, sodic sulphate for sulphate of soda, and zincic oxide for oxide of zinc, may, like most changes, appear at first to some extent awkward and pedantic. Yet the system possesses advantages in brevity and precision which will, there can be little doubt, lead to its gradual substitution for the nomenclature till lately in general use.

The change in notation is now practically acquiesced in; for in none of the recent investigations made in this country, and in

very few of those on the Continent, is the old method made use of.

It is remarkable that the ratios expressive of atomic weights in the symbols employed by Berzelius, at their first introduction by him nearly fifty years ago, should be, with few exceptions, those to which Cannizzaro and Wurtz with other writers of the present day have returned.

In order to facilitate the use of this new notation, a table of the symbols and atomic weights adopted in the present volume has been prefixed.

To the names of the friends who have aided him in revising the work for the press the author must add those of Dr. E. A. Cook and Mr. J. T. Bottomley, to whose accuracy and patient care he is much indebted.

KING'S COLLEGE, LONDON.

July, 1869.



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*The reader is requested to make the following corrections in
Part III.*

- Page 23, 17 lines from bottom, for equal read two, and insert one of before nitrogen.
 ,, 76, 8 lines from top, for with read while.
 ,, 175, second equation, for H_2PHO_3 read H_2PHO_3 .
 ,, 231, last line of table, for 517 read 617.
 ,, 282, 20 lines from top, transpose in heading glycol, acetic acid.
 ,, 283, last line but one of table, for 48.5 read 84.5.
 ,, ,, last line of table, for 6.845 read 6.485.
 ,, 324, 13 lines from top, for $CH_{10}Cl_2O_3$ read $C_5H_{10}Cl_2O_3$.
 ,, 346, 8 lines from top, for $C_nH_{n-6}O_2$ read $C_nH_{n-8}O_2$.
 ,, 348, 16 lines from bottom, for 5 H_2SO_4 read 5 H_2SO_4 .
 ,, 368, 7 lines from top, for $HC(C_3H_7)O_2$ read $HC(C_3H_7)O_2$.
 ,, 379, 19 lines from top, for $CaNa_3 2 SO_4$ read $CaNa_2 2 SO_4$.
 ,, 405, 19 lines from top, for less read more.
 ,, ,, 9 lines from bottom, for $C_4H_6O_2$ read $C_4H_6O_4$.
 ,, 410, last line, for HC_6H_9O read $HC_6H_9O_6$.
 ,, 446, 21 lines from bottom, for $C_{12}H_8N_2$ read $C_6H_8N_2$.
 ,, 487, 2 lines from bottom, for azodiphenyldiamine read diazophenyldiamine.
 ,, ,, 5 lines from bottom, for azophenyldiamine read azodiphenyldiamine.
 ,, ,, last line, for 2 H_3N read 3 H_2O .
 ,, 506, dimethyltoluylia, for $C_{91}H_3N$ read $C_9H_{13}N$.
 ,, 516, add another H at bottom of long formula in margin.
 ,, 517, 16 lines from bottom, for $(C_2H_4)''(C_2H_5)''_2N_2$ read $(C_2H_4)''_2(C_2H_5)''_2N_2$.
 ,, 571, the last equation should be $2 C_{10}H_{16}O + KHO = KC_{10}H_{15}O_2 + C_{10}H_{18}O$.
 ,, 584, 15 lines from top, for $(C_7H_5)_2O$ read $(C_7H_5O)_2$.
 ,, 596, 16 and 18 lines from bottom, for C_8H_9O read $C_8H_{10}O$.
 ,, 614, 23 and 24 lines from top, for C_7H_3 read C_7H_4 four times.
 ,, 665, 9 lines from top, twice for orcein read orcin.
 ,, 669, 19 lines from bottom, for $C_9H_{10}O_2$ read $C_8H_{10}O_2$.
 ,, 704, 11 lines from bottom, for 2 H_2O read H_2O .
 ,, 707, 30 lines from bottom, for $C_{10}H_5(H_2N)N_2$ read $C_{20}H_{15}N_3$.
 ,, 715, 12 lines from top, for 0.8938 read 0.8398.
 ,, 776, heading of table, for $\left. \begin{array}{l} \text{Diureides with loss of} \\ H_2O \mid 2 H_2O \end{array} \right\}$ read $\left\{ \begin{array}{l} \text{Diureides with loss of} \\ 3 H_2O \mid 4 H_2O \end{array} \right.$
 ,, ,, in table Glycoluric acid, for $CH_6N_2O_3$ read $C_8H_6N_2O_3$.
 ,, 777, 1 line from top, for 1 atom read 3 atoms.
 ,, ,, 3 lines from top, for 2 atoms of water read 4 atoms.
 ,, 818, 6 lines from top, after process add varies.
 ,, 827, 18 lines from top, for $C_{12}H_{28}N_2O_{11}$ read $C_{17}H_{23}N_2O_{11}$.
 ,, 839, 8 lines from top, after air-pump add or.
 ,, 927, opposite Indium, for 636 read 63.6, and for 10.2 read 10.88.
 ,, 940, 4 lines from bottom, for $C_2H_5, C_{47}HO_2$ read $C_2H_6, C_4H_7O_2$.

Additional corrections in Part II., 4th edition.

- Page 332, 13 lines from top, for three read two.
 ,, 533, table in heading, for °C, read 0° C.
 ,, 540, 10 lines from bottom, for $CoCl_2, 3 [(H_4N)_2O]$ read $CoCl_2, 6 H_3N, H_2O$.
 ,, 541, 19 lines from bottom, for 7 H_2O read 5 H_2O .
 ,, 607, 3 lines from top, for $NaHCrO_4, H_2O$ read 2 $(NaHCrO_4), H_2O$.
 ,, 610, last line, for 2 $K_2C_2O_4$ read 2 $K_2C_2O_4$.
 ,, 643, 6 lines from top, for 186.8 read 231.5.
 ,, 701, 21 lines from top, for Cu_2P_2 read Cu_3P_2 .
 ,, 703, 13 lines from top, for (H_4N) read $(H_4N)_2$.
 ,, 707, 2 lines from bottom, for to oxidize read to be oxidized by.
 ,, 713, 7 lines from bottom, for conduct read condensc.
 ,, 743, 16 lines from top $\left\{ \begin{array}{l} \text{sal alembroth, for } 6 H_4NCl \\ \text{read } 2 H_4NCl. \end{array} \right.$
 ,, 745, 6 lines from bottom $\left\{ \begin{array}{l} \text{sal alembroth, for } 6 H_4NCl \\ \text{read } 2 H_4NCl. \end{array} \right.$
 ,, 799, 5 lines from top, for 2 H_2O read H_2O .
 ,, ,, 11 lines from top, add H_2O at end of line.
 ,, 819, 6 lines from bottom, for 20° read 30°.
 ,, 831, 7 lines from bottom, for 1865, 1866, read 1866, 1867.
 ,, 868, 22 lines from top, for cases read causes.

*Symbols and Atomic Weights of the Elements
as used in this Volume.*

| Names of Elements. | Symbol. | At. wt. | Names of Elements. | Symbol. | At. wt. |
|---------------------|---------|---------|----------------------|---------|---------|
| Aluminum . . . | Al | 27·5 | Molybdenum . . . | Mo | 96 |
| Antimony . . . | Sb | 122 | Nickel | Ni | 59 |
| Arsenicum . . . | As | 75 | Niobium | Nb | 94 |
| Barium | Ba | 137 | Nitrogen | N | 14 |
| Bismuth | Bi | 210 | Osmium | Os | 199 |
| Boron | B | 10·9 | Oxygen | O | 16 |
| Bromine | Br | 80 | Palladium | Pd | 106·5 |
| Cadmium | Cd | 112 | Phosphorus | P | 31 |
| Cæsium | Cs | 133 | Platinum | Pt | 197·1 |
| Calcium | Ca | 40 | Potassium | K | 39·1 |
| Carbon | C | 12 | Rhodium | Rh | 104·3 |
| Cerium | Ce | 92 | Rubidium | Rb | 85·3 |
| Chlorine | Cl | 35·5 | Ruthenium | Ru | 104·2 |
| Chromium | Cr | 52·5 | Selenium | Se | 79·5 |
| Cobalt | Co | 59·0 | Silicon | Si | 28 |
| Copper | Cu | 63·5 | Silver | Ag | 108 |
| Didymium | Di | 96 | Sodium | Na | 23 |
| Erbium | E | 112·6 | Strontium | Sr | 87·5 |
| Fluorine | F | 19·0 | Sulphur | S | 32 |
| Glucinum | G | 9·5 | Tantalum | Ta | 182 |
| Gold | Au | 196·6 | Tellurium | Te | 129 |
| Hydrogen | H | 1 | Thallium | Tl | 204 |
| Indium | In | 75·6 | Thorium | Th | 238 |
| Iodine | I | 127 | Tin | Sn | 118 |
| Iridium | Ir | 197·1 | Titanium | Ti | 50 |
| Iron | Fe | 56 | Tungsten | W | 184 |
| Lanthanum | La | 92 | Uranium | U | 120 |
| Lead | Pb | 207 | Vanadium | V | 51·3 |
| Lithium | L | 7 | Yttrium | Y | 61·7 |
| Magnesium | Mg | 24·3 | Zinc | Zn | 65 |
| Manganese | Mn | 55 | Zirconium | Zr | 89·5 |
| Mercury | Hg | 200 | | | |

PART III.

ORGANIC CHEMISTRY.

CHAPTER I.

INTRODUCTORY.

§ I. *Analysis of Organic Compounds*;—§ II. *Principles of Classification*;—§ III. *Metamorphoses of Organic Compounds*.

(1035) ORGANIC CHEMISTRY, in its primary signification, is that division of the science which treats of the chemistry of organized beings, and of the products of their chemical actions upon matter in its various forms.

It is important to draw a clear distinction between *organic compounds* and *organized bodies*.

Organic compounds, like those derived from the mineral kingdom, possess a definite composition, and in many cases exhibit a perfectly definite crystalline structure. Bodies, such as sugar, oxalic acid, urea, taurin, and quinia, belong to this class; such substances are often spoken of as the *proximate principles* of animals and vegetables: and many of them may be obtained from inorganic bodies by synthesis.

On the other hand, *organized bodies*, such as muscular tissue, nervous structure, cellulin, and ligneous fibre, never exhibit any tendency to a crystalline arrangement, but show a rounded, vesicular, or fibrous configuration; and are so connected with each other as to form parts of a system, each of which is incomplete if severed from the remainder. Bodies such as these cannot be prepared synthetically: they are the result of the action of living bodies upon inanimate matter; every living body having the power of assimilating fresh matter from without, and of arranging its particles in the special form which characterizes the class to which the individual organism belongs.

The study of the chemical changes that occur during these transformations constitutes *physiological chemistry*, the most diffi-

cult branch of the science. Its difficulty depends, however, not simply upon the obscurity which enshrouds the nature of life itself; for the essential nature of every description of force, and the mysterious tie which exists between matter and force, has baffled the penetration of the profoundest philosophers, and belongs to an order of truths to which the human intellect probably may not be permitted in this sphere of its existence to attain.

A part of the difficulty attendant on the study of the chemical changes that occur in the living animal or plant depends upon the extreme delicacy of the arrangements by which these metamorphoses are effected; and upon the complicated nature of those arrangements, which are liable to injury from a multiplicity of causes that have eluded scrutiny. Important changes may in consequence often be effected in the organism itself without being appreciable to human sense, save in their results, although they may even proceed so far as to occasion death. We can at once appreciate the effect produced by the tying of a large artery or the division of a nerve; but when an animal is poisoned by a fraction of a grain of aconitina or by a few drops of hydrocyanic acid, there is nothing to indicate to the anatomist, to the microscopic observer, or to the chemist, the mode in which these bodies operate in suddenly cutting short the life of the animal. The organization still appears to be perfect, yet the once living laboratory no longer continues to perform its wonted operations, and the inanimate mass speedily falls under the dominion of ordinary chemical laws. In the living body, ordinary chemical actions are modified, and new compounds are produced, many of which, when released from the influences under which they originated, quickly undergo fresh changes; and these are manifested by the occurrence of putrefaction and decay, to which both animal and vegetable tissues are liable when they no longer form parts of the living frame. A perpetual tendency to the renewal of their constituents is one of the distinguishing and essential characteristics of living bodies. When the plant or the animal is performing its functions in a healthy manner, a series of changes succeed each other in a defined and regular order; but if this sequence be modified, even in a slight degree, disease generally ensues, and when the alteration reaches a certain amount or degree, death is the speedy and inevitable consequence.

In the present work the attention of the reader will be only incidentally directed to the physiological portion of the subject, the main object being to exhibit the mutual relations which the different chemical compounds bear to each other, and to trace

the laws of their formation. Even with these limitations the subject of organic chemistry is one of great extent and complexity.

(1036) *Organic products* are composed of a small number of elements: yet such products present properties as much opposed to each other as it is possible to imagine: some of these products constitute the daily food of man, others act as direct and violent poisons: yet these very different bodies rarely consist of more than four elements, viz., carbon, hydrogen, nitrogen, and oxygen; a few contain minute proportions of sulphur and phosphorus, with certain earthy and saline matters.

Carbon is the characteristic element of organic bodies, so that commonly the most convenient means of ascertaining if an unknown body be of organic origin, is to heat a fragment of it in a narrow test tube; the carbon is thus separated, and the substance becomes charred and blackened, except in a few cases where the material may be wholly volatilized without undergoing decomposition. Several of the essential oils, such as those of turpentine, elemi, juniper, and attar of roses, consist of carbon and hydrogen only: the same may be said of naphthalin, benzol, and the illuminating constituents of coal gas; but the larger number of organic bodies contain carbon, hydrogen, and oxygen; this occurs, for example, in the case of sugar, acetic acid, alcohol, the fixed oils, and the greater part of the proximate principles of vegetables. Nitrogen is superadded to these elements in many instances, though such compounds are of less frequent occurrence, except in highly organized portions of the plant or animal, such as the seed, or the muscular and other animal tissues; albumin, fibrin, indigo, quinia, and the vegetable alkalies generally, contain nitrogen as an essential component. The presence of nitrogen may in most cases be ascertained readily by heating a small fragment of the substance in a tube with solid caustic potash, when the odour of ammonia is perceived.

The organs by which these various compounds are produced always contain small quantities of salts of the alkalies and earths, among which the compounds of potassium, sodium, calcium, and magnesium, in the form of chlorides, sulphates, phosphates, and silicates, are the most frequent: in rarer cases salts of iron and manganese are met with, and in still rarer instances, fluorides, iodides, and bromides. The presence of certain of these saline bodies appears to be as essential to the chemical activity of the growing plant or animal as that of carbon, of hydrogen, or of oxygen; for no organized tissue has ever been found free from some of these saline substances. Besides these natural compo-

nents of organic products, the chemist often artificially introduces other elements for the purpose of, as it were, dissecting these compounds, and ascertaining the probable rational composition of the body under experiment. With this view he either produces new compounds which contain sulphur, phosphorus, chlorine, bromine, iodine, peroxide of nitrogen, or sulphuric acid; or he obtains others in which arsenicum, antimony, zinc, and a variety of metallic bodies, have been introduced into the original substance.

(1037) *Organic and Inorganic Compounds.*—Many distinguished philosophers have attempted to draw the line which separates organic from inorganic chemistry. Laurent, for instance, has termed organic chemistry 'the chemistry of carbon,' and Liebig has defined it as 'the chemistry of compound radicles.' Few persons, however, would be disposed to consider with Laurent, carbonic anhydride as an organic compound, and many chemists regard sulphurous anhydride, which is undoubtedly a compound inorganic substance, as the radicle of a somewhat numerous series of bodies of inorganic origin.

There is, in fact, no definite line of demarcation between inorganic and organic products. Amongst the productions of organized nature, we meet with acids, alkalies, salts, and other bodies, similar in chemical functions to those derived from inanimate nature: and all organic compounds, when once formed, are subject to precisely the same chemical laws as those which regulate the combinations and decompositions of bodies confessedly inorganic; but while the composition of the former is generally much more complicated than that of the latter, the balance of chemical attractions in organic bodies is disturbed by slighter causes; and there are, consequently, an unnumbered variety of products generated by slight modifications of the various forces to which organic substances can be subjected.

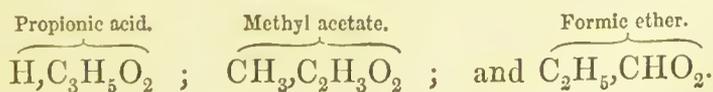
Still, it is convenient to subdivide chemical compounds into organic and inorganic; since those derived from the inorganic world, from the greater simplicity of their composition, afford to the student the most favourable instances for examining the fundamental laws of chemical combination, before he proceeds to the investigation of the more complicated products obtained from the operations of the living plant or animal.

The number of elementary atoms which enter into the formation of an inorganic compound rarely exceeds ten or twelve; whereas in bodies of organic origin they may have any degree of complexity, from the simplest known organic compound, hydro-

cyanic acid, which contains only three elements (HCN), to the complex substance stearin ($C_{57}H_{110}O_6$) with its 173 atoms, or the still more complex compound albumin, the molecule of which ($C_{72}H_{112}N_{18}SO_{22}$) contains not less than 225 atoms, and perhaps even more.

(1038) *Frequency of Isomerism.*—The number of organic compounds known to chemists is very great, and the list is perpetually undergoing increase; it therefore cannot excite surprise, if amongst them numerous instances of isomerism, metamerism, and polymerism should occur.

The formation of *isomerides*, *metamerides*, and *polymerides* (as bodies which possess the same percentage composition may be termed), can only be accounted for on the supposition that differences of chemical arrangement occur in these different cases. In some instances a rational explanation of the cause of difference may be given. A familiar example is afforded in the case of the three metamerides, propionic acid, methyl acetate, and formic ether. These bodies are liquids, each of which contains $C_3H_6O_2$, they yield vapours of the same density, the latter two even have nearly the same boiling point and specific gravity in the liquid form; but there can be no doubt that they are all differently constituted. Propionic acid is one of the acids of the stearic series: methyl acetate is prepared by the action of acetic acid upon wood spirit, and potassic acetate may be extracted from it by means of an alcoholic solution of caustic potash, whilst wood spirit is liberated: formic ether is the result of an action of formic acid upon ordinary alcohol, and when treated with caustic potash in the same way as the methyl acetate it betrays its origin by yielding potassic formiate and alcohol. Each of these bodies must therefore be represented as possessing a different molecular constitution, as for example:—



In other cases, such for example as the ordinary sugar of fruits ($C_6H_{12}O_6$), no reasonable hypothesis of their constitution has been offered; yet we know of the existence of several bodies, isomeric with fruit-sugar, such as lactic and acetic acids, for which rational formulæ are in common use.

Even in substances of comparatively simple composition, the difficulty of framing a conclusive theory of their molecular arrangement is very great, as may be seen by inspecting the

following table, which represents a few of the views which have been taken respecting the nature of acetic acid :—

| | | | | |
|----------------|---------|-------------------|-------------------|----------------------|
| $C_2H_4O_2$ | . . . | Acetic acid | . . . | (Empirical Formula.) |
| $H_2C_2H_3O_2$ | . . | Binary theory. | | |
| $(C_2H_4)O_2$ | . . . | Nucleus theory. | | |
| $H(C_2H_3O)O$ | . . | Radicle theory. | | |
| C_2H_3O H | } O_2 | . . . | Water type theory | (Gerhardt.) |
| $H(CH_3)CO_2$ | . . | Methyloxalic acid | . . | (Kolbe.) |
| $H,C(CH_3)O_2$ | . . | Methylformic acid | . . | (Wurtz.) |

Formulae such as these do but represent probabilities as to the internal arrangement of organic bodies. We cannot assert positively in any instance what the actual grouping of the component elements or the relative collocation of the atoms in space really is; but we may infer, with reasonable confidence, that that grouping, be it what it may, is similar in allied or homologous (1058) compounds. The rational formulae which embody these views should therefore be regarded chiefly in the light of a *memoria technica*; a means by which facts may be fixed upon the memory, and by which analogies that otherwise would escape the notice of the observer may be traced; and, above all, as instruments by which that precision may be given to our ideas which is so essential to the reception and advancement of solid philosophical knowledge.

§ I. ON THE ANALYSIS OF ORGANIC COMPOUNDS.

(1039) A. PROXIMATE ANALYSIS.—In the analysis of organic compounds, two problems are presented to the chemist for solution:—the object of the first is to separate the proximate components of the vegetable or animal product from each other; while the object of the second is to determine the elementary composition of the proximate principles thus isolated. The separation of wheat flour into starch, sugar, gluten, ligneous fibre, and oily matter, affords an instance of *proximate* analysis; and the determination of the proportions in which the carbon, hydrogen, and oxygen are united in the component starch, sugar, or fibre, furnishes an illustration of what is meant by *ultimate* organic analysis.

The proximate analysis of an organic compound is often a matter of great difficulty. The first process generally consists

in the complete desiccation of a given weight of the substance under examination, by exposing it to a temperature of from 212° to 250° in a *water oven* or box of sheet copper, made double, as shown in fig. 377; *a* being an aperture for the introduction of water or of oil into the interval between the external and internal plates, the heat being supplied by a gas flame below, and the temperature being regulated by a thermometer introduced into the opening at *b*. The loss of weight which the substance under examination experiences during the drying can be accurately ascertained when needed.

The dried material is then pulverized, and subjected to the action of several solvents in succession, such as ether, alcohol, and water.

A convenient apparatus for the digestion of the substances for analysis in these menstrua, is shown in fig. 378:—*A* is a glass flask containing the liquid solvent: this can be kept in steady ebullition by means of the lamp beneath. *B* is a tube of glass or of tin-plate, in the contracted portion of which is a plug of cotton wool, *c*; in this tube the substance for analysis is to be placed: *d*, is a short lateral tube to which the tube, *e*, of glass or of flexible metal is attached by india-rubber tubing. The tube *e* should be kept warm by enveloping it in flannel, with a view to prevent the premature condensation of the vapour as it rises from the flask. *M*, is a tin-plate condenser, which can be filled with water; *h*, is a funnel for conveying cold water to the bottom of this vessel, whilst the hot water flows off at the spout above. A tube, *g*, open at both ends, passes through the axis of *M*; the lower projecting extremity of this tube is fitted by a cork to the tube *B*. *f* is a worm tube, the upper extremity of which

FIG. 377.

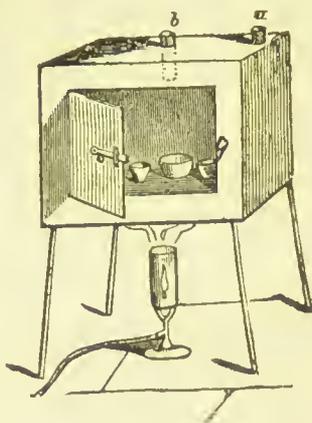
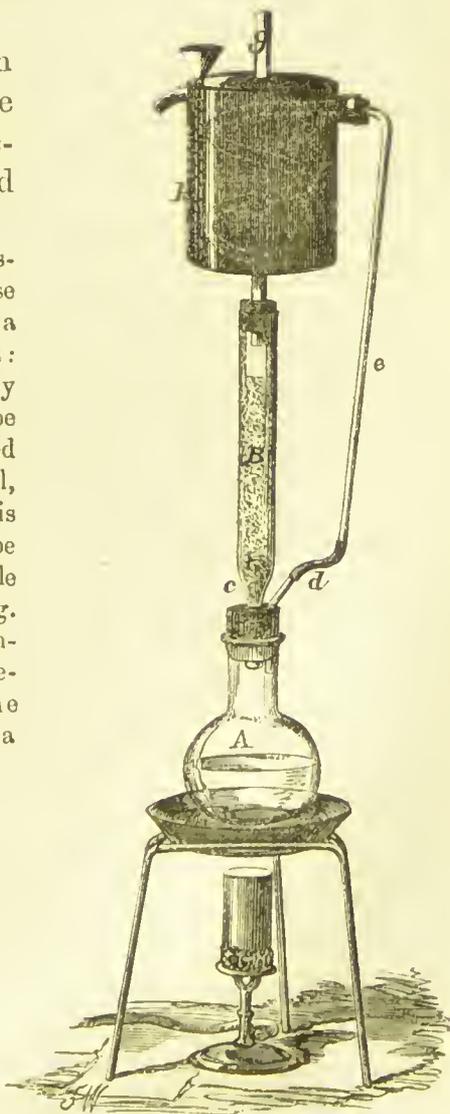


FIG. 378.



passes through the side of the refrigerator, and is adapted by a cork to the tube *e*, whilst its lower extremity is soldered to the tube *g*, into which its contents flow after they have been condensed in their passage through the refrigerator. It is obvious that by this arrangement a perpetual distillation of the liquid in the flask *A* may be readily maintained; the vapour which passes through the tube *e* becomes condensed in the spiral tube *f*, and percolates, in the liquid form, through the material contained in *B*, carrying the soluble matters into the flask *A*, where they gradually accumulate. If the employment of metal be in any case objectionable, glass vessels may be used.

Ether is particularly valuable as a solvent for fatty substances, and for caoutchouc and camphor; *alcohol* may be used for the solution of many crystallizable organic principles, such as the vegetable alkalies; whilst *water* dissolves sugar, gum, starch, and other highly oxidized bodies which are nearly insoluble in alcohol and in ether. In some cases *benzol*, in others *chloroform*, and in others *carbon disulphide* (CS_2) may be substituted for ether, which they most resemble in their solvent action. In particular cases *dilute acids*, and in others *dilute alkalies* may be employed, but they must be used with caution, since they are liable to act not merely as solvents, but also to produce important chemical changes in the compounds submitted to them. No general rule can be laid down for the extraction of the different proximate principles; each class of substances requiring special modifications, which experience alone can indicate.

In all cases of proximate analysis, the employment of the microscope will afford valuable aid whilst watching the progress of the separation of the various principles, and in enabling the operator to ascertain whether or not the substances which he has isolated are mixed with other bodies which may resemble them in chemical habitudes. When a substance or a deposit assumes the crystalline state, such an examination, by revealing the similarity or difference in form of its component particles, is often more valuable for ascertaining the purity of the body than the use of ordinary chemical reagents.

(1040) It frequently happens that two or more substances, of different degrees of solubility in the same menstruum, occur together: in such a case, if crystallizable, they may often be separated by repeated crystallizations, care being taken always to separate those crystals which are first deposited, from those which are formed subsequently: by successive recrystallizations of the first portions from each crop, the less soluble compound may be obtained in a state of purity.

In other cases, if the different compounds yield precipitates with the same reagent, but differ in the degree of their attraction for it, a separation by *fractional precipitation* may be effected by

adding a quantity of the precipitant insufficient to throw down, for example, more than one-half of the amount of the substances that may be present. The salts of silver or of lead may thus be added to mixtures of various organic acids, particularly to such as, like the fatty or the resinous acids, greatly resemble each other in properties. The precipitate is then to be suspended in water, and decomposed by means of sulphuretted hydrogen, or of a dilute mineral acid, in order to separate the metal, and liberate the organic acid, which is to be again submitted to a similar incomplete precipitation; and this process must be repeated until the fusing point becomes constant, or till some other guarantee of the purity of the body is obtained.

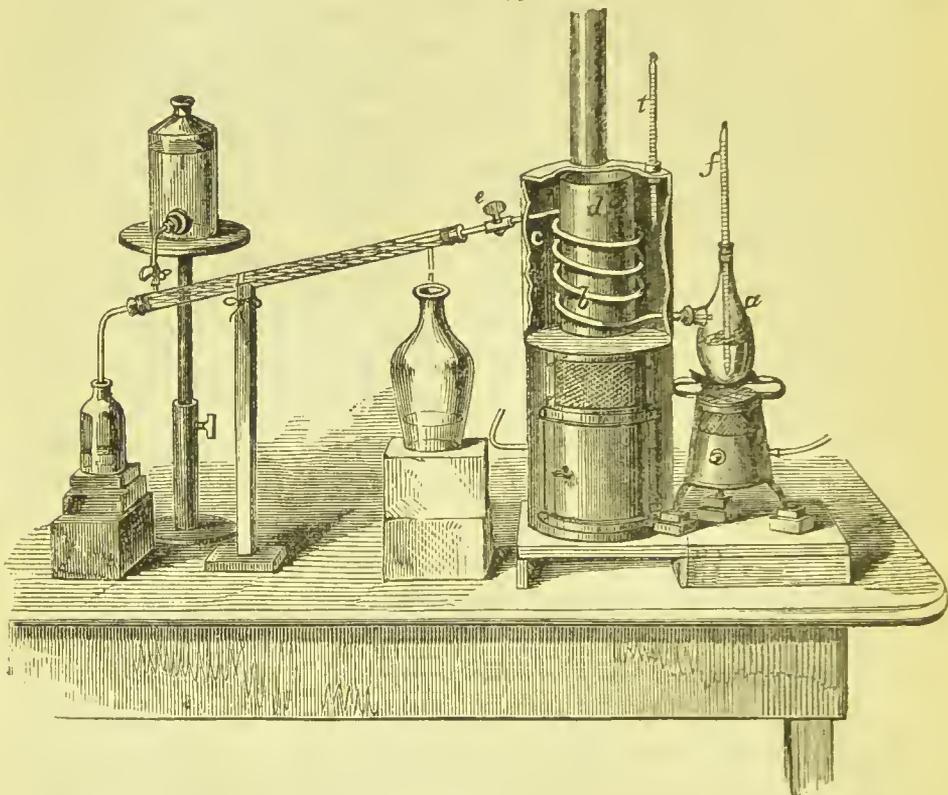
In other cases, where a mixture of two solids of unequal solubility in the same menstruum is operated on, *fractional solution* may be employed. In this case, by using successive small portions of the same solvent, a separation of the more soluble ingredient from the less soluble one may be gradually effected, till at length the last portions which remain undissolved consist of the least soluble ingredient nearly pure.

In the rectification of mixtures of volatile liquids, analogous principles are to be acted on; in these cases the boiling point is the guide. The liquid is placed in a retort, into the tubulure of which a thermometer is fitted, and the temperature is raised till the liquid boils. So long as the temperature of the boiling liquid continues to rise, the substance which distils must consist of a mixture; but as soon as the point of ebullition becomes nearly stationary, the distillate may be supposed to have a composition nearly uniform; and by rectifying again those portions which distil at the same fixed temperatures, the different components of a mixed liquid may be obtained in a state of purity. Where large quantities can be operated on, this process of *fractional distillation* is well adapted to the separation of liquids the boiling points of which differ considerably from each other; but it is much less satisfactory when the quantities are small, or where the boiling points are within 20° or 30° (10° or 15° C.) of each other.

A considerable improvement in the mode of conducting fractional distillation has recently been introduced by Warren, who applied it successfully in examining the volatile products of American petroleum. (*Memoirs of the American Academy*, New Series, vol. ix.) This mode of distillation will be understood from an examination of fig. 379, in which *a* shows the retort or two-necked flask containing the liquid for distillation together with a thermometer *f*. The flask is connected with an ascending spiral worm *b*, which is maintained at a steady temperature by being made to pass through the oil bath *c*, the heat of which is regulated by the aid of the thermometer, *t*. *d* is a vessel ordinarily

empty, but which can, if necessary, be filled with ice. The upper end of the worm *e* is connected with a Liebig's condenser or other suitable apparatus for condensation. By this arrangement it is easy to ensure the condensation of nearly all the less volatile portions, which flow back into the retort, whilst the more volatile portions pass on and are obtained in the colder part of the appa-

FIG. 379.

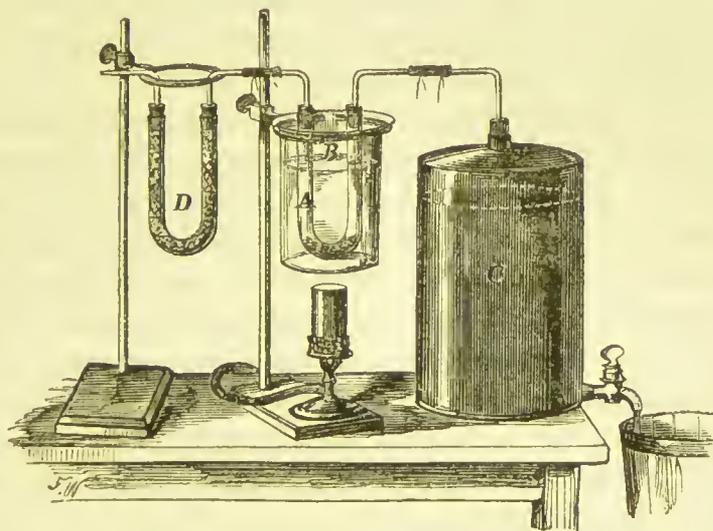


ratus. The apparatus should be made of brazed copper; the worm is about 5 feet, or 1.5 metre in length, and $\frac{3}{8}$ inch or 10 millimetres in internal diameter.

Wanklyn has shown (*Proceed. Roy. Soc.* xii. 534) that the proportions in which the mixed liquids distil over must vary not only with the relative amount of each in the mixture, and with the tension of the vapour of each at the boiling point of the mixture, but also with the adhesion of the liquids to each other and with the vapour density of each. In most cases the effect of adhesion is trifling, but the variation in vapour density is important. According to his experiments, a mixture of equal weights of two liquids of different boiling points will furnish a distillate in which the proportion of each liquid may be calculated by the product of the tension of its vapour into the specific gravity of the vapour. In consequence of this circumstance, the less volatile liquid may distil over more rapidly than the other; for example, a mixture containing 18 parts of wood spirit (boiling at 151° , vapour density 1.107) and 17 parts of ethyl iodide (boiling at $161^{\circ}.6$, vapour density 5.397) yielded in the first third a mixture consisting of 6 parts of wood spirit and 8.7 of ethyl iodide. If the vapour density and the tension at the boiling point of the mixed liquid are inversely proportional in the case of the two liquids, the mixture distils over without change. These observations explain the facility with which bodies of high boiling point, but of considerable vapour density, such as the essential oils, pass over with the vapour of water. Berthelot has made similar observations.

A method, which may be termed *fractional saturation*, was applied by Liebig to the separation of certain volatile acids from each other. This process consists in saturating a portion only of the acid with potash or with soda, and then proceeding with the distillation; when the more volatile acid passes over with the distillate. Suppose that it be desired to effect the separation of butyric from valeric acid:—a certain amount of potash is added, and if this be more than sufficient to saturate the valeric acid, the distillate will consist of butyric acid only, while the residue will be a mixture of potassic valerate and butyrate. If, on the other hand, the valeric acid be more than sufficient to saturate the potash, the residue in the retort will consist of pure potassic valerate, and the distillate will be a mixture of butyric and valeric acids, which may be separated by a repetition of the same process.

FIG. 380.



(1041) B. ULTIMATE ANALYSIS.— Before proceeding to the ultimate analysis of a body, it is necessary first to dry it carefully, either by means of the water oven (1039), or of an apparatus similar to that shown in fig. 380.

A represents a bent glass tube, for the reception of the substance to be dried; B, is a vessel of glass or of metal, containing water, or some saline solution; C, an aspirator, by which a current of atmospheric air can be maintained through the apparatus; and D, a bent tube filled with fragments of pumice-stone, soaked in oil of vitriol, for drying the air as it enters. The tube A is weighed at the beginning of the operation, and the desiccation must be continued so long as this tube ceases to lose weight. If the desiccation be effected in the water oven, the capsule or crucible which contains the compound must be allowed to cool under a bell glass, over a dish of oil of vitriol, and must be kept covered whilst being weighed, in order to prevent the absorption of moisture.

(1042) *Determination of the Mineral Components.*—If any mineral substances be present in the compound under examination, their amount must be ascertained by the incineration of a

weighed quantity of the material. This operation, though simple in appearance, is one which it is difficult to perform with exactness; owing to the partial volatilization of the alkaline chlorides at a red heat, and the reduction of the sulphates to the form of sulphides. The incineration should therefore always be performed at a low temperature, which need not exceed a barely visible red, but must be prolonged for many hours if the mass for incineration be considerable. Caillat finds it advantageous in a large number of cases, before incinerating to treat the substance with dilute nitric acid, by which means almost the entire saline ingredients may be extracted in the soluble form; on incinerating the insoluble portion, scarcely anything is left except silicea and a small quantity of ferric oxide. The quantity of saline matters, and particularly of sulphates, thus obtained always exceeds that furnished by burning only; since in the digestion with nitric acid the loss occasioned by reduction of the calcic sulphate, and the partial expulsion of sulphur from the calcic sulphide so formed is avoided.

(1043) *Analysis of Organic Compounds by Combustion.*—Since the four elements, carbon, hydrogen, oxygen, and nitrogen, constitute the bulk of most organic substances, the operation of organic analysis resolves itself mainly into the accurate quantitative determination of these elements. We are indebted to Gay Lussac and Thénard for the fundamental principle that regulates our operations in this respect. The process proposed by them has subsequently been modified and improved by many chemists, especially by Berzelius, Prout, and Liebig, and it was by the last named eminent philosopher that the method now in general use was contrived.

The object of this operation being to determine the relative proportion in which each of the ultimate elements occurs in the compound under examination, it becomes necessary to the success of any analytical process that these elements should be procured either separately in a state of purity, or in the form of definite compounds that can easily be collected. In practice it has been found most convenient to supply the substance to be analysed with a quantity of oxygen sufficient to convert the carbon which it contains into carbonic anhydride, and the hydrogen into water. An arrangement is made for absorbing the carbonic anhydride by means of a known weight of a solution of potash; whilst the water is caused to pass over a weighed quantity of a substance that has a powerful attraction for it, such as calcic chloride, or pumice moistened with sulphuric acid; and the nitrogen

is measured in the form of gas, over mercury. In certain cases where nitrogen is present, the substance to be analysed may be mixed with caustic soda or potash, and heated; all the nitrogen is thus converted into ammonia, in which form it admits of being weighed as easily as carbonic anhydride and water.

Having proceeded thus far it is easy to find by calculation the weight of the carbon, the hydrogen, and the nitrogen respectively contained in the carbonic anhydride, the water, and the ammonia collected. When the proportion of saline matter has been determined by incineration of a portion of the mass, the quantity of oxygen which the substance contains may be known by deducting the united weight of the carbon, the hydrogen, the nitrogen, and the salts, from the total weight of the body analysed; the deficiency (supposing sulphur and phosphorus not to have been present) is reckoned as oxygen.

Serupulous attention to the purity of the matter submitted to analysis is of course of primary importance, a very slight admixture with other compounds being sufficient to vitiate the conclusions deducible from the experiments. Having by suitable means ascertained the purity of the substance to be analysed, the next care is to insure its complete desiccation. Solids should be dried in the water oven. Volatile liquids that are unchanged by distillation should be allowed to stand for two or three days upon fragments of fused caloric chloride; the liquid should then be decanted and distilled in a small retort. In other cases, as in the examination of fats or fixed oils, it may be more convenient to dry the material in a watch-glass placed in an ordinary water-bath, or in the hot-water oven. The further progress of the analysis will vary according to the form and composition of the substance to be examined.

We shall describe the methods of analysing—

1. A *solid*, which does not contain nitrogen.
2. A *liquid*, which does not contain nitrogen.
3. A substance which does contain nitrogen.

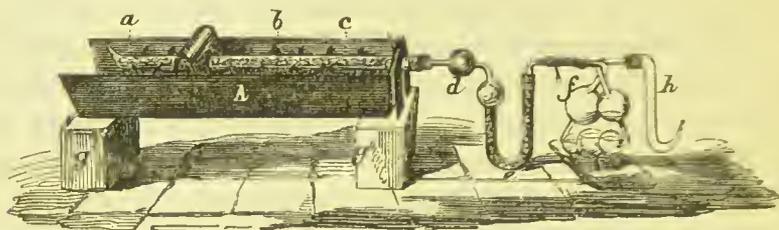
1. *Analysis of a Solid not containing Nitrogen.*

(1044) The combustible which is generally used in these experiments is charcoal; it is very manageable, but the dust occasioned by it is troublesome. Hofmann has contrived a furnace in which gas is made use of as a fuel, and which answers its purpose admirably. (*Q. J. Chem. Soc.*, xi. 33.)

The best form of furnace to be used with charcoal is repre-

sented at A, fig. 381 : it is made of stout sheet-iron bent into the form of a trough, open at one end ; the plate which closes the other end is perforated with an aperture three-quarters of an inch in diameter, to allow the passage of the combustion tube ; the furnace is about 20 inches long, 5 inches wide at top, $2\frac{3}{4}$ inches at bottom, and 3 inches high ; or about 50 centimetres long, 13 cm.

FIG. 381.



wide at top, 7 cm. at bottom, and 8 cm. high. Transverse slits are made at intervals of 2 inches along the bottom of the trough for the admission of air, and in each of the spaces between these slits is riveted a vertical stiff piece of sheet-iron, 1 inch high, terminating in a concave edge above, for the support of the combustion tube. During the operation, the apparatus may rest on bricks, *g*, *g*.

The *combustion or retort tube* (*a b c*), in which the mixture is burned, is about 15 inches long and half an inch in diameter (25 centimetres long and 12 millimetres in diameter) ; it is made of glass of difficult fusibility and free from lead, such as the hard Bohemian glass. The tube may on certain occasions be drawn out into a fine but strong tail bent upwards at an obtuse angle, and the mouth should be smoothed by making it red-hot in the flame of the blowpipe, so that a cork may not be torn in adjusting it.

The water is collected in a bent tube, *e*, filled with calcium chloride. At *d* is a small bulb, in which the greater part of the water becomes condensed ; it may be emptied from time to time. The calcium chloride must not be fused, but should be prepared by merely evaporating the solution of the chloride to dryness by a strong sand heat. A porous mass is thus obtained, which does not expand by absorbing moisture, as the fused variety does, to the destruction of the tube that contains it. The cork through which passes the bent tube by which it is connected with the potash bulb *f*, should be trimmed close to the large tube and covered neatly with melted sealing-wax ; and lastly, air should be drawn through the apparatus by the mouth to ascertain that no

obstruction exists. Pumice-stone moistened with concentrated sulphuric acid may be advantageously substituted for calcium chloride in the drying tube. The connexion between this tube and the retort, *a b c*, is effected by means of a sound elastic cork, or a plug of vulcanized caoutchouc, which is made to close the mouth of the tube accurately; it is pierced with a round file, and fitted firmly upon the fine tube proceeding from the bulb *d* of the drying tube; the cork is to be dried on the sand-bath immediately before the apparatus is mounted.

The solution of potash employed in the bulb tube, *f*, should have a sp. gr. of from 1.25 to 1.27, and must be renewed for every experiment.* To the free end of the potash bulbs, a tube *h*, filled with fragments of caustic potash, is adjusted by means of a cork; this is weighed with the bulbs, and is employed to dry the nitrogen and other gases which escape during the course of the analysis.

The compound commonly used for supplying oxygen to the substance to be burned is cupric oxide, which readily imparts oxygen to combustible matter in contact with it, but when heated alone, bears a very high temperature without being decomposed. It is best procured by dissolving copper in pure nitric acid, evaporating to dryness, and decomposing the nitrate by heating it strongly in an earthen crucible. Ignition is to be kept up till red fumes cease to appear: if the heat be too great the oxide becomes agglutinated, and requires strong pounding in an iron mortar to pulverize it. The powdered oxide is to be sifted through a fine copper sieve, and reserved in stoppered glass bottles.

Immediately before each analytical operation, a sufficient quantity of cupric oxide is to be ignited in a crucible, and while still hot, transferred to a dry tube, by plunging the mouth of the tube into the oxide in the crucible, and then shaking it in piecemeal: the tube is to be immediately closed with a dry cork, and allowed to cool. Meantime the interior of the retort is to be dried completely by heating each portion of it in succession in the flame of a gas or spirit-lamp, beginning at the closed end, and drawing air through the heated tube by means of a narrower tube passed down just beyond the heated part, and exhausting by the mouth. When every part has thus been dried, the retort is to be corked and allowed to cool.

* The portions of the potash solution that have been used in this way may be put aside, and afterwards, when a sufficient quantity has been collected, may again be rendered caustic in the usual way by means of quicklime.

Five or six grains, or about 0.3 grm., of the substance to be analysed, when powdered and dried, are to be put into a perfectly dry test tube, and this tube with its contents very accurately weighed; its contents are then to be mixed with cupric oxide in a mortar, and the empty tube again weighed; the difference gives the weight of the substance employed. Much caution is requisite in charging the retort. The mortar, having been first made dry and warm, is to be placed on a sheet of glazed paper, and cleared out with a little of the dried cupric oxide, which is then to be thrown aside. Cupric oxide to the depth of an inch (2.5 centimetres) is to be poured into the combustion tube; after which a small quantity of the oxide is to be put into the mortar, then the substance to be analysed, then more oxide. The mixture must be made quickly and carefully, so much oxide being added as shall be sufficient to fill a little more than half the retort tube. The mortar is now to be taken in the palm of the left hand, and the mixture introduced, carefully picking it up piece-meal by means of the retort tube itself; fresh portions of oxide are to be rubbed in the mortar to clear out the last traces of the mixture, and the retort is finally to be filled up with pure cupric oxide to within two inches (5 centimetres) of the extremity.

The proportions of the mixture are represented in fig. 381: in which the portion from the tail of the tube to the letter *a* consists of pure cupric oxide; that from *a* to *b* of the mixture, that from *b* to *c* of the rinsings of the mortar, and that from *c* to within an inch of the cork of pure oxide. The tube having been closed by a cork is to be struck smartly in a horizontal position on the table, so as to clear the tail-like prolongation, and make an air-way above the oxide from end to end.

The drying tube *e* having been accurately weighed, is next to be fitted to the dry perforated cork, and connected by it airtight to the tube *a b c*. The retort tube is now to be placed in the furnace; the potash apparatus *f*, also previously weighed, is to be attached to the drying tube by means of a connecting piece of caoutchouc, care being taken that the largest bulb is on the arm connected with the drying tube. The potash apparatus should be slightly inclined by placing a cork under the end of the horizontal portion nearest the open extremity. Matters being thus arranged, the next process is to ascertain if the whole be tight, and for this purpose the air in the large bulb is to be gently heated so as to expel a few bubbles; if, on cooling, the liquid rise in the limb and maintain its elevation steadily for a few minutes, the combustion may safely be begun. Charcoal

broken into pieces about the size of a walnut is to be ignited, and applied to the portion of the tube nearest the cork, where the pure cupric oxide lies: the action of the heat is limited by a double sheet-iron screen which fits into the furnace, and has a central slit in order to allow it to bestride the tube; this screen can by degrees be moved further and further down the furnace until the whole tube is heated. An additional screen of single iron plate is hung over the closed end of the furnace to protect the cork, care being taken that the heat never rises so high as to scorch it, or falls so low as to allow of the condensation of moisture in the portion of the retort which projects from the furnace.

When the fore part of the retort is red-hot and the escape of air due to expansion has ceased, about an inch more of the tube may be heated; and in this way the fire is gradually carried down. At first only a small portion of the escaping gas is absorbed, but when the substance is fairly undergoing decomposition, and the atmospheric air in the apparatus has been expelled, the gas is almost entirely taken up by the potash-ley. When the whole tube is ignited, the heat must be continued till bubbles are no longer disengaged. The potash-ley will now gradually recede into the large bulb; as soon as this motion is observed, the charcoal must be removed from the tail of the tube; and when the solution of potash has risen sufficiently to fill half the large bulb, the tip of the tail must be nipped off: gentle suction is then to be effected by means of a tube of vulcanized caoutchouc, fitted to the free extremity of the potash apparatus, and air drawn through the combustion tube by the mouth, in order to displace the carbonic anhydride and aqueous vapour which the apparatus contains. Dumas prefers to connect the extremity of the retort with a drying tube, and this again with a receiver containing oxygen, which gas is carefully driven over the contents of the tube in the manner shown in our former volume, fig. 298, Part II., p. 82. This renders the operation somewhat more complicated, but it is more exact, especially for compounds where the proportion of carbon is great. The tube for supplying oxygen is easily adjusted to the retort by drawing out the tail horizontally instead of obliquely, and fitting it on by a caoutchouc connector, care being taken to screen the junction from the influence of heat.

The apparatus is now to be dismantled, and allowed to cool. In about an hour the drying tube *e* may be weighed; one-ninth of the gain which it has experienced indicates the quantity of hydrogen contained in the compound analysed; the potash apparatus *f*,

is also to be weighed, and three-elevenths of what it has gained shows the quantity of carbon. The deficiency is reckoned as oxygen.

The cupric oxide used in these experiments may again be rendered serviceable by moistening it with nitric acid, and igniting it as before, or by reoxidizing it whilst red-hot, in a current of air directed through the tube.

In some cases, where chlorine, bromine, or iodine is present in the compound to be analysed, *plumbic chromate* (PbCrO_4) may be advantageously substituted, as the chloride, bromide, or iodide of copper are somewhat volatile, and would be carried by the current of gas into the condensing tubes. The chromate is also useful with substances difficult of combustion, since by a bright red heat alone it gives off a portion of its oxygen. It is easily prepared by precipitating the potassic chromate or dichromate with a solution of plumbic acetate: it should be well washed and heated to incipient fusion before it is used for analysis. Plumbic chromate has the advantage of being much less hygroscopic than cupric oxide. In some cases the body to be burned may be mixed with potassic dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) which parts with oxygen by heat more freely than the lead salt.

2. Analysis of a Liquid not containing Nitrogen.

(1045) If the liquid be *volatile*, a piece of tube rather less than a quarter of an inch or 6 millim. in diameter is to be heated in the blowpipe flame, and drawn out into a capillary portion, *a* fig. 382, about four inches (10 centimetres)

FIG. 382.



long: about a quarter of an inch below this the tube is to be sealed, and the little piece of tube, *b*, thus left connected with the capillary part, heated and blown into a small bulb about as big as a good-sized pea; this is to be cut off, leaving a capillary neck of about two inches (5 centimetres) long. Having made a sufficient number of these small bulbs, two of them, which it has been ascertained will freely enter the combustion-tube, are to be accurately weighed; a little of the liquid to be analysed is to be put into a small tube, and the capillary neck of the bulbs inverted into the liquid; the bulbs are then to be warmed by the flame of a spirit-lamp, so that on cooling they shall be about three-fourths filled with the liquid. The necks are now to be sealed by the blowpipe flame, and the bulbs again weighed; the increase of weight gives the quantity of the liquid which has entered, and which is to be analysed. The cupric oxide having been heated and allowed to cool with the usual precautions, about an inch and a half (36 millimetres) of the retort is to be filled with pure oxide; next a file is to be drawn across the capillary neck of one of the bulbs, and the bulb having been placed in the retort, the neck is to be broken by pressure against the glass, and the broken portion of the neck to be dropped in with the bulb; dried cupric oxide is then to be poured in to the depth of two inches more; the second bulb is to be introduced in the same manner as the first, and the tube is to be filled up with oxide; after which it is to be corked and struck smartly upon its side on the table, to secure free air-way. The combustion tube is now to be adjusted in the furnace, and the first half of the tube is to be gradually heated; when this is red-hot, the liquid must be volatilized by cautiously approximating a piece of

ignited charcoal to the part of the tube where the bulb nearest the open end of the retort lies, taking especial care not to raise the temperature too rapidly: when by degrees all the liquid in the first bulb has been expelled, the other is to be proceeded with in like manner; the whole tube is finally to be heated carefully, and the gases are to be swept out of the apparatus by means of air or oxygen in the manner already described.

If the liquid be *not volatile* it may be weighed in a small tube the weight of which, when empty, is known; and after the tube with its contents has been introduced into the retort tube, the liquid is to be distributed over the sides of this tube; dry cupric oxide is then filled in, and the combustion is conducted in the usual way.

Substances which contain a great excess of carbon, sometimes escape complete combustion by the foregoing process: when this is to be feared, the tube is connected with a receiver filled with oxygen, upon the plan of Dumas, already mentioned; or some finely pulverized, carefully dried potassic chlorate may be mixed with about four times its weight of cupric oxide, and about an inch of the retort near *a* (fig. 381) may be filled with it; the tail-like prolongation may in this case be dispensed with. At the close of the operation, instead of sucking air through the apparatus, heat is to be very cautiously applied to the chlorate; the oxygen that is evolved burns the last traces of carbon and displaces the gas and aqueous vapour contained in the tubes. The heat must not be too suddenly applied, for if it be, a portion of the chlorate is apt to be carried forward mechanically, a circumstance which constitutes the chief objection to its use.

3. *Analysis of a Body containing Nitrogen.*

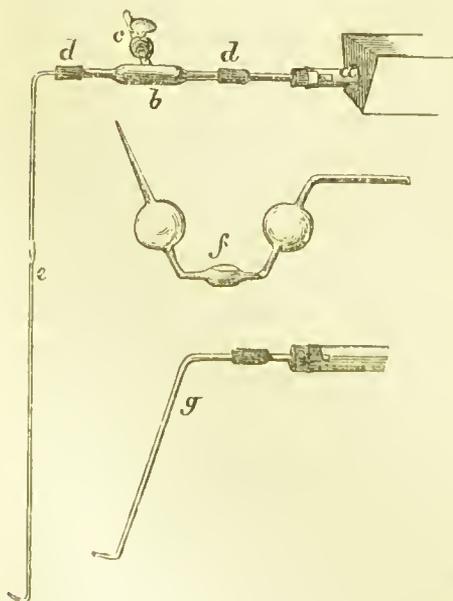
(1046) The presence of nitrogen in an organic compound is ascertained by mixing a small quantity of such compound with a portion of solid caustic potash, and heating it in a small test tube: if nitrogen be present, vapours of ammonia will be evolved. Two separate analyses are in this case required: the first, to discover the proportion of carbon and hydrogen; and the second, to determine the proportion of nitrogen. When bodies containing nitrogen are burned with cupric oxide, a variable proportion of the lower oxides of nitrogen is formed, which being retained by the calcic chloride, or by the potash, would render the analysis incorrect. A precaution is therefore employed which renders it necessary to make use of a retort-tube rather longer than common; this tube is to be charged as usual to within six inches (15 centimetres) of the opening, and then filled up with clean copper turnings. The apparatus having been arranged as before directed, the copper turnings are to be brought to a full red-heat, and the analysis is to be cautiously conducted in the ordinary manner. As the oxides of nitrogen pass slowly over the ignited copper they are decomposed, the oxygen combining with the copper, while pure nitrogen escapes. The quantity of carbon and hydrogen is determined exactly in the manner previously described.

(1047) *Method of Varrentrapp and Will.*—The most accurate method for ascertaining the proportion of nitrogen is that devised by Varrentrapp and Will; and the fundamental fact upon which this method is based consists in the observation of Gay-Lussac, that when azotised matters are heated with a large excess of potassic or sodic hydrate, the whole of the nitrogen is expelled in the form of ammonia. In order to render this method available for the purposes of analysis, the subjoined precautions are requisite.

A mixture of two parts of quicklime and one of sodic hydrate is prepared by slaking some well-burned lime with the necessary quantity of a solution of soda; the whole is evaporated to dryness, and ignited; the dry mass is pulverized as quickly as possible, and then transferred to well-closed bottles, in order to exclude carbonic acid and moisture. When an analysis is required, the substance under examination is very intimately mixed in a warm mortar with a portion of this alkalinized lime, or *soda-lime* as it is frequently termed, instead of with eupric oxide: the accidental presence of a little moisture after the weight of the material for analysis has been accurately determined, is, in this case, of no consequence.

Having introduced the mixture into the retort tube, it is better to plug the aperture loosely with a few fibres of asbestos,

FIG. 383.



(which has been ignited just before) in order to prevent any mechanical transport of the mixture into the apparatus through which the gases are made to pass. On applying heat to the combustion-tube in the ordinary way, and with the usual precautions, the substance is decomposed, and the whole of the nitrogen escapes as ammonia. The drying-tube and the potash apparatus are not used, but the ammonia is collected in a bulb-tube of the form represented at *f*, fig. 383, which is connected air-tight with the retort-tube *a*, by means of a good cork, the bulbs *f*

having been previously charged with hydrochloric acid of sp. gr. 1.1.

Pure hydrochloric acid is easily procured for this purpose by diluting the ordinary acid of the shops till it has a sp. gr. of 1.1, and distilling it in glass vessels; the first eighth may be rejected, and the distillation proceeded with until three-fourths of the acid employed have passed over. It is better for the operator always to rectify his own acid, in order to be quite sure of the absence of every trace of ammonia.

The tube connecting the bulbs *f* should be somewhat larger in diameter than that of the ordinary potash apparatus, in order to allow the liquid to be poured out readily. When the operation is complete, absorption will take place, and the liquid will rise in the bulb nearest the fire; at this moment the tail of the combustion-tube should be nipped off, and air carefully drawn through the apparatus in the usual way. When the combustion is completed, the contents of the bulb-tube are to be emptied into a small evaporating dish, and the bulbs washed out first with a mixture of alcohol and ether, and afterwards several times with water; solution of platinum chloride is to be added in excess, and the whole evaporated to dryness in a water-bath or a chloride of calcium bath. The residue when dry is to be digested with a mixture of two parts of alcohol, sp. gr. 0.833, and one of ether, which dissolves the excess of platinum chloride, and leaves the double chloride of platinum and ammonium in a crystalline form. This must now be brought upon a weighed filter, and washed repeatedly with the mixture of two parts of alcohol and one of ether, until nothing further is taken up. The precipitate and filter must be dried at a heat of 212°, and the weight accurately observed; 223 parts of the ammonio-platinum chloride are equivalent to 14 of nitrogen, or 100 parts to 6.278 of nitrogen. Instead of collecting the ammonia in hydrochloric acid, it may be condensed in a certain volume of dilute sulphuric acid of known strength. About 150 grains, or 10 grammes, of an acid of which 100 parts will neutralize 2.5 parts by weight of ammonia, will answer the purpose. The acid liquor is then to be washed out of the bulbs *f*, diluted, and carefully neutralized by means of a solution of caustic soda, or of lime in dilute syrup, the strength of which has been accurately ascertained.

(1048) *Method of Dumas.*—The foregoing method of determining nitrogen answers for nearly all cases excepting those in which this element occurs in the form of a cyanide or a nitrate, when it must be determined by volume, and its weight thence deduced. For this purpose the process of Dumas is the most trustworthy:—A retort-tube of about 30 inches (75 centimetres)

long is employed, not drawn out into a tail, but sealed with a rounded extremity; about 3 inches (75 millimetres) of the tube are filled with hydrie-sodie carbonate (NaHCO_3) and then the mixture with cuprie oxide is added, and covered as usual with a layer of pure oxide; beyond this, the last 3 or 4 inches of the tube are filled with clean copper turnings, as already directed, with a view of decomposing any of the oxides of nitrogen which may be formed. The retort-tube is then connected with a three-legged apparatus of brass or copper (fig. 383, *b*), one limb of which is furnished with a stopcock *c*. The connexion with the retort-tube *a* is best made by passing a piece of glass tubing through a cork fitting accurately into the mouth of the tube *a*, and connecting the brass apparatus to this small glass tube by means of a caoutchouc connector, *d*; the third limb is fastened with a similar joint to a glass tube *e*, bent at right angles near one end, with a straight portion upwards of 30 inches (760 mm.) long, the other extremity of which is turned up at an acute angle for the convenience of safely delivering the gas; this tube is placed with its long portion in a vertical direction and with its lower upturned extremity dipping into a small mercurial trough; the stopcock tube, *c*, is connected with an exhausting syringe, by which a vacuum is produced; the apparatus is left for half an hour to ascertain that all the joints are tight: if the mercury after this lapse of time still stands at the same level, the experiment may be proceeded with. A moderate heat is then applied by means of a spirit lamp at the end of the retort containing the carbonate; carbonic anhydride is thus set free, and displaces the last portions of air: the exhaustion and the disengagement of gas are repeated alternately three or four times, care being taken to leave an amount of the carbonate undecomposed sufficient to renew this expulsive process at the termination of the experiment. The stopcock, *c*, is now closed, the air-pump is removed, and a graduated jar containing some solution of potash is inverted in the mercury over the recurved extremity of the long glass tube. The copper turnings are then brought to redness in the usual way by means of a charcoal fire, the decomposition being caused to take place less rapidly than usual. When the part of the retort containing the matter for analysis is red-hot through its entire extent, heat is gradually applied to the hydrie-sodie carbonate, and the last portions of gas furnished by the combustion are driven into the receiver by the carbonic anhydride disengaged from the carbonate.

The products of the combustion are water, carbonic anhydride, and nitrogen; the two former are retained by the solution

of potash, so that the nitrogen alone presents itself for measurement. When by standing for an hour or two, the apparatus has reached the temperature of the atmosphere, the height of the barometer and thermometer must be carefully noticed; and since the gas will be saturated with moisture, its volume must be corrected for the three points of temperature, pressure, and moisture. Then, since a litre of nitrogen at 0° C. and 760 mm. barometric pressure weighs 1.256 gm., or 100 cubic inches of nitrogen at 60° F. and under a pressure of 30 inches of mercury weigh 30.15 grains, it is easy to calculate the weight of the nitrogen contained in a given quantity of the matter analysed. In this process, as in every case where the proportion of nitrogen alone forms the object of the experiment, after the weight of the material for analysis has been once accurately ascertained, it is evident that there is nothing to fear from a slight absorption of moisture.

(1049) *Method of Relative Volumes.*—When the quantity of nitrogen present is not less than one-fourth of the weight of the carbon contained in the compound, its proportion may be advantageously determined by conducting the combustion just as if we were going to ascertain the proportion of carbon and hydrogen; but, instead of condensing the carbonic anhydride and weighing it, the whole of the gases produced are to be collected over mercury. A bent gas-delivering tube, *g*, fig. 383, is used instead of the usual apparatus for the absorption of water and carbonic anhydride. In this case it is best to begin at the closed extremity of the tube, and having expelled the atmospheric air by means of a portion of gas generated from the substance, to collect the remainder of the gaseous products in a graduated jar. Then, by agitating the gas with a solution of potash, the proportion of nitrogen to the carbon can be at once determined, since equal volumes of carbonic anhydride and nitrogen gases represent single atoms of carbon and nitrogen. It is not necessary in this case to weigh accurately the quantity of material acted upon.

Experience has shown that in the preceding process for organic analysis, the quantity of hydrogen deduced from it is always slightly in excess, usually about 0.2 parts in 100; whilst, unless plumbic chromate or potassic chlorate be employed, the carbon is sometimes deficient to the same extent. A deficiency of carbon also occurs if the ash contain carbonates of the metals of the alkalis or of the earths.

(1050) *Determination of Sulphur, Phosphorus, and Arsenicum.*—One of the methods employed for ascertaining the amount of unoxidized sulphur in an organic compound, consists in mixing 1 part of the substance for analysis with 10 parts of nitre, 2 of dried sodic carbonate, and 30 of pure sodic chloride, and heating the mass to redness in a tube of hard glass. The sulphur is thus converted into sulphuric acid, which forms a salt with a portion

of the alkali. The object of adding the sodie chloride is simply to moderate the violence of the deflagration. The residue is to be dissolved in water rendered slightly acid by means of hydrochloric acid, and the sulphuric acid is to be precipitated by the addition of barie chloride. If phosphorus or arsenicum be present, it will remain in the acid liquor in the form of phosphoric or arsenic acid. Its amount may be determined by adding sulphuric acid in order to throw down the excess of barium salt; then filtering, supersaturating with ammonia, and adding an ammoniacal solution of magnesian sulphate: the phosphoric or arsenic acid is precipitated as the ammonio-magnesian phosphate or arseniate, and is to be collected in the usual manner.

Another method, and one less liable to error, consists in sealing up the substance in a tube with strong nitric acid (of sp. gr. 1.52) and heating it for twenty-four hours to about 392° (200° C.); then neutralizing with soda, and after evaporating to dryness, fusing the residue in a platinum dish; after which the amount of sulphate, phosphate, or arseniate can be determined in the usual way.

When a large quantity of sulphur is present, an error may easily occur in the estimation of the amount of carbon, since a portion of the sulphur becomes converted during the process of combustion with cupric oxide into sulphurous anhydride, and this would be condensed by the potash along with the carbonic anhydride, which would thus be estimated in excess. This source of error may be avoided by interposing a short tube filled with peroxide of lead between the tube of calcie chloride and the potash bulbs; the sulphurous anhydride is by this means arrested, and is retained as plumbic sulphate, the anhydride passing into a higher state of oxidation, $PbO_2 + SO_2$ becoming $PbSO_4$.

(1051) *Determination of Chlorine, Bromine, and Iodine.*—When the quantity of chlorine, or of any other halogen, is to be estimated, the substance for analysis is to be mingled with about 10 times its weight of lime, and introduced into a tube of Bohemian glass 10 or 12 inches (25 or 30 centim.) long, and sealed at one end. The tube is filled up with fragments of pure lime, and gradually brought to a red heat, commencing at the open extremity. When the combustion is complete, the tube is corked, its outer surface cleared from ashes, and whilst hot it is plunged into a beaker of cold water. It thus becomes cracked; its contents are then treated with nitric acid, and the chlorine, iodine, or bromine is precipitated from the filtered liquid by means of argentic nitrate.

(1052) *Calculation of the Combining Proportion of an Organic Body.*—We will suppose the labour of analysis thus brought to a successful issue. It is evident that the information derived from this source alone is but scanty; for it furnishes no idea either of the number of atoms of each element entering into the molecule of the organic body, or of the relations of the body to the substances concerned in its production or obtainable from it by its decomposition. Whenever it is possible, the combining proportion of the compound must be determined. This is effected by preparing a compound of the body with some substance the combining proportion of which is well known, and proceeding to analyse the new product. If the organic substance be soluble in water and capable of forming a compound with silver, this compound is for many reasons to be preferred. Silver forms with many organic bodies compounds insoluble or but sparingly soluble in water; and they may generally be obtained by double decomposition, by adding a solution of the nitrate or some soluble salt of silver to an aqueous or alcoholic solution of the substance under examination; the precipitate must then be washed from all adhering impurities. Supposing a silver compound to have been prepared in a state of purity, a gramme or more of it is to be accurately weighed in a counterpoised porcelain crucible. It is then to be carefully incinerated till pure silver alone remains. On again weighing, the loss will give that of the body combined with the silver. The residual silver should be soluble without remainder in nitric acid. From the weight of the metallic silver, the combining number of the organic body that had combined with it may be readily calculated.

An example will best explain the method of proceeding:—

4·873 grms. of silver acetate left
3·149 grms. of metallic silver.

1·724 grms. will therefore express the loss, due to the weight of acetic acid (the acetic acid radicle) combined with silver; then,

3·149 : $\left\{ \begin{array}{l} \text{at. wt. silver.} \\ 108 \end{array} \right. : : 1·724 : x (=59); \text{ and}$

59 = the combining number of acetic acid.

Another example will show the method of calculating the number of atoms of each element in a molecule of the compound:—

By combustion with cupric oxide it is found that 1 gramme of silver acetate yields

| | |
|-----------------------------------|-------------------|
| | Grm. |
| 0.5277 grm. of carbonic anhydride | = 0.1439 carbon |
| 0.1620 grm. of water | = 0.0180 hydrogen |
| And (from previous expt.) . . . | 0.6462 silver |
| The deficiency | = 0.1919 oxygen. |
| | 1.0000 |

Then by proportion :—

| | | | | |
|---------|-----------------|----|-------------|--------------------------|
| Silver. | at. wt. silver. | | { Carbon. | |
| 0.6462 | : 108 | :: | { 0.1439 | : x (= 24), or C_2 . |
| | | | { Hydrogen. | |
| 0.6462 | : 108 | :: | { 0.0180 | : y (= 3), or H_3 . |
| | | | { Oxygen. | |
| 0.6462 | : 108 | :: | { 0.1919 | : z (= 32), or O_2 . |
| | | | Total | = 59 |

From this the formula of glacial acetic acid can be easily deduced, as it contains one atom of hydrogen in the place of the atom of silver in the argentic acetate; argentic acetate = $AgC_2H_3O_2$, and glacial acetic acid = $HC_2H_3O_2$.

In some cases the required compound with silver cannot be obtained: a salt of lead is then, if practicable, substituted for it. The residue after incineration in this case does not consist entirely of metallic lead, nor is it all plumbic oxide. In order to determine the proportion of each, the residue is carefully weighed, and treated with acetic acid in the crucible itself; the plumbic oxide is thus dissolved and washed away. When the contents of the crucible have been carefully dried, a second weighing gives the quantity of metallic lead, whilst the loss furnishes that of the oxide. From the metal, the quantity of oxide to which it is equivalent may be calculated; this, added to the portion dissolved by acetic acid, furnishes the whole quantity of oxide contained in the compound: a calculation, similar to that employed for the silver salt, then supplies the equivalent number of the body analysed. The method is not quite so accurate as the preceding one; it involves more manipulation, and the compounds of lead are apt at a high temperature to undergo loss by volatilization.

Salts of barium or of potassium may be substituted when needful for those of silver or of lead.

Just as the combining number of an acid can be ascertained by determining the amount of any metallic element with which it forms a salt, so may the combining number of a body possessed of marked basic properties—morphia or aniline, for example—be

discovered by causing it to enter into combination with a well-defined acid, such as the hydrochloric, and ascertaining the amount of such acid with which a given weight of the base will unite. The hydrochlorates of many bases form crystallizable double salts with platinum chloride; when this is the case, the double salt is frequently employed in the determination of the combining proportion of the organic base which it contains.

(1053) *Distinction between the Combining Proportion and the Molecular Weight.*—It is comparatively easy to determine the *combining proportion*, or chemical equivalent of compounds possessing decided acid or basic characters, when referred for comparison to some well-known acid, such as the hydrochloric or the nitric; or to some base, such as potash; and up to this point the chemist is strictly within the domain of facts. But these facts do not decide the question of the *molecular weight* of a compound, which is necessarily based on theoretical considerations.

If, for instance, we analyse the normal and neutral potassium tartrate after it has been dried sufficiently to expel the water of crystallization, we shall find that the composition of a quantity of the salt equivalent to KCl, (containing, that is to say, a quantity of potassium equal to that in the amount of chloride represented by the formula KCl), may be expressed by the formula $KC_2H_2O_3$. A second salt of potassium with tartaric acid, the sparingly soluble acid tartrate, may however be obtained; and this, when subjected to analysis, is found to contain, combined with the same amount of potassium as is present in KCl, other elements, in proportions which must be indicated by the formula $KHC_4H_4O_6$. Now if we imagine the potassium of these two salts to be displaced by hydrogen, we obtain two different formulæ, either of which may be the molecular formula for tartaric acid. These formulæ are—1. $HC_2H_2O_3$, and 2. $H_2C_4H_4O_6$. The first of these formulæ indicates the amount of tartaric acid equivalent to the quantity of hydrochloric acid represented by the formula HCl, or of nitric acid expressed by the formula HNO_3 ; yet it is not the true representation of the molecule of tartaric acid, as a further examination of the tartrates will show. The acid is, indeed, dibasic, requiring two atoms of a metallic monad to neutralize it, so that the second formula is the least by which its molecule can be indicated.

Supposing that each of the undermentioned tartrates be sufficiently dried to expel its water of crystallization, the results of their analysis may be expressed by the following formulæ, in which the proportions of carbon and oxygen are alike:—

| | |
|--|--|
| Tartaric acid (hydric tartrate) | $\text{HHC}_4\text{H}_4\text{O}_6$ |
| Cream of tartar (hydric-potassic tartrate) | $\text{KHHC}_4\text{H}_4\text{O}_6$ |
| Normal potassic tartrate | $\text{K}_2\text{C}_4\text{H}_4\text{O}_6$ |
| Potassic-sodic tartrate (Rochelle salt) . | $\text{KNaC}_4\text{H}_4\text{O}_6$ |

Of the two atoms of basylous hydrogen in the first of these four formulæ, one atom only is displaced by a metallic basyl in cream of tartar; but both atoms are displaced by potassium in the normal potassic tartrate; whilst in potassic-sodic tartrate one atom is displaced by sodium, the other by potassium. No such double salts as cream of tartar and Rochelle salt could be formed from the monobasic acid $\text{HC}_2\text{H}_2\text{O}_3$.

The determination of the molecular formula of a body demands a careful investigation of a number of its compounds and derivatives, and frequently exercises all the sagacity of the chemical investigator. The study of the physical properties of a compound often affords great assistance in the determination of its molecular formula; and amongst these physical properties the connexion between the vapour density and the molecular constitution is the most important.

(1054) *Relation of Vapour Density to Molecular Formulæ.*—All bodies in the aeriform condition, whether simple or compound, if compared at equal temperatures, increase by an equal fraction of their volume, for equal increments of temperature (134): in other words, they have the same coefficient of dilatation when heated. In like manner equal bulks of all gases and vapours undergo equal amounts of compression for equal increments of pressure, if the comparison be made under similar circumstances (27). It appears therefore that the elastic force of all gases, whether simple or compound, is equal and uniform; and hence it has been concluded that under similar circumstances of temperature and pressure equal volumes of all gases and vapours contain an equal number of molecules. This is commonly known as Ampère's hypothesis of the constitution of gases.

Assuming then that equal bulks of vapours contain an equal number of their constituent molecules, it is easy, if the vapour density of any compound be known, to calculate its molecular formula; whilst from the molecular formula it is equally easy to calculate the vapour density of the body. In order to calculate the vapour density of any compound from its molecular formula, it is assumed, in accordance with the results of observation, with few exceptions,* that the volume of the molecule of the body in

* Among these exceptions are chlorous anhydride and some of the oxides of nitrogen, as well as many of the salts of ammonia—such as the hydrochlorate,

the state of vapour is double that of the atom of hydrogen; or, that it corresponds to H_2 ; H_2 being the representative of the molecule of hydrogen when in the *free* state. Now, according to Regnault's experiments, the weight of a given bulk of atmospheric air is 14.47 times that of an equal bulk of hydrogen under similar circumstances of temperature and pressure; consequently, doubling this for H_2 (the molecule of free hydrogen), we obtain $\frac{2}{2 \times 14.47} = 0.0691$ as the vapour density, or specific gravity, of hydrogen. And in like manner by dividing the molecular weight m , of any organic compound, by 2×14.47 (or 28.94), we obtain the vapour density d of the compound; $\frac{m}{28.94} = d$. As a necessary consequence, if the weight of an atom of hydrogen be taken as the unit of reference, the relative weight of the molecule of every vapour which occupies $\square \square$ will be represented by half its molecular weight. The term *relative weight* will therefore in this work be employed to indicate the vapour density of a substance when compared with an equal volume of hydrogen under the like conditions of temperature and pressure.

For example, the molecular formula of marsh gas is CH_4 , and its *molecular weight*, or the sum of the atomic weights of its component elements, is 16. Now $\frac{16}{28.94} = 0.55$, and this number agrees with Thomson's experimental determination of the density of the gas.

On the other hand, if the vapour density of a compound be known, and if its percentage composition have been determined, the accuracy of the molecular formula of the body may be checked by reversing the foregoing process; that is to say, by multiplying the vapour density by 28.94, we obtain a very close approximation to the molecular weight, since $d \times 28.94 = m$. The numbers obtained by this calculation are never absolutely correct, owing to unavoidable experimental errors in ascertaining the vapour density; but the errors do not affect the value of the result in controlling the molecular formula; the atomic constitution of the molecule may be safely inferred from the calculated result; and thus the accuracy of the formula deduced from the analytical operations may be checked.

For example, the experimental determination of the specific gravity of the vapour of ether shows it to be 2.586. Now, $2.586 \times 28.94 = 74.26$. The simplest formula deducible from the analysis of ether is $C_4H_{10}O$, and the corresponding molecular weight ($= 74$)

hydrocyanate, and hydrobromate. The anomalies which they present will be considered hereafter.

agrees as closely as can be desired with the result of the calculation from the vapour density.

Important as this subject is, it would exceed our limits to enter further into the methods of checking the correctness of an analysis in its various parts. For fuller information upon this point the reader is referred to Liebig's *Handbook of Organic Analysis*.

(1055) *Distinction between Atomic Weight and Molecular Weight.*—It is obvious that if the atom of oxygen be taken as $O=16$, the formula for the smallest particle of water cannot be less than $H_2O=18$: and in like manner the simplest formula for the atom of sulphuretted hydrogen must be $H_2S=34$; consequently, the formulæ H_2O and H_2S constitute the atomic as well as the molecular formulæ of these bodies.

But though the *atomic weight* of an element or of a compound may sometimes coincide with the *molecular weight*, the two expressions are by no means necessarily synonymous, and are to be carefully distinguished from each other. The atomic weights are the numbers which represent the relative weights of the atoms of the different elements, when referred to some arbitrary but recognized standard, such as the atom of hydrogen = 1. The molecular weights, whether of the elements or of compounds, represent the relative weights of the molecules; and the molecular weight, when once the magnitude of the molecule is agreed upon, is determined by the sum of the weights of all the atoms which enter into the formation of the molecule itself. The molecular formula of a compound body may frequently be ascertained by considerations analogous to those adduced in the cases of water and of sulphuretted hydrogen, when the density of its vapour cannot be ascertained by experiment. (See p. 46.)

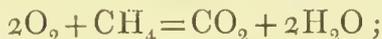
(1056) *On the Use of Molecular Formulæ.*—A knowledge of the fact that the densities of the vapours are exactly in the ratio of their molecular weights facilitates the calculation of the vapour density of a body from its molecular formula; and, conversely, the vapour density affords a valuable control over the calculated molecular formula. The use of molecular formulæ in our equations sometimes renders them less simple in appearance, but by their employment in ordinary equations for the representation of chemical changes, a real simplicity is introduced into our calculations of vapour volume. This affords a strong argument in favour of their uniform employment; for by such a method the gaseous volume of each constituent is at once placed before the eye. If we continue to assume as the unit of volume that of hydrogen H , with the atomic weight 1, the molecule of hydrogen, or H_2 , will

represent \square or 2 volumes. Now the gaseous volume occupied by each molecule of any compound will (with the exceptions already specified) also occupy 2 volumes.

For example, the formulæ H_2 and Cl_2 represent a molecule of hydrogen and of chlorine respectively, whilst HCl represents a molecule of hydrochloric acid; and we see by the equation $H_2 + Cl_2 = 2HCl$, that a molecule of hydrogen and one of chlorine unite without condensation to form 2 molecules of hydrochloric acid; whilst, when oxygen and hydrogen unite to form water, from the equation $O_2 + 2H_2 = 2H_2O$, it is manifest that 1 molecule of oxygen and 2 molecules of hydrogen unite to form 2 molecules of steam, and that the 3 volumes which the gases occupied in their separate condition become condensed into 2 when they have united.

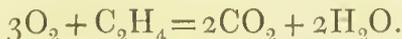
So, again, it is clear from the equation employed, that a similar condensation occurs when carbonic oxide and oxygen unite to form carbonic anhydride; for $O_2 + 2CO = 2CO_2$, 1 molecule of oxygen and 2 of carbonic oxide yielding 2 molecules of carbonic anhydride, 3 volumes again becoming 2 by combination.

Again, when marsh gas is detonated with oxygen, the molecular formula at once gives the volume of oxygen required, and the gaseous products which are obtained:—



1 volume of marsh gas and 2 volumes of oxygen yielding 1 volume of carbonic anhydride and 2 volumes of steam.

If olefiant gas be detonated with oxygen we find that 3 volumes of oxygen and 1 volume of olefiant gas furnish 2 volumes of carbonic anhydride and 2 of steam, as indicated by the molecular formulæ,



The formulæ which express the composition of salts cannot in strictness be regarded as molecular, or formulæ of uniform vapour volumes: they indicate the relative proportions of their constituents in the solid form, and have no reference to gaseous volume.

Some further discussion of the relation between the atom or molecule of elementary and compound bodies will be found in par. 1061, at p. 43.

§ II.—CLASSIFICATION OF ORGANIC COMPOUNDS.

(1057) *General Principles of Classification.*—The classification of the immense variety of compounds that are presented to the

chemist, either naturally by the organs of the living plant or animal, or that are derivable from the bodies so obtained, by the employment of chemical reagents, may be effected upon one of two principles. The first of these, which rests upon analogies of function (according to which bodies are arranged under the head of acids, bases, &c.) might seem to be the more natural; but the second, which is based on the chemical relations of the different compounds, is the truly philosophical system. The first method of arrangement was the only practicable one in the infant state of organic chemistry, and it still presents certain advantages to the student in the early stage of his career; but the second method will eventually prevail, as it greatly facilitates the important study of the true analogies of the different compounds with each other.

The true relations of a great number of bodies to each other have, however, been as yet only imperfectly traced; so that the most devoted admirer of a strictly chemical classification is obliged to make a large appendix of unclassified bodies, and to bring into the more systematically arranged portion of his subject many substances which have but a questionable title to the place accorded to them. Moreover, a rigid adherence to such a principle of classification would lead to the separation of bodies which in their applications and in general properties are closely allied. We shall, therefore, in this, as in other portions of the present work, be guided rather by considerations of convenience than by the rigid requirements of system; and shall endeavour to select such a method of arrangement as shall most facilitate the progress of the student.

For this purpose the various compounds of organic chemistry will be examined in the following order:—

1. Sugar, starch, and ligneous fibre.
2. Alcohols, ethers, and their derivatives.
3. Fats, fixed oils, and their allied acids.
4. Certain organic acids of vegetable origin.
5. Amides and organic bases.
6. Essential oils and resins.
7. Colouring matters.
8. Products of destructive distillation.
9. Cyanogen and its derivatives.
10. Nitrogenized principles of plants and animals.
11. Certain products peculiar to animals.

(1058) *Classification in Homologous Series.*—Before, however, we proceed with this examination it will be advantageous to

illustrate more fully the principle of the chemical classification by means of a few examples. This purpose may be answered by examining the relations of alcohol or spirit of wine to other bodies which resemble it.

1. *Alcohols*.—Alcohol or spirit of wine is the most important member of a group of compounds which manifest a close analogy with each other, both in chemical composition and in the decompositions of which they are susceptible. In the following table the composition of most of the different bodies which may be classed under the generic term of alcohols is exhibited:—

| | $C_n H_{2n+2}O$ | Boiling Point. | |
|-------------------------------------|--|----------------|-------|
| | | ° F. | ° C. |
| Wood spirit | $C H_4 O$ | 149·9 | 65·5 |
| Alcohol (ethyl alcohol) | $C_2 H_6 O$ or $CH_4O + (CH_2)$ | 173·1 | 78·3 |
| Trityl (propyl) alcohol | $C_3 H_8 O$ or $CH_4O + 2 (CH_2)$ | 204·8 | 96 |
| Tetryl (butyl) alcohol | $C_4 H_{10} O$ or $CH_4O + 3 (CH_2)$ | 226·4(?) | 108 |
| Amyl alcohol (fousel oil) | $C_5 H_{12} O$ or $CH_4O + 4 (CH_2)$ | 269·8 | 132·1 |
| Hexyl (caproic) alcohol | $C_6 H_{14} O$ or $CH_4O + 5 (CH_2)$ | 300·2(?) | 149 |
| Octyl (capryl) alcohol | $C_8 H_{18} O$ or $CH_4O + 7 (CH_2)$ | | |
| Lauryl alcohol | $C_{12} H_{26} O$ or $CH_4O + 11 (CH_2)$ | | |
| Cetyl alcohol (ethal) | $C_{16} H_{34} O$ or $CH_4O + 15 (CH_2)$ | | |
| Ceryl alcohol | $C_{27} H_{56} O$ or $CH_4O + 26 (CH_2)$ | | |
| Melissyl alcohol | $C_{30} H_{62} O$ or $CH_4O + 29 (CH_2)$ | | |

Now, on inspecting the formulæ of the alcohols contained in the foregoing table, it will be seen that each of the first six compounds contains a quantity of carbon and of hydrogen less by CH_2 than the compound immediately beneath it: so that each may be regarded as a compound analogous to wood spirit, but containing a certain additional number of multiples of the hydro-carbon CH_2 . Bodies of analogous properties which stand thus related to each other, or which differ by a multiple of CH_2 , are said to be *homologous* (from ὁμοῦς, like, λόγος, a word) because a similar description is applicable to each member of the series. Wood spirit and fousel oil, as well as ethal and ceryl alcohol, are termed *homologues* of wine alcohol. These different compounds may be represented under a common formula, viz., $C_n H_{2n+2} O$, where n represents 1, 2, 3, 4, 5, 6, or any whole number. The boiling point of these homologous bodies, it will be observed, rises with each additional increment of CH_2 by about 33° (18° C.).

(1059) *Collateral Series*.—This principle of classification admits of extension in other directions. Every compound in a homologous series when subjected to the action of chemical reagents furnishes other compounds, differing in composition from

that from which they are obtained, but yet bearing a definite relation to it. For instance, alcohol yields under various circumstances ether, aldehyd, acetic acid, &c.; and these *heterologous* (from ἕτερος different, and λόγος) or differently constituted bodies belong to collateral, and intimately related, but different series: for it is found that the different members of a homologous series exhibit an analogous deportment when submitted to similar chemical reagents, and furnish derivative series in which the homology is still preserved. We may exemplify the formation of these collateral series in the derivatives obtained from the alcohols.

2. *Vinic Acids*.—When ordinary alcohol is mixed with an equal weight of strong sulphuric acid, a large portion of the alcohol and of the acid decompose each other, water is formed, whilst a new compound acid, termed sulphovinic or ethyl-sulphuric acid ($\text{H}_2\text{C}_2\text{H}_5\text{SO}_4$) is produced; one molecule (H_2SO_4) of sulphuric acid acting upon the elements of 1 molecule ($\text{C}_2\text{H}_6\text{O}$) of alcohol, whilst one molecule of water (H_2O) is liberated; $\text{C}_2\text{H}_6\text{O} + \text{H}_2\text{SO}_4 = \text{HC}_2\text{H}_5\text{SO}_4 + \text{H}_2\text{O}$. Now wood spirit, fusel oil, and each of the other alcohols, when similarly treated, furnishes a compound perfectly analogous to ethylsulphuric acid, as is represented in the following table:—

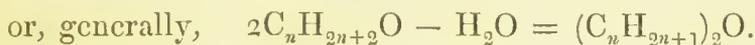
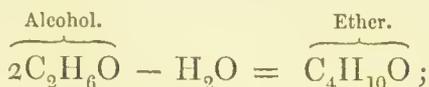
| | |
|--|---|
| Methylsulphuric acid | $\text{H}_2\text{C}_2\text{H}_5\text{SO}_4$ |
| Ethylsulphuric (sulphovinic) acid | $\text{H}_2\text{C}_4\text{H}_9\text{SO}_4$ |
| Tritylsulphuric (propylsulphuric) acid | $\text{H}_2\text{C}_6\text{H}_{13}\text{SO}_4$ |
| Tetrylsulphuric (butylsulphuric) acid | $\text{H}_2\text{C}_8\text{H}_{17}\text{SO}_4$ |
| Amylsulphuric acid | $\text{H}_2\text{C}_{10}\text{H}_{21}\text{SO}_4$ |

the general formula for these vinic acids being $\text{HC}_n\text{H}_{2n+1}\text{SO}_4$.

3. *Ethers*.—If ethylsulphuric acid, or if a mixture of equal volumes of sulphuric acid and alcohol, be exposed to heat in a retort and distilled, a volatile liquid which has been long known under the name of *ether* passes over; and a similar body may be obtained from the other alcohols. The composition of these different ethers is such that they all admit of being represented by formulæ which contain the same elements as two molecules of the alcohol which yields them, minus water in the proportion of 1 molecule, or H_2O ; for example:—

| General formula | = | $(\text{C}_n\text{H}_{2n+1})_2\text{O}$ |
|-------------------------------------|---|---|
| Methylic ether | | $\text{C}_2\text{H}_6\text{O}$ |
| Vinic (or ordinary) ether | | $\text{C}_4\text{H}_{10}\text{O}$ |
| Tritylic (propylic) ether | | $\text{C}_6\text{H}_{14}\text{O}$ |
| Tetrylic (butylic) ether | | $\text{C}_8\text{H}_{18}\text{O}$ |
| Amylic ether | | $\text{C}_{10}\text{H}_{22}\text{O}$ |

the general formula for these ethers being $(C_nH_{2n+1})_2O$; consequently they may be regarded as being formed by the coalescence of the residues of two molecules of the corresponding alcohol after the abstraction of the elements of a single molecule of water; for instance:—



4. *Hydrochloric and other corresponding Ethers.*—If alcohol be treated with hydrochloric, hydrobromic, or hydriodic acid, instead of with sulphuric acid, water is separated, and ethyl chloride, ethyl bromide, or ethyl iodide is formed: for example; $C_2H_6O + HCl = C_2H_5Cl + H_2O$.

The following table exhibits the analogy and the homology of these compounds:—

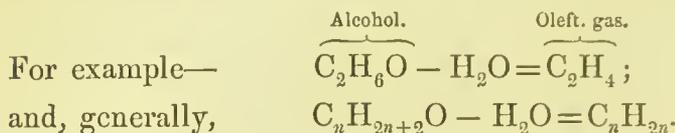
| Compounds. | Chloride. | Bromide. | Iodide. |
|------------------------------|----------------|----------------|---------------|
| Dimethyl . . . $(CH_3)_2$ | $C H_3 Cl$ | $C H_3 Br$ | $C H_3 I$ |
| Diethyl . . . $(C_2H_5)_2$ | $C_2H_5 Cl$ | $C_2H_5 Br$ | $C_2H_5 I$ |
| Ditryl (propyl) $(C_3H_7)_2$ | $C_3H_7 Cl$ | $C_3H_7 Br$ | $C_3H_7 I$ |
| Ditryl (butyl) $(C_4H_9)_2$ | $C_4H_9 Cl$ | $C_4H_9 Br$ | $C_4H_9 I$ |
| Diamyl . . . $(C_5H_{11})_2$ | $C_5H_{11} Cl$ | $C_5H_{11} Br$ | $C_5H_{11} I$ |

5. *Hydrocarbon Radicles of the Ethers.*—When ethyl iodide is sealed up in a strong tube and heated to about 302° (150° C.) in contact with metallic zinc, zincic iodide, and a quantity of a peculiar hydrocarbon $(C_2H_5)_2$ is set at liberty. This substance has been termed *ethyl*, and has been regarded as the basis of ether, which has the composition of an oxide of this hydrocarbon. By analogous means bodies corresponding in composition to the radicles of several of the other ethers have also been isolated. The general formula of the molecule of these compounds when isolated may be represented as $(C_nH_{2n+1})_2$; the atom, or the proportion which enters into combination being represented by C_nH_{2n+1} ; *e.g.*—

| | Molecule. | Atom. |
|---------------------------|-----------------|-------------|
| Methyl | $(C H_3)_2$ | $C H_3$ |
| Ethyl | $(C_2H_5)_2$ | C_2H_5 |
| Trityl (propyl) | $(C_3H_7)_2$ | C_3H_7 |
| Tetryl (butyl) | $(C_4H_9)_2$ | C_4H_9 |
| Amyl | $(C_5H_{11})_2$ | C_5H_{11} |

6. *Homologous Hydrocarbons of the form C_nH_{2n} .*—If alcohol be treated with three or four times its volume of sulphuric acid,

or with phosphoric anhydride, and be distilled, each molecule of alcohol loses all its oxygen and two atoms of hydrogen in the form of water (H_2O), and a gaseous compound of carbon and hydrogen, (C_2H_4), which constitutes olefiant gas, is liberated. A similar hydrocarbon may be obtained from each of the other alcohols.—

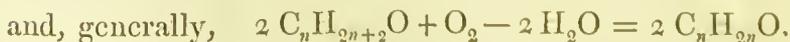
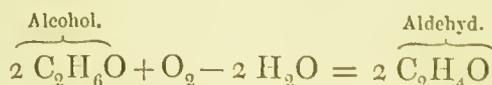


| General formula | = | C_nH_{2n} |
|---------------------------------|---|-------------|
| Ethylene (olefiant gas) | | C_2H_4 |
| Tritylene (propylene) | | C_3H_6 |
| Tetrylene (oil gas) | | C_4H_8 |
| Amylene | | C_5H_{10} |

7. *Aldehyds.*—If alcohol be distilled with black oxide of manganese and diluted sulphuric acid, or with other oxidizing agents the oxidating influence of which can be applied with sufficient slowness and regularity, a very volatile liquid may be obtained (1249), each molecule of which contains the elements of one molecule of alcohol, minus 2 atoms of hydrogen. This substance is known as aldehyd. By similar means, corresponding compounds may be obtained from the other alcohols, these aldehyds possessing the

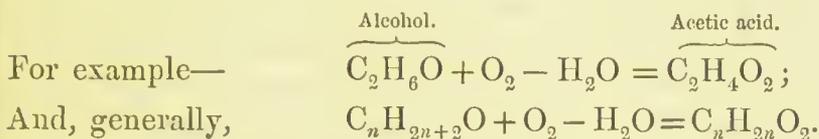
| General Formula | = | $C_nH_{2n}O$ |
|---------------------------------|---|--------------|
| Formic aldehyd | | $C H_2O$ |
| Acetic aldehyd | | C_2H_4O |
| Propionic aldehyd | | C_3H_6O |
| Butyric aldehyd (butyral) . . . | | C_4H_8O |
| Valeric aldehyd (valeral) . . . | | $C_5H_{10}O$ |

the action of oxygen in the proportion of one atom (=O) upon one molecule of any alcohol is to convert it into an aldehyd, with the removal of one molecule of water (H_2O);



8. *Homologous Volatile Acids.*—The aldehyds are neutral substances, but they absorb oxygen rapidly from the air, in the proportion of 1 atom for each molecule of the aldehyd, and thus become converted into powerful monobasic acids, the general formula of these acids being, $H, C_nH_{2n-1}O_2$, or $C_nH_{2n}O_2$. These

acid compounds are therefore derived by a process of oxidation from the alcohols; the formation of the aldehyd being the intermediate stage in their production. Each molecule of the alcohol, when acted on by oxygen in the proportion of O_2 , is converted into one molecule of a corresponding volatile acid, whilst two atoms of hydrogen are eliminated in the form of water:—



The volatile fatty acids belong to this series, which is indeed more complete than that of the alcohols. Compounds of several of these acids exist in many of the vegetable and animal fats and oils; but chemists have not as yet succeeded in obtaining a simple general method of reconverting the fatty acids into alcohols, though the alcohols are readily converted into their corresponding acids. The more important of these acids are the following:—

| General Formula | = | $HC_nH_{2n-1}O_2$ | or | $C_nH_{2n}O_2$ |
|-----------------------|---|----------------------|----|---------------------|
| Formic acid | | $HC H O_2$ | or | $C H_2 O_2$ |
| Acetic | | $HC_2 H_3 O_2$ | or | $C_2 H_4 O_2$ |
| Propionic | | $HC_3 H_5 O_2$ | or | $C_3 H_6 O_2$ |
| Butyric | | $HC_4 H_7 O_2$ | or | $C_4 H_8 O_2$ |
| Valeric | | $HC_5 H_9 O_2$ | or | $C_5 H_{10} O_2$ |
| Caproic | | $HC_6 H_{11} O_2$ | or | $C_6 H_{12} O_2$ |
| Enanthylic | | $HC_7 H_{13} O_2$ | or | $C_7 H_{14} O_2$ |
| Caprylic | | $HC_8 H_{15} O_2$ | or | $C_8 H_{16} O_2$ |
| Pelargonic | | $HC_9 H_{17} O_2$ | or | $C_9 H_{18} O_2$ |
| Capric | | $HC_{10} H_{19} O_2$ | or | $C_{10} H_{20} O_2$ |
| Lauric | | $HC_{12} H_{23} O_2$ | or | $C_{12} H_{24} O_2$ |
| Myristic | | $HC_{14} H_{27} O_2$ | or | $C_{14} H_{28} O_2$ |
| Palmitic | | $HC_{16} H_{31} O_2$ | or | $C_{16} H_{32} O_2$ |
| Stearic | | $HC_{18} H_{35} O_2$ | or | $C_{18} H_{36} O_2$ |
| Cerotic | | $HC_{27} H_{53} O_2$ | or | $C_{27} H_{54} O_2$ |
| Melissic | | $HC_{30} H_{59} O_2$ | or | $C_{30} H_{60} O_2$ |

The molecule of each of these acids furnishes 2 volumes of vapour, $\square\square$, (if $H=1$ represent 1 vol., \square), and it requires 1 atom of a monad metal like potassium for its saturation.

This group of acids, which is one of the most complete of the homologous series, illustrates in a very interesting manner the general similarity in properties which always exists in homologous bodies. This statement may appear paradoxical when the extreme terms of the series are compared together, since formic acid is an

exceedingly pungent, corrosive, volatile liquid, which requires cooling below 32° (0° C.) in order to render it solid, and it is miscible with water in all proportions; whilst melissic acid requires a temperature of $192^{\circ}\cdot 2$ (89° C.) for its fusion, is insoluble in water, and has the properties of a fat. But if we compare together the contiguous terms of the series, such as the formic with the acetic, the acetic with the propionic acid, and so on, no abrupt change in properties will be perceived between the contiguous terms; as the proportion of carbon and hydrogen increases, each becomes gradually less and less volatile, less fusible, less susceptible of solution in water, until we reach the true fatty acids. Now this similarity in properties, which is observed equally in other groups of homologous substances,* naturally leads to the supposition that

* Table to illustrate the Arrangement of

| Hydrocarbons. $C_n H_{2n}$ | Positive Radicles. $C_n H_{2n+1}$ or when free $(C_n H_{2n+1})_2$ | Simple Ethers. $C_n H_{2n+1} \} O$ $C_n H_{2n+1} \} O$ | Sulphides. $C_n H_{2n+1} \} S$ $C_n H_{2n+1} \} S$ | Chlorides. $C_n H_{2n+1} Cl$ | Alcohols. $C_n H_{2n+2} O$ or $C_n H_{2n+1} \} O$ H |
|-------------------------------|--|--|--|---------------------------------|---|
| 1. $C H_2$ | $(C H_3)_2$ | $(C H_3)_2 O$ | $(C H_3)_2 S$ | $C H_3 Cl$ | $C H_3 HO$ |
| 2. $C_2 H_4$ | $(C_2 H_5)_2$ | $(C_2 H_5)_2 O$ | $(C_2 H_5)_2 S$ | $C_2 H_5 Cl$ | $C_2 H_5 HO$ |
| 3. $C_3 H_6$ | $(C_3 H_7)_2$ | | | $C_3 H_7 Cl$ | $C_3 H_7 HO$ |
| 4. $C_4 H_8$ | $(C_4 H_9)_2$ | $(C_4 H_9)_2 O$ | | $C_4 H_9 Cl$ | $C_4 H_9 HO$ |
| 5. $C_5 H_{10}$ | $(C_5 H_{11})_2$ | $(C_5 H_{11})_2 O$ | $(C_5 H_{11})_2 S$ | $C_5 H_{11} Cl$ | $C_5 H_{11} HO$ |
| 6. $C_6 H_{12}$ | $(C_6 H_{13})_2$ | | | | $C_6 H_{13} HO$ |
| 7. $C_7 H_{14}$ | | | | | $C_7 H_{15} HO$ |
| 8. $C_8 H_{16}$ | | | | $C_8 H_{17} Cl$ | $C_8 H_{17} HO$ |
| 9. $C_9 H_{18}$ | | | | | |
| 10. $C_{10} H_{20}$ | | | | | |
| 11. | | | | | |
| 12. | | | | | $C_{12} H_{25} HO$ |
| 13. | | | | | |
| 14. | | | | | |
| 15. | | | | | |
| 16. $C_{16} H_{32}$ | | $(C_{16} H_{33})_2 O$ | $(C_{16} H_{33})_2 S$ | $C_{16} H_{33} Cl$ | $C_{16} H_{33} HO$ |
| 17. | | | | | |
| 18. | | | | | |
| 19. | | | | | |
| 20. $C_{20} H_{40}$ | | | | | |
| 27. $C_{27} H_{54}$ | | | | | $C_{27} H_{55} HO$ |
| 30. $C_{30} H_{60}$ | | | | | $C_{30} H_{61} HO$ |
| Relation to Hydrogen | H } H } | H } H } O | H } H } S | HCl | H } H } O |

A somewhat similar hypothesis might be extended to the different alcohols themselves (1124).

It will be perceived that all these groups, derived from the alcohols by decomposition, are produced by an analogous decomposition of the several alcohols, and that they all preserve a strict homology in their respective groups. This will be more easily traced by the aid of the table in the preceding page, in which the different classes of compounds just described are so arranged that all those compounds which are placed in the same vertical column are homologous; whilst those which are placed in different columns are heterologous, or dissimilar in molecular constitution and in chemical characters. But it will be seen that those bodies in the same horizontal line are all related to the same alcohol; they are all formed from it by reactions similar to those by which each of the corresponding compounds in the other horizontal lines are formed from their alcohol.

Exceptions to this uniformity occur in the last column in the case of the compound ethers, the formula for which, in the majority of instances, represents the ether formed by the union of the acid with ethyl ether, since these compounds have been more generally formed and studied than any other kind of compound ether; though in a few instances the compound ether resulting from the union of the acid of the series with its corresponding ether, is given, and there can be no doubt that such ethers might in all cases be formed if any sufficient inducement to their preparation existed; or if the necessary materials could be had in sufficient quantity.

The column headed *mercaptans* contains a series of compounds which correspond to the alcohols, and are strictly analogous to them; they contain sulphur in the place of oxygen; the *sulphides* are analogous in like manner to the ethers; and there are *bromides* and *iodides*, which are not included in the table, analogous to the chlorides. The quantities represented by the formulæ given in the table yield, in all cases where the compound is volatile without decomposition, 2 volumes of vapour, $\square\square$, if $H=1$ be taken as 1 vol, \square . In this table many blanks occur, which could in most cases be filled up if the compounds which correspond to them presented sufficient interest to induce the chemist to prepare them. New compounds are indeed being continually added to the list. By thus mapping out the territory which has been explored, the progress of future research is materially aided, and each new compound, as it is discovered, more readily falls into its true place, while its relations to other bodies previously known are anticipated, and readily verified.

Exact observations upon the crystalline form of homologous bodies are still wanted; but it appears that in many cases homologous compounds are isomorphous, though this is not by any means uniformly true. The baric methyl-sulphate and ethyl-sulphate appear to be isomorphous; such is the case also with the alums formed with aluminic sulphate by the sulphates of the alcohol bases, methylica, ethylica, amylica, and trimethylica; but the double salts formed by the hydrochlorates of these bases with platinic chloride are decidedly not isomorphous. The double salt of trimethylica hydrochlorate and platinic chloride is isomorphous with the corresponding salt of ammonia; but the corresponding double salt of ethylica crystallizes in rhombohedra, and that of diethylica in oblique prisms.

(1060) *Theory of Compound Radicles.*—Liebig explained the similarity in properties between the terms of homologous series by supposing the existence in each, of a certain group of elements which he regarded as the radicle of the series. He, in fact, made the theory of *compound radicles*,* as it is termed, the basis of his classification, and defined organic chemistry to be the chemistry of compound radicles. According to this supposition, the basis of each ether is a hydrocarbon, from which all the *heterologous* bodies of the series, or bodies not analogous in composition, are derived: for example,

| <i>Compound Radicle.</i> | <i>Ether, or Oxide of the Radicle.</i> |
|--|--|
| Methyl (CH ₃) | Methylic ether . . (C H ₃) ₂ O |
| Ethyl (C ₂ H ₅) | Ethylic ether . . (C ₂ H ₅) ₂ O |
| Amyl (C ₅ H ₁₁) | Amylic ether . . (C ₅ H ₁₁) ₂ O |
| <hr/> | |
| <i>Alcohol, or Hydrated Oxide.</i> | <i>Compound Ether.</i> |
| Wood spirit . . . (C H ₃) HO | Methyl formiate . . (CH ₃) (CH)O ₂ |
| Alcohol (C ₂ H ₅) HO | Ethyl acetate . . (C ₂ H ₅) (C ₂ H ₃)O ₂ |
| Fousel oil (C ₅ H ₁₁)HO | Amyl valerate . . (C ₅ H ₁₁) (C ₅ H ₉)O ₂ |

Upon this theory the simple ethers are oxides of the peculiar electro-positive hydrocarbon which forms the radicle of the series; the alcohols are the hydrated oxides of the same radicle, and the so-called hydrochloric, hydrobromic, hydriodic, and hydrosulphuric ethers, are compounds in which chlorine, bromine, iodine, or sulphur have united with the radicle—just as in the corresponding compounds of a metal; in the ethyl series, for instance, the compound group termed ethyl (C₂H₅) discharges a function in these

* The German term *radikal* (from the Latin *radix*, a root) is commonly, but inaccurately, translated *radical*, which is properly an adjective, the word *radicle* being the appropriate rendering.

compounds analogous to that of potassium in the salts of this metal : so that calling ethyl (C_2H_5) = Et, the two series would run as follows:

| | | | |
|-------------------|--------|-------------------|---------|
| Potassic oxide . | K_2O | Ethyl oxide . . | Et_2O |
| Potassic chloride | KCl | Ethyl chloride . | $EtCl$ |
| Potassic iodide . | KI | Ethyl iodide . . | EtI |
| Potassic sulphide | K_2S | Ethyl sulphide . | Et_2S |
| Potassic hydrate | KHO | Ethyl hydrate . . | $EtHO$ |

The mercaptans correspond in composition to alcohol in which the place of the oxygen is supplied by sulphur ; whilst the compound ethers, such as the formic, the acetic, and the valeric, are regarded in the light of salts, in which the hydrogen of the formic, the acetic, or valeric acid is displaced by methyl, ethyl, or some other compound radicle, by which its acid properties are completely neutralized.

It is true that the theory of compound radicles supposes the existence of a number of substances which have not been isolated, and also of many which probably have no separate existence. The theory indeed cannot be supposed to afford a correct representation of the molecular constitution of organic bodies ; but it is a convenient fiction, which materially facilitates the retention of their composition in the memory, and the comprehension of the metamorphoses which such compounds experience. One of the first groups to which it was systematically applied by Liebig and Wöhler was that derived from the essential oil of bitter almonds. This oil was regarded by these chemists as containing an organic radicle, to which they gave the name of benzoyl (C_7H_5O), and which may be conveniently distinguished by the symbol Bz. Although unsuccessful in the attempt to isolate this radicle, they succeeded in transferring the group of which it was supposed to consist from one elementary substance to another, and in causing it to enter into combination with other organic groups ; and by the aid of this hypothesis they were enabled to give as simple and intelligible an account of the mode in which the compounds derived from the oil were formed, as though they had been dealing with the salts or other compounds of a metal. The advantages thus obtained may be rendered evident by comparing the empirical formulæ of some of these compounds with those in which the same bodies are represented as containing the organic radicle :—

| | Empirical Formula. | $C_7H_5O=Bz$ |
|-------------------------|-----------------------|-------------------------------------|
| Oil of bitter almonds . | C_7H_6O | BzH, Benzoyl hydride |
| Benzoic acid | $C_7H_6O_2$ | H BzO, Benzoyl hydrate |
| Chlorinated compound . | C_7H_5OCl | BzCl, Benzoyl chloride |
| Sulphur compound . . | $C_7H_5O_2S$ | Bz ₂ S, Benzoyl sulphide |
| Cyanogen compound . | C_7H_5ON | BzCy, Benzoyl cyanide |

It is, moreover, to be observed, that many substances corresponding in composition to certain of the organic radicles may be isolated. The existence of cyanogen as an electro-negative organic radicle, and the remarkable analogy in its mode of combination to that of chlorine and the halogens, were known long before Liebig had attempted to generalize the theory of organic radicles. Bunsen subsequently isolated kakodyl $(C_2H_6As)_2$, which is an excellent representative of the electro-positive class of radicles, and other bodies of analogous composition have since been obtained; whilst several compounds having the composition of such radicles as ethyl and methyl, which are supposed to form the bases of the alcohols and ethers, have been obtained in a separate form by Frankland and others.

(1061) *Theory of Isolated Radicles—Atoms and Molecules.*—The recent progress of research has nevertheless rendered it very probable that the bodies thus isolated are not really the radicles that they were once supposed to be. Later writers indeed usually follow Gerhardt, who expressly rejects isolability as constituting any part of the idea of a radicle (*Traité*, t. iv. p. 569). He says: "Let it be clearly understood that, in speaking of a radicle, I do not indicate any substance under the form and with the properties which it would have in an isolated condition; but I distinguish by it simply the proportion in which certain elements, or groups of elements, may be substituted for others, or may be transferred from one body to another in the process of double decomposition."

A radicle may consist of a single elementary atom, and it then forms a *simple radicle*; or it may consist of a group of atoms, in which case it constitutes a *compound radicle*.

A body when in combination presents characters and properties very different from those which it exhibits in what is usually regarded as its free or isolated condition. The chemical attractions of bodies in their 'nascent state,' or at the moment of their liberation from combination with others, are by all chemists admitted to be much more active than those which they possess in their 'free state.'

In fact, it appears to be highly probable that at least the monad elementary substances in their uncombined condition are unknown to us,—such so-called elementary bodies being really compounds of at least two atoms of the true element with each other. Hydrogen gas, upon this view, is not simply H, but is H_2 or $\left. \begin{array}{c} H \\ H \end{array} \right\}$, or hydride of hydrogen, *dihydrogen*; metallic potassium

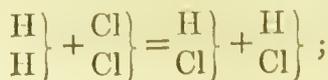
is not simply K, but K_2 , or $\left. \begin{matrix} K \\ K \end{matrix} \right\}$, potasside of potassium, or *dipotassium*; in like manner chlorine gas $\left. \begin{matrix} Cl \\ Cl \end{matrix} \right\}$ is chloride of chlorine, or *dichlorine*. This hypothesis has also been extended to the monatomic so-called compound organic radicles; cyanogen gas being not CN, but $\left. \begin{matrix} CN \\ CN \end{matrix} \right\}$, or cyanide of cyanogen (*dicyanogen*); and liquid kakodyl is $\left. \begin{matrix} Kd \\ Kd \end{matrix} \right\}$, or kakodylide of kakodyl (*dikakodyl*). Indeed, it admits of experimental proof in many cases, as in that of methyl (1204), that the formula which represents the molecule of the compound must be thus doubled, the molecule of methyl being truly $\left. \begin{matrix} CH_3 \\ CH_3 \end{matrix} \right\}$, or dimethyl; that of ethyl being $\left. \begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix} \right\}$, or diethyl; that of acetic anhydride, $\left. \begin{matrix} C_2H_3O \\ C_2H_3O \end{matrix} \right\} O$, or acetic acetate; and so on.

The important influence which this view has exerted and is still exerting upon the progress of the science, renders it necessary to develop it somewhat further.

A distinction has already been drawn (p. 28, Part I.) between, 1. the *Atom*, or smallest and chemically indivisible particle of each element which can exist in a *compound* united with other particles either of the same or of different kinds of matter, but which is not known in a separate form; and 2, the *Molecule*, or the smallest quantity of any elementary substance which is capable of existing in a *separate form*. H, for instance, indicates the *atom* of hydrogen, whilst $\left. \begin{matrix} H \\ H \end{matrix} \right\}$ represents its *molecule*.

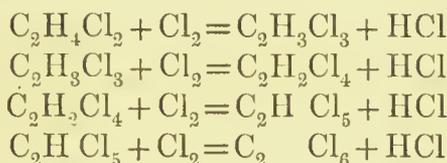
The molecule of a compound must, it is obvious, consist of at least two atoms, since it cannot consist of less than one atom of at least two different kinds of matter; and in like manner it is probable that the molecules of the bodies hitherto described as isolated elements are, at least in the case of the monads, and triads, compounds of the element with itself. If this view be correct, it must happen that when such bodies unite with other so-called elements of the same group, the act of combination is in most cases attended by double decomposition, and not by direct union.

When, for example, hydrogen and chlorine unite to form hydrochloric acid, the change should be thus represented:—



the equation indicating that one of the atoms of hydrogen in the molecule of this gas changes places with one of the atoms of chlorine in the molecule of chlorine gas; and the result is, the formation of *two* molecules of hydrochloric acid gas.*

In further justification of this view, it may be stated as a uniform result of observation, that in all the reactions in which chlorine gas is concerned, not one is known in which less than two atoms of chlorine is required. Take, for example, the successive steps of the action of chlorine upon Dutch liquid (488):—



and the same is true in all other cases. Hence it has been concluded on chemical grounds, independently of physical considerations equally strong, that the smallest particle of chlorine which can exist in the free state—its molecule, in short—must contain two atoms of chlorine.

A similar necessity for the presence of at least two atoms of bromine, and of iodine, has been observed in every reaction in which they take part; and the same thing is true of hydrogen and of all the metals which correspond to hydrogen in atomic character. Many of the simpler compound substances may be indeed looked upon as intermediate between the elements or the radicles which enter into their formation; as for instance,

| | |
|--------------------------|----------------------|
| 1. Hydrogen . . . HH | Sodium . . . NaNa |
| 2. Hydrochloric acid HCl | Sodic iodide . . NaI |
| 3. Chlorine . . . ClCl | Iodine . . . II |

| | |
|---------------------------|---|
| 1. Potassium . . . KK | Bromine . . . BrBr |
| 2. Potassic cyanide K(CN) | Ethyl bromide . . (C ₂ H ₅)Br |
| 3. Cyanogen . (CN) (CN) | Ethyl . . . (C ₂ H ₅) (C ₂ H ₅) |

In like manner the hydrated alkalis and the ordinary acids may be regarded as compounds intermediate between water and the anhydrous oxides. So also hydric-potassic sulphide is intermediate between sulphuretted hydrogen and dipotassic sulphide,

* Sir B. Brodie explains this phenomenon by a different hypothesis, for the development of which the reader is referred to his paper, "On the Calculus of Chemical Operations." (*Phil. Trans.* 1866, 781).

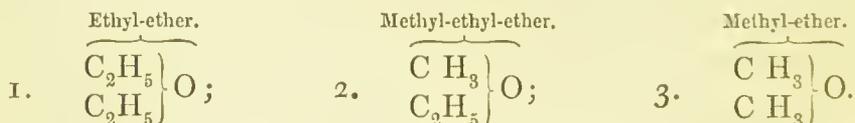
and mereaptan between sulphuretted hydrogen and diethyl sulphide :—

| | | | | |
|-------------------------------|-----|--|----------------------------------|-------|
| 1. Water | HHO | | Water | HHO |
| 2. Potassic hydrate | KHO | | Hypochlorous acid | HClO |
| 3. Anhydrous potash | KKO | | Hypochlorous anhydride | ClClO |

| | | | | |
|---------------------------------------|-----|--|--|------------------------------------|
| 1. Sulphuretted hydrogen | HHS | | Sulphuretted hydrogen | HHS |
| 2. Hydric-potassic sulphide | KHS | | Mercaptan | H(C ₂ H ₅)S |
| 3. Dipotassic sulphide | KKS | | Diethyl sulphide (C ₂ H ₅)(C ₂ H ₅)S | |

And upon this view an argument has been founded for regarding the formula of water as H₂O, and not as HO, and that of sulphuretted hydrogen as H₂S, not HS. (O=8, and S=16.)

It is indeed frequently upon the formation of such intermediate compounds that the most probable inference respecting the magnitude of the molecule of a body, the vapour density of which cannot be ascertained, is founded; for in no case can any such intermediate compound be formed, unless two atoms of each of the original bodies concerned in the reaction take part in the metamorphoses under consideration. For example, it is hence urged that the molecule of ethylic (or ordinary) ether cannot be less than (C₄H₁₀O) because of the existence of the compound methyl-ethyl ether, which is a body intermediate between ethyl ether and methyl ether: for we have



It must not, however, be supposed that there is no such thing as direct combination between two bodies: the molecules of compounds frequently exhibit the power of uniting in this manner, in which case the number of molecules of the new body is smaller than the sum of those of its components: in other words, condensation occurs. When, for instance, 1 molecule of carbonic oxide and 1 of chlorine unite, they form 1 molecule of carbon oxychloride; $\text{CO} + \text{Cl}_2$, yielding COCl_2 . One molecule of mercury and 1 of chlorine yield 1 of corrosive sublimate; $\text{Hg} + \text{Cl}_2 = \text{HgCl}_2$; and 1 molecule of ethylene and 1 of bromine yield 1 of ethylene dibromide; $\text{C}_2\text{H}_4 + \text{Br}_2 = \text{C}_2\text{H}_4\text{Br}_2$. In like manner, ammonia and hydrochloric acid gases combine directly; $\text{H}_3\text{N} + \text{HCl}$ becoming H_4NCl . Nitric oxide with oxygen forms nitrogen dioxide; $\text{NO} + \text{O}$ becoming NO_2 . Antimonious chloride and chlorine yield antimonie chloride; $\text{SbCl}_3 + \text{Cl}_2 = \text{SbCl}_5$. It

may indeed be stated as a general rule, that whenever a body formed upon the type of ammonia combines with a body formed on the type of hydrochloric acid, that direct or *additive* combination occurs: though these are not the only compounds which exhibit this tendency; for example, aldehyd (C_2H_4O) combines directly with 1 atom of oxygen to form acetic acid, ($C_2H_4O_2$). Double salts belong to a different category, although nearly always formed by this additive process, as when platinic chloride and potassic chloride unite, $2KCl + PtCl_4$ yielding $2KCl, PtCl_4$: because, so far as we know, such combination exists only so long as the compound is in the solid form; whereas the other bodies, previously cited, are known in the aeriform condition, in which state the relations by volume of the molecules of different compounds are definite, whilst we know but little of the relative volumes of solid molecules.

(1062) *Arguments for doubling the Atomic Weight of Oxygen.*— We can now review with advantage the chemical line of argument which has induced chemists to adopt the proposal of Gerhardt to double the atomic weight of oxygen, of sulphur, and of carbon, and of several other important elements.

It is urged in the case of oxygen and sulphur, for example, that there is a marked distinction between the number of the compounds which these elements form with other bodies, as compared with the compounds which chlorine and bromine are known to form with the same bodies. There are, in fact, numerous oxides and sulphides which have no corresponding representatives among the chlorides and bromides. This will be rendered evident by an examination of the following table, where a certain number of the compounds of each of these elements are enumerated.

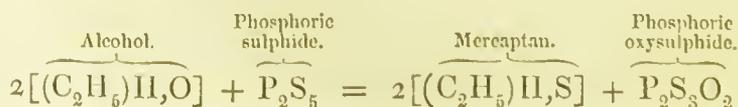
In all cases, intermediate oxides and sulphides, such as those shown at 2, 4, 5, 7, 8, and 9, may be traced, whilst in no case can any intermediate chlorides or bromides be formed: in other words two different radicles may be united into one compound when oxygen or sulphur is combined with them; whilst this is never the case with chlorine or with bromine. Hence it is argued, that the quantities of oxygen and of sulphur indicated by O and S in the foregoing formulæ are not really two atoms, as was formerly supposed, but rather that they represent an indivisible whole, or, in fact, *one* atom. In consequence of this, two atoms of each of the other elements or radicles are united with O or S, and are held together as one group, owing to the indi-

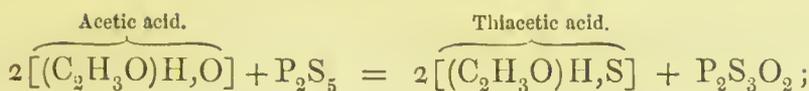
visibility of the quantities of the elements represented by the symbols O and S. On the other hand, the non-existence of such intermediate compounds, or compounds containing two *different* elements or radiels, amongst the chlorides and the bromides, is an indication that no such cause of union exists in the atomic constitution of chlorine and of bromine; but that the quantities represented respectively by the symbols Cl and Br correspond truly to the atoms of these bodies.

| | Oxides. | Sulphides. | Chlorides. | Bromides. |
|-----|--|---|--|---|
| 1. | Water HHO | Sulphuretted hydrogen HHS | Hydrochloric acid HCl | Hydrobromic acid HBr |
| 2. | Caustic potash KHO | Hydric-potassic sulphide HKS | Wanting. | |
| 3. | Anhydrous potash KKO | Dipotassic sulphide KKS | Potassic chloride KCl | Potassic bromide KBr |
| 4. | Alcohol (C ₂ H ₅)H,O | Mercaptan (C ₂ H ₅)H,S | Wanting. | |
| 5. | Potassium alcohol (C ₂ H ₅)K,O | Potassic mercaptide (C ₂ H ₅)K,S | Wanting. | |
| 6. | Ether (C ₂ H ₅) (C ₂ H ₅)O | Diethyl sulphide (C ₂ H ₅) (C ₂ H ₅)S | Ethyl chloride (C ₂ H ₅)Cl | Ethyl bromide (C ₂ H ₅)Br |
| 7. | Acetic acid (C ₂ H ₃ O)H,O | Thiacetic acid (C ₂ H ₃ O)H,S | Wanting. | |
| 8. | Argentiacetate (C ₂ H ₃ O)Ag,O | Argentiacetate (C ₂ H ₃ O)Ag,S | Wanting. | |
| 9. | Acetic ether (C ₂ H ₃ O) (C ₂ H ₅)O | Thiacetic ether (C ₂ H ₃ O) (C ₂ H ₅)S | Wanting. | |
| 10. | Acetic anhydride (C ₂ H ₃ O) (C ₂ H ₃ O)O | Thiacetic anhydride (C ₂ H ₃ O) (C ₂ H ₃ O)S | Acetyl chloride (C ₂ H ₃ O)Cl | Acetyl bromide (C ₂ H ₃ O)Br |

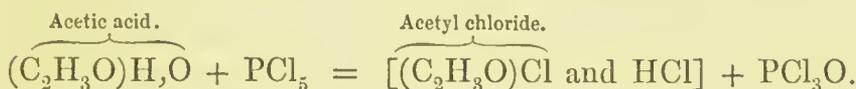
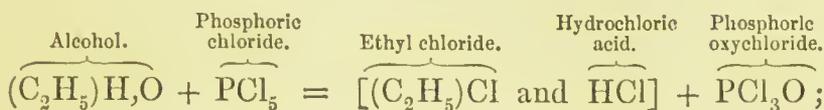
The different metamorphoses which many bodies undergo under the influence, on the one hand, of certain sulphuretted, and on the other of certain chlorinated compounds, have been further adduced in support of this view.

When, for instance, alcohol or acetic acid is acted upon by a sulphuretted body such as diphosphorus pentasulphide, a *single* new sulphuretted organic body is formed; but when the same compounds are acted upon by a body which furnishes chlorine, such as phosphoric chloride, *two* new chlorinated derivatives are produced; for example —





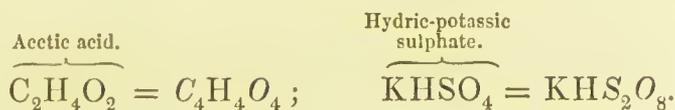
whilst



The groups C_2H_5 and H, on the one hand, and the groups C_2H_3O and H on the other, are held together by the indivisible quantity O or S; whilst they separate into two distinct bodies as soon as chlorine takes the place of the oxygen, because the quantity of chlorine (Cl_2) which displaces the quantity of oxygen (O) is really not a single atom, but two atoms.

Analogous reasoning may be extended to the case of the compounds of carbon, the atomic weight of which has also been doubled on similar grounds.

Selenium and tellurium, from their analogy with sulphur, are also indicated with doubled atomic weights; and we have already, on other grounds, shown the advantage of doubling that of silicon and of many of the metals. If it be desired to translate formulæ written with the new symbols into those formerly made use of, it is simply necessary to multiply the numbers of the atoms of oxygen, sulphur, carbon, silicon, and the dyad elements by 2, whilst the monads and triads remain unaltered; for instance:—



(1063) *Chemical Types*.—The homologous series of the alcohols which has already been briefly reviewed (1059) has its representatives among the simpler compounds contained in the department of inorganic chemistry; for by deducting (CH_2) from the formula of each atom of methyl and the compounds of the methylic group (contained in the horizontal line 1 in the Table, p. 38), we arrive at hydrogen and some of its most important compounds of simple constitution. For example, the double atom or molecule of dimethyl, if deprived of 2 (CH_2) would leave a residue consisting of hydrogen only; $(CH_3)_2 - 2(CH_2) = H_2$. The molecule of methylic ether deprived of 2 (CH_2) would leave water; $(CH_3)_2O - 2(CH_2) = H_2O$: the residue from each molecule of methyl sulphide and of methylic mereaptan would be sulphuretted hydrogen.

Methyl chloride after a deduction of CH_2 would leave the elements of hydrochloric acid. Hence it appears that the radicles methyl, ethyl, trityl, tetryl, amyl, &c., are bodies which correspond to hydrogen, and that they may be regarded as homologues of a series in which hydrogen forms the lowest term; that the simple ethers and alcohols are homologues of water, whilst the chlorides and iodides are homologues of hydrochloric and hydriodic acid, and the sulphides and mereaptans are homologues of hydrosulphuric acid. Water, hydrochloric and hydrosulphuric acid may, therefore, be regarded as the patterns or *types* upon which these several bodies are formed.

This idea of referring organic compounds to some simple representative or type was systematically worked out by Laurent and by Gerhardt.

The four principal types to which most of the compounds of organic chemistry are referred are the following:—

- | | | | | |
|--|---|--|-----------------|-----------------------------|
| 1. The hydrogen or metallic type | . | $\left. \begin{array}{l} \text{H}' \\ \text{H}' \end{array} \right\}$ | , | or H_2 ; |
| 2. The oxide or water type | . | $\left. \begin{array}{l} \text{H}' \\ \text{H}' \end{array} \right\}$ | O'' | , or H_2O ; |
| 3. The nitride or ammonia type | . | $\left. \begin{array}{l} \text{H}' \\ \text{H}' \\ \text{H}' \end{array} \right\}$ | N''' | , or H_3N ; |
| 4. The marsh gas type. | . | $\left. \begin{array}{l} \text{H}' \\ \text{H}' \\ \text{H}' \end{array} \right\}$ | C ^{iv} | , or H_4C . |

It is important to remark, that many bodies are referred to the same type, though they present no analogy in chemical properties, either to it or to each other. The various radicles which have been proved or assumed to exist in organic compounds vary in character as much as the elementary bodies themselves. Some, like cyanogen (CN), being strongly electro-negative, may be arranged with chlorine, oxygen, and sulphur, on the right-hand side of a double converging series; such as the following:—

| | |
|------------|-----------|
| POTASSIUM. | CHLORINE. |
| SODIUM. | OXYGEN. |
| CALCIUM. | SULPHUR. |
| IRON. | GOLD. |
| &c. | &c. |
| ANTIMONY. | |
| ARSENICUM; | |

whilst others, like aldehyd and acetone, agree with arsenieum and antimony in occupying a central or intermediate position; and others, like kakodyl (C_2H_6As) and the metallie derivatives of alcohol, would be arranged with the electro-positive bodies, potassium, sodium, calcium, &c., on the left-hand side of such a series. When we compare together different compounds belonging to the same series, a progressive change in properties is observed, so that the differences observable between any two such compounds become greater, the wider is the interval between the respective places in the series of the two terms submitted to the comparison. Following this idea to its extreme limits, the same type may therefore comprehend bodies belonging to the three classes of acids, of bases, and of neutral bodies; the acids or electro-negative bodies being at one extremity of the series, and the neutral bodies occupying the intermediate positions, provided that the bases or electro-positive bodies be arranged at the opposite extremity.

These types are to be regarded as *types of double decomposition*; and are chiefly useful as representing the fact that the bodies which are referred to them experience a similar mode of decomposition when subjected to the action of the same chemical reagents.

The application of these types to the compounds of organic chemistry will be best understood by means of a few examples:—

1. *The Hydrogen or Metallic type* $\left\{ \begin{array}{l} H' \\ H' \end{array} \right.$

To this class may be referred the monad metals, as well as the dyad metals, such as zinc and cadmium, of which the molecule consists of a single atom; and amongst organic compounds, the radicles of the monatomic alcohols, the hypothetical oxidized radicles of the monatomic acids, certain bodies formed by the union of two different monatomic radicles, such as the aldehyds and the ketones, as well as the dyad organic radicles of which the molecule consists of a single compound atom, such as ethylene—*e.g.*

| | |
|---------------------------------------|---|
| Potassium | $\left\{ \begin{array}{l} K \\ K \end{array} \right.$ |
| Dimethyl (methyl methylide) | $\left\{ \begin{array}{l} C H_3 \\ C H_3 \end{array} \right.$ |
| Diethyl (ethyl ethylide) | $\left\{ \begin{array}{l} C_2 H_5 \\ C_2 H_5 \end{array} \right.$ |
| Diacetyl | $\left\{ \begin{array}{l} C_2 H_3 O \\ C_2 H_3 O \end{array} \right.$ |
| Dibenzoyl | $\left\{ \begin{array}{l} C_7 H_5 O \\ C_7 H_5 O \end{array} \right.$ |

| | |
|--------------------------------------|---|
| Aldehyd (acetyl hydride) | $\left\{ \begin{array}{l} C_2H_3O \\ H \end{array} \right.$ |
| Aectonc (acetyl methylide) | $\left\{ \begin{array}{l} C_2H_3O \\ C H_3 \end{array} \right.$ |
| Zinc | Zn'' |
| Ethylene (olefiant gas) | (C ₂ H ₄)'' |

Hydrochloric acid was originally proposed by Gerhardt as an additional typical body, but the *hydrochloric acid type* $\left. \begin{array}{l} H \\ Cl \end{array} \right\}$ is now usually included under the hydrogen type. It forms a subtype which comprehends the chlorides, fluorides, bromides, iodides, and cyanides of any monad radicle, including, therefore, the ethers of the hydracids, and the chlorides of the radicles of the monobasic acids; for example:—

| | |
|--|---|
| Hydrochloric ether (ethyl chloride) | $\left\{ \begin{array}{l} C_2H_5 \\ Cl \end{array} \right.$ |
| Amyl iodide | $\left\{ \begin{array}{l} C_5H_{11} \\ I \end{array} \right.$ |
| Benzoic oxychloride (benzoyl chloride) | $\left\{ \begin{array}{l} C_7H_5O \\ Cl \end{array} \right.$ |
| Aectie oxyehloride (acetyl chloride) | $\left\{ \begin{array}{l} C_2H_3O \\ Cl \end{array} \right.$ |
| 2. <i>The Water type</i> | $\left. \begin{array}{l} H' \\ H' \end{array} \right\} O''.$ |

This series includes the oxides (comprising under this term acids, bases, and salts), sulphides, selenides, and tellurides of all the monad radicles, such as the alcohols, the hydrosulphuric ethers and mereaptans, the simple and compound ethers, the double ethers, the monobasic organic acids and their anhydrides: for instance:—

| | |
|---|---|
| Wood spirit | $\left. \begin{array}{l} CH_3 \\ H \end{array} \right\} O$ |
| Alcohol | $\left. \begin{array}{l} C_2H_5 \\ H \end{array} \right\} O$ |
| Ethyl sulphide (hydrosulphuric ether) | $\left. \begin{array}{l} C_2H_5 \\ C_2H_5 \end{array} \right\} S$ |
| Mereaptan | $\left. \begin{array}{l} C_2H_5 \\ H \end{array} \right\} S$ |
| Ordinary ether | $\left. \begin{array}{l} C_2H_5 \\ C_2H_5 \end{array} \right\} O$ |

| | | |
|---|--|---|
| Amyl-ethyl ether | $\left. \begin{array}{l} C_5H_{11} \\ C_2H_5 \end{array} \right\}$ | O |
| Acetic ether | $\left. \begin{array}{l} C_2H_3O \\ C_2H_5 \end{array} \right\}$ | O |
| Acetic acid | $\left. \begin{array}{l} C_2H_3O \\ H \end{array} \right\}$ | O |
| Acetic anhydride | $\left. \begin{array}{l} C_2H_3O \\ C_2H_3O \end{array} \right\}$ | O |
| Hydrated tetrethylum } oxide | $\left. \begin{array}{l} (CH_3)_4N \\ H \end{array} \right\}$ | O |

includes the nitrides, phosphides, as well as arsenides and antimonides of the alcohol radicles, together with the compound ammonias, and the amides; *e.g.*:—

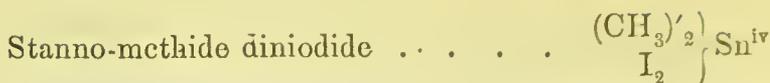
3. *The Ammonia type* $\left. \begin{array}{l} H' \\ H' \end{array} \right\} N'''$,

| | | |
|--|---|---|
| Ethylia (ethylamine) | $\left\{ \begin{array}{l} C_2H_5 \\ H \\ H \end{array} \right\}$ | N |
| Phosphodiethylia | $\left\{ \begin{array}{l} C_2H_5 \\ C_2H_5 \\ H \end{array} \right\}$ | P |
| Trimethylia (trimethylamine) | $\left\{ \begin{array}{l} CH_3 \\ CH_3 \\ CH_3 \end{array} \right\}$ | N |
| Acetamide | $\left\{ \begin{array}{l} C_2H_3O \\ H \\ H \end{array} \right\}$ | N |
| Benzoyl-salicylamide | $\left\{ \begin{array}{l} C_7H_5O \\ C_7H_5O_2 \\ H \end{array} \right\}$ | N |

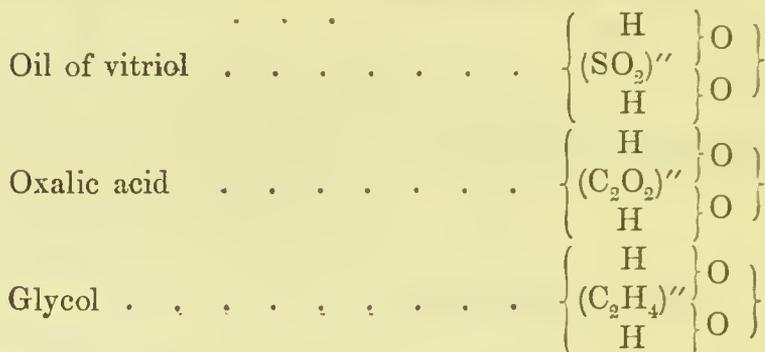
4. *The Marsh Gas type* $\left. \begin{array}{l} H' \\ H' \\ H' \\ H' \end{array} \right\} C^{iv}$

The members of this group have hitherto been but little studied; they comprise compounds like carbonic anhydride and some of the more complex organo-metallic bodies.

| | |
|------------------------------|---|
| Carbonic anhydride | $\left. \begin{array}{l} O'' \\ O'' \end{array} \right\} C^{iv}$ |
| Plumbic tetrethyl | $\left. \begin{array}{l} (C_2H_5)' \\ (C_2H_5)' \\ (C_2H_5)' \\ (C_2H_5)' \end{array} \right\} Pb^{iv}$ |



It will be seen, as we advance, that bodies are also known which are formed upon condensed types, or upon the plan of the preceding types doubled, tripled, quadrupled, &c., such as the type of 2 molecules of water $\left. \begin{array}{c} \text{H}_2 \\ \text{H}_2 \end{array} \right\} \text{O}_2$ condensed into one, as is more fully explained at p. 58; among these, for instance, are



whilst there are others formed upon the type of 3 molecules of water, $\left. \begin{array}{c} \text{H}_3 \\ \text{H}_3 \end{array} \right\} \text{O}_3$, as



and so on.

These condensed types are represented only in the case of compounds which contain multivalent radicles, such as sulphuryl $(\text{SO}_2)''$ and glycyll, $(\text{C}_3\text{H}_5)'''$ as in the instances just cited, where the radicle serves as the link to bind the several molecules into one.

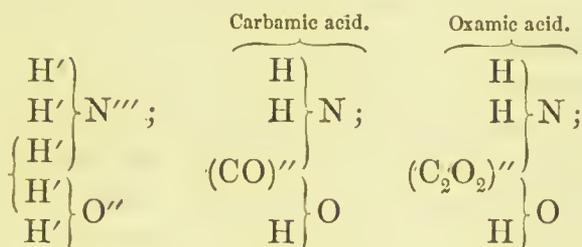
It will be seen that each of the four substances, hydrogen, water, ammonia, and marsh gas, thus selected as types to one of which the various chemical compounds are referred, is a compound of hydrogen; and other bodies are supposed to be formed from these typical substances by the substitution of a portion, or of the whole of the hydrogen of the type, by hydrocarbons or by other simple or compound radicles. For the sake of precision it is often found to be necessary to distinguish the unaltered hydrogen of the type from any hydrogen which may have been subsequently introduced into the molecule.

Alcohol, for example, is said to be a compound formed upon the water type by the introduction of a hydrocarbon C_2H_5 in the

place of one of the original atoms of hydrogen in the type; alcohol being $\left. \begin{matrix} \text{C}_2\text{H}_5 \\ \text{H} \end{matrix} \right\} \text{O}$; whilst water is $\left. \begin{matrix} \text{H} \\ \text{H} \end{matrix} \right\} \text{O}$.

In such cases the original hydrogen in the type is distinguished as *typical* hydrogen.

Many compounds, not included under the preceding types, may be referred to the union of two of the foregoing types with each other, as was first suggested by Williamson, such compounds being represented as derived from *mixed types*. Kekulé, for example (*Lehrbuch der Org. Chemie*, i. p. 121,) proposes to consider the amidated acids, such as the carbamic and the oxamic, as formed upon the combination of the types of ammonia and water:—



the tie between the two typical groups is in one case the bivalent radicle $(\text{CO})''$, in the other $(\text{C}_2\text{O}_2)''$

(1064) *Theory of Multivalent Elements*.—The tendency of bodies to assume these typical forms of combination is supposed to be due to the existence of special peculiarities in the nature of the elementary bodies themselves.

This principle, first suggested by the consideration of certain organic compounds, has since been extensively applied to the explanation of the formation of chemical compounds in general. A new theory of chemical combination has been founded upon it; and although the theory has not yet been worked out in all its details, it has, in the hands of Kekulé, Frankland, Wurtz, and many other eminent chemists, already proved a fertile source of new discoveries, and has led to generalizations of great interest and growing importance.

Although, therefore, it is still of a speculative character, it will be necessary to give a sketch of the general features of the view of the *atomicity* or *equivalency* of elements which is at present under discussion among chemists.

Observation has shown that each elementary substance has a tendency to unite with the other elements in a particular manner, and the special peculiarities of these combinations have rendered it necessary to arrange the more important of the elements in six principal groups (see also Part I., p. 32), viz. :—

1. *Monatomic* or *univalent* elements, *Monads*, each atom of which is in combination usually equivalent to H, or one atom of hydrogen.

2. *Diatomic* or *bivalent* elements, *Dyads*, each atom of which in combination is usually equivalent to H_2 , or two atoms of hydrogen.

3. *Triatomic* or *tervalent* elements, *Triads*, each atom of which is in combination usually equivalent to H_3 , or three atoms of hydrogen.

4. *Tetatomic* or *quadrivalent* elements, *Tetrads*, each atom of which in combination is generally equivalent to H_4 , or four atoms of hydrogen.

5. *Pentatomic* elements, or *Pentads*, each atom of which usually represents five atoms of hydrogen, or is equivalent to five atoms of a monad.

6. *Hexatomic* elements, or *Hexads*, each atom of which is equivalent in combination to six atoms of hydrogen or some other monad.

The particular class of the element or radicle may, when needful, be pointed out as proposed by Odling, by affixing the marks (") (""') (""') (""') (""') (""') to indicate its dyad, triad, tetrad, pentad, or hexad character.

All the members of the same group exhibit a certain similarity in chemical characters. Further, when any one of them enters into combination with any given element, *A*, the compound so formed is usually similar in atomic composition to the compounds which the other members of the group form with the same given element, *A*. For example:—

a. To the *monad* group are regarded as belonging—hydrogen, potassium, and the allied metals of the alkalis, and silver, as well as chlorine and bromine.

Each molecule of a monad consists of two atoms of the element united one with the other. Each of the monad elements may combine with a single atom of some other element of the same group; for instance:—

| | |
|---|------|
| Chloric ehloride (chlorine gas) | ClCl |
| Hydric hydride (hydrogen gas) | HH |
| Hydrochloric acid | HCl |
| Potassic iodide | KI |
| Argentie bromide | AgBr |

b. To the *dyad* group the following elements are considered to belong:—Oxygen ($O=16$), sulphur ($S=32$), and a large number of the metals, including those of the alkaline earths, with those of the magnesian group, besides mereury, copper, and several others.

One atom of each of these elements may unite with two atoms of some one monad element, or with one atom of two different monads; for example:—

| | |
|------------------------------------|----------|
| Water | (HH)O'' |
| Hydric-potassic sulphide | (KH)S'' |
| Sodic hydrate | (NaH)O'' |

The molecule of the dyad metals usually contains but one atom of the metal; whilst the non-metallic dyads contain two atoms in their molecule.

c. To the *triad* group belong boron, gold, and rhodium, and as still admitted by most chemists, nitrogen, phosphorus, arsenicum, antimony, and bismuth. One atom of each of these triad elements may combine with three atoms of an element of the monad group. As for instance:—

| | |
|----------------------------------|----------------------|
| Boric chloride | B'''Cl ₃ |
| Auric bromide | Au'''Br ₃ |
| Rhodic chloride | Ro'''Cl ₃ |
| Ammonia | N'''H ₃ |
| Arseniuretted hydrogen | As'''H ₃ |

d. To the *tetrad* group carbon (C=12), and silicon (Si=28) belong, besides tin, titanium, zirconium, platinum, and some other metals.

The elements of this group unite with four atoms of the monad or with two of the dyad group; for example:—

| | |
|---------------------------------|-----------------------------------|
| Marsh gas | C ^{iv} H ₄ |
| Silicon tetrachloride | Si ^{iv} Cl ₄ |
| Carbonic anhydride | C ^{iv} O'' ₂ |
| Carbon disulphide | C ^{iv} S'' ₂ |
| Silica | Si ^{iv} O'' ₂ |

e. Among the *pentad* group, Frankland and some other chemists include nitrogen, phosphorus, arsenicum, and antimony, relying on the existence of such compounds as—

| | |
|---------------------------------------|---|
| Phosphoric chloride | PCl ₅ |
| Antimonic chloride | SbCl ₅ |
| Sal ammoniac | NH ₄ Cl |
| Arsenio-tetretylum chloride | As(C ₂ H ₅) ₄ Cl. |

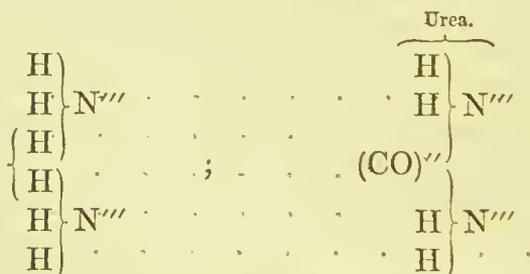
f. Among the *hexads* are included molybdenum, tungsten, and some of the metals of rare occurrence.

Observation shows, as indeed theory requires, that no monad element can effect the union of other monads into a compound group of multivalent combining power.

Further, it appears that complex groups or compound radicles exist which possess the powers of monad, dyad, or polyad elements. No monad radicle has the power of effecting the union of two or more monad molecules into one polyad radicle; but just as each polyad element can unite the atoms of several monads into one indivisible group, so also when a polyad radicle enters into the composition of a body it may cause the union of several compound molecules of more or less simple constitution into one indivisible group or compound molecule: sulphuric acid may, for instance, be regarded as formed upon the type of two molecules of water, the bivalent group $(SO_2)''$, forming the link which, by displacing two atoms of hydrogen, connects the two molecules together:—



In like manner urea may be supposed to be formed upon the type of two molecules of ammonia, the bivalent group $(CO)''$ furnishing the link which connects the molecules into an indivisible whole:—



(1065) *Application of the Theory of Multivalent Elements.*—The following statement of the hypothesis which is now usually admitted in explanation of these facts, will be necessary to complete our sketch of this part of the subject.

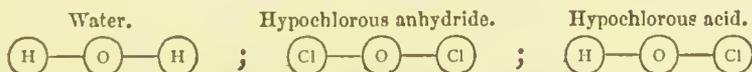
Each atom of every element is supposed to have a certain definite number of centres of attraction, or *bonds* as they have been called by Frankland, by which, and by which alone, it enters into chemical combination with other elements. To aid in giving precision to our ideas, these bonds or points of attachment may be represented graphically; and this has been done in various

ways, the most convenient perhaps being that employed by Crum Brown.

The atom of a monad, such, for example, as hydrogen, is believed to have but a single such bond, the existence of which is indicated by a single line, *e.g.* $(\text{H})-$; the same is supposed to be true of each monad, the atom of chlorine being $(\text{Cl})-$. In the *molecule* of hydrogen as it exists in the gas, $(\text{H})-(\text{H})$, the attraction of each atom is saturated by that of its fellow; and the same thing is assumed to hold good in the molecule of other elementary monads, such as gaseous chlorine $(\text{Cl})-(\text{Cl})$. When combination occurs between two monads, they can only unite in one proportion; and a single molecule of one element, by reaction upon a single molecule of the other element, gives rise to two molecules of the compound; $(\text{H})-(\text{H}) + (\text{Cl})-(\text{Cl})$ becoming $(\text{H})-(\text{Cl}) + (\text{Cl})-(\text{H})$.

Each atom of a dyad is supposed to have two such points of union. Consequently it may unite with two atoms of the same monad, or with one atom of two different monads, or it may form a more complex group by uniting with other dyads in various ways.

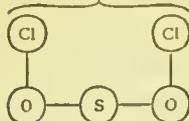
One atom of oxygen, for instance, may unite with two atoms of hydrogen, with two of chlorine, or with one of chlorine and one of hydrogen; or it may unite with a second atom of oxygen, or with an atom of some other dyad, such as zinc; as for instance—



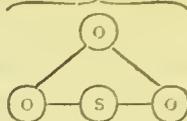
Oxygen gas. Zinc oxide. In this case the different elements are re-
 $(\text{O})=(\text{O})$ $(\text{O})=(\text{Zn})$ presented as being so united that both the
 bonds of the dyad are saturated. But, on the other hand, two
 atoms of the same or of two different dyads may be so united that
 only one of the two points of union is saturated, leaving there-
 fore two other bonds unsaturated and ready to enter into com-
 bination to that extent with some other element or compound.
 Such a union would give rise to a dyad or diatomic radicle with
 two unsaturated bonds, such as $-(\text{O})-(\text{O})-$, $-(\text{S})-(\text{S})-$ &c.

Again, 3 dyad molecules, in combining, must leave two
 bonds unsaturated, giving rise to a dyad radicle such as sul-
 phuryl, $(\text{SO}_2)''$, $-(\text{O})-(\text{S})-(\text{O})-$, which requires two atoms of a
 monad for saturation, as in forming the compound SO_2Cl_2 . One
 atom of a dyad, such as oxygen, in uniting with sulphuryl,
 would form the compound SO_3 .

Sulphuryl dichloride.

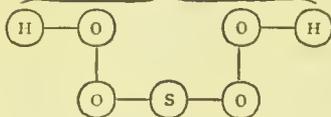


Sulphuric anhydride.



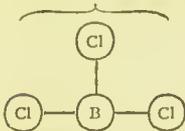
Again, sulphuryl, by displacing two atoms of hydrogen in two atoms of water, forms the more complex group of sulphuric acid, $H_2SO_4^*$ which is a stable or *saturated* molecule in the sense in which the word saturated is here used.

Sulphuric acid.

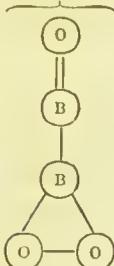


In the case of a triad like boron or gold, there are supposed

Boron trichloride.



Boric anhydride.

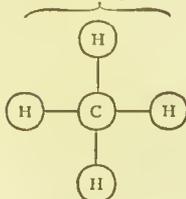


to be three such centres of attraction. In such a saturated compound as boron trichloride (BCl_3)^o combination may be therefore represented as in the annexed diagram; saturation in a molecule being indicated by the mark ^o.

Combination with a dyad such as oxygen, to form a saturated molecule, like boric anhydride (B_2O_3)^o, might be represented as indicated in the margin.

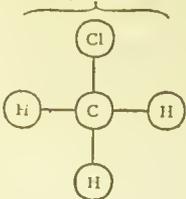
The relations of the tetrads, of which carbon is by far the most important, are still more complex, and hence the vast variety of combinations which we meet with among the compounds of carbon.

Marsh gas.



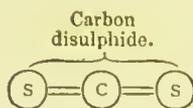
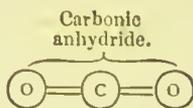
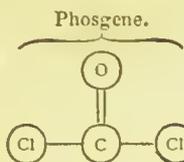
Marsh gas may be taken as the simplest instance of a saturated molecule containing carbon, (CH_4)^o.

Methyl chloride.

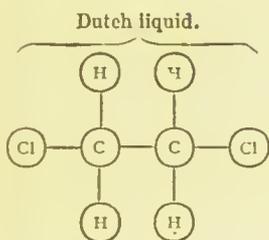
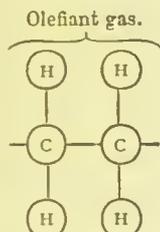
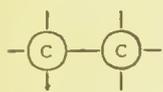


It will also afford a good illustration of the effect of the removal of hydrogen, and the substitution for it of a monad such as chlorine in methyl chloride, (CH_3)'Cl; a monad and a dyad, as in phosgene (CO)''Cl₂; or two dyads, as oxygen in carbonic anhydride CO_2 , or sulphur in carbon disulphide CS_2 .

* It is scarcely necessary to remind the reader that the graphic illustrations employed to aid the conception are not intended in any way to represent the relative position of the atoms, but merely to show whether the compound is a saturated or an unsaturated group or molecule.



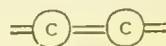
When substances are formed, into the composition of which more than one atom of carbon enters, it is supposed that the atoms of carbon are riveted together by partial saturation. If the pair of atoms be united by single points, the group C_2 will be hexad in power. Consequently, if olefiant gas (C_2H_4) contains two atoms of carbon so united, it will furnish a radicle of dyad power; that is to say, as indeed is the fact, that it should show a readiness to unite with two atoms of some monad, such as chlorine, when it forms Dutch liquid (C_2H_4) $''Cl_2$. Indeed we may regard most of the dicarbon compounds as formed from 2 atoms of carbon retaining a hexad power; as for instance in



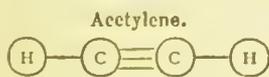
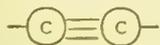
| | |
|---------------------------------|-------------------|
| Ethyl hydride | $C_2^{vi}H_5H$ |
| Ethyl chloride | $C_2^{vi}H_5Cl$ |
| Solid carbon chloride | $C_2^{vi}Cl_6$ |
| Aldehyd | $C_2^{vi}H_4O$ |
| Chloral | $C_2^{vi}HCl_3O$ |
| Acetonitrile | $C_2^{vi}N'''H_3$ |
| Cyanogen gas | $C_2^{vi}N'''_2$ |

Each of these formulæ represents a quantity of its corresponding compound which yields two volumes of vapour.

But it is quite possible that the two atoms of carbon may be united by two of their bonds, in which case a tetrad group would be the result; and in other instances the union may be by three out of the four bonds,

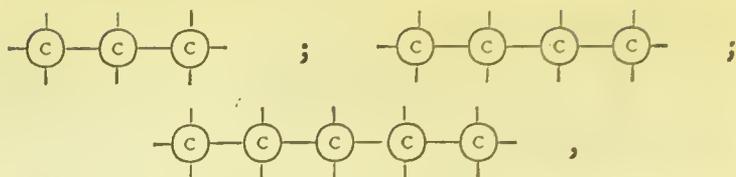


leaving only two unsaturated points. In the last case, by their union with two atoms of a dyad, a



molecule like acetylene (C_2H_2) would be the result. Union of the carbon by single bonds is, however, the more common case. Com-

pounds containing 3 atoms of carbon would, if united by single bonds, require 8 atoms of a monad to complete the molecule: with 4 atoms of carbon, 10 bonds would require saturation; with 5 atoms, 12 atoms of a monad would be needed; and generally if n represent the number of atoms of carbon, the number of bonds in the molecule requiring saturation would be $2n + 2$, as will be seen by inspecting the diagrams subjoined:—



and so on. In fact, no hydrocarbon is known in which the number of atoms of hydrogen exceeds this proportion, nor does it seem to be probable that any class containing a larger proportion of hydrogen can exist.

(1066) *Mode of determining the Equivalency of an Element.*—

It is not surprising that in the application of a new theory of such generality, some difficulties have been experienced. Chemists, indeed, are not yet agreed in all cases, as has been already stated, as to the class in which some even of the most important elements are to be placed, because they are not yet agreed as to the mode in which the equivalency of an element is to be determined, and because that equivalency in some cases seems, at first sight, to be variable.

The method of determining the equivalency of an element theoretically, least open to objection, appears to be that followed by Naquet. It consists in ascertaining the greatest number of atoms of any monad with which a single atom of the element in question is capable of combining. Chlorine combines with but a single atom of hydrogen; and these two elements have been uniformly regarded as the types of the monad group. The maximum number of atoms of chlorine or of hydrogen with which a single atom of any element is capable of uniting, may therefore be employed to determine its equivalency. Yet there are difficulties when we attempt to carry out the principle rigidly.

Iodine and thallium are both usually recognized as monads, but if this rule be applied, each ought to be regarded as a triad, inasmuch as the compounds ICl_3 and TlCl_3 are known.

Each atom of oxygen and sulphur may unite with two atoms of hydrogen or with two of chlorine, but never with a larger proportion of either of these elements. They are therefore regarded as dyads; but selenium and tellurium, which are often included in the same class, must according to this rule be reckoned as tetrads, for they form compounds with four atoms of chlorine, SeCl_4 and TeCl_4 . Sometimes the rule fails in the opposite direction. No compound of lead with hydrogen has hitherto been formed, and the combination PbCl_4 is unknown. Yet it can scarcely be doubted that lead, from its power of forming plumbic tetrethyl, $\text{Pb}(\text{C}_2\text{H}_5)_4$, should be referred to the group of tetrads.

It has already been stated that Frankland regards phosphorus and antimony as pentads, since each forms a compound with five atoms of chlorine; and nitrogen and arsenium are by him also referred to the same group, from their close analogy with phosphorus and antimony, as well as from the composition of several of their compounds, such as the haloid salts of ammonium and the ethyl compounds of arsenium.

Excepting in the case of lead, there are, however, difficulties in the way of admitting these alterations; inasmuch as the groups of the closely allied elements at present exhibited in the classification shown at p. 33 of Part I., would be disturbed. Iodine would be severed from the other halogens; selenium and tellurium would be separated from sulphur; and the nitrogen group, at present regarded by most chemists as triads, owing to the well marked character of its hydrogen and chlorine compounds, would be displaced. In the group last named, it is, moreover, a significant fact that the vapour volume of many of their pentad combinations is anomalous, for it has been found that in most cases the atom of these compounds yields four volumes of vapour instead of two. This it has been attempted to account for on the principle of dissociation (*note* § 67), but the explanation is not applicable in every case. Most of these pentad compounds exhibit instances of additive combination (p. 47).

Again, chromium forms with fluorine a hexad compound, Cr F_6 , of which the vapour density has not hitherto been determined. Chromium, by Naquet's rule, must be a hexad; and if this be so, iron, aluminum, manganese, as well as cobalt and nickel, would require to be transferred to this group, from their close chemical analogies with chromium, and to this there are serious objections.

It is, however, not improbable that all these metals should be regarded, not as dyads but as tetrads, for reasons which we shall proceed now to consider, as it will help us towards a solution of some of the difficulties which the fact of combination in multiple proportion seems to present to the theory as above stated.

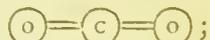
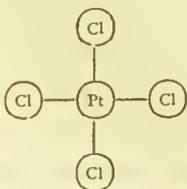
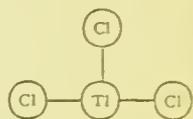
(1067) *Bearing of the Law of Multiple Proportion on the Theory of Equivalency.*—It has been observed that the elementary bodies may be subdivided into two principal groups: one of these comprises the monads, triads, and pentads, and combines with the monads, according to the progression of the uneven numbers 1, 3, 5: the other group comprises the dyads, tetrads, and hexads, and combines with the monads in the progression of even numbers, 2, 4, 6. In a few remarkable instances the same element appears

to form compounds belonging to both the odd and the even series: this is the case with iron, chromium, manganese, and iridium.

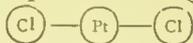
There are two ways in which it has been attempted to explain this tendency of an element always to combine either with 1, 3, 5, or an odd number of atoms of a monad, or else as regularly with 2, 4, or some even number of atoms. First, taking Naquet's rule, it is supposed that the highest known compound determines the equivalency of an element, and that in each of the lower compounds two of the centres of attraction neutralize each other (Frankland). In thallic chloride ($TlCl$), for instance, two of the three points of thallium neutralize each other; whilst in the rarer instances, as when thallic chloride $TlCl_3$ is formed, each of the three centres is saturated by chlorine. In such cases of partial saturation of the atom as $TlCl$, the other centres of attraction in each atom neutralize each other in pairs; and hence the tendency of all the elements to preserve their mode of combination, either always with an odd number of atoms of a monad, or else always with an even number. Every element tends to form one particular class of compounds, which are more stable than any other series into the formation of which it enters. For example, the stable thallium compounds are generally those in which the metal appears to act the part of a monad, not of a triad; corresponding, that is, to $TlCl$, not to $TlCl_3$. With gold, on the contrary, though compounds like aurous chloride ($AuCl$) may be obtained, the most stable series is that in which the triad character of the metal is distinctly shown, as in the trichloride ($AuCl_3$).

Again, in the group of tetrads, though platinum generally forms compounds on the type of platonic chloride, $PtCl_4$, it occasionally forms them on that of platinous chloride, $PtCl_2$, in which it may be supposed that the two unsaturated centres are neutralized by reacting one against the other. Such a mode of representing the formation of the inferior compounds seems to be suited especially to gaseous compounds like carbonic oxide, as compared with carbonic anhydride $O=C=O$; where the specific gravity of the gas defines distinctly the molecule of each.

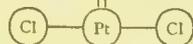
There is, however, a second explanation of the method of combination in multiple proportion, which is admissible in certain cases. Upon this view it is supposed that in the lower compounds,



such as the aurous and platinous groups, two atoms of the element have partially neutralized each other; for instance, aurous chloride, (Au_2Cl_2) may be represented $\text{Cl}-\text{Au}=\text{Au}-\text{Cl}$ and



platinous chloride (Pt_2Cl_4) as $\begin{array}{c} \text{Cl} - \text{Pt} - \text{Cl} \\ || \\ \text{Cl} - \text{Pt} - \text{Cl} \end{array}$. In each case, how-

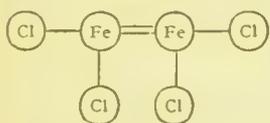


ever, it becomes necessary to double the formula ordinarily employed to represent the molecule.

Upon either hypothesis a reasonable explanation may be given of the remarkable cases presented where the same element, like iron, seems to combine with the monads in proportions represented by both odd and even numbers.

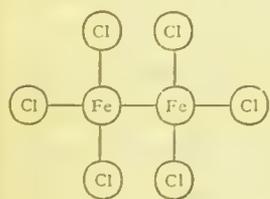
It is, however, necessary to suppose that in such cases as those of iron and the other metals allied to it, viz., cobalt, nickel, manganese, chromium, uranium, and aluminum, instead of being regarded as dyads, these metals should be viewed as tetrads. If this be granted, the ferrous compounds, such as ferrous

chloride, may be represented either as $FeCl_2$, $\text{Cl}-\overset{\circ}{\text{Fe}}-\text{Cl}$



where the two of the centres neutralize each other; or as (Fe_2Cl_4) , where the two atoms of iron are represented as united by two points of attraction. In *ferric* compounds (like ferric chloride, of

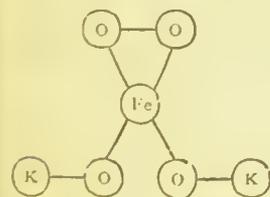
which we know from the density of its vapour that the molecule cannot be less than that indicated by the formula $Fe_2^{vi}Cl_6$), each atom of iron in the molecule must be united to its fellow by a single point only, as represented in the diagram below.

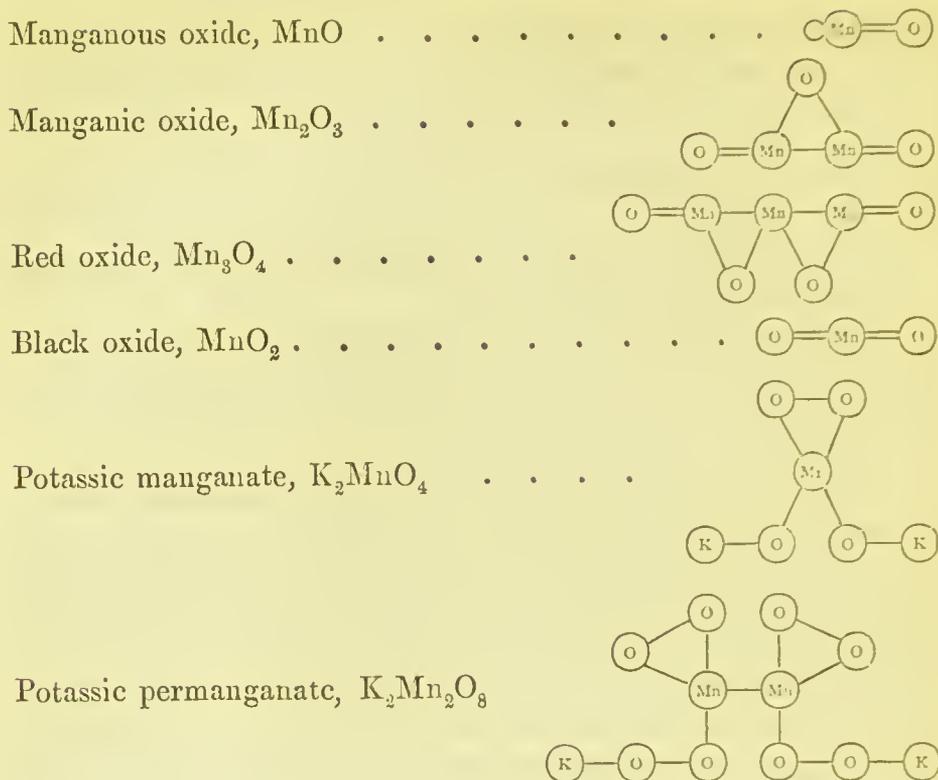


A similar plan would be supposed to prevail in the constitution of the molecule of aluminic chloride, the density of which corresponds with the formula $Al_2^{vi}Cl_6$, as well as in the case of the analogous body, chromic chloride.

The existence of the ferrates, such as potassic ferrate, K_2FeO_4 , would be equally easily accounted for, as may be seen in the diagram in the margin.

Indeed it may be shown that even in so complex a multiple series as that exhibited by the oxides of manganese, there is no difficulty in representing the mode of combination upon this principle; for example:—





Even if the systematic carrying out of this view should occasionally necessitate the doubling of a formula hitherto regarded as adequate to represent the molecular constitution of a body, this can scarcely be regarded as an objection; for at present our knowledge of the molecule of any substance not reducible to the condition of vapour is extremely uncertain, and our view consequently liable to modification if reasonable grounds be shown.

It is manifest that whatever theory of chemical combination be adopted we must admit of an additional species of combination by *apposition*. Such, for example, are the cases when water of crystallization enters into the formation of a salt; and such probably is also the cause of the formation of double salts, like the platonic double chlorides, the alums, and the numerous cases where the union between the two salts is less stable than in these.

(1068) *Causes of the Multivalent Character of Radicles.*—The study of polyad compounds has been prosecuted with great activity and success within the last few years, and the circumstances under which an organic radicle exhibits a multivalent type have consequently attracted much attention. The foregoing observations will have prepared the reader to seize the bearing of the principal points which have been ascertained regarding this interesting subject.

A large number of the hydrocarbon radicles which have at present been studied are monads, others are dyads, and a few are triads. No isolated radicle is known, the molecule of which contains an *uneven* number of atoms of hydrogen; though so called isolated radicles with an even number of atoms of hydrogen are of frequent occurrence.

1. All radicles hitherto admitted of the form C_nH_{2n+1} , such as methyl, (CH_3) , ethyl (C_2H_5) , or amyl (C_5H_{11}) , are *monads*: as is seen in ethyl chloride $(C_2H_5)Cl$, and amyl iodide $(C_5H_{11})I$; and, in isolated ethyl, ethyl ethylide (C_2H_5, C_2H_5) .

2. Radicles of the form C_nH_{2n} , such as ethylene (C_2H_4) , tritylene (C_3H_6) , octylene (C_8H_{16}) , are *dyad*, as in Dutch liquid $(C_2H_4)''Cl_2$. Such radicles may exist in the free state.

3. A radicle of the form C_nH_{2n-1} is in certain cases *triad*, in others *monad*; (C_3H_5) , for example, is triad in glycerin, $(C_3H_5)'''O_3$, but monad in allyl alcohol, $(C_3H_5)H\}O$, and in allyl chloride $(C_3H_5)Cl$.

A radicle may as a rule be made to change its equivalency, or basic power, by the removal of hydrogen. As an example of this we may take marsh gas, which is usually regarded as a neutral or saturated body of the methyl series: * by acting upon this gas with chlorine, 1, 3, and 4 atoms of hydrogen may be removed in succession, and a corresponding number of atoms of chlorine substituted;

| | | |
|----------------------------|-----------|-----------|
| Marsh gas (methyl hydride) | | CH_3H |
| Methyl chloride | | CH_3Cl |
| Methylene diiodide | | CH_2I_2 |
| Chloroform | | $CHCl_3$ |
| Carbon tetrachloride | | CCl_4 |

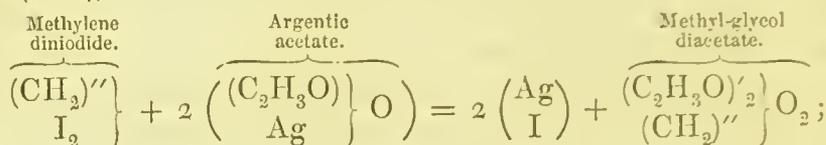
The third term in the series is not known with chlorine, but it has been obtained with iodine by Butlerow.

Now from these substitution-products of marsh gas, compounds of four different equivalencies have been obtained, corresponding to the following different radicles, viz. :—

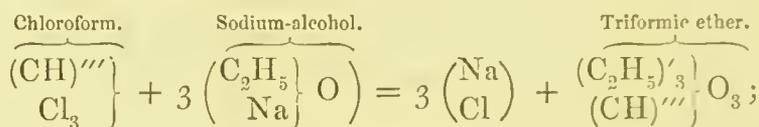
| | | | | |
|--------|-----------|------------|----|---------------|
| Monad | | $(CH_3)'$ | or | C_nH_{2n+1} |
| Dyad | | $(CH_2)''$ | or | C_nH_{2n} |
| Triad | | $(CH)'''$ | or | C_nH_{2n-1} |
| Tetrad | | C^{iv} | or | C_nH_{2n-2} |

* By a saturated or neutral molecule is here understood a compound which will not unite directly with an elementary monad, or a monad radicle: whenever it forms compounds, such compounds are produced by substitution, methyl chloride CH_3Cl , for example, being obtained from marsh gas by substituting 1 atom of chlorine for 1 of hydrogen.

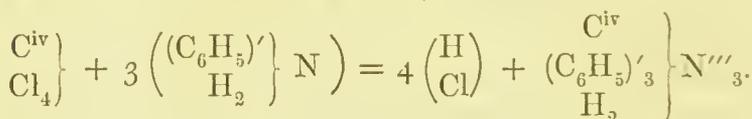
The compound $(\text{CH}_2)'\text{Cl}$ is manifestly a chloride of a monad radicle. If methylene diiodide be treated with argentic acetate, methyl-glycol diacetate, the ether of a diatomic alcohol is procured (1214):—



and if chloroform be treated with sodium alcohol a tribasic formic ether is obtained:—



Whilst, finally, if carbon tetrachloride be acted upon by aniline, a base is obtained containing $\text{C}_{19}\text{H}_{17}\text{N}_3$:—

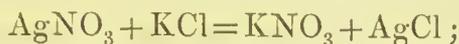


The *equivalency*, or as it is sometimes called, the *basicity*, of a radicle, is therefore increased by unity for each atom of hydrogen which is withdrawn, so that a univalent radicle becomes bivalent by the loss of an atom of hydrogen; a bivalent radicle becomes trivalent by the loss of another atom of hydrogen, and by the further removal of an atom of hydrogen the trivalent radicle becomes quadrivalent.

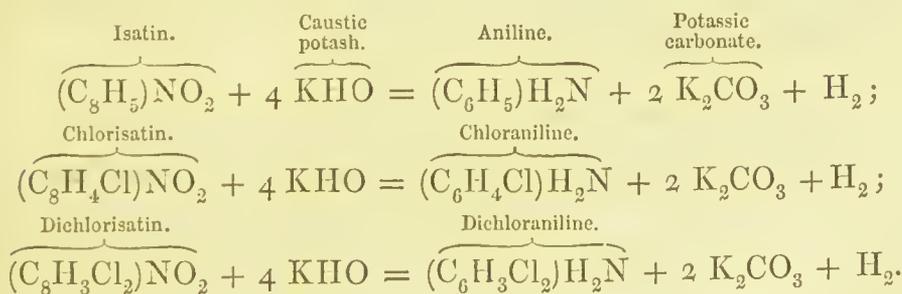
For the further prosecution of these speculations the reader may consult Kekulé (*Org. Chemie*, i. pp. 158—183).

(1069) *Influence of Arrangement of Atoms in a Compound on its Properties.*—From what has been already stated it is obvious that a body does not necessarily belong to a given type merely because it may contain one of the characteristic elements which contribute to form the typical compound. It would be wrong, for example, to infer that a compound was formed on the hydrochloric acid type simply in consequence of the presence of chlorine among its components; since the properties of a body are dependent, not only upon the nature and number of atoms of its component elements, but also in a very important manner upon the molecular arrangement of those components. Indeed, in many cases the arrangement of the atoms in the compound has a greater influence upon its properties than even the nature of the elements of which it is composed. It may in fact be said that

the whole theory of types is founded upon the dissimilar activity of atoms otherwise identical save in their relative position in the molecule of the compound. For example, the chlorine in potassic chlorate does not perform the same part that it does in potassic chloride; in the latter instance it is susceptible of displacement when mixed with argentic nitrate; the soluble potassic nitrate and insoluble argentic chloride being formed when solutions of the two salts are mixed—



whereas, when potassic chlorate and argentic nitrate are mixed, no precipitation of argentic chloride takes place. So it is in organic substances; for example, when isatin, $\text{C}_8\text{H}_5\text{NO}_2$ (a compound derived from indigo) is distilled with caustic potash, a powerful volatile base termed aniline ($\text{C}_6\text{H}_5\text{H}_2\text{N}$) is obtained. Now derivatives of isatin may be formed in which one and two atoms of chlorine may be successively substituted in each molecule of isatin for an equal number of atoms of hydrogen; and when these chlorinated compounds are distilled with caustic potash, they yield substances corresponding in composition to aniline, but in which a certain number of atoms of hydrogen in the group (C_6H_5) are displaced by a corresponding number of atoms of chlorine; for instance:—

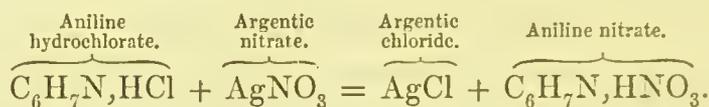


By the action of chlorine upon aniline, another compound has been obtained, termed trichloraniline ($\text{C}_6\text{H}_2\text{Cl}_3\text{H}_2\text{N}$), in which three atoms of chlorine have taken the place of three atoms of hydrogen in a certain group in the molecule of aniline.

It is particularly to be remarked that the basic properties of the aniline are preserved in these compounds, though with gradually decreasing distinctness; and it is not until the third atom of chlorine has been introduced, that the basic power finally disappears; aniline, for example, is powerfully basic; chloraniline is distinctly basic; dichloraniline, feebly so; and trichloraniline is a neutral body.

Not one of these bodies when in solution, combined with nitric

or sulphuric acid for instance, gives any precipitate of chloride when mixed with argentic nitrate; yet a single atom of chlorine, in the form of hydrochloric acid, will neutralize the basic power of an atom of any of these compounds. If, for instance, hydrochloric acid be combined with aniline so as to form the hydrochlorate of this base (C_6H_7N, HCl), the solution will have all the characters of a normal salt, and will occasion an immediate precipitate when its solution is mixed with one of argentic nitrate:—



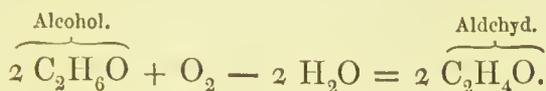
These differences may be accounted for upon the supposition that chlorine, when in combination, may discharge different functions; in the different chlorinated anilines, for example, it is evident that the chlorine has entered more intimately into the composition of the body than in the instance just cited, since part of the hydrogen in the molecule of the base has been actually displaced by chlorine in the first cases; whereas, in the last, the chlorine is external to the base. The full importance of such processes of substitution will be made manifest as the reader proceeds; and in order to facilitate the acquirement of distinct notions upon this point we pass next to the consideration of a few of the principal modes in which the chemist effects the metamorphoses of the compounds which come before him.

§ III. PRODUCTION OF CHEMICAL METAMORPHOSES.

(1070) Three principal methods are employed in examining the chemical composition of organic bodies, and in tracing their relations to other compounds. These three methods are—1. That of *oxidation*. 2. That of *reduction*. 3. That of *substitution*, including double decomposition.

1. *Oxidation*.—It will be unnecessary to consider minutely the effects of rapid direct oxidation, or combustion, since the general result in all cases where a sufficient amount of air is supplied is to convert the carbon into carbonic anhydride, and the hydrogen into water, whilst the nitrogen is commonly liberated in the free state. It is the study of the process of gradual oxidation which affords results so instructive to the chemist. When an organic body is placed in contact with a powerful oxidizing agent, such as nitric acid, chromic acid, or a mixture of sulphuric acid and black manganese oxide, the effects which are produced will vary in different cases.

1. The oxygen may simply remove hydrogen; as when alcohol is submitted to distillation with chromic acid. In this case water is formed, and a new body, aldehyd, containing all the carbon of the alcohol, is produced:—



2. The newly-formed substance, by absorbing oxygen, may give rise to a body in which the hydrogen, like that removed from the alcohol, is represented by an equivalent amount of oxygen, as when aldehyd passes into acetic acid; $2 \text{C}_2\text{H}_4\text{O} + \text{O}_2$ becoming $2 \text{C}_2\text{H}_4\text{O}_2$.

Or, 3. The complex molecule may be broken up more or less completely, in which case both the carbon and the hydrogen are partially removed in the form of carbonic anhydride and water, whilst an organic body of less complex composition is left; as when stearic acid is treated with nitric acid: in this case the products vary with the strength of the nitric acid employed, and with the time during which it is left to act upon the organic substance; so that the following compounds, each successively simpler in composition, might be obtained from stearic acid ($\text{C}_{18}\text{H}_{36}\text{O}_2$):—

| | | | |
|--------------------|--|---------------------|-------------------------------------|
| Rutic acid . . . | $\text{C}_{10}\text{H}_{20}\text{O}_2$ | Adipic acid . . . | $\text{C}_6\text{H}_{10}\text{O}_4$ |
| Suberic acid . . . | $\text{C}_8\text{H}_{14}\text{O}_4$ | Succinic acid . . . | $\text{C}_4\text{H}_6\text{O}_4$ |
| Œnanthylie acid | $\text{C}_7\text{H}_{14}\text{O}_2$ | Butyric acid . . . | $\text{C}_4\text{H}_8\text{O}_2$ |
| Pimelic acid . . . | $\text{C}_7\text{H}_{12}\text{O}_4$ | | &c. |

But it is not only to the processes of oxidation effected in the laboratory that it is necessary to attend. Oxidizing actions are in constant operation unperceived on every side of us. The gradual decay of organic compounds is owing to their spontaneous slow oxidation; for decay is, in reality, only a slow process of combustion: a fact which Liebig indicated by substituting the term *eremacausis* for that of decay (from ἡρεμος, gentle, καῦσις, combustion). The decay of wood is a familiar instance of this kind; the hydrogen of the wood becomes more rapidly oxidized than its carbon, and the result is the formation of a brown powder termed ulmin or humus, in which the carbon preponderates over the hydrogen and the oxygen, to a much greater extent than in the wood from which it was formed. Such actions take place generally under the combined influence of moisture and of a temperature of about 59° (15° C.) or upwards. If the substance be perfectly dry, or if the temperature fall to the freezing point, oxidation is usually completely arrested.

Contact with a body which is itself actively undergoing slow oxidation will frequently induce this oxidizing action in substances possessed of a strong attraction for oxygen, but which do not, when in a pure state, themselves undergo oxidation. Alcohol, for example, does not undergo oxidation when allowed to evaporate in air; but if it be mixed with a little must or some substance susceptible of oxidation, the alcohol, when brought into contact with atmospheric air, becomes oxidized, and furnishes aldehyd and acetic acid (1250). Sometimes the steps of the process may be pretty clearly traced; for example, a solution of grape sugar in an alcoholic solution of potash does not absorb oxygen when exposed to the air; but the addition of a minute quantity of sulphindylie acid (1514) effects the oxidation of the sugar: probably, as Traube suggests, by the absorption of oxygen on the part of the sulphindylie acid, and the transfer of oxygen to the sugar; the sulphindylie acid absorbing fresh oxygen and again parting with it to fresh portions of sugar, acting in fact as a carrier of oxygen, just as nitric oxide does to sulphurous acid, during the manufacture of oil of vitriol (412). Another analogous experiment of Traube's consists in heating a solution of cupric oxide containing a large quantity of hydrochlorate of ammonia with grape sugar: no reduction takes place even when the liquid is boiled; but if a small quantity of reduced and colourless sulphindylie acid be added, the blue colour of the indigo reappears, owing to the absorption of oxygen by the indigo acid from the cupric oxide; the acid then gives up its oxygen to the sugar, after which it again takes up more oxygen from a fresh quantity of cupric oxide; so that in a short time the whole of the sugar is oxidized, and the cupric oxide reduced to cupreous oxide, whilst the sulphindylie acid is left apparently unaltered. The sulphindylie acid is in fact much more easily reduced than cupric oxide, and yet it has the power of easily absorbing oxygen from this oxide. An action similar to this of the sulphindylie acid in favouring oxidation in the sugar is supposed to exist in many other cases; as for example in the ordinary process of vinegar-making from sugar and water, where the presence of certain oxidizable matters is found by experience to be necessary.

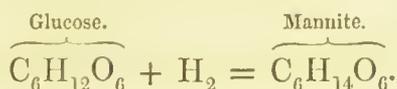
These slow processes of combustion are intimately connected with the development of ozone. In certain cases the formation of ozone is so abundant during such actions, that they furnish some of the best means of obtaining this singular body. Ozone, for instance, is always formed during the slow oxidation of phosphorus in air; and it appears also to be produced in the oxidation

of oil of turpentine and of ether under particular circumstances, as when a hot platinum wire is suspended in a mixture of the vapour of ether and atmospheric air. The ozone thus developed has in its turn a powerful influence in promoting the oxidation of the organic body, though of course it cannot be supposed that the presence of ozone is essential to the production and development of such oxidations, for they constantly occur where no ozone can be believed to exist; whilst in other cases the production of ozone appears to be a consequence rather than a cause of the process.

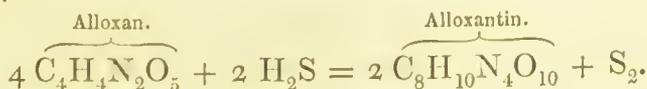
The importance of studying the action of such cases of oxidation must be obvious, when it is borne in mind that it is always by the agency of oxygen that the various complex substances contained in the animal body are gradually resolved into carbonic acid, water, and ammonia; in one or other of which forms the organic products return again to the domain of inorganic chemistry.

(1071) 2. *Metamorphoses by Reduction.*—From the foregoing observations it is manifest that processes of oxidation are essentially analytic and destructive in their nature. The synthetic processes, or processes of reduction, are, however, not less important. They are in perpetual operation in the growing plant, and less frequently occur in the animal; they may also in a limited degree be imitated in the laboratory. These reducing operations, however, are less completely under the control of the chemist than those of oxidation, but they are gradually becoming better understood.

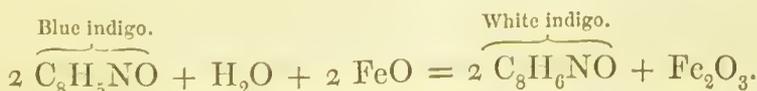
Nascent hydrogen may act in four ways. 1. It may combine directly with an organic compound. When, for instance, sodium amalgam is made to act upon inverted cane sugar (1086), mannite is produced:—



A similar effect is sometimes produced by the action of sulphuretted hydrogen, as when alloxan is by its means converted into alloxantin:—

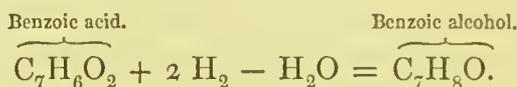


And in a somewhat similar manner blue indigo, under the combined action of ferrous oxide and alkalis, becomes converted into white indigo, whilst ferric oxide is formed:—

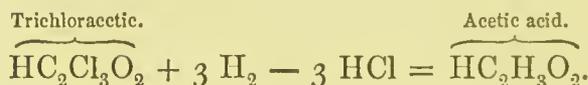


2. Sometimes simple removal of oxygen may take place, as in the deoxidation which occurs during the process of fermentation; as when calcic malate is allowed to ferment in contact with decayed cheese; succinic, acetic, and carbonic acids being the result. The formula of malic acid differs from that of succinic acid by containing 1 atom more of oxygen, malic acid being $C_4H_6O_5$, and succinic acid, $C_4H_6O_4$.

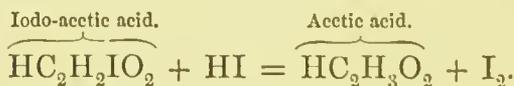
3. It may remove oxygen, or one of the halogens, whilst combining with the compound, as when benzoic acid is reduced to benzoic alcohol (Hermann).



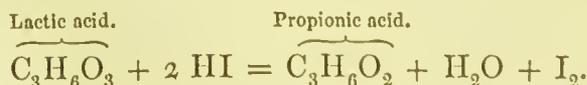
And, 4. It may remove oxygen, chlorine, or one of the halogens, whilst an equivalent amount of hydrogen takes its place, occasioning what has been called inverse substitution (1074): as in the reconversion of trichloroacetic into acetic acid:—



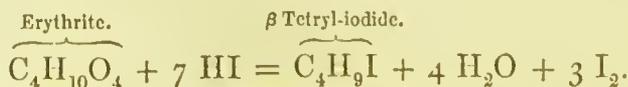
The action of hydriodic acid upon organic compounds is remarkable. When a basic substance like ammonia or ethylia is presented to it, direct combination ensues, as might have been expected; but hydriodic acid does not usually produce compounds into which iodine is introduced by substitution or double decomposition, though if heated with an iodized compound it often furnishes a substance in which hydrogen is substituted for iodine, whilst iodine is set at liberty, as for instance:—



In other cases hydriodic acid acts as a reducing agent; as for example when lactic acid is by its means converted into propionic (1284, 1310):—



or when erythrite is converted into β tetryl-iodide by its means (1243):—



(1072) 3. *Metamorphoses by Substitution.*—The method to be

adopted in the formation of new compounds by displacement or substitution, constitutes an important object of chemical inquiry, for the prosecution of such researches often gives the most satisfactory proof of the molecular grouping of the body under examination, and points out most distinctly its relations to other compounds. The ordinary method of preparing insoluble inorganic compounds by double decomposition, is simply a case of the substitution of one metal or one salt-radicle for another: when solutions such as those of potassic carbonate, and baric nitrate are mingled, the barium is exchanged for potassium, and reciprocally potassium for barium: $K_2CO_3 + Ba\ 2\ NO_3$ becoming $BaCO_3 + 2KNO_3$. This species of substitution is also a familiar operation amongst the compounds of organic chemistry; for the chemist has learned to displace* various elementary substances by compound groups, as when by the mutual action of hydrocyanic acid and mercuric oxide, mercuric cyanide and water are produced; $2HCy + HgO = HgCy_2 + H_2O$: the hydrogen and the mercury being substituted the one for the other; whilst 2 atoms of the monad group Cy (=CN), takes the place of 1 atom of the dyad oxygen in the oxide of mercury. Substitutions of groups of greater complication than these are also readily effected, and it is even possible in many instances to produce true organic compounds from inorganic elements (1075).

Few instances of substitution are more remarkable than those by which ammonia may be converted into a complex organic base. When ethyl bromide, for example, is mixed with a solution of ammonia in alcohol, placed in a sealed tube and heated for a few hours to 212° , a reaction occurs, in consequence of which, as the mixture cools, crystals of ethylia hydrobromate (C_2H_7N, HBr) are produced; and if this compound be distilled with caustic potash, potassic bromide, water, and a new base, ethylia (C_2H_7N), will be formed.

Now the molecule of ammonia may be represented as consisting of

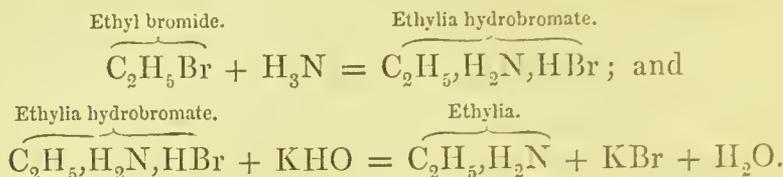
$$\left. \begin{array}{l} H \\ H \\ H \end{array} \right\} N;$$
 and the molecule of ethylia in like manner may

$$\left. \begin{array}{l} C_2H_5 \\ H \\ H \end{array} \right\} N;$$
 be viewed as

or as ammonia in which 1 atom of hydrogen has been displaced

* The French term *remplacement* is usually but inaccurately rendered *replacement*; the true meaning of the latter word is putting back into its place and not *displacement* or *substitution*, which conveys the meaning of the French word more correctly.

by C_2H_5 : that is to say, by its equivalent of ethyl. The substitution will be understood from the following equations:—



Again, if ethyl bromide be heated similarly with this new base, a second atom of hydrogen may be displaced, with a hydrobromate of a second more complicated base, diethylia, ($C_4H_{11}N$) will be obtained; and from this hydrobromate the pure base is liberated by distillation with caustic potash. In diethylia two atoms of hydrogen have been displaced by ethyl. For example:—



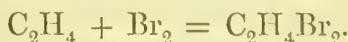
And again, if ethyl bromide be made to act upon diethylia, the third atom of hydrogen is displaced, and triethylia ($C_6H_{15}N$) in combination with hydrobromic acid is produced; and thus a

complex ammonia $\left. \begin{array}{l} C_2H_5 \\ C_2H_5 \\ C_2H_5 \end{array} \right\} N$, is built up step by step, by the suc-

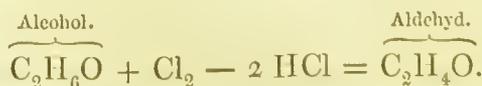
cessive removal of hydrogen and the substitution of a corresponding number of atoms of ethyl. Many cases of the same nature will be exhibited when the artificial formation of organic bases comes under the notice of the reader (1360).

(1073) *Action of Chlorine and the Halogens upon Organic Compounds—Substitution for Hydrogen.*—The action of chlorine and bromine upon the compounds of organic chemistry resembles that of oxygen, but the action of bromine is weaker than that of chlorine.

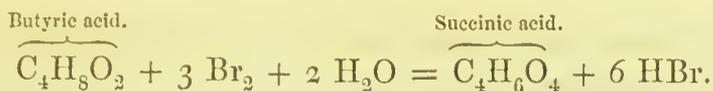
1. They may enter into direct combination, as when olefiant gas is converted into ethylene dibromide:—



2. They may simply remove hydrogen, as in the conversion of alcohol into aldehyd:—



3. They may act as oxidizing agents by liberating oxygen from water, as when butyric is converted into succinic acid:—



Secondary products, however, accompany this reaction, and a quantity of carbonaceous matter is deposited; (Friedel and Maehuca.)

4. Or they may produce compounds by substitution, in which hydrogen is displaced atom for atom by chlorine or bromine, while hydrochloric or hydrobromic acid escapes. It is advantageous, in conducting this experiment with chlorine, to transmit a current of the dry gas through the organic liquid; the chlorine is rapidly absorbed, especially if the action be aided by exposure to light or to the direct rays of the sun: the organic compound undergoes decomposition, abundance of hydrochloric acid escapes, and a new organic body, into the composition of which chlorine enters, is formed. In the majority of cases the new product is perfectly analogous to the compound from which it is procured, and contains the same number of elementary atoms, but a certain number of atoms of its hydrogen has been displaced by a corresponding number of atoms of chlorine. This very singular species of substitution was originally observed by Gay-Lussac to take place when wax is acted upon by chlorine; and a good example of its occurrence has already been considered, when we were engaged in tracing the conversion of Dutch liquid into Faraday's chloride of carbon (C_2Cl_6 ; 488).

This kind of substitution is of frequent occurrence, and some of the most instructive instances are afforded by the action of chlorine upon ether and upon other derivatives of alcohol. For example, when the vapour of hydrochloric ether ($\text{C}_2\text{H}_5\text{Cl}$) is subjected to the action of chlorine in the direct rays of the sun, the chlorine immediately begins to act upon the ether, and the process may then be continued in diffused daylight. By attention to a number of precautions a succession of compounds is furnished, in which, atom for atom, the hydrogen is displaced by chlorine, until at length the last product obtained is the solid chloride of carbon. The table on the next page exhibits the successive steps of the reaction, and indicates some of the properties of the different compounds. The density of these compounds, both in the state of liquid and of vapour, increases as the proportion of chlorine increases; the volume of a molecule of vapour is the same for all, being \square when the volume of the atom of hydrogen $\text{H}=1$, is taken as \square . It will also be seen that the boiling point rises as the quantity of chlorine increases. Every molecule

of each of these bodies contains the same number of elementary atoms, which appear to be grouped in the same order in each compound. The chlorine seems to have taken the place of hydrogen in the group without disturbing the relative position of the other elements which enter into its formation: just as a brick in an edifice may be conceived to admit of being removed, whilst its place is supplied by a block of wood or of stone, without altering the form or the symmetry of the building.

| Name of Compound. | Formula. Mol. Vol. □ | Boiling Point. | | Specific Gravity. | |
|------------------------------------|----------------------------|----------------|------|-------------------|---------|
| | | ° F. | ° C. | Liquid. | Vapour. |
| Hydrochloric ether | C_2H_5Cl | 51·8 | 11 | 0·874 | 2·219 |
| Chlorinated ditto | $C_2H_4Cl_2$ | 147·2 | 64 | 1·174 | 3·478 |
| Dichlorinated ditto | $C_2H_3Cl_3$ | 170·6 | 77 | 1·372 | 4·530 |
| Trichlorinated ditto | $C_2H_2Cl_4$ | 215·6 | 102 | 1·530 | 5·799 |
| Tetrachlorinated ditto | C_2HCl_5 | 294·8 | 146 | 1·644 | 6·975 |
| Solid chloride of carbon | C_2Cl_6 | 359·6 | 182 | 2·4 | 8·15 |

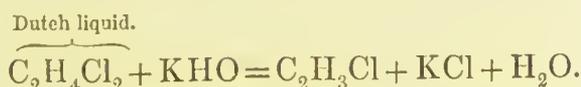
A striking proof of the persistence of the molecular arrangement of the compound, and of the preservation of the relative collocation of its component particles, is afforded when two parallel series of isomeric substitution-compounds are compared with each other. Such a parallel is afforded by the chlorinated compounds derived from hydrochloric ether and from Dutch liquid.

| Name of Compound. | Formula. Mol. Vol. □□ | Boiling Point. | | Specific Gravity. | |
|--|-----------------------------|----------------|------|-------------------|---------|
| | | ° F. | ° C. | Liquid. | Vapour. |
| Dutch liquid | $C_2H_4Cl_2$ | 184 | 84·5 | 1·280 | 3·450 |
| Monochlorinated hydrochloric ether | $C_2H_4Cl_2$ | 147·2 | 64 | 1·174 | 3·478 |
| Monochlorinated Dutch liquid, Dichlorinated HCl ether | $C_2H_3Cl_3$ | 239 | 115 | 1·422 | 4·613 |
| Dichlorinated Dutch liquid, Trichlorinated HCl ether | $C_2H_2Cl_4$ | 170·6 | 77 | 1·372 | 4·530 |
| Dichlorinated Dutch liquid, Trichlorinated HCl ether | $C_2H_2Cl_4$ | 275 | 135 | 1·576 | 5·767 |
| Trichlorinated Dutch liquid, Tetrachlorinated HCl ether | C_2HCl_5 | 215·6 | 102 | 1·530 | 5·799 |
| Trichlorinated Dutch liquid, Tetrachlorinated HCl ether | C_2HCl_5 | 307·4 | 153 | 1·663 | 6·975 |
| Tetrachlorinated Dutch liquid, Pentachlorinated HCl ether | C_2HCl_5 | 294·8 | 146 | 1·644 | 6·975 |
| Solid carbon chloride | C_2Cl_4 | 359·6 | 182 | Solid. 2·40 | 8·157 |
| Solid carbon chloride | C_2Cl_6 | | | | |

It has already been explained (488), that when equal volumes of gaseous chlorine and olefiant gas are mixed together, they gradually enter into combination, and form the oily fragrant body known as Dutch liquid ($C_2H_4Cl_2$); and further, that when this

liquid is submitted to the action of chlorine in excess, a series of compounds is obtained from it, in which each atom of hydrogen in succession is displaced by an atom of chlorine. Now it will be found, on comparing these bodies with those furnished by acting upon hydrochloric ether, that a certain number of them are metameric in pairs, although the two members of each pair possess very different properties, as may be seen by examining the preceding table, where the metameric pairs are placed side by side.

A molecule of each of these compounds in the gaseous state occupies two volumes; consequently the vapour densities of each metameric pair nearly coincide. Indeed it is a necessary condition that equal weights of all metameric bodies yield equal volumes of vapour, and therefore, allowing for errors of experiment, metamerides must always coincide in density in the gaseous state: but in the liquid form, the densities of the components of each pair are widely different, and the temperatures at which they boil are also different. There is likewise a marked difference in their chemical properties, and in the mode of their decomposition. The following are some of the points of difference:—the substitution compounds derived from hydrochloric ether are scarcely affected even when boiled with an alcoholic solution of potash, or with one of hydric potassic sulphide (KHS); and potassium may remain in them at ordinary temperatures without being acted upon. On the other hand, when the compounds derived from Dutch liquid are treated with an alcoholic solution of potash they are rapidly decomposed; potassic chloride and water are formed, and a new substance, considerably more volatile than the original chlorinated compound is obtained: for example:—



| By the action of Caustic Potash:— | New Compounds. | Boiling Point. | | Sp. Gr. of Liquid. |
|---|---|----------------|------|--------------------|
| | | ° F. | ° C. | |
| Dutch liquid . . . C ₂ H ₄ Cl ₂ yields | C ₂ H ₃ Cl | 14 | -10 | 1·250 |
| Monochlorinated ditto C ₂ H ₃ Cl, Cl ₂ „ | C ₂ H ₂ Cl ₂ | 95 | 35 | |
| Dichlorinated ditto . C ₂ H ₂ Cl ₂ , Cl ₂ „ | C ₂ HCl ₃ | 251·6 | 122 | 1·619 |
| Trichlorinated ditto . C ₂ HCl ₃ , Cl ₂ „ | C ₂ Cl ₄ | | | |

If an alcoholic solution of hydric potassic sulphide be employed instead of the caustic alkali, various sulphuretted compounds are produced; and the chlorinated derivatives of Dutch liquid are violently decomposed by potassium.

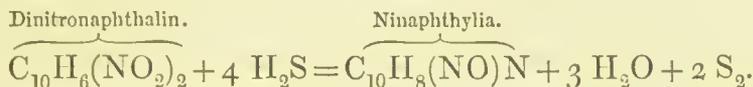
Now it is obvious that the original difference of molecular grouping is preserved throughout, both in the series of Dutch liquid and in that of hydrochloric ether, so that the chemist is thus, as it were, enabled to dissect these compounds by the agency of chlorine; and it is not until the last atom of hydrogen is removed that the molecular arrangement breaks down; both groups in that case yielding the same compound—viz., Faraday's chloride of carbon.

The discovery that the substitution of chlorine for hydrogen was practicable, at first excited the greatest astonishment amongst chemists, since owing to the powerful attractions of chlorine, particularly when its electrical opposition to hydrogen is borne in mind, the possibility of such an occurrence was never suspected. The displacement of oxygen by chlorine was familiar to the mind of the chemist, but the displacement of hydrogen by chlorine was a circumstance in opposition to the doctrines of chemical attraction then prevalent. The discovery of this remarkable fact has led to the production by substitution of an immense number of analogous compounds in other groups of organic bodies. The new products so obtained, however, are in general possessed of but little intrinsic interest. The importance of accurately studying the steps by which these substitutions are effected, can, however, be scarcely over-estimated, owing to the light which they frequently throw upon the views of the constitution of the different compounds, and of their relations to others where no obvious connexion had been previously traced.

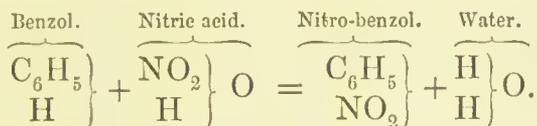
It seldom happens that the process of substitution can be followed through its successive stages so completely as in the case of hydrochloric ether or of Dutch liquid; the products of the operation are mingled with each other, and often cannot be satisfactorily separated. The first atoms of hydrogen are displaced more readily than the others, and frequently the last atom is removed with great difficulty. It is often necessary at first to moderate the action by cooling the liquid artificially, and by placing it either in obscurity or only in the diffused light of day; while to complete the displacement of the last portions, the strongest sunlight, aided by a temperature of ebullition, is frequently requisite (1174 *et seq.*).

Substitutions of bromine for hydrogen may also be effected by analogous methods, although, owing to its feebler chemical attractions, the reactions take place with less vehemence; and with iodine the products of substitution can only be obtained by indirect means.

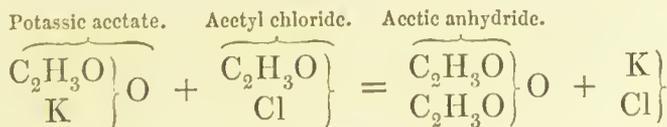
In a few cases the substitution of an atom of nitric oxide, (nitrosyl NO), for an atom of hydrogen has been observed; dinitronaphthalin, for instance, by the reducing action of sulphuretted hydrogen, yields a compound termed nitrosonaphthylamine, or ninaphthylia—



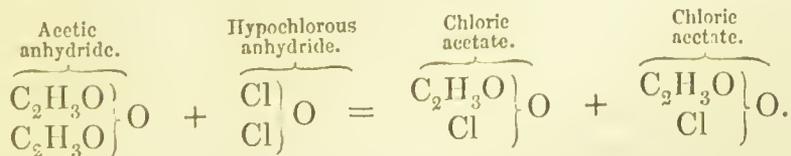
In other instances peroxide of nitrogen (nitroxyl NO_2), may be substituted for hydrogen, atom for atom, as when benzol (C_6H_6) is acted upon by nitric acid, and is converted into nitrobenzol ($\text{C}_6\text{H}_5\text{NO}_2$) whilst water is formed. Each molecule of nitric acid (HNO_3) in these cases exchanges an atom of nitroxyl for an atom of the hydrogen of the benzol; thus:—



Schutzenberger (*Comptes Rendus*, lii. 135) appears to have succeeded, in some cases, in effecting the indirect substitution of electro-negative bodies, such as chlorine, iodine, and cyanogen, for even the *basylous* hydrogen of certain organic acids; and thus, in a certain sense, chlorine and its analogues are shown to be chemically equivalent to potassium. In order to effect these transformations it is necessary to displace the hydrogen of the acid, or the metal which occupies its place, by some electro-negative group. For instance, if potassic acetate be treated with acetyl chloride (1266) acetic anhydride is obtained:—



and if acetic anhydride (1279) be digested at a very low temperature with hypochlorous anhydride (379), the red-coloured liquid at first obtained gradually becomes colourless, and chloric acetate is formed:—



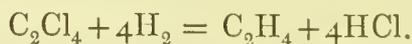
Similar compounds may be obtained with bromine, with iodine, and with cyanogen. All these bodies are extremely unstable, and

most of them undergo gradual decomposition at common temperatures; the compound with bromine even explodes spontaneously, that with chlorine at 212° , and that with iodine at a temperature somewhat higher.

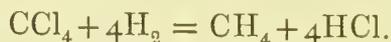
These compounds are respectively metameric with chloroacetic (1281), bromoacetic, and iodoacetic acids, but they bear no resemblance to them in properties. Similar combinations with butyric and benzoic acids have been obtained.

(1074) *Inverse Substitutions*.—A series of substitutions the reverse of those just described, and in which the chlorine or iodine is displaced by a corresponding number of atoms of hydrogen, often furnishes results of very great interest; but the methods of effecting these inverse substitutions are only beginning to attract the notice which their importance demands.

1. Berthelot (*Ann. de Chimie*, III. li. 48) has pointed out that when the compounds for experiment are of a very stable character, *free hydrogen*, at an elevated temperature may effect this species of substitution, though a good deal of the chlorinated compound is always destroyed. Several of the chlorides of carbon yield such results; for instance, ethylene-chloride of carbon (C_2Cl_4) when transmitted in vapour with hydrogen through a glass tube filled with fragments of pumice and heated to redness, furnishes hydrochloric acid and olefiant gas:—



Carbon tetrachloride (CCl_4) yields marsh gas and olefiant gas:—

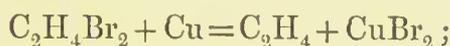


The olefiant gas is the result of the effect of heat upon the carbon tetrachloride, which is partially decomposed into ethylene chloride (C_2Cl_4) and free chlorine; and this ethylene chloride is then converted into olefiant gas by the action of the hydrogen, as already explained.

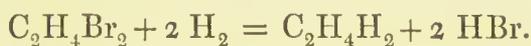
2. *Nascent hydrogen* may generally be more advantageously resorted to in effecting reductions of this description. In this way Melsens, by acting upon trichloroacetic acid with an amalgam of potassium, reproduced acetic acid; Frankland, by means of zinc, has obtained the hydrocarbon radicles of the alcohols and their hydrides (1203, 1206) from their iodides; and Berthelot, by enclosing the bromide of ethylene, of propylene, of butylene, and of amylene, in strong glass tubes in contact with water, copper foil, and potassic iodide, and subsequently heating the mixture to 527° (275° C.) in an oil bath, procured olefiant gas, propylene,

butylene, and amylene, accompanied by some gaseous bodies which are products of a secondary decomposition. If the use of copper be omitted, the products of secondary decomposition are more considerable; so that it would appear that a part of the organic body had taken the place of the copper, and had undergone oxidation at the expense of the oxygen of the water, whilst the hydrogen had effected an inverse substitution and formed *hydrides* of ethylene, propylene, butylene, and amylene.

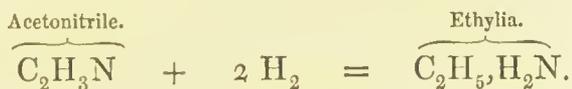
When the copper is present the reaction is probably of the following nature:—



and when the copper is not added, the decomposition may be represented as follows:—



Another important reaction of this kind was observed by Mendius, who has succeeded in converting the nitrile of an acid into the corresponding ammoniated base of its alcohol (1124). The nitrile is to be mixed with alcohol and hydrochloric acid, and digested upon granulated zinc; after the reaction has terminated, about half the liquid is to be distilled over; a good deal of unaltered nitrile comes off, leaving the new base in combination with the acid, mixed with zincic chloride; on then adding potash or lime the alcohol-base may be distilled off. The reaction is a simple case of hydrogenation; for example:—



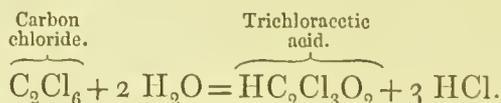
(1075) *Synthetic Production of Organic Compounds.*—A combination of the operations of direct chemical action with those of substitution, enables the chemist in many instances to build up a truly organic compound from inorganic materials. This is well exemplified in the artificial production of acetic acid in the manner first pointed out by Kolbe (Liebig's *Annal.* liv. 186):—When carbon is heated to bright redness in the vapour of sulphur, combination between the two elements takes place, and carbon

* The base may then be converted into the alcohol by Hofmann's reaction with nitrous acid; aniline ($\text{C}_6\text{H}_5\text{H}_2\text{N}$) thus yields carbolic acid ($\text{C}_6\text{H}_6\text{O}$) $\text{C}_6\text{H}_5\text{H}_2\text{N} + \text{HNO}_2 = \text{C}_6\text{H}_5\text{O} + \text{H}_2\text{O} + \text{N}_2$; and the nitrites of the alcohol bases when boiled with water yield the corresponding alcohol, and nitrogen; ethylia nitrite ($\text{C}_2\text{H}_7\text{N}, \text{HNO}_2$) for instance, becoming $\text{C}_2\text{H}_6\text{O} + \text{N}_2 + \text{H}_2\text{O}$.

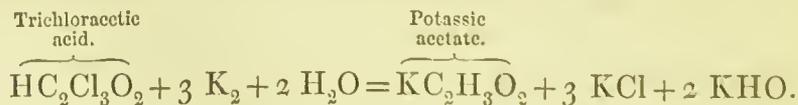
disulphide (CS_2) is formed. When carbon disulphide is digested for several days with aqua regia, a white volatile crystalline compound is obtained which is insoluble in water, but soluble in alcohol and in ether: it melts at 275° (135° C.), and at 338° (170° C.) it enters into ebullition: it has a peculiar odour which brings tears into the eyes, and its vapour has a sp. gr. of 7.43. This substance, discovered by Berzelius and Marcet, has the composition represented by the formula (CCl_4SO_2), and is termed by Kolbe *sulphite of perchloride of carbon*. When this compound is transmitted in vapour through a porcelain tube at a dull red heat it is decomposed into liquid carbon ethylene-chloride (C_2Cl_4), sulphurous anhydride, and free chlorine:—



If the carbon ethylene chloride thus obtained be placed beneath a layer of water, and exposed to the sun's rays in a large vessel filled with chlorine gas, Faraday's solid carbon chloride (C_2Cl_6) is formed abundantly, and at the same time an acid solution is obtained, which, after saturation with lime or with some other base, is found to contain a chloride and a trichloracetate of the basyl; if lime be used, the formula of the salt is $\text{Ca } 2 \text{C}_2\text{Cl}_3\text{O}_2$. Kolbe attributes its production to the reaction of water upon solid carbon chloride at the moment of its formation, as shown by the following equation:—



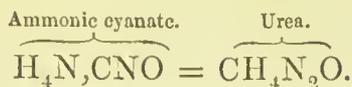
Now if trichloracetic acid be treated with an excess of potassium in the form of an amalgam, the chlorine is entirely withdrawn from this compound, and its place is supplied by hydrogen; in other words, it is converted into a salt of acetic acid:—



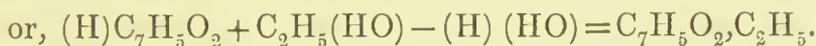
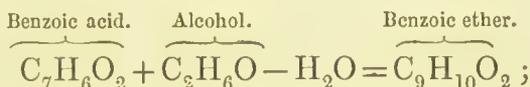
Thus a complex organic acid is obtained from inorganic materials:—the successive steps of the operation being, 1. carbon disulphide; 2. sulphite of carbon tetrachloride; 3. ethylene chloride of carbon; 4. trichloracetic acid; and 5. acetic acid.

The earliest and one of the most remarkable instances of the synthetic formation of an organic compound was afforded in the case of urea, which Wöhler discovered might be artificially obtained by the action of cyanic acid on ammonia; for if it be attempted to

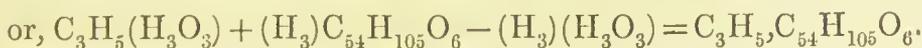
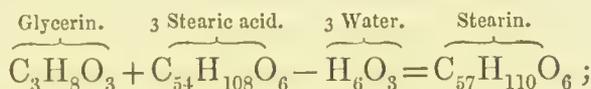
evaporate a solution of ammoniac cyanate, this salt undergoes an isomeric transformation, and yields urea :—



In a large number of cases it has been ascertained that the complex molecules constituting many organic compounds are obtained by the union of two or more molecules of different bodies of simpler constitution, with the separation of the elements of water; the *residues* of the original molecules having entered into combination to form a new more complex molecule, still retaining the characteristics of its origin, and ready to break up again with the assimilation of the elements of water to reproduce its parent molecules. For example, benzoic ether ($\text{C}_9\text{H}_{10}\text{O}_2$) may be procured by the reaction of alcohol upon benzoic acid with elimination of water :—

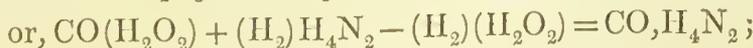
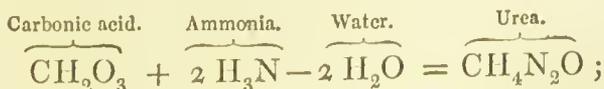


And in like manner stearin ($\text{C}_{57}\text{H}_{110}\text{O}_6$) may be obtained from the residues of 3 molecules of stearic acid and 1 molecule of glycerin, after the separation of 3 molecules of water :—



Benzoic ether, when left long in contact with water, slowly combines with it, benzoic acid and alcohol being reproduced. And when, as in the process of soap-making, stearin is broken up by the action of an alkali such as soda, 3 molecules of sodic stearate and 1 molecule of glycerin are produced from each molecule of stearin, while water is assimilated.

In like manner urea itself may be regarded as a product obtained from 1 molecule of carbonic acid and 2 molecules of ammonia, with elimination of 2 molecules of water :—



and this explains the rapid conversion of urea into ammoniac carbonate during the putrefaction of urine, since in this case

the elements of water reunite with those of urea, and produce the salt.

It has been well remarked by Berthelot (*Chimie Organique fondée sur la Synthèse*, Vol. I. p. 133), "In order to accomplish the reproduction of a natural compound, it is often necessary to erect an entire edifice founded upon the formation of artificial products. The examination of these enables us to ascertain the general laws which regulate the composition of compounds presented by nature, and the method by which their study, whether analytical, or synthetical, may be followed with some hope of a successful result." No experimenter has laboured so successfully in this field as the eminent chemist just quoted, who has indeed established new modes of investigation by his researches. Among many remarkable discoveries which he has made in this direction, is the method of obtaining a formiate synthetically by combining carbonic oxide with caustic potash: $\text{CO} + \text{KHO}$, becoming KCHO_2 (1275).

Berthelot has likewise obtained olefiant gas by the reaction of copper and sulphuretted hydrogen upon carbon disulphide; and from olefiant gas he has procured alcohol. He has further, by heating carbon intensely by means of the voltaic arc, obtained synthetically the hydrocarbon acetylene (C_2H_2). The same chemist has also, conjointly with De Luca, converted the hydrocarbon propylene into glycerin, and he has further shown that glycerin may be transformed into one variety of sugar; he has also succeeded in producing from the simpler hydrocarbons, such as acetylene (C_2H_2), others more complex, as benzol (C_6H_6), styrol (C_8H_8), and various others of still more complicated structure.

Strecker succeeded a few years ago in obtaining taurin by synthesis; and as researches in this direction are multiplied, new methods of preparing bodies till lately obtainable only from the products of the living plant or animal are daily being devised; so that the number of organic products which can be formed synthetically is now very considerable.

CHAPTER II.

THE SACCHARINE OR AMYLACEOUS GROUP.—VARIETIES OF
FERMENTATION.

(1076) THE compounds which belong to the group to which the following chapter is mainly devoted are among the most important and abundant constituents of plants. They all contain carbon in the proportion of 6 atoms, or some multiple of 6, in their molecule. One of the most remarkable features of their chemical composition is the circumstance that they all contain oxygen and hydrogen exactly in the proportions requisite to form water, and hence they have by some writers been spoken of as *hydrates of carbon*. This term, however, is by no means intended to signify that all the hydrogen and oxygen exist in them united in the form of water, but merely to indicate that the proportion of their components is such as might allow of their elements being so arranged. Owing to this peculiarity of composition, many of these bodies admit of being readily transformed one into the other by the addition or abstraction of the elements of water, and several of them are especially prone to undergo the changes produced by fermentations of various kinds. - In the presence of dehydrating agents, the sugars, lignin, and many bodies of this class yield humus-like products. When submitted to oxidation by the action of nitric acid, most of them yield oxalic acid; and under the influence of a mixture of concentrated nitric and sulphuric acids, substitution compounds are obtained, in which a portion of their hydrogen is displaced by peroxide of nitrogen. The most remarkable of these substitution compounds is pyroxylin (gun-cotton), the peculiar inflammability and explosive character of which is well known; but all of the nitrous substitution products of this class partake more or less of the inflammable and explosive properties which are so signally exhibited by pyroxylin. The bodies of the saccharine group readily undergo oxidation, especially in the presence of uncombined alkalies, and reduce many metallic oxides, such as those of copper and silver. Many of them, including cane sugar, amidin, inulin, and gum, allow of a substitution of portions of their hydrogen by metals; and in this manner compounds containing calcium, barium, and lead, may be obtained. In other cases the oxides appear to unite with the original body.

The researches of Berthelot and others seem to have ren-

dered it probable that the sugars, as well as mannite and the bodies allied to it, are polyatomic alcohols, like glycerin (1238); for they possess the power of entering into combination with various acids, with elimination of water, in some cases yielding peculiar colligated acids, analogous to the tannic, and in others furnishing neutral bodies closely allied to the fats. Linnemann has also shown that certain sugars may by the action of sodium amalgam be combined with hydrogen and converted into mannite (1244).

In the present chapter the compounds mentioned in the following table will be described. In a few of the substances enumerated in the lower part of the table, the proportion of oxygen and hydrogen differs from that of the sugars and starches.

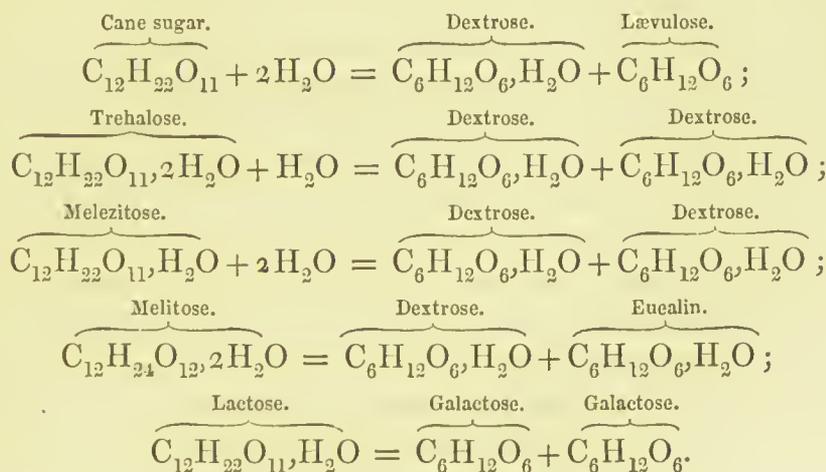
Amylaceous and Saccharine Group.

| | |
|-----------------------------------|-------------------------------|
| Sucrose (cane sugar) | $C_{12}H_{22}O_{11}$ |
| Mycose, or trehalose | $C_{12}H_{22}O_{11}, 2H_2O$ |
| Melczitose | $C_{12}H_{22}O_{11}, H_2O$ |
| Laetose (milk sugar) | $C_{12}H_{22}O_{11}, H_2O$ |
| Lævulose (fruit sugar). | $C_6H_{12}O_6$ |
| Dextrose (starch sugar) | $C_6H_{12}O_6, H_2O$ |
| Galactose | $C_6H_{12}O_6$ |
| Melitose | $C_{12}H_{24}O_{12}, 2H_2O$ |
| Eucalin | $C_6H_{12}O_6, H_2O$ |
| Sorbin | $C_6H_{12}O_6$ |
| Inosin | $C_6H_{12}O_6, 2H_2O$ |
| <hr/> | |
| Amidin (starch) | $x C_6H_{10}O_5$ |
| Dextrin | $C_6H_{10}O_5$ |
| Inulin | $C_6H_{10}O_5$ |
| Glycogen | $C_6H_{10}O_5$ |
| Arabin (gum arabic) | $2(C_6H_{10}O_5), H_2O.$ |
| Bassorin (tragacanth) | $x C_6H_{10}O_5$ |
| Cellulin (cellulose) | $3 C_6H_{10}O_5$ |
| Tunicin | $x C_6H_{10}O_5$ |
| <hr/> | |
| Erythrite | $C_4H_{10}O_4$ |
| Dulcite | $C_6H_{14}O_6$ |
| Mannite | $C_6H_{14}O_6$ |
| Pinite | $C_6H_{12}O_5$ |
| Quercite | $C_6H_{12}O_5$ |
| Pectin | $C_{32}H_{40}O_{28}, 4H_2O ?$ |

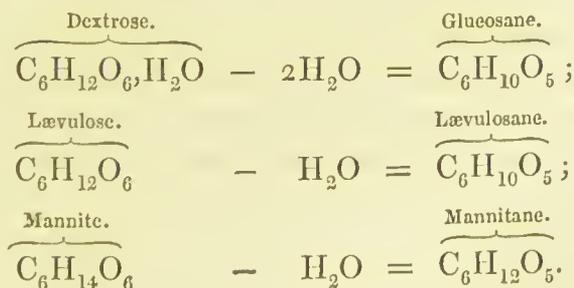
Certain of these substances are soluble in cold water, such as the sugars and the gums. Others, like starch, become dissolved in water by the aid of heat, or rather become diffused through the liquid, though the solution is of a very imperfect character; whilst a third variety, including cellulin or ligneous fibre, is quite insoluble in water, whether cold or hot.

With the exception of sorbin and inosin, all compounds which have the constitution of hydrates of carbon are convertible either by prolonged boiling with dilute sulphuric acid, or by digestion in the strong acid and boiling after subsequent dilution, into one of the forms of glucose—viz., dextrose, lævulose, or galactose. But neither of these three forms of sugar appears to be convertible into either of the others.

The action of acids on some of these bodies may be illustrated by the following formulæ (Kekulé, *Org. Chemie*, ii. p. 334):—



By the effect of heat certain of these sugars lose water, and become converted into other hydrates of carbon, which, by boiling with acids, are reconverted into the original compounds; for example:—



When heated with caustic potash to a temperature not exceeding 482° (250° C.), most of the members of this group yield considerable quantities of potassic oxalate; whilst an evolution of gas containing hydrogen and carburetted hydrogen takes place.

§ I. THE SUGARS.

(1077) SEVERAL varieties of sugar are known to the chemist; but they may all be referred to three principal forms, viz., cane sugar or sucrose, milk sugar or lactose, and grape sugar or glucose. The most important of these is the common sugar furnished by the sugar cane, hence termed *cane sugar*, related to which are some others of small importance, viz., trehalose, melezitose, and melitose, represented by the general formula $(C_{12}H_{22}O_{11}, xH_2O)$. The second variety is that to which milk owes its sweetness: it has never been met with excepting in the milk of animals, and hence it is termed *milk sugar* $(C_{12}H_{22}O_{11}, H_2O)$. The third variety constitutes the hard granular sweet masses common in old dried fruits, such as raisins, figs, &c., when it is known as *grape* or *starch sugar*, the latter name being derived from a method of preparing it artificially by boiling starch with a dilute acid. Connected with this variety are fruit sugar (lævulose), malt sugar, and galactose, the product of dilute acids upon milk sugar, all of which may be represented by the general formula $(C_6H_{12}O_6, xH_2O)$.

These different varieties of sugar agree in possessing a powerfully sweet taste. Each, when pure, has always a definite degree of sweetness, but there are great differences in the relative sweetness of the different varieties. A pound of cane sugar, for example, will produce a greater sweetening effect than a pound of fruit or inverted sugar; and at least two pounds and a half of starch sugar are required to produce a sweetening effect equal to that of one pound of the cane sugar; while a given weight of the sugar from milk possesses less sweetening power than an equal quantity even of starch sugar.

These varieties of sugar differ greatly in external appearance as well as in chemical characters; and they also differ in chemical composition. If quantities of the different kinds of sugar which contain equal amounts of carbon be compared together, it will be found that they differ in the proportion in which the elements of water are present. Comparing together quantities of sugar which contain 12 atoms of carbon, the proportion of water in each variety will be as follows;—

| Name of Sugar. | Formulae. | Carbon. | Water. |
|--------------------------|----------------------------|---------|--------|
| Cane sugar | $C_{12}H_{22}O_{11}$ | 144 | 198 |
| Inverted sugar | $2C_6H_{12}O_6$ | 144 | 216 |
| Starch sugar | $2(C_6H_{12}O_6, H_2O)$ | 144 | 252 |
| Milk sugar | $C_{12}H_{22}O_{11}, H_2O$ | 144 | 216 |

There are few plants from which sugar is absent, and to which, at some period of their growth, it does not form an important article of nutriment.

(1078.) I. CANE SUGAR or *Sucrose* ($C_{12}H_{22}O_{11}=342$).—This variety of sugar is chiefly obtained from the sugar cane: but the sugar maple and the beetroot furnish a considerable quantity for the market; it is also contained in carrots and turnips, as well as in the pumpkin, the chestnut, the young shoots of the maize, the ripe sorgho grass, and a large number of tropical fruits.

Properties.—Cane sugar has a sp. gr. of 1.6. It is soluble in about one-third of its weight of cold water, producing the thick viscid liquid known as syrup. It is also somewhat soluble in dilute alcohol, especially when heated with this liquid. It is insoluble in ether, and nearly so in cold absolute alcohol. By the spontaneous evaporation of its aqueous solution, it is deposited in large four-sided oblique rhomboidal prisms, which are often hemihedral, and are terminated by dihedral summits; these crystals constitute sugar-candy, which is colourless or brown according as the syrup employed is more or less free from colour. Ordinary loaf sugar consists of a congeries of minute transparent crystals, and the dazzling whiteness of the purest specimens is produced by the numerous reflections and refractions which the rays of light experience within the mass, from the numberless crystals of which it is composed. When two pieces of loaf sugar are rubbed together, a pale violet phosphorescent light is emitted.

If a solution of sugar be long boiled, it acquires an acid reaction, generally becoming less viscid, and irrecoverably losing its property of crystallizing; this change is attended by the assimilation of an additional quantity of the elements of water, and the consequent formation of the uncrystallizable inverted sugar (1086) ($C_6H_{12}O_6$). This prejudicial alteration is effected still more rapidly by the addition to the sugar of one-twentieth of its weight of oxalic, citric, malic, or any of the stronger acids. If the solution be kept boiling for some hours, the change proceeds still further, water being assimilated by the inverted sugar, which thus becomes converted into grape sugar ($C_6H_{12}O_6, H_2O$); and at the same time a certain quantity of formic acid, and of a brown sparingly soluble substance termed *ulmin*, are produced. Smaller quantities of the acids produce similar effects, but to an extent proportioned to the degree of acidity. It is to prevent these injurious changes that a small amount of lime is always added to

the cane juice immediately after its expression from the plant, and before it is heated. The crystallization of sugar is also prevented by the presence of 2 or 3 per cent. of many salts, such as common salt and calcium chloride; these salts appear to form definite but deliquescent compounds with cane sugar. Péligré's analysis of the compound with sodic chloride gives results which may be represented by the formula $(2\text{NaCl}, \text{C}_{12}\text{H}_{20}\text{O}_{10}, \text{C}_{12}\text{H}_{22}\text{O}_{11})$.

The uses of sugar as an article of food are well known. Alone, it is insufficient for the support of life; but, when mixed with other suitable food, it has a fattening tendency, which, however, is not greater than that of a corresponding weight of starch (Lawes and Gilbert). Sugar is largely used as an antiseptic, in syrups and preserves. If dusted abundantly over meat, fruit, or fermentable matters, it prevents the usual process of decay from occurring, provided that the substances to be preserved are at the same time tolerably well excluded from the air.

(1079) *Action of Bases on Sugar*.—Sugar has the property of dissolving many metallic oxides when its solution is boiled with them. For example, freshly precipitated plumbic oxide is taken up by it in considerable quantity; and, on cooling, a white powder consisting of $\text{C}_{12}\text{H}_{20}\text{Pb}_2\text{O}_{12}$ is deposited; this if dried at 212° loses H_2O , and becomes $\text{C}_{12}\text{H}_{18}\text{Pb}_2\text{O}_{11}$; and a compound containing $\text{C}_{12}\text{H}_{16}\text{Pb}_3\text{O}_{11}$, may be obtained by adding a solution of lime in syrup to a boiling solution of plumbic acetate. Lime is also dissolved by syrup to a large extent; the compound $(\text{C}_{12}\text{H}_{22}\text{O}_{11}\text{CaO}; \text{Péligré})$ is that which is produced in cold moderately dilute solutions; it has a bitterish taste, and is very soluble in cold water. Its solution, however, if tolerably concentrated, becomes opaque when heated, and presents an appearance of coagulation, resembling that of white of egg; and a deposit occurs on boiling, which may even be washed with boiling water, though it is readily redissolved by the mother liquor on cooling. If this precipitate be filtered from the boiling solution it is found to contain $\text{C}_{12}\text{H}_{22}\text{O}_{11}, 3\text{CaO}$, and is nearly insoluble both in cold and hot water, though freely soluble in cold syrup. Baryta also forms a soluble compound with sugar $(\text{C}_{12}\text{H}_{22}\text{O}_{11}, \text{BaO})$.* The compounds produced with other bases are sparingly soluble in water, but are

* Dubrunfaut and Péligré have taken advantage of the insolubility of these compounds in boiling water, to separate crystallizable sugar from treacle. Péligré has obtained from common treacle one-fourth of its weight of crystallized sugar, by dissolving the precipitated sugar-lime in water, and separating the lime by means of a current of carbonic acid.

readily taken up by alkaline liquids. This fact explains an observation that the presence of sugar prevents the precipitation by alkalis of many metallic oxides from their salts,—the oxides of copper and iron being amongst the number thus retained in solution. Many metallic oxides experience reduction, either partial or complete, when boiled with sugar; if the chromates, for instance, be mingled with a little free acid, and heated with a solution of sugar, the chromic acid is reduced to chromic oxide, which is dissolved by the excess of acid, whilst the liquid becomes green; but the solutions of cupric salts containing excess of alkali are not reduced except by prolonged heating. The mercuric salts are converted into mercurous compounds, and salts of gold give a precipitate of the reduced metal in fine powder. This reducing action is also possessed, though to a less extent, by other compounds analogous to sugar.

If sucrose be mixed with 8 times its weight of quick-lime, and distilled in an earthenware retort, it is decomposed, and amongst the products of the distillation are a mixture of acetone (C_3H_6O), and *metacetone* ($C_6H_{10}O$). The latter is an oily liquid, which does not mix with water, but is soluble in alcohol and in ether; by washing the distilled liquid with water the acetone may, therefore, be removed, whilst the metacetone is left. Metacetone boils at $183^{\circ} \cdot 2$ ($84^{\circ} C.$; Fremy). When treated with a mixture of potassic dichromate and sulphuric acid it undergoes oxidation, and is converted into propionic acid ($HC_3H_5O_2$; 1284). If sucrose be treated with three times its weight of caustic potash containing excess of water, but not enough to liquefy it at ordinary temperatures, propionic acid, mixed with a large proportion of formic and acetic acids, is formed, and the three acids enter into combination with the potash. If heated with the solid hydrate (KHO), sucrose furnishes potassic oxalate.

(1080) *Other Modes of Decomposition of Sugar.*—Concentrated sulphuric acid rapidly chars and destroys cane sugar. If equal measures of strong syrup and oil of vitriol be mixed, much heat is evolved, the mass froths up and emits carbonic and formic acids, whilst a black carbonaceous residue containing ulmic acid is left. A similar blackening effect is produced by some of the metallic chlorides, such as stannic chloride. Dry chlorine likewise attacks sugar at a temperature of 212° , and produces a similar brown substance, which is only partially soluble in water. Nitric acid, of sp. gr. of 1.25, converts sugar into saccharic acid (1090), with evolution of carbonic anhydride; but if the nitric acid be more concentrated oxalic acid is formed.

Cane sugar undergoes an important change under the influence of the yeast of beer, which causes it to experience the alcoholic fermentation; it first assimilates the elements of water, and is then decomposed into carbonic anhydride and alcohol (1115). In contact with putrefying casein and chalk, lactic fermentation is

induced in sugar, the chief product being calcic lactate (1119); under other circumstances, not as yet thoroughly investigated, sugar undergoes the viscous fermentation, and becomes changed into a mucilaginous substance, and sometimes into mannite (1244).

(1081) *Action of Heat on Sugar.*—At a temperature of about 320° (160° C.) sucrose undergoes fusion, and on cooling forms the transparent amber-coloured solid, sold by the confectioners as *barley sugar*. If long kept in this form it loses its transparency, and gradually becomes crystallized. This change may be retarded, but not altogether prevented, by adding a small proportion of vinegar to the melted sugar. This alteration in structure is strictly analogous to that in consequence of which the tough, transparent variety of sulphur resumes its crystalline state. It has been observed that in both these cases an evolution of heat occurs during the passage of the bodies from the vitreous to the crystalline condition. Another interesting point of resemblance between these two phenomena is presented in the remarkable difference between the melting-points both of crystallized and vitreous sulphur, and of crystallized sugar and barley sugar. The latter becomes liquefied between 194° and 212° (90° and 100° C.), while loaf sugar does not melt below 320° . According to Gélis, when sugar has thus been melted, a mixture of dextrose and lævulosane is produced—



This mixture, when dissolved in water, and fermented with yeast, yields only half the quantity of alcohol that the original sugar would have produced, the lævulosane (1086) remaining unaltered in solution.

A solution of cane sugar exerts a right-handed rotation upon a ray of polarized light (126); but sugar which has long been kept in a melted state, when redissolved in water, has lost its power of crystallizing, and exerts a reduced right-handed rotatory action on the polarized ray. Soubeiran also observed that when a solution of sugar is long exposed to an elevated temperature, even when air is excluded, it undergoes a molecular change; the liquid becomes brown, and gradually acquires a left-handed rotatory action upon the ray. The simple boiling of cane sugar with water, if long continued, causes the sucrose to combine gradually with the elements of water, and it thus becomes converted into starch sugar. This change is effected much more rapidly in the presence of ammoniac chloride, or of any of the chlorides of the metals of the earths, such as calcic chloride: dilute acids effect the change still more rapidly.

If the application of heat to the melted sugar be continued, and it be gradually raised to 401° (205° C.), or 420° ($215^{\circ}5$ C.) each molecule ($C_{12}H_{22}O_{11}$) of sugar loses $2H_2O$, and a brown deliquescent and nearly tasteless mass ($C_{12}H_{18}O_9$?) remains, which is known as *caramel*, the French name for burnt sugar. This body is often used by cooks and confectioners as a colouring matter. It is probably a mixture. Caramel is soluble in water, and is precipitated from its solution as a brown powder, by adding a large excess of alcohol. It is not susceptible of fermentation with yeast. Caramel forms an insoluble compound with baryta; and if its solution be mixed with one of the basic plumbic acetate, a precipitate is formed. If sugar or caramel be heated beyond 420° , inflammable gases, containing carbonic oxide, marsh gas, aldehyd, acetone, acetic acid, and oily hydrocarbons, escape, and the compound is completely decomposed, leaving a porous brilliant mass of charcoal.

(1082) *Melitose* ($C_{12}H_{24}O_{12}, 2H_2O$).—This is the name (from *mel*, honey), given by Berthelot (*Ann. de Chimie*, III. xlv. 66) to a singular modification of sugar observed by Johnston to be contained in the manna of some species of the *Eucalyptus*. It is soluble in water, and somewhat soluble in alcohol. Its aqueous solution crystallizes by spontaneous evaporation in slender needles, which have a feebly sweet taste. When heated to 212° it loses $2H_2O$, or 9.2 per cent. of water; if heated to 266° (130° C.) it loses about 1 atom more of water, melts, and emits an agreeable odour, whilst it assumes the aspect of barley-sugar. The aqueous solution of melitose produces right-handed rotation of a polarized ray more powerfully than one of cane sugar. Basic plumbic acetate produces a precipitate in its solutions. It does not reduce the cupric salts when boiled with an alkaline solution of these compounds; but if boiled with sulphuric acid, the resulting liquid acquires the power of reducing the cupric salts, and its rotatory power on light is reduced by two-fifths, but it is not inverted like that of cane sugar. With nitric acid it yields, amongst other products, mucic acid. When mixed with yeast, melitose experiences the vinous fermentation, but it gives off one-half only of the quantity of carbonic anhydride which an equal weight of glucose would have yielded. These peculiarities depend upon the fact that under the influence of acids and of yeast melitose becomes broken up into two portions, one of which is susceptible of fermentation like glucose, whilst the second portion remains unacted on in the liquid. To the latter body the name of *eucalin* has been given. It is a substance of syrupy consistence, and a feebly sweet taste; when dried *in vacuo* at the ordinary temperature, it consists of $C_6H_{12}O_6$, H_2O , and at 212° it parts with H_2O . It produces right-handed rotation upon a polarized ray. Eucalin has the properties of sorbin (see table p. 111) in every respect, except that sorbin produces left-handed rotation and is crystallizable. When heated with alkalis it assumes a brown colour, and reduces the cupric salts; at a heat of 392° (200° C.) it becomes converted into a black insoluble mass.

(1083) 2. SUGAR OF MILK; *Lactin* or *Lactose* ($C_{12}H_{24}O_{12}$ or $C_{12}H_{22}O_{11}, H_2O$), *Sp. Gr.* 1.543.—This variety of sugar is an animal product, being obtained solely from the milk of the mammalia, and hence its name, from *lac*, milk. It is produced by the

herbivora in greatest abundance, but it is secreted also by the carnivora, although their diet is exclusively of an animal nature.

Preparation.—After the milk has been coagulated, the curd is separated, and the whey is concentrated by evaporation until it reaches the crystallizing point; small pieces of wood are then introduced to act as nuclei, upon which the crystals of lactose are deposited. It is thus procured in mammillated masses composed of groups of right four-sided prisms, terminated by four-sided pyramids. The crystals are white and semitransparent; they feel hard and gritty between the teeth, and require 5 or 6 parts of cold water for solution; the liquid thus formed is less sweet to the taste than that produced by an equal weight of starch sugar. Lactose is insoluble in alcohol and in ether. Its aqueous solution produces right-handed rotation of a ray of polarized light; the fresh solution has a higher rotatory power than it exhibits after standing for a few hours, or after heating it to 212° . If lactose be heated gradually to 284° (140° C.), 1 atom of water is expelled; but it is remarkable that if the temperature be suddenly raised to about 401° (205° C.), the crystals melt, and then lose $2\frac{1}{2}\text{H}_2\text{O}$. When boiled with dilute acids it is very slowly converted into a very soluble, crystallizable and fermentable sugar, *galactose*, which exerts a right-handed rotatory action upon polarized light, and furnishes twice as much mucic acid when treated with nitric acid as an equal weight of lactose. When pure, milk sugar is not susceptible of fermentation, but milk itself may be fermented. In this case, Berthelot was unable to find any evidence of the conversion of the lactose into glucose before it underwent fermentation. If the milk be allowed to ferment spontaneously in contact with chalk, a considerable quantity of calcic lactate is formed simultaneously with the alcohol. Lactose may be combined with plumbic oxide, which it dissolves freely; it likewise forms with it a white insoluble compound ($4\text{C}_{12}\text{H}_{24}\text{O}_{12}, 5\text{PbO} = \text{C}_{48}\text{H}_{86}\text{Pb}_5\text{O}_{48}, 5\text{H}_2\text{O}$). It also yields compounds with the alkalis and with the alkaline earths, and absorbs both ammoniacal and hydrochloric acid gases. An alkaline solution of lactose when boiled with cupric salts reduces them, and precipitates cuprous oxide. It also reduces the salts of mercury and of silver when heated with their solutions. The reaction upon the salts of silver has been made the basis of a process for silvering glass (936). When lactose is oxidized by nitric acid it yields mucic acid, with small quantities of saccharic, tartaric, racemic, and oxalic acids. If distilled with potassic dichromate and sulphuric acid, aldehyd is amongst the products.

(1084) 3. GRAPE OR STARCH SUGAR; *Glucose*,* *Dextrose*, ($C_6H_{12}O_6, H_2O = 180 + 18$).—*Preparation*.—Starch sugar is prepared upon a considerable scale by allowing a mixture of starch with a sufficient quantity of water to render it liquid, to flow gradually at a temperature of about 131° (55° C.), into a vat containing water acidulated with 1 per cent. of sulphuric acid; this liquor is kept constantly at the boiling point, by which means the starch is at once altered so as not to produce a mucilage. The liquid, after all the starch has been added, is maintained in a state of ebullition for about half an hour, at the end of which time the starch is usually completely converted into sugar. The portion of starch used amounts to one half of the weight of the water employed. The liquid is drawn off, and the acid is neutralized, by adding chalk in small quantities at a time, until it ceases to occasion any effervescence; the precipitate is allowed to subside, and the clear solution is concentrated by evaporation until it acquires a density of 1.28. It is drawn off from the deposited calcic sulphate, after which it is set aside for some days to crystallize. The molasses is allowed to drain off, and the sugar is dried at a gentle heat in a current of air.

The formula assigned to starch is $C_{12}H_{20}O_{10}$, and since that of starch sugar may be represented as $(C_6H_{12}O_6, H_2O)$, the conversion of starch into sugar may be regarded in the light of a combination of starch with the elements of water, 1 atom of starch and 4 atoms of water yielding 2 atoms of dextrose.

By the action of diastase (1096) starch is also converted partially into a fermentable sugar, which is one of the varieties of glucose.

A similar conversion of ligneous fibre into this form of sugar may be effected under the influence of acids, but in this case the acid is employed in a more concentrated form; 2 parts of clean linen or calico cut into shreds, are added gradually to 3 parts of oil of vitriol, and allowed to stand for 24 hours. The mixture is afterwards diluted largely with water, and boiled for a few hours.

* Under the name *glucose* (from $\gamma\lambda\upsilon\kappa\upsilon\varsigma$, sweet) several distinct modifications of sugar have been comprised, such as linen sugar, uncrystallizable diabetic sugar, and honey sugar, as well as sugar from malt, modified cane sugar, and the modification of milk sugar produced by acids; but these bodies, though closely resembling each other, present differences in their molecular structure, as may be proved by the differences in the effects produced by them on polarized light. In order to avoid this ambiguity it will be convenient to designate starch sugar by the term *dextrose*, employed by Kekulé, whilst the term *glucose* may still be retained as generic for the group.

The acid may then be neutralized by the addition of chalk, or what is better, of baric carbonate, and the sugar can afterwards be separated from the insoluble calcie or baric sulphate.

True dextrose is also produced from glycogen (1095) by prolonged boiling with diluted acids, as well as from trehalose and melezitose when similarly treated. One of the forms of glucose is also furnished by amygdalin, salicin, phloridzin, and other glucosides (1492) when decomposed by acids. Tunicin (1106), or the horny covering of beetles and other insects, also yields it when treated with dilute acids. Cane sugar, when so acted on, furnishes a mixture of dextrose with lævulose in equal proportions.

Glucose, usually in the form of dextrose, is the variety of sugar met with as a morbid constituent of the urine in cases of diabetes. It has been shown by Bernard to be produced rapidly from one of the normal constituents of the liver (glyeogen), and the same physiologist has remarked, that by irritating with a needle the fourth ventricle of the brain in a dog or a rabbit, sugar is developed in the blood and in the urine, after a few minutes.

Properties.—Grape sugar is distinguished from cane sugar by several characters; it crystallizes with difficulty in warty concretions, composed of hard transparent cubes. It requires about its own weight of water for solution, so that it is less soluble in water than cane sugar, though it is more readily taken up by alcohol; 100 parts of alcohol of 83 per cent. dissolve 2 of dextrose at 68° (20° C.), and about 21 parts at the boiling point. It crystallizes from a hot solution in alcohol containing not more than 5 per cent. of water, in anhydrous acicular prisms ($C_6H_{12}O_6$) fusible at 294°·8 (146° C.). It requires fully 2½ parts of glucose to produce the same sweetening effect as is produced by 1 part of cane sugar. The action of sulphuric acid upon grape sugar is quite different from its effect upon cane sugar, since, instead of decomposing it, as occurs with sucrose, it forms with glucose a definite compound acid, which has been termed *sulpho-saccharic* acid, and which, according to Péligot, yields a soluble salt with calcium and with barium.

Dextrose forms with common salt a compound that crystallizes with facility ($NaCl, H_2O, 2 C_6H_{12}O_6$); this furnishes another distinctive character of this variety of saccharine matter. This compound when heated to 212° gives off H_2O , and if the temperature of the residue be raised to 320° (160° C.) it loses an additional atom of water. When grape sugar is heated, it begins to soften at about 140° (60° C.) and at 212° it melts and loses

H_2O ; at about 338° (170° C.) it loses another atom of water and is converted into *glucosane** $C_6H_{10}O_5$, and at a still higher temperature an additional quantity of water is expelled, and the residue consists of caramel, which, when heated still further, is decomposed into gaseous products.

Grape sugar forms definite but unstable combinations with the alkaline bases. These compounds, even at ordinary temperatures, gradually undergo change; their solution, which is at first strongly alkaline, becomes neutral, owing to the formation of a powerful, colourless, but uncrystallizable acid, *glucic acid* ($H_3C_{12}H_{15}O_9$, Pélilot), which remains in combination with the base. Glucic acid, when boiled with water, absorbs oxygen and becomes brown; a new acid is formed ($H_2C_9H_9O_5$), which Mulder terms *apoglucic acid*, (from ἀπο, at a distance from, and glucose): it is not crystallizable. If an alkaline solution of grape sugar be heated, the sugar is rapidly destroyed, and a different body of dark brown colour, also possessed of acid characters, is produced; this substance is not crystallizable; it has been termed *melassic acid*. This body has a powerful tendency to combine with oxygen, and when boiled with an alkaline solution to which a cupric salt has been added, speedily reduces the cupric to a cuprous salt, whilst the red oxide is precipitated. The compounds obtained by the combination of dextrose with the acids and the alcohols, will be described hereafter (1246, 1247).

(1085) *Estimation of Sugar*.—Upon the foregoing facts Barreswil has founded a simple method of estimating the amount of sugar which any mixture may contain. For this purpose he prepares an alkaline solution of potassic-cupric tartrate ($K_2Cu 2 C_4H_4O_6$), of known strength. A given volume of this solution is placed in a porcelain capsule, and heated to near its boiling point; the solution of sugar to be tested is then added by degrees from a burette, until the addition of the syrup ceases to produce any further precipitate. The proportion of sugar which is present in the liquid will be inversely as the volume of the saccharine solution consumed.

Cane sugar does not reduce the alkaline solution of cupric tartrate; consequently no indication of the presence of cane sugar is afforded by this reagent. Nevertheless, a quantitative determination even of this variety of sugar may be effected by means of this method, provided that a given volume of the saccharine liquid, acidulated slightly with sulphuric acid, be diluted with water, and boiled for a short time; the cane sugar is thus converted into *inverted* sugar (1086),

* This is a colourless uncrystalline, unfermentable substance, not sweet, but reconvertible into dextrose by boiling with dilute acids.

and on diluting this liquid with water till it occupies a definite volume, the proportion of altered sugar which it contains may be ascertained. Supposing both kinds of sugar to be present, a preliminary experiment is made before boiling with acid, in order to estimate the amount of inverted or of grape sugar, and by deducting this from the quantity found after acidulating the liquid and boiling, the proportion of cane sugar is ascertained. Fehling recommends for the preparation of the standard copper solution, the following proportions, as reduced to English weights:—437·5 grains of crystallized cupric sulphate, 3 ounces of cream of tartar, $1\frac{1}{2}$ ounce of pure potassic carbonate, 14 or 16 ounces of a solution of caustic soda (sp. gr. 1·12), and water, which is added until the solution measures 12630 water grains. Two hundred measured grains of this solution contain a quantity of copper, which would be reduced by 1 grain of sugar ($C_6H_{12}O_6$); each atom of sugar reducing 5 atoms of cupric oxide to the state of cupreous oxide. The test is often conveniently resorted to as a preliminary trial for sugar in urine: little or no action occurs when a solution of grape or diabetic sugar is mixed with an alkaline solution of copper in the cold; but on the application of a gentle heat, the yellow hydrated cupreous oxide is thrown down, and on raising the temperature to the boiling point the anhydrous red oxide is deposited.

When a solution of any of the varieties of glucose is mixed with an ammoniacal solution of plumbic acetate, a precipitate is formed, containing ($2 C_6H_{12}O_6, 3PbO$). Lead dioxide converts glucose into a mixture of plumbic formiate and carbonate, whilst water is eliminated.

(1086) 4. FRUIT SUGAR—LÆVULOSE ($C_6H_{12}O_6$).—The researches of Baignet (*Ann. de Chimie*, III. lxi. 268) have shown that many ripe acidulous fruits, such as apricots, peaches, pine-apples, citrons, plums, and strawberries, contain cane sugar mixed with a variable proportion of *inverted* sugar; other fruits, among which are grapes, cherries, gooseberries, and figs, contain inverted sugar only.

Inverted sugar has received this appellation from its inverted action upon polarized light, which distinguishes it from sucrose; it appears to be procurable only from sucrose, by the action either of acids or of a peculiar albuminous ferment, present in the juice of many ripening fruits. Honey and manna contain inverted sugar.

Inverted sugar is soluble in alcohol of 85 per cent. It is not crystallizable, nevertheless it gradually separates into crystallized starch sugar, and an uncrystallized syrup. It is, in fact, a mixture of two different kinds of sugar; and if a solution of 5 parts of this sugar in 50 of water be mixed intimately with 3 parts of slaked lime, the solution, which is at first very liquid, becomes pasty: on straining it through linen, and expressing the fluid portion, the sugar is separated into two equal portions of different properties. One of these varieties, ordinary starch

sugar, remains in solution, and exerts a right-handed rotation upon a beam of polarized light, as may be ascertained by removing the lime by means of oxalic acid; whilst the other, which remains combined with the lime, exerts a left-handed rotation, and may be in like manner separated from the lime by suspending the compound in water and decomposing it by means of oxalic acid (Dubrunfaut).

Lævulose is the name from *lævus*, left-handed, given by Berthelot to the uncrystallizable variety of sugar found in fruits, and characterized by its *left-handed* rotation of a ray of polarized light. The rotatory power of this sugar diminishes rapidly as the temperature rises; it amounts to -106° at 56° (13° C.), and only to -53° at 194° (90° C.). With lime, lævulose forms a sparingly soluble compound ($2\text{ C}_6\text{H}_{12}\text{O}_6, 3\text{ CaO}$) which crystallizes in needles. Lævulose reduces alkaline cupric tartrate when heated with it. Lævulose is the sole fermentable product obtained from inulin (1100) by prolonged boiling with dilute acids. It is sweeter than starch sugar, and is less readily fermentable by yeast. When a solution of lævulose is digested with an amalgam of sodium, the sugar unites directly with a portion of the hydrogen, and mannite is formed.

When heated to 338° (170° C.) lævulose gradually loses water, and is converted into *lævulosane* ($\text{C}_6\text{H}_{10}\text{O}_5$), a soluble amorphous unfermentable substance, which, by boiling with water, especially if acidulated, is reconverted into lævulose. By heating cane sugar to 320° (160° C.) it becomes converted without loss of weight into starch sugar and lævulosane; the sugar may then be destroyed by fermentation, whilst the greater part of the lævulosane remains unaltered.

The foregoing observations will explain the fact that the sugar of fruits under the influence of diluted acids becomes combined with an additional quantity of water, and by continued boiling of this acid liquid the sugar gradually passes into the form of dextrose. When this solution, after the neutralization of the acid by baric carbonate, is evaporated, the grape sugar is obtained in the form of crystals. This passage of the sugar in fruits into grape sugar sometimes takes place spontaneously, as is seen in the gradual crystallization of the sugar in dried fruits. The sugar contained in honey also undergoes a spontaneous change by long keeping into a mass composed chiefly of crystalline grains of starch sugar. If such crystalline honey be washed with alcohol, the lævulose is removed and pure dextrose remains.

(1087) *Effects of the Varieties of Sugar on Polarized Light.*—Both sucrose, or cane sugar, and dextrose produce rotation upon a ray of polarized light. The plane of polarization is rotated to the right by sucrose rather less powerfully than by dextrose. It is remarkable that the uncrystallizable sugar of fruits produces an opposite rotation, viz., to the left. Since the degree of rotation is proportionate in columns of equal length to the quantity of sugar present, it has been proposed to employ this property in order to determine the quantity of sugar present in syrups. The following, according to Berthelot, are the rotatory powers of the different varieties of sugar, if equal weights of each are dissolved in an equal bulk of water: the quantities of each sugar are calculated for the formulæ annexed:—

| Variety. | Formula. | Rotation. | Temperature. | |
|--|--|-------------|--------------|------|
| | | | ° F. | ° C. |
| Sucrose (cane sugar) | (C ₁₂ H ₂₂ O ₁₁) | right 73°·8 | 56 | 13·3 |
| Melczitose | (C ₁₂ H ₂₂ O ₁₁) | „ 94°·1 | | |
| Mycose | (C ₁₂ H ₂₂ O ₁₁) | „ 193° | | |
| Melitose | (C ₁₂ H ₂₄ O ₁₂) | „ 102° | | |
| Dextrose (grape sugar) | (C ₆ H ₁₂ O ₆) | „ 57°·4 | | |
| Malt sugar | (C ₆ H ₁₂ O ₆) | „ 172° | | |
| Lævulose (fruit sugar) | (C ₆ H ₁₂ O ₆) | left 106° | | |
| Eucalin | (C ₆ H ₁₂ O ₆) | right 50° | | |
| Sorbin | (C ₆ H ₁₂ O ₆) | left 46°·9 | | |
| Laetose (milk sugar) | (C ₆ H ₁₂ O ₆) | right 56°·4 | | |
| Glucose of ditto (galactose) | (C ₆ H ₁₂ O ₆) | „ 83°·3 | 57 | 13·9 |
| Inverted cane sugar | (C ₆ H ₁₂ O ₆) | left 28° | | |

The specific rotatory power of a sugar or other organic compound may be thus calculated:—Let a represent the observed angle of rotation of the ray, for the *teinte de passage* (126); V the volume of the solution; l the length of the column of liquid; t the temperature of observation; p the weight of the substance in solution; R the rotatory power: then $R = a \frac{V}{lp}$ at the temperature t .

The following are quoted by Kekulé, as corresponding rotations of some other substances of the amylaceous group:—

| | |
|--------------------------|----------------|
| Soluble starch | right 211° |
| Dextrin | „ 138°·7 |
| Inulin | left 34°·4 |
| Arabin | „ 36° (about). |
| Inosin | inactive. |

In a paper contained in the *Ann. de Chimie*. III. xxvi. 175, Clerget gives a detailed account of the application of polarized light to the analysis of saccharine solutions by the aid of an instrument invented by Soleil. Bence Jones has applied the method to the determination of the quantity of sugar which remains in the unfermented state in wines. Diabetic urine may also be examined by the same process. According to Clerget, if the right-handed rotatory power of a given weight of cane sugar be taken as 100, that of an equal weight of diabetic sugar is 73, the rotation in this case also being right-handed. In connexion with the optical examination of syrups, the following facts are important:—Starch sugar presents three modifications when examined by its effect upon polarized light. A solution of anhydrous dextrose, crystallized from alcohol, when freshly made, possesses a rotatory power double of that which it retains after having been kept in solution for some hours; and the rotatory power of a solution of sugar from malt when freshly made, is three times as great as that of the same solution after long keeping. These different va-

rieties may all be immediately reduced to the one possessed of the minimum rotatory power, by simply heating the solution to 176° (80° C.) or upwards, and then allowing it to cool. If the rotatory power of starch sugar, of minimum effect, be taken as 1, that of a fresh solution of crystallized starch sugar will be 2, that of sugar of malt 3, and that of an equivalent quantity of dextrin (1099) will be equal to 4. Sugar of milk and the modified fermentable sugar obtained from it by the action of acids (galactose), resemble starch sugar in the circumstance that when first dissolved in water their solutions exert a greater rotatory power than after they have been in solution for a few hours. After the lapse of a certain interval of time the rotatory effect becomes stationary, and is represented by the numbers given in the table.

Starch sugar, after it has been thus reduced to its minimum power of rotation, undergoes no change when heated for a short time with an acid; but the rotatory power from left to right possessed by a solution of cane sugar is reversed by mixing the liquid with one-tenth of its bulk of a concentrated solution of pure hydrochloric acid, and heating it by means of a water bath for ten minutes to the temperature of 158° (70° C.); the crystalline sugar is thus converted into the uncrystallizable form, distinguished as *inverted* sugar (1086). It has been remarked, that the addition of a solution of potash or of soda to a solution of sugar, reduces the rotatory action of the liquid upon the polarized ray, but on neutralizing the alkali the original effect is restored. An excess of acid exerts no sensible effect upon the rotatory power of the liquid. Mitscherlich has shown that elevation of temperature produces a very singular effect upon the rotatory power. In the case of cane sugar, the rotatory power diminishes slowly as the temperature rises. If the rotatory power at 32° be = 1, it will at 212° be less by 0.0232 (or = 0.9768 Dubrunfaut); and in the case of cane sugar altered by acids the effect is so considerable, that according to Buignet it amounts to about 0.205 for each rise of 1° F.: indeed, not only is its rotatory power to the left greatly reduced, becoming at 126° only one-half of that which it had at 57° , but at 187° it becomes null, and beyond this it is actually reversed, and becomes right-handed.

(1088) *Manufacture of Sugar*.—The chief source of sugar in the state in which it is offered for sale is the sugar-cane, of which there are three or four varieties. This plant is a solid jointed reed, which grows to a height varying from 6 to 15 feet (1.8 to 4.5 metres). It is found most advantageous to cut the canes before they are allowed to flower, the produce of sugar being much reduced after inflorescence. The canes are cut as close to the soil as possible, since the juice contained in the lowest joints is the sweetest. The ripe canes immediately after cutting are stripped of their leaves, and subjected to strong pressure by passing them between grooved iron cylinders. In that hot climate the juice, if left to itself even for half an hour, begins to ferment: it is, therefore, immediately mingled with from $\frac{1}{3000}$ to $\frac{1}{800}$ of its weight of lime, and heated to 140° (60° C.) in large flat-bottomed copper pans or clarifiers, which hold from 300 to 400 gallons each (from 1360 to 1814 litres). At this temperature the albuminous portions of the juice become coagulated and rise to the surface in the form of scum, whilst the free acid is

nearly neutralized by the lime.* After allowing it to cool for an hour, the clear liquid is drawn off for concentration by boiling. The fuel used for this purpose generally consists of the crushed canes, the ashes of which, in well-managed plantations, are always returned to the soil, and furnish manure for future crops. When the syrup has acquired sufficient consistence, it is run into shallow wooden coolers, and immediately stirred briskly for a few minutes; it is then left to stand for an hour, when a crust like thin ice becomes formed over the top; this is broken up, after which the mass is left at rest for twenty-four hours: the semi-solid mass is then transferred to the curing-house, and is put into the *potting casks*, which are vessels furnished with perforated bottoms, to allow the molasses or treacle to drain off. In each perforation, a reed, or the stem of a plantain leaf, is placed, extending to the top of the cask, with the view of facilitating the drainage, which requires from four to five weeks for its completion. The crystals are finally dried off in the sun, and form the raw sugar of commerce. On an average, one gallon of juice furnishes one pound of sugar, or one tenth of its weight. Much waste is always incurred in the extraction of the saccharine matter, for according to Dumas 100 parts of fresh cane contain 90 of juice, and of this 18 or 20 parts are pure sugar. Péligot states that no uncrystallizable sugar is contained in the fresh juice of sound canes, though it occurs in decayed ones. Leery, who has specially studied this subject in the Mauritius, finds, however, that even sound canes contain a small but variable proportion of lævulose. (*Ann. de Chimie*, IV. v. 387.) Much of the waste arises from the conversion of the crystallizable sugar into treacle or uncrystallizable syrup, by the high temperature and frequent boilings to which it is subjected. Great improvements have recently been effected in the apparatus for boiling down syrups, by means of which a beautiful crystallized product may with care be obtained from the juice at the first crystallization.

Maple Sugar.—The American Indians manufacture a considerable quantity of sugar from a species of maple (*Acer saccharinum*). In order to obtain the

* According to the experiments of Leery, there are three azotised substances present in the juice of the cane: one a granular matter separable by filtration, which acts as an alcoholic ferment, a second coagulable by heat, of the nature of albumin, and a third substance precipitable by alcohol and by normal plumbic acetate. Both these soluble substances act injuriously by favouring the production of acids during ebullition. The liquid should not be alkaline when boiled, however, as it would then become strongly coloured. The addition of sulphurous acid is very effectual in checking the tendency of the juice to rapid alteration.

juice, they make perforations which penetrate through the bark, from a quarter to half an inch (from 6 to 12.5 millimetres) into the wood. Each tree usually has two borings; these perforations are always made upon the side of the tree facing the south, at a height of from 16 to 20 inches (0.4 to 0.5 metre) from the surface of the soil. Reeds are placed in each aperture, to convey the juice into suitable vessels. The best season of the year is during the months of March, April, and May, while the sap is rising; from the 22nd of March to the middle of April being the period preferred. Sometimes a second running is taken in the autumn from the same tree, but it is more injurious to the tree than the spring tapping; in autumn the juice does not run for more than four or five days, but it is twice as strong as that which is drawn in spring. A good run gives daily six gallons from each incision, and in an old tree or 'old bush' these six gallons yield one pound of sugar. In a 'new bush,' twelve gallons are required for each pound of sugar: the average quantity of sugar from each tree is about three pounds. If properly treated, the same tree may be tapped for twenty or thirty years in succession. The higher the perforations the sweeter is the juice. Every twenty-four hours the liquid that has collected is concentrated, and the raw crystallized sugar is sold in blocks without further refining.

Beet-root sugar is extracted by pressing out the juice from the ripe roots of the white beet, which are usually gathered in October. The expressed juice contains about 10 per cent. of sugar, which in the fresh juice is entirely of the crystallizable kind; but it is seldom possible to extract in the crystallizable form more than half the quantity which the root contains.*

The expressed juice is first mingled with a small quantity of lime, and then boiled; a large portion of the albumin and azotised matters are thus coagulated, and rise to the top in the form of a scum, which is carefully removed. The juice is next filtered through a column of animal charcoal; it is concentrated in the vacuum pan, and is then filtered a second time through charcoal; it is again evaporated still further, and filtered through coarse cloth bags to remove any suspended particles; after which it is boiled down to the crystallizing point; the syrup at this stage having a sp. gr. of about 1.39.

The crystals of beet-root sugar are longer and flatter than those furnished by sugar from the cane, but they cannot otherwise be distinguished from the latter.

The manufacture of sugar from this root was called into existence by the wars of Napoleon, during which the ordinary

* An application of dialysis on a large scale has been made in the extraction of sugar from the beet-root by M. Robert: the fresh roots are cut into thin slices, and these are placed in tanks with rather more than their own weight of water at 122° (50° C.), the crystallizable sugar diffuses out and leaves the colloid, pectous, and albuminous impurities; by a methodical process of progressive washing a strong solution of sugar is ultimately obtained, whilst comparatively little is left in the pulp. The syrup is afterwards concentrated and purified as usual. It is stated that the process has also been applied successfully to the sugar-cane.

supply of the article was cut off from the French. In France, where the principal manufactories of this sugar exist, a good deal of the molasses, which is inferior to that of the cane, is fermented, and furnishes a considerable quantity of spirit of wine, amounting in weight to nearly one-third of the treacle employed; this spirit is purified by distillation: the residuum is evaporated to dryness, and then incinerated for the sake of the alkaline salts which it yields; these salts consist principally of potassic and sodic carbonates, with a small proportion of potassic sulphate and chloride. Beet-roots contain a large proportion of soluble saline matters, which are by this means economized. The crushed pulp is either employed while fresh as food for cattle, or used as manure for the land.

(1089) *Refining of Sugar.*—The process of refining sugar, whether from the cane or the beet-root, is alike for each. Two or three parts of sugar are dissolved in one part of lime-water mixed with 3 or 4 per cent. of bone black, and the whole is heated in large cisterns by allowing steam to blow up into them through pipes which open into the bottom of the vessel; from these cisterns the syrup is transferred to a filtering apparatus consisting of tubes of twilled cotton, where it is freed from mechanical impurities, and runs through as a reddish brown syrup. Formerly this clarification was aided by adding to the syrup a certain quantity of the serum of bullock's blood. The albumin of the serum, on the application of heat, became coagulated and rose to the surface, carrying with it entangled in its meshes the greater part of the solid impurities, which were afterwards removed by skimming.

The reddish syrup which has run through the filters has next to be freed as much as possible from colouring matter, and for this purpose it is a second time filtered; but the filter on this occasion is of a different nature, and consists simply of a bed of animal charcoal, prepared by calcining bones in closed vessels, and subsequently grinding them into a coarse powder. The filters consist of extensive vats twelve or fourteen feet deep, and sometimes much deeper, with perforated false bottoms; upon these a layer of ticking is placed, and above this, charcoal to the depth of twelve feet or more; above this is another layer of ticking covered with a perforated metallic plate. The syrup is allowed to flow evenly over the surface, and by the time it has run through it is colourless (54).

Owing to the viscosity of the filtered liquid, a high temperature (230° F. or 110° C.) is necessary to make it boil under

ordinary circumstances: and at this temperature the sugar quickly passes into the uncrystallizable modification, especially when exposed to the action of the atmosphere. By an ingenious application of the mode in which liquids may be boiled *in vacuo* at a temperature far below their ordinary boiling point (182), this difficulty has been in a great measure overcome; and the syrups are now universally boiled down in the *vacuum pan*. In this apparatus the pressure of the atmosphere is removed by means of a powerful air-pump, and a partial vacuum is maintained above the surface of the liquid in the evaporating vessel, which is a closed pan or boiler constructed of a spheroidal form, in order to enable it to resist the pressure of the external atmosphere. The lower half of the pan is double, for the purpose of admitting steam between the coatings; and a spiral steam pipe is also coiled within the boiler, with a view of increasing the extent of heating surface. By this arrangement a supply of steam can be admitted from a neighbouring boiler, the heat being sufficient to cause the syrup to enter into rapid ebullition, whilst all danger of burning the syrup is completely avoided, since the boiling point does not rise above 150° or 158° (70° C.). The evaporation is continued until a small quantity of the liquid when placed between the thumb and finger can be drawn out into a thread which breaks near the thumb and curls back to the finger. When it reaches this point the syrup is emptied into a vessel heated by steam to about 170° ; in this *heater* it is strongly agitated with wooden oars until it appears to be thick and granular. It is upon this agitation in the heater that the whiteness and fineness of the grain in refined sugar depend. Fresh portions of the evaporated liquor are two or three times added to the first, and thus the temperature is alternately raised and suffered to fall. From the heating vat it is transferred into inverted conical moulds, either of sheet iron or of unglazed earthenware; in the apex of each of these is an aperture, which is at first closed by means of a plug. The syrup is again well stirred in these moulds, to favour the escape of air-bubbles, which would otherwise give the mass a honeycombed appearance. After this operation it is left at rest for several hours, at the end of which time the plug is removed, and the uncrystallized syrup runs into vessels placed below for its reception. The sugar, however, is not yet white; for though the crystals consist of pure sugar, the loaves retain mechanically a large quantity of coloured syrup. In order to get rid of this, a quantity of fine colourless syrup is poured upon the base of each loaf, and this syrup, as it gradually percolates through the porous mass, dis-

places the impurities. The loaf is finally dried in a heated chamber, and finished for the market by turning it in a lathe.

In many refineries, after the finest quality of sugar has been obtained in the form of loaves in the manner already described, the syrup which drains from them is boiled down again in the vacuum pan, and is obtained in the form of what is termed *crushed sugar*, which is freed from the uncrystallized syrup with great rapidity by an ingenious application of the centrifugal force. The apparatus employed is similar in principle to that which has been long used for drying clothes in laundries. It consists of a cylindrical drum mounted upon a vertical axis, to which a very rapid rotatory movement can be given. The outer wall of this revolving drum is formed of a stout but close metallic network. This drum is enclosed in a second somewhat larger fixed cylindrical vessel, in which the liquid portion of the syrup is collected. In order to use the apparatus, a charge of concentrated syrup, which has been allowed to cool, and has thus become converted into a crystalline magma, is transferred to the inner drum of the centrifugal machine. The drum is now put into rapid rotatory motion, the uncrystallized syrup escapes through the pores of the metallic gauze, whilst the crystals are retained upon its inner surface. Between the withdrawal and the introduction of each charge the drum is cleansed by a jet of high-pressure steam, and thus the pores of the metallic network are kept clear.

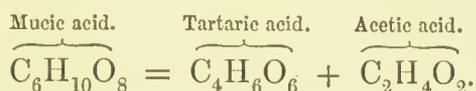
(1090) *Action of Nitric Acid on the Sugars.*—The action of nitric acid upon the different varieties of sugar is remarkable and characteristic. Sucrose and dextrose, when treated with $3\frac{1}{2}$ times their weight of nitric acid, of sp. gr. 1.25 [care being taken that the temperature be not allowed to rise beyond 158° (70° C.)], yield a peculiar acid, the *saccharic*; and the same substance may also be obtained from starch, gum, and lignin by similar treatment.

Saccharic Acid ($\text{H}_2\text{C}_6\text{H}_8\text{O}_8$).—This acid forms a colourless, inodorous, deliquescent, gummy, uncrystallizable mass, which is freely soluble in alcohol, but sparingly so in ether. It yields two salts with potassium, one of which is the normal salt; this contains 2 atoms of metal to 1 of acid, and is very soluble; the other is a sparingly soluble acid saccharate which crystallizes in oblique rhombic needles. Saccharic acid is sufficiently powerful to dissolve iron and zinc with extrication of hydrogen. Its normal baric salt is amorphous and sparingly soluble. Saccharic acid has a tendency to form double salts, so that it appears to be dibasic.

If sucrose or dextrose be acted upon by nitric acid of a specific gravity higher than 1.27, and the temperature be allowed to rise, a large quantity of oxalic acid is formed.

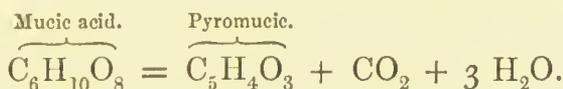
Mucic Acid ($\text{H}_2\text{C}_6\text{H}_8\text{O}_8$).—Sugar of milk, when treated with

excess of nitric acid, furnishes *mucic* acid, accompanied by saccharic acid, with which the mucic is isomeric; mucic acid may also be produced from gum and mannite by similar treatment, hence its name, derived from *mucilage*. When sugar of milk is used, Liebig found the mother-liquor to contain tartaric acid; indeed it may be remarked that one molecule of mucic acid contains the elements of one molecule each of tartaric and acetic acids, for



One part of gum or of sugar of milk, when boiled with 4 parts of nitric acid of sp. gr. 1.35 and 1 part of water, on cooling deposits mucic acid in minute, colourless, transparent, tabular crystals, which assume the appearance of a sparingly soluble white gritty powder, insoluble in alcohol. It is a dibasic acid, the salts of which are all insoluble in water with the exception of those of the metals of the alkalis: it forms two classes of salts, a normal and an acid series. Normal potassic mucate consists of $2 \text{K}_2\text{C}_6\text{H}_8\text{O}_8, \text{H}_2\text{O}$; the acid mucate of the same metal, of $2 \text{KHC}_6\text{H}_8\text{O}_8, \text{H}_2\text{O}$. Mucic acid is soluble in concentrated sulphuric acid, with which it forms a crimson solution.

When mucic acid is heated, carbonic anhydride and water are expelled, and a new monobasic acid, the *pyromucic* ($\text{HC}_5\text{H}_3\text{O}_3$), is sublimed in delicate needles:—



Pyromucic is isomeric with pyromeconic acid, but it is distinguished from this body by the formation of a white insoluble pyromucate when added to a solution of basic plumbic acetate.

If mucic acid be simply boiled in water for some time, it passes into an isomeric variety known as *paramucic acid*, which is much more soluble in water than mucic acid, and is also freely taken up by alcohol; when its aqueous solution is evaporated, paramucic acid is left in quadrangular tables.

(1091) The action of polybasic acids upon the sugars gives rise to a remarkable series of bodies which we shall describe hereafter (1246). The products thus obtained lead to the conclusion that glucose is intimately connected with the class of polyatomic alcohols.

Some steps have been made recently towards the artificial production of sugar. Amongst the products obtained from oxalic ether by the action of sodium amalgam (1324) Löwig found a fermentable sugar, and Carius has procured from benzol a variety of sugar which he calls *phenose* (1548).

The following table contains a summary of the leading characters of the principal varieties of sugar, including those of a few saccharine substances of less importance—viz., *trehalose*, (a term taken from *trehala*, the commercial name for Turkish manna), *melezitose*, (from *melèze*, the French name for the larch), *sorbin*, *dulcite*, *quercite*, (from *quercus* the oak, indicative of its origin in the acorn), and *pinite*, none of which it will be necessary to describe more minutely.

Sugars and some allied Bodies.

| VARIETY AND ORIGIN OF SUGAR. | PRINCIPAL PROPERTIES. |
|--|--|
| Sucrose, or Cane Sugar, $C_{12}H_{22}O_{11}$; from sugar cane. | Crystallizes in four or six-sided rhomboidal prisms—is very soluble in water, less so in diluted alcohol—sp. gr. 1.6—fuses at about 320° (160° C.)—is not precipitated by basic plumbic acetate, but is so by an ammoniacal solution of plumbic acetate—does not reduce an alkaline solution of potassic-cupric tartrate on boiling—produces <i>right</i> -handed rotation = $73^{\circ}.8$,—undergoes alcoholic fermentation with yeast—combines with alkalies—yields dextrose and lævulose when boiled with dilute acids—with nitric acid yields saccharic and oxalic acids. |
| Inverted Cane Sugar, $C_6H_{12}O_6$; from many recent fruits. | Is not crystallizable—is soluble in dilute alcohol—is not precipitated by basic plumbic acetate—reduces an alkaline solution of potassic-cupric tartrate by boiling—produces <i>left</i> -handed rotation = -26° at 59° (15° C.)—undergoes alcoholic fermentation with yeast—turns brown when treated with alkalies—is partially converted into grape sugar by boiling with dilute acids. |
| Dextrose, or Grape Sugar, $C_6H_{12}O_6, H_2O$; from dried fruits, or from starch altered by acids. | Crystallizes in cubes or square tables—is less soluble in water than cane sugar, but more soluble in alcohol—yields a precipitate with ammoniacal plumbic acetate—reduces potassic-cupric tartrate, and the salts of mercury, silver, and gold when boiled with them—ferments readily with yeast—produces <i>right</i> -handed rotation = $57^{\circ}.4$ —becomes brown when treated with alkalies—with nitric acid yields saccharic and oxalic acids. |
| Lactose, or Sugar of Milk, $C_{12}H_{22}O_{11}, H_2O$; from whey of milk. | Crystallizes in four-sided prisms—is less soluble in water than grape sugar—is nearly insoluble in alcohol and ether—is precipitated from its solutions by ammoniacal plumbic acetate—reduces the salts of copper, silver, and mercury, when its alkaline solution is boiled with them—produces <i>right</i> -handed rotation = $56^{\circ}.4$ —is not directly susceptible of alcoholic fermentation—is converted into galactose by boiling with dilute acids—yields mucic and oxalic acids with nitric acid. |
| Trehalose, or Mycose, $C_{12}H_{22}O_{11}, 2 H_2O$; (Berthelot) Turkish Manna, product of insect, <i>Larinus nidificans</i> . | Crystallizes in brilliant rectangular octohedra or in rhombic prisms—produces <i>right</i> -handed rotation = 220° —if heated quickly it fuses at 212° , and at 266° (130° C.) loses H_2O , and becomes solid—may be heated without decomposition to 410° (210° C.), when it melts again—loses its water of crystallization—is very soluble in water, and in hot alcohol—is sparingly soluble in cold alcohol and ether—is precipitated by ammoniacal plumbic acetate—does not reduce potassic-cupric tartrate—ferments slowly and imperfectly with yeast—yields dextrose when heated with dilute acids—does not give mucic with nitric acid, but when heated with it yields saccharic and oxalic acids. |

| VARIETY AND ORIGIN OF SUGAR. | PRINCIPAL PROPERTIES. |
|---|--|
| <p>Melezitose, $C_{12}H_{22}O_{11}, H_2O$; (Berthelot) from larch manna.</p> | <p>Crystallizes in short, hard, efflorescent rhombic prisms—is very soluble in water—sparingly soluble in alcohol, either hot or cold—insoluble in ether—has a sweetness about that of glucose—fuses at 280° (138° C.)—is precipitated by ammoniacal plumbic acetate—does not reduce the alkaline potassic-cupric tartrate—produces <i>right</i>-handed rotation = 94°—ferments with difficulty—yields dextrose when heated with dilute acids—gives no mucic acid with nitric acid.</p> |
| <p>Melitose, $C_{12}H_{24}O_{12}, 2 H_2O$; (Berthelot) from the <i>Eucalyptus</i>.</p> | <p>Crystallizes in slender prisms—is freely soluble in water—slightly soluble in alcohol—is feebly sweet—melts and loses water at 266° (130° C.)—yields a precipitate with ammoniacal plumbic acetate—does not reduce an alkaline solution of potassic-cupric tartrate—exerts <i>right</i>-handed rotation = 102°—undergoes alcoholic fermentation with yeast, at the same time half the sugar is separated in an unfermentable form as eucaliu—furnishes mucic acid with nitric acid—is little affected by alkalies.</p> |
| <p>Eucalin, $C_6H_{12}O_6, H_2O$; (Berthelot) from fermentation of melitose.</p> | <p>Is not crystallizable—precipitates ammoniacal plumbic acetate, and reduces the alkaline potassic-cupric tartrate when boiled with it—produces <i>right</i>-handed rotation = about 50°—is not susceptible of alcoholic fermentation with yeast—becomes brown when treated with alkalies—is not altered by boiling with dilute acids.</p> |
| <p>Sorbin, $C_6H_{12}O_6$; (Pelouze) from berries of the service tree, <i>Sorbus aucuparia</i>.</p> | <p>Crystallizes in octohedra with a rectangular base—is very soluble in water—nearly insoluble in alcohol—sp. gr. 1.65—is fusible without loss of weight—gives a white precipitate with ammoniacal plumbic acetate—reduces the alkaline solution of potassic-cupric tartrate on heating it with it—occasions <i>left</i>-handed rotation = 46°—is not fermentable with yeast, but with cheese and chalk slowly yields lactic and butyric acids and alcohol—becomes brown when treated with alkalies—yields a red solution with oil of vitriol—is converted into oxalic and a little racemic acid by nitric acid.</p> |
| <p>Inosin, $C_6H_{12}O_6, 2 H_2O$; (Scherer) from muscular tissue.</p> | <p>Crystallizes in radiated tufts—is soluble in water—insoluble in absolute alcohol and ether—loses water by heat, and fuses at 410° (210° C.)—has no rotatory power on polarized light—does not reduce the alkaline potassic-cupric tartrate when boiled with it—is not susceptible of alcoholic fermentation, but with cheese and chalk yields lactic and butyric acids—is not altered by boiling with dilute acids or alkalies—forms a precipitate with ammoniacal plumbic acetate.</p> |
| <p>Mannite, $C_6H_{14}O_6$; from the juice of <i>Fraxinus ornus</i>.</p> | <p>Crystallizes in silky anhydrous four-sided prisms—is soluble in water and alcohol—fuses at 320° (160° C.)—gives a precipitate with ammoniacal plumbic acetate—reduces the salts of silver or gold by heat—does not reduce the alkaline potassic-cupric tartrate when boiled with it—exerts no rotatory power on polarized light—is not easily fermentable—with nitric acid yields saccharic and oxalic acids—is soluble without coloration in oil of vitriol, and in alkaline solutions.</p> |
| <p>Erythrite, $C_4H_{10}O_4$; (V. Luynes) from Roccella and other lichens.</p> | <p>Crystallizes in broad voluminous crystals of the pyramidal system—is soluble in water and in alcohol—fuses at 248° (120° C.)—has no rotatory power—gives no precipitate with ammoniacal plumbic acetate—does not reduce the alkaline potassic-cupric tartrate—yields no mucic acid with nitric acid—is not fermentable.</p> |
| <p>Dulcite, $C_6H_{14}O_6$; (Laurent) origin unknown.</p> | <p>Crystallizes in brilliant prisus—is soluble in water and in alcohol—fuses at 356° (180° C.)—gives no precipitate with normal or with basic plumbic acetate—does not reduce argentic nitrate or auric chloride—produces no rotation on polarized light—is not susceptible of fermentation with yeast—is not affected by dilute alkalies—is converted into mucic acid by nitric acid.</p> |

| VARIETY AND ORIGIN OF SUGAR. | PRINCIPAL PROPERTIES. |
|---|---|
| Quercite, $C_6H_{12}O_5$; from acorns. | Crystallizes in transparent prisms—is soluble in water and dilute alcohol—is fusible at 420° ($215^\circ.5$ C.)—does not reduce the alkaline potassic-cupric tartrate—is not fermentable by yeast—is soluble without change of colour in oil of vitriol and in the alkalis—yields oxalic acid with nitric acid. |
| Pinite, $C_6H_{12}O_5$; (Berthelot) from <i>Pinus Lambertiana</i> . | Crystallizes slowly in hard hemispherical radiated masses—has a very sweet taste—is very soluble in water—is sparingly soluble in alcohol—gives a precipitate with ammoniacal plumbic acetate—does not reduce the alkaline potassic-cupric tartrate—sp. gr. 1.52—produces <i>right</i> -handed rotation—is not fermentable—fuses below 480° ($248^\circ.9$ C.)—does not yield mucic with nitric acid. |

§ II. VARIETIES OF STARCH AND GUM.

(1092) STARCH x ($C_6H_{10}O_5$).—The term *starch*, or *amylaceous matter*, or *fecula*, is applied to an organized substance which occurs in rounded or oval grains in the cellular tissue of certain parts of plants. It is met with in great abundance in all dicotyledonous seeds, particularly in those of leguminous plants, such as peas and beans. The monocotyledonous seeds of the *Cereal*ia or corn tribe contain it still more largely; it is also abundant in the tubers of the potato, in the roots of the tapioca and arrow-root, and in a variety of other plants. On examining the grains of starch with a magnifying power of 300 or 400 diameters, they are seen to consist of flattened ovate granules, which in the same plant are tolerably uniform in size, but which vary in magnitude in different species of plants; those of the *canna*, or *tous les mois*,

FIG. 384.



No. 1, fig. 384, being about $\frac{1}{2500}$ of an inch (0.1 millimetre) in diameter; those of the potato are somewhat smaller, but the

grains become larger as the age of the plant increases ; those of the arrow-root, No. 2, do not exceed $\frac{1}{500}$ of an inch ; those of wheat starch, No. 3, are more circular, and about $\frac{1}{1000}$ of an inch (0.025 millimetre) in diameter, and do not exhibit rings ; those of rice No. 4, are angular and often adherent to each other ; they do not usually exceed the $\frac{1}{3000}$ of an inch, whilst those contained in the cells of the beet root are still smaller.

Each of the larger grains exhibits a series of concentric rings ; some observers consider this appearance to indicate that they have been formed by a deposition of successive layers of starchy matter within an external envelope ; Busk believes that the rings are occasioned by a plication of the envelope itself : in many instances the *hilum*, or point of attachment of the grain to the cellular tissue of the plant from which it was developed, is distinctly perceptible, as shown at *a, a*, fig. 384.

The structure of the grains of starch is very beautifully displayed by placing some of them in contact with a drop of concentrated solution of zincic chloride, (tinged with a little free iodine), on the field of the microscope. No change takes place in the granules until a little water is added. They then become of a deep blue colour, and gradually expand ; at first a frill-like plicated margin is developed around the globule ; by degrees this opens out ; the plications upon the globule may then be seen slowly unfolding, and may be traced in many cases into the rugæ of the frill ; ultimately the granules swell up to 20 or 30 times their original bulk, and present the appearance of a flaccid sac. During these changes no extrusion of anything within the granules is observed to take place (Busk, *Quart. Jour. Microscop. Soc.*, vol. i.).

The grains of potato starch, if illuminated by polarized light, with a Nicol's prism interposed between the object and the eye, present a well-marked black cross, the centre of which corresponds with the hilum. When wheat starch is subjected to a similar test this cross is not perceptible ; its presence may therefore be of service as a means of distinguishing the fraudulent addition of potato starch or flour to wheat flour.

(1093) *Properties*.—As sold in the shops, starch exhibits the appearance of a white glistening powder, or of columnar masses which are easily reduced to powder ; when pressed between the fingers it emits a peculiar sound, and produces a certain feeling of elasticity. Starch is heavier than water, having a sp. gr. of about 1.5. It is insoluble in cold water, alcohol, and ether. If

placed in a solution of soda or of potash which contains 2 per cent. or upwards of alkali, the granules of starch swell up and become converted into a tenacious paste. A mixture of starch and water may be preserved without alteration at ordinary temperatures for an indefinite period; but it undergoes a remarkable change when heated to a temperature a little above 140° (60° C.). Under these circumstances the exterior layer of the granules absorbs water, the grain swells up, and the mixture suddenly assumes a viscid, pasty condition, in which form it is extensively employed by laundresses for stiffening linen. If this paste be largely diluted with water, the swollen granules of the starch subside slowly, whilst a certain quantity of amylaceous matter remains in solution. The starch paste thus obtained does not, when evaporated, recover its former insolubility. Its solutions are precipitated by alcohol, and the precipitate may be redissolved by the immediate addition of water; but after a few hours the flocculi become more coherent and are no longer soluble in cold water. A solution of starch produces right-handed rotation of a polarized ray. The soluble portion of starch is often termed *amidin*, from the French *amidon*, starch. Soluble starch, free from dextrin, is readily obtained by boiling the grains of starch with a strong solution of zinc chloride, or with glacial acetic acid. Prolonged boiling with water alone has a similar effect, but dextrin is gradually formed (Masehke).

It is remarkable that if starch be boiled under pressure, at about 302° (150° C.), with from 5 to 15 times its weight of water, a thin solution is obtained, which may be filtered from the insoluble portion; this liquid, as it cools, deposits minute spherical granules, which, when dried, have the whiteness of starch without its glistening appearance. These granules are sparingly soluble in cold water, but are readily dissolved when the water is raised to 158° (70° C.) or upwards. Iodine tinges them blue, and alcohol causes a precipitate when added to their aqueous solution.

Starch, in the form in which it is usually sold, contains about 18 per cent. of water; in order to render it anhydrous, it should be dried *in vacuo*, at a temperature of 257° (125° C.).

When dry starch is heated sufficiently, it becomes soluble in cold water, and forms aropy solution much resembling gum in properties. The grains of anhydrous starch may be heated to 320° (160° C.) without becoming soluble, but at 401° (205° C.) the change is complete in the course of an hour or two. Commercial starch, on the contrary, from the water which it retains, is rendered completely soluble by raising the temperature suddenly to

320°, and maintaining it at this point for some time. The change produced in these cases consists in the formation of a substance isomeric with starch, which is termed dextrin (1099). This soluble torrefied starch is known under the name of *British gum*, and constitutes the *leïogomme* of the French manufacturers; it is largely employed by calico printers for mixing with their colours, in order to give them the requisite consistence. When starch is subjected to dry distillation, acetic acid and marsh gas are among the products.

Like most organized structures, starch appears to retain as an essential component a small quantity of saline matter, consisting partly of potash; and it likewise contains a perceptible amount of some azotised compound, which is present chiefly in the tegument of the grains (Jacquelain).

A solution of tannic acid occasions a precipitate in one of starch. When a dilute solution of starch is mixed with one of the ammoniacal plumbic acetate, an insoluble compound with oxide of lead ($C_{12}H_{13}O_9, 2PbO$) is formed. Starch may be recognized when present by the deep blue colour which it acquires on the addition of free iodine to its solution; this colour disappears if the solution be heated, but it re-appears as the liquid cools (394). If boiled with diluted sulphuric acid, starch quickly loses its viscosity, and is ultimately converted into dextrose. Before the transformation is complete, it passes through the same modification that exists in British gum, which has received the name of dextrin, from its property of causing the rotation of a polarized ray from left to right. During germination, the diastase of the seed converts the starch into a soluble mixture, containing, according to Musculus, 1 part of dextrose to 2 of dextrin. A solution of starch does not ferment with yeast; but Berthelot obtained as much as 16 per cent. of its weight of alcohol, when it was exposed for several weeks at a temperature of 104° (40° C.) in contact with chalk and cheese: no sugar could be detected in the liquid during this process; probably because it was decomposed as fast as it was formed. When oxidized by nitric acid, starch yields oxalic acid in abundance. When fused with caustic potash containing water, it furnishes oxalate, mixed with formiate, acetate, and propionate of potassium. Concentrated sulphuric acid furnishes with it a colligated acid, the *amidinsulphuric*.

(1094) *Preparation*.—In the extraction of starch from the vegetable tissues in which it is contained, advantage is taken of its insolubility in cold water.

1. *Potato Starch*.—This variety is prepared on a large scale

from potatoes, which contain about 20 per cent. of amylaceous matter; the cellular tissue of the tuber does not exceed 2 per cent. of the mass, whilst of the remainder, about 76 per cent. consists of water, and the rest of small quantities of sugar, salts, and azotised matters.* In order to extract the starch, the tubers are first freed from adhering earth by a thorough washing, and are then rasped by machinery. The pulp thus obtained is received upon a sieve, and is washed continuously by a gentle stream of water, so long as the washings run through milky. This milkiness is due to the granules of starch which are held in suspension. The milky liquid is received into vats, in which the amylaceous matter is allowed to subside; the supernatant water is drawn off, and the deposit is repeatedly washed with fresh water until the washings are no longer coloured. The starch is next suspended in a small portion of water, run through a fine sieve to keep back any portions of sand, and after having been again allowed to settle, is drained in baskets lined with ticking: the mass is then placed upon a porous floor of half-baked tiles, and dried in a current of air, which is at first of the natural temperature; the drying is completed by the application of a moderate artificial heat. Potato starch emits a characteristic odour when made into an emulsion with hot water, owing to the presence of a small quantity of some volatile compound.

2. *Wheat Starch*.—A finer species of starch is obtained from the grains of the *Cerealia*, in the preparation of which wheat is largely employed. In making wheat starch a more complicated process is necessary, for in this grain the starch, which amounts to nearly 60 per cent. of the whole, is accompanied with an azotised material termed gluten (1117), amounting to from 14 to 19 per cent. of the weight of the grain, which also contains a certain quantity of cellular tissue and of sugar. The grain is first coarsely ground and wetted with water. After the lapse of three or four

* The following, according to Boussingault, is the average composition of the tubers of the potato:—

| | Moist. | Dry. |
|---------------------|------------|-------|
| Water | 75.9 . . . | |
| Albumin | 2.3 . . . | 9.6 |
| Oily matter | 0.2 . . . | 0.8 |
| Fibre | 0.4 . . . | 1.7 |
| Starch | 20.2 . . . | 83.8 |
| Salts | 1.0 . . . | 4.1 |
| | ————— | ————— |
| | 100.0 | 100.0 |
| | ————— | ————— |

days it begins to ferment, and is then transferred to a large vat, where it is mixed with an additional quantity of water, and the fermentation is allowed to proceed for three or four weeks. During this operation, the gluten undergoes putrefaction, the sugar and part of the starch become converted into alcohol, and carbonic anhydride is evolved, while the fermenting mass emits a powerful putrescent odour. A portion of the alcohol and of the starch become converted into acetic and lactic acids, which dissolve that portion of the gluten that has escaped putrefaction, and thus the starch is separated from the materials by which it was accompanied in the grain. It is then repeatedly washed, drained, and dried, as before. The blocks into which it is divided in order to facilitate the desiccation, shrink during the drying into columnar fragments, which are readily pulverized by gentle pressure.

3. *Rice Starch*.—In the foregoing method of preparing starch from wheat, much of the amylaceous matter is wasted, the whole of the gluten is lost, and the operation is attended with the continual evolution of gases of an offensive odour, which are a source of annoyance to the neighbourhood in which the manufacture is carried on. These inconveniences were overcome by Mr. O. Jones, who, in the year 1840, took out a patent for the manufacture of starch, by a method which he applied particularly to rice, though it may be used with other cereal grains. Undried rice contains about 83 per cent. of starch, and about 7.0 per cent. of gluten. The process of Mr. Jones consists in separating these two materials by means of a very weak solution of alkali, which dissolves the gluten, but leaves the starch granules unaltered:—100lb. of rice in the form of grain are macerated in 5 times its weight, or 50 gallons of a solution containing $\frac{1}{350}$ of its weight of caustic soda; after the lapse of 24 hours the alkaline liquid is drawn off, and the rice is allowed to drain; a fresh portion of alkaline ley is gradually added whilst the rice is being ground into a paste. It is then digested in the ley for 24 hours longer with frequent agitation; at the end of that time the fibrous matter of the grain, which is heavier than the fine grains of starch, is easily freed from the latter, by stirring up the whole with water, allowing the mixture to rest for an hour, during which time the vegetable fibre subsides, and then running off the milky liquid into a separate vessel, where the starch is deposited: finally the starch is washed, mixed with a little smalt, to give it the blue tinge preferred in the market, drained, and dried in the usual manner. The liquid which floats above the starch is turbid, has a yellow colour, and

contains the gluten of the grain in solution. From this liquid the gluten may be recovered by carefully neutralizing the solution with sulphuric acid.

Other Sources of Starch.—If, during the preparation of starch the temperature employed in its desiccation be raised to 140° (60° C.), a transparent jelly is produced, which, when dry, is no longer farinaeous, but assumes the form of semitransparent granules. *Sago* is the fecula procured from the pith of the sago palm by making it into a paste with water, and pressing the mixture through a perforated metallic plate; the little cylinders thus obtained are granulated by placing them in a revolving vessel; these are then exposed upon a sieve to a jet of steam, and subsequently dried. *Tapioca* is the starch of the *Jatropha manihot*, which is pressed through a colander, and dried upon a metallic plate heated to 212° . It is thus formed into granular, semitransparent, irregular masses. *Arrow-root* is the starch of the root of the *Maranta arundinacea*, and of one or two other tropical plants. *Salep* is the name given to the starch yielded by the *Orchis mascula*.

The occurrence of starch has been supposed not to be confined to the vegetable kingdom. Granules of a substance, which, after being moistened with oil of vitriol, becomes blue on the addition of iodine, have been found in the brain: in certain cases of scrofulous caries, the liver assumes the peculiar hard, semitransparent, waxy appearance described by Dr. G. Budd; and a similar deposit has been found in the kidney in the same cases. The deposition of small quantities of this material in the animal tissues, even in health, is not uncommon. This compound is, however, not true starch, but is azotised in composition. It does not yield sugar when heated with acids, nor any of the characteristic products of starch.

(1095) *Glycogen* ($C_6H_{10}O_5, H_2O$; air dried) is the name given to the sugar-producing substance discovered by Bernard in the liver and the placenta. When dried at 212° each molecule loses 1 atom of water and becomes $C_6H_{10}O_5$. It may be extracted nearly pure by forming a solution of glycogen by boiling thin slices of perfectly fresh liver in a small quantity of water, and precipitating by the addition of a great excess of glacial acetic acid (Bernard). The boiled liquid may also be precipitated by the addition of 4 or 5 times its bulk of alcohol, but then the precipitate contains, in addition to glycogen, albumin and fat. To remove these it must be boiled with caustic potash in concentrated solution so long as ammonia escapes, and then be precipitated by alcohol. This precipitate must be redissolved in dilute acetic or hydrochloric acid, and again precipitated by alcohol, repeating the process two or three times.

Glycogen is rapidly converted into sugar by one of the con-

stituents of the liver. It furnishes an opalescent solution in water, but is not soluble in alcohol or in ether. When boiled with dilute sulphuric acid it yields dextrose. Nitric acid converts it into oxalic acid. It is tinged violet or brownish red by iodine. Alkaline potassium-euphratic tartrate is not reduced when boiled with it. With basic plumbic acetate it gives a white precipitate.

(1096) *Diastase*.—During the germination of seeds the starch undergoes a species of fermentation, and is converted into a mixture of dextrin and sugar, in which state it is assimilated by the young shoot. This conversion is due to the action of a peculiar ferment termed *diastase* (from $\delta\acute{\iota}\alpha\sigma\tau\alpha\sigma\iota\varsigma$, separation), which exists in all germinating seeds during the act of growth, being probably merely albumin or gluten in a particular stage of decomposition. An impure solution of diastase may be readily obtained from malt or freshly-germinated barley by grinding it, moistening it with half its weight of warm water, allowing it to stand for a few minutes, and pressing out the liquid. Malt does not contain more than $\frac{1}{300}$ of its weight of diastase. One part of this substance suffices to convert 2000 parts of starch into dextrin and sugar (Persoz and Payen): the temperature of 149° (65° C.) is most favourable to the change; the diastase is coagulated at about 167° (75° C.), above which point this conversion is arrested.

Long before the discovery of diastase, the distillers had found that by mixing a portion of unmalted barley with their malt, and digesting the mixture in warm water for some hours, they obtained an infusion or wort equally sweet with that furnished by an equal weight of malt: 1 part of malt having the power to change into dextrin and sugar the starch contained in 4 or 5 parts of barley. Now unmalted barley contains but very little sugar, whereas after it has been malted the proportion of sugar is much increased, whilst that of the starch is diminished. Malt is simply barley allowed to germinate up to a certain point, after which its growth is suddenly checked by the application of heat; and it contains a considerable quantity of diastase which has not been expended in the conversion of its starch into sugar. When the mixture of ground malt and barley is digested with water, or *mashed*, this excess of diastase acts upon the starch of the unmalted barley, converting it into a mixture of dextrin and sugar; a saccharine liquid is thus obtained which is susceptible of fermentation. Museulus asserts (*Ann. de Chimie*, III. lx. 203) that only one-third of the starch undergoes this conversion into sugar, two-

thirds remaining in the form of dextrin ; but Payen still maintains the correctness of his original statement. The preparation of such a sweet wort is the first step in the process of brewing. In malted barley this saccharification of the starch has already taken place during the act of germination, and simple digestion in water extracts the sugar. But since raw barley is less expensive than malt, a certain quantity of it is often substituted for a portion of the germinated grain by the distiller, who sometimes adds as much as 4 parts of unmalted grain to 1 of malt, and thus effects a considerable pecuniary saving.

(1897) *Action of Ferments*.—The exact manner in which diastase acts in producing this singular change is unknown, and the same may be said of the mode in which sugar is converted into alcohol and carbonic anhydride through the intervention of yeast. These actions, however, exhibit considerable analogy with each other, and are connected in some way with a molecular change of the matter serving as a ferment. Moist yeast and moist diastase both very rapidly undergo alteration. Diastase when in a state of decomposition, however, produces changes on other matter entirely distinct from the transformation of starch into dextrin ; and an examination of these changes has thrown considerable light on the obscure subject of ferments in general.

It has already been stated that if starch be acted on for some time by diastase, it is partially converted into sugar ; but in a certain stage of its decomposition diastase may give rise to products of a different kind :—An infusion of malt, if kept for a few days, converts the starch into gum instead of into sugar ; at other times mannite is formed ; in other cases the starch is converted first into sugar, and this compound if mixed with chalk is then rapidly transformed into calcic lactate ; whilst the same infusion, at a still later period of its decomposition, becomes turbid, and acquires the power of exciting the alcoholic fermentation. These observations seemed to indicate that the same body during its different states of decay may give rise to the formation of products quite different in properties from each other, though all these products, except mannite, have the same ultimate composition. Hence it was concluded, that the formation of each of these compounds corresponds to a particular phase of decay in the ferment. The observations of Pasteur have, however, rendered it probable that each product of fermentation is produced by the action of particular fungi or organisms developed successively during the decay of the albuminous substance. If this explanation be admitted, it is easy to see why in many instances the products of ferment-

tation are of a more or less mixed nature, according as the body undergoing decomposition contains a greater or smaller variety of each kind of the different germs which act as special ferments.

All substances susceptible of putrefactive decomposition—such as casein, albumin, mucous membrane, muscular tissue, and the albuminoid azotised principles of plants—may furnish a pabulum for the development of these special ferments, each of which appears to have the power of inducing decomposition of a particular kind, in bodies—like sugar, starch, urea, and various others—which undergo no change unless some agent susceptible of putrefaction be mixed with them. All these azotised putrescible substances possess certain properties in common, whilst they are undergoing putrefaction; and some seem to have the power of producing special changes peculiar to themselves. For example, the synaptase of the almond (1431) acts upon starch and sugar in a way resembling that in which yeast and gluten act, converting starch into sugar, and sugar into alcohol and carbonic anhydride; but it has, in addition, the peculiar property, not possessed by yeast or gluten, of converting amygdalin into hydrocyanic acid and essential oil of bitter almonds, and also of changing salicin into saligenin and sugar.

We have still much to learn respecting the progress of putrefaction. Pasteur describes putrefaction as a peculiar species of fermentation produced and maintained by an animal ferment of the genus *vibrio*. Each of the six known species of this genus he regards as possessing the property of producing a special mode of putrescence. During putrefaction, the substance, if exposed to the air, always experiences slow oxidation. If a liquid susceptible of putrefaction and containing air in solution be sealed up in glass vessels and left to itself, infusoria (*Monas crepusculum* and *Bacterium termo*) are first developed. They absorb the oxygen of the air, and evolve carbonic acid, after which they die and produce a sediment. Then, if the germs of the vibrio are present, these become developed, and at the same time putrefaction commences. The vibriones cannot exist in a liquid which contains free oxygen.

If the putrescible liquid be freely exposed to the air, the monads and bacteria are developed at first, and continue to be produced in great abundance. Over the surface of the liquid they form a pellicle, which is perpetually being renewed, and which, by absorbing oxygen, entirely prevents its access to the interior of the liquid. Then putrefaction commences, but the newly-formed products of putrescence are partially decomposed

under the influence of the superficial layer of infusoria ; and by the agency of these monads they become oxidized and converted into water, carbonic acid, and ammonia.

Pasteur further considers that he has proved that the slow oxidation of animal and vegetable matters, such for instance, as moistened sawdust, is dependent upon the influence of the lower cryptogamic and infusorial organisms, such as the mycelia, muceors, or ' moulds,' and monads and bacteria, without the presence of which dead organized matter would scarcely be subject to change ; and he altogether rejects the theory of albuminoid ferments.

Lemaire has pointed out the important influence which the condition of the liquid exerts upon the products of putrefaction, the same ferment producing different results according as the liquid is neutral, acid, or alkaline.

The observations of Schröder (*Liebig's Annal.* cix. 35, and cxvii. 273) upon the processes of fermentation and putrefaction are remarkable. He has shown that any organic liquid may be prevented from fermenting or putrefying, if it be heated under pressure to about 266° (130° C.), then transferred to a flask and boiled, the mouth of the flask being plugged whilst boiling with a pellet of cotton wool which is left in the neck of the flask. In this way he preserved, during a hot summer, various liquids, including freshly boiled wort, blood, white of egg, whey, urine, broth, and milk ; but when afterwards the plug of cotton was withdrawn, these liquids in a few days began to undergo decomposition. He explains these results by supposing that the spores of some organism must find access to the substance in order to set up the process of decomposition ; by a temperature of 260° ($126^{\circ}\cdot7$ C.) any such spores which the substance itself might contain are destroyed, and as the air is filtered through the cotton before it reaches the interior of the flask, none of these organic germs can afterwards obtain access to the body under experiment. I have repeated some of these experiments with complete success. If air be transmitted with suitable precautions slowly through narrow ignited platinum tubes, so as to destroy all suspended organic particles, no fermentation or putrefaction will take place on admitting such air to contact with putrescible substances previously heated to 260° for an hour. Pasteur has shown the existence of these floating germs in the air by drawing a large volume of atmospheric air, by means of an aspirator, through a narrow tube obstructed with collodion wool. On subsequently dissolving this wool in a mixture of alcohol and ether, various microscopic sporules were left

undissolved. An elaborate experimental discussion of the subject occurs in a paper of Pasteur (*Ann. de Chimie*, III. lxiv. 5).

(1098) *Preparation of Malt*.—Upon the proper management of the process of malting much of the success of the subsequent brewing depends. The seasons most favourable for malting are spring and autumn, when the temperature is neither very high nor very low. The barley first undergoes the operation of steeping. This is effected in stone troughs, where the grain is covered with water to a depth of about 6 inches (15 centimetres). The lighter and decayed seeds float, and are skimmed off, whilst the sound grain, being heavier than the water, subsides. The steeping is continued until the grain becomes uniformly soft, and this occupies generally from 40 to 60 hours, the water being changed twice or thrice. During this stage the barley swells considerably from the water which it imbibes, and increases in weight nearly one-half. After a final washing it is drained, and then *couched*, or placed in heaps of about 15 inches in height upon the floor. In these heaps it becomes warm, and continues to swell for the next twenty-four hours; by this time it begins to sprout; as soon as the first whitish protuberance shows itself, the heaps are evenly distributed over the floor of a darkened apartment, and the process termed *sweating* follows. In this state it is allowed to remain for several days, usually fourteen; the workmen turning it twice or thrice daily with wooden shovels. This step is employed for the purpose of equalizing the heat, in order that the process of germination may proceed at all points with equal rapidity. By this manipulation the temperature is maintained at a point varying between $55^{\circ}\cdot4$ and $62^{\circ}\cdot6$ (13° and 17° C.). In from 10 to 20 days, according to the heat of the weather, the germination is complete; as soon as the radicle, or *acrospire*, as the maltster calls it, has shot to the length of about half an inch, when it bifurcates, and just as the plumula or leaf-shoot is about to make its appearance, the vitality of the seed is extinguished by rapidly drying the grain. In order to effect this object, the malt is spread to the depth of about $2\frac{1}{2}$ inches, upon floors made of perforated metallic plates. Here it is left to dry in a current of air for some hours, at a temperature not exceeding 90° ($32^{\circ}\cdot2$ C.); and at the end of this time a fire is lighted underneath. It is necessary that the greater part of the moisture be expelled before the fire be kindled; afterwards the heat is allowed to rise gradually, but not to exceed 140° (60° C.) otherwise the starch of the grain would be acted on, and much of the diastase would lose its efficacy. *High dried* malt is subjected to a much higher temperature, and is actually scorched on the outside. Such malt, however, is used only in small quantity as a colouring ingredient, to give the customary deep brown tinge to *porter*. During the drying, which occupies two or three days, the grain requires frequent stirring, in order that the desiccation may take place regularly. Barley generally yields about 80 per cent. of malt after drying and sifting from the radicles. According to Thomson, 12 per cent. of this loss is due to water, only 8 per cent. being actually wasted in the form of carbonic anhydride and trimmings. During the germination, oxygen is absorbed, and a large quantity of carbonic anhydride is set at liberty. Other grains, such as wheat, oats, rye, and even Indian corn, may be malted, but experience has shown that barley is the grain best adapted to this process. It yields the largest quantity of diastase, although this does not exceed $\frac{1}{300}$ of the weight of the grain. The diastase appears to be developed at the expense of the azotised constituents of the grain. It is generated chiefly in the neighbourhood of the young germ, not of the rootlet.

According to the experiments of Lawes, 100 parts of dry barley yield $90\cdot22$ of malt, and $3\cdot99$ of malt and kiln dust. It is remarkable that the malt dust, consisting chiefly of the radicles of the seed, carries off with it a great deal of the

nitrogen of the grain, amounting to nearly one-ninth of the entire quantity contained in the barley. The loss in nitrogen which barley suffers in becoming converted into malt rises to as much as 13.5 per cent. of the total quantity of nitrogen contained in 100 parts of dry barley. Lawes found the nitrogen in the barley to amount to 1.78 per cent. of the weight of the dry grain: that contained in dry malt being 1.70 per cent.

(1099) DEXTRIN ($C_6H_{10}O_5$) is a transparent, brittle solid, with a vitreous fracture, and is indeed an artificial gum produced by a transformation of starch. It is soluble in water and in dilute alcohol, but is insoluble in anhydrous alcohol or in ether; wood spirit dissolves it freely. Dextrin is distinguished by producing *right-handed* rotation upon a ray of polarized light, and it derives its name from this property. It differs from starch in not yielding any coloration with iodine. It does not reduce cupric potassium tartrate on boiling. It is not susceptible of fermentation. By boiling for several hours with dilute sulphuric acid, it combines with water, and is converted into dextrose. It may be distinguished from gum by yielding with nitric acid, oxalic acid only, and no mucic acid. Payen has contrived a method of preparing crude dextrin on a large scale, which consists in moistening 10 parts of starch, with 3 of water containing $\frac{1}{150}$ of its weight of nitric acid, allowing the mixture to dry spontaneously, then spreading the starch upon shelves in layers of an inch and a-half in depth, and heating them for an hour or an hour and a half in an oven to about 239° (115° C.) It consists of a mixture of dextrin with glucose and unchanged starch. When pure dextrin is required, Museulus recommends it to be prepared as follows:—Starch is diffused through water and boiled with diluted sulphuric acid till it gives no blue or red coloration with tincture of iodine. Well washed yeast is then added to destroy the glucose by fermentation. When this process is complete, the solution is filtered, evaporated, and the residue treated with absolute alcohol; the undissolved residue is dextrin, nearly pure. Dextrin is likewise largely manufactured in a form more or less coloured by heating starch to about 400° (p. 114), when it yields British gum. It may also be obtained by heating an infusion of ground malt in water to about $165^\circ.2$ (74° C.), and adding starch in small quantities at a time: as soon as the starch is dissolved the temperature is raised rapidly to 212° , and the liquid filtered, and evaporated with constant agitation, until it has acquired a syrupy consistence. Pure dextrin gives no precipitate with basic plumbic acetate (Museulus).

(1100) INULIN (dried at 212° , $C_6H_{10}O_5$; Dubrunfaut).—The roots of many plants, among which are those of the dahlia, elecampane (*Inula helenium*), col-

chicum, dandelion, and chicory, contain a variety of starch, to which the name of *inulin* has been given. It is a white, pulverulent, inodorous, tasteless powder, insoluble in alcohol, sparingly soluble in cold water, but readily so in boiling water, from which it is partially deposited again on cooling, in a pulverulent form. Its solution produces left-handed rotation upon a ray of polarized light. By long boiling it assumes the characters of gum. If heated beyond 212° it melts, gives off water, and leaves a scaly, sweetish, gummy mass, which is readily soluble in water. Iodine turns inulin yellow. By boiling with dilute acids it is converted first into dextrin and then into pure lævulose. If heated with nitric acid in the concentrated form, it is converted into oxalic acid, with acetic but no mucic acid. It forms an insoluble precipitate when its solution is mixed with one of plumbic acetate and ammonia is added.

(1101) GUM is found in the juices of almost all plants, but is met with in its purest form in transparent tears which exude from various species of acacia. Gum arabic (*Arabin*) may be taken as its type. According to Fremy, ordinary gum is a mixture of the calcium and potassium salts of a feeble vegetable acid termed *gummic* or *arabic* acid, which according to the analysis of Gélis may be represented by the formula $C_{12}H_{22}O_{11}$; it loses H_2O when dried at 257° (125° C.). This acid renders litmus distinctly red, and is soluble in water when freshly precipitated by the addition of a mixture of hydrochloric acid and alcohol to an aqueous solution of gum arabic; but if it has been allowed to become dry, and is again moistened, it passes when quite free from bases, into the isomeric modification, *metagummic acid*, a substance which swells up to a jelly in water, but does not dissolve. Salts of metagummic acid may also be obtained by heating the gummates to about 260° . The insoluble cherry-tree gum, or *cerasin* (so called from *cerasus*, a cherry), consists chiefly of calcic metagummate. Crude gum always has a slightly acid reaction in solution. It forms a tasteless, ropy, mucilaginous liquid, which from its adhesive quality often forms a useful substitute for paste or glue. A solution of gum arabic produces left-handed rotation of a polarized ray. It is not susceptible of the alcoholic fermentation under the influence of yeast; but if digested with cheese and chalk it may be made to furnish alcohol, which amounted in one experiment to 12 per cent. of the gum employed: calcic lactate is formed at the same time, but no formation of sugar is perceptible (Berthelot). A solution of arabin is precipitated by alcohol and by ether in white flocculi, or, if dilute, in the form of a milky turbidity. If boiled with dilute sulphuric acid, it is gradually converted first into dextrin, and then into a fermentable variety of sugar; concentrated nitric acid converts it into mucic and oxalic acids, showing its relation to sugar of milk in this respect:

iodine does not alter its colour. Pure solution of gummie acid may be prepared by mixing a concentrated solution of gum arabic, with 4 or 5 per cent. of hydrochloric acid, and subjecting the solution to dialysis till it no longer precipitates argentic nitrate (Graham). A solution of gum arabic is not precipitated by admixture with solutions of alum, stannous chloride, the ferric salts, cupric sulphate or nitrate, or normal plumbic acetate; but when mixed with one of ammoniacal plumbic acetate it produces a curdy precipitate ($3\text{C}_6\text{H}_{10}\text{O}_5, 2\text{PbO}$). Some other metallic salts, such as the mercurous and mercuric nitrates, also precipitate its solution, and the precipitate is dissolved by an excess of the metallic salt.

Mucilage or *Bassorin* $x(\text{C}_6\text{H}_{10}\text{O}_5)$ is a modification of gum which is insoluble in water; but when moistened with this liquid it swells up into a gelatinous mass. It is contained abundantly, combined with lime, in gum tragacanth, and accompanies the gum which exudes from the cherry tree. Many seeds, such as linseed, quince-seed, and certain roots, such as those of the marsh-mallow, furnish it in large quantity: alkalis change it into a gum soluble in water, and long boiling in water has a similar effect. Nitric acid converts it into mucic and oxalic acids. Bassorin, as contained in an infusion of linseed, is precipitated by alcohol, mercurous nitrate, and corrosive sublimate, as well as by normal and by basic plumbic acetate. The various kinds of mucilage from different plants, however, present some differences in their reactions; for example, the mucilage from quince seeds yields oxalic acid only, when treated with nitric acid; moreover, it is coloured blue when moistened with oil of vitriol containing iodine, and a solution of iodine in zincic iodide produces in a few days a beautiful red tint: the mucilage of linseed is not so coloured by either of the agents last named.

(1102) VEGETABLE JELLY (formerly called *pectin*).—Another principle which, like starch and gum, extensively pervades the vegetable kingdom, is that peculiar body which gives to the juice of many succulent fruits and roots the faculty of gelatinizing. Braconnot first called attention to this substance under the name of *pectin* (from *πηκτικόν*, a jelly); it has since been particularly studied by Mulder and by Chodnew; as well as by Fremy (*Ann. de Chimie*, III. xxiv. 5) especially in relation to the ripening of fruits.

According to the last-mentioned chemist, the cellular tissue of most fruits, and of turnips, carrots, parsnips, &c., contains a sub-

stance which he terms *pectose*, and which is quite insoluble in water, alcohol, and ether. It is the material which gives the hardness to green fruits, and it possesses the characteristic property of becoming converted, under the influence of dilute acids aided by a gentle heat, into pectin.

Pectin may be obtained from the juice of ripe pears or apples, by throwing down the lime which they contain by the cautious addition of oxalic acid, and then adding a concentrated solution of tannin so long as it occasions a precipitate; the albumin is thus coagulated, and may be separated by filtration. On adding alcohol to the clear liquid, the pectin is thrown down in the form of gelatinous strings. If this precipitate be redissolved in cold water, and again precipitated by alcohol, it may be obtained tolerably pure: when dry, it forms a friable mass, which is soluble in water, but insoluble in alcohol and in ether. Its aqueous solution is somewhat viscous: it gives a gelatinous precipitate when mixed with basic plumbic acetate, but none with the normal acetate. Pectin exerts no action on polarized light. When boiled with water it loses its viscosity, and becomes converted into a modification (*parapectin*), which occasions a precipitate in a solution of normal plumbic acetate. If boiled with dilute acids, an isomeric substance (*metapectin*) is formed, which occasions a precipitate when mixed with a solution of baric chloride, even if the liquid be somewhat acid.

Pectic Acid ($H_2C_{16}H_{20}O_{15}$; Fremy).—All the above modifications of pectin are rapidly converted into salts of pectic acid by being treated with a solution of a caustic alkali, or of an alkaline carbonate, care being taken to avoid any excess of the alkali. Pectic acid is characterized by its gelatinous nature. It forms soluble compounds with the alkalies, but they do not crystallize; the other pectates are insoluble. Pectic acid is likewise soluble in many of the salts of the alkalies. It is most easily obtained by boiling the washed pulp of carrots or turnips in a weak solution of sodic carbonate; sodic pectate is thus formed by the action of the alkali upon the insoluble pectose contained in the vegetable tissue; and on mixing the solution with calcic chloride, a gelatinous calcic pectate is precipitated. This when well washed and treated with dilute hydrochloric acid, to remove the calcium, furnishes pectic acid as a transparent insoluble jelly.

If this jelly be long boiled with water it is gradually dissolved, and a deliquescent uncrystallizable acid is the result (*parapectic acid*), which yields a precipitate with baric chloride. Parapectic acid in its turn, when treated with alkalies, passes into another

uncrystallizable acid, the *metapectic*, which has a strongly sour taste; it is no longer precipitable by baric chloride, though it yields a precipitate with basic plumbic acetate.

According to Fremy, pectin is susceptible of a specific fermentation, produced by a peculiar ferment, *pectase*, present in the cellular tissue of the vegetable. This change is not attended by any disengagement of gas, but simply by the conversion of the soluble pectin into two gelatinous acids, which are insoluble in water: one of these acids he terms *pectosic acid*. It is almost insoluble in cold water, but it becomes dissolved by boiling water, and the liquid gelatinizes on cooling. This acid appears to be the one formed in the first instance, but it gradually passes into a second, which is the pectic acid already described: the gelatinizing of many juices of fruits arises from the gradual conversion of the pectin which they contain into these gelatinous acids. The composition of these gelatinous bodies cannot be said to be established with certainty; since there is no means of determining whether or not they have been prepared in a pure condition, nor is it easy to procure them in a uniform state of desiccation. But whatever may be the true composition of these bodies, it is clear that pectose is readily susceptible of modification under the influence of acids, of alkalis, and of a peculiar ferment contained in the plant or fruit itself; and these modifications are probably connected with the assimilation or separation of the elements of water. None of these compounds exert any rotatory action upon polarized light, a character which indicates an important molecular distinction between them and the class of sugars. All these closely related bodies, it may be observed, contain oxygen in larger proportion than would be required to convert their hydrogen into water. When treated with nitric acid they furnish mucic and oxalic acids.

Fremy assigns to these different bodies the composition given in the following table, but the formulæ require confirmation:—

| | | |
|---------------------------|----------------------------------|-----------------|
| Pectose | Composition unknown. | Not gelatinous. |
| Pectin | $C_{32}H_{40}O_{28}, 4 H_2O$ | Viscous. |
| Parapectin | $C_{32}H_{40}O_{28}, 4 H_2O$ | Not gelatinous. |
| Metapectin | $C_{32}H_{40}O_{28}, 4 H_2O$ | Not gelatinous. |
| Pectosic acid | $2 (H_2C_{16}H_{20}O_{15}) H_2O$ | Gelatinous. |
| Pectic acid | $H_2C_{16}H_{20}O_{15}$ | Gelatinous. |
| Parapectic acid | $H_4C_{24}H_{30}O_{23}$ | Not gelatinous. |
| Metapectic acid | $H_4C_8H_{10}O_9$ | Not gelatinous. |

§ III. CELLULIN AND WOODY FIBRE.

(1103) CELLULIN, or CELLULOSE ($C_{18}H_{30}O_{15}$).—If a thin slice of wood be examined under the microscope, it is immediately apparent that it is not a homogeneous structure, but that it is composed of a cellular or fibrous substance, the texture of which assumes a different appearance, according as the slice has been cut across the grain of the wood, or parallel to it. This ligneous fibre, or true woody matter, consists, according to the researches of Payen, of two essentially distinct portions. One of these has received the name of *cellulose* (which it is better to change into

cellulin, reserving the termination *ose* for the different varieties of sugar); it constitutes the basement tissue, found in all vegetables; it occurs nearly pure in cotton, linen, elder pith, and in the pith of the *Aralia papyrifera*, from which *rice paper* is prepared: the other portion is a deposit of inerusting matter which lines the interior of these cellules in amorphous layers, varying in thickness according to the age or character of the ligneous substance.

Cellular tissue forms the groundwork of every plant, and when obtained in its pure state, its composition is the same, whatever may have been the nature of the plant which furnished it, though it may vary greatly in appearance and physical characters. For instance, it is loose and spongy in the succulent shoots of germinating seeds, and in the roots of plants such as the turnip and potato; it is porous and elastic in the pith of the rush and the elder; it is flexible and tenacious in the fibres of hemp and flax; it is compact in the branches and wood of growing trees, and it becomes very hard and dense in the shells of the filbert, the peach, the cocoa-nut, and the *Phytelphas* or vegetable ivory. Vegetable cellular tissue, in its succulent form, is easily digestible; but when it has become compact and inerusted with true woody matter, as in the husks of the seed and in the hard portions of the stems, and even when simply condensed into tenacious fibres, like those of hemp and flax, it is no longer digestible, or in a condition to serve as nutriment to the higher orders of animals.

It is scarcely possible to obtain celluline free from ligneous tissue by artificial means, since the inerusting woody matter, when once deposited within its meshes, is retained with great obstinacy; but it is presented in a pure condition in finely carded cotton, in linen, and in the finest kinds of filtering paper; to these sources the chemist usually has recourse when he desires to examine the properties of celluline.

Pure celluline is a white, tasteless substance, insoluble in water, alcohol, ether, or oils. It is heavier than water: its fibres are transparent, and exert a depolarizing influence upon a ray of polarized light. A solution of well-washed freshly precipitated hydrated cupric oxide, or cupric carbonate, in dilute ammonia, dissolves the fibre in most of its forms, though in some cases, as in that of the *rice paper*, this solution does not take place until the vegetable fibre has been boiled with diluted acids. Celluline is precipitated from the cupric solution, unaltered in composition, on acidulating the solution with an acid. Cold concentrated sulphuric acid dissolves it, and produces a treacly-looking liquid, converting it, after dilution and boiling, first into dextrin, and subse-

quently into grape sugar. Weak acids exert but little effect upon cellulin, but the action of these and of all other solvents is materially greater upon the recently formed celluloses than upon the old ones. By prolonged boiling with dilute sulphuric acid the less compact forms of cellulin are gradually converted into glucose. Hydrochloric acid, in its concentrated form, dissolves cellulin, and deposits it on immediate dilution with water; but if it be left undiluted for 2 or 3 days, no precipitate occurs on the addition of water. Alkaline liquids when dilute do not act upon cellulin, but when concentrated they gradually destroy its texture. According to Péligot, if cellulin be moistened with water and submitted to distillation with an equal weight of solid caustic potash, wood spirit distils over, and potassic oxalate is formed in the residue. A solution of chlorine acts but very slowly upon cellulin.

Cellulin, in its natural state, is not coloured blue by iodine; but after it has been digested for a short time with concentrated sulphuric acid, it becomes of a fine blue when free iodine is added. This reaction is sometimes serviceable in the microscopic examination of vegetable tissues; cellulin being thus easily distinguished from most tissues into the composition of which nitrogen enters. By the prolonged action of sulphuric acid, the property of being coloured blue by iodine disappears, the dextrin and sugar which are formed not being susceptible of the blue coloration.

A remarkable modification in the vegetable fibre is effected by the action of zincic chloride or of sulphuric acid, in consequence of which paper may be converted into a material which, in toughness and appearance, much resembles parchment, and is known under the name of *vegetable parchment*. It is more transparent than true parchment. In order to prepare it, thin paper, which must not be sized, is plunged for a few moments, at a temperature of 59° (15° C.) into a mixture of oil of vitriol with half its bulk of water. The paper must be quickly withdrawn and washed, first with water, then with a weak solution of ammonia, and, lastly, with water again. In this process the outer surface of the fibres appears to have become converted into a glutinous substance by which the fibres are cemented together. This substance, according to Hofmann, is intermediate between cellulin and dextrin, with both of which it is isomeric, having neither acquired nor given up the elements of water, nor entered into permanent combination with sulphuric acid.

Hofmann found the toughness of this vegetable parchment to be five times as great as that of the paper which furnished it, and

to be about three-fourths that of ordinary parchment. It takes ink well. Water, even at 212° , exerts very little action on it for several hours, but if immersed for many months in water it gradually loses its tenacity. It may be substituted for bladder as a septum in dialysis, and in electrolytic operations, with great advantage.

Cellulin, when subjected to destructive distillation, yields acetic acid and a variety of hydrocarbons, mixed with carbonic anhydride and carbonic oxide.

When oxidized by means of nitric acid of moderate strength cellulose yields oxalic acid in abundance, but no mucic acid. With concentrated nitric acid it yields various remarkable substitution products, some of which we proceed to notice. These reactions with nitric acid about to be described show that the formula of cellulose cannot be less than $C_{18}H_{30}O_{15}$.

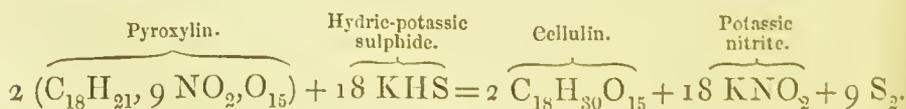
(1104) PYROXYLIN, or *Gun Cotton* ($C_{18}H_{21}NO_2O_{15}$; Hadow).

—When cellulose in any form, such as cotton, tow, linen, sawdust, or paper, is dipped into a mixture of equal measures of oil of vitriol and of nitric acid of sp. gr. 1.520, no change of form ensues, but a remarkable chemical alteration takes place: a certain number of atoms of hydrogen are abstracted, and an equal number of atoms of peroxide of nitrogen (NO_2) supply their place. The fibre in undergoing this change becomes increased about 82 per cent. in weight (Hadow), and acquires completely new properties. In order to prepare this remarkable body—called *gun cotton* by its discoverer, Schönbein—1 part of finely carded cotton is immersed in 15 parts of a mixture of equal measures of strong nitric acid (sp. gr. 1.5), and sulphuric acid (sp. gr. 1.845). The cotton must be completely immersed in the mixture, otherwise it becomes so hot as to undergo instant decomposition. After a few minutes' immersion it must be plunged into a large volume of cold water, and then washed, so long as the least trace of acid is perceived when the moist mass is placed upon litmus paper; it is then to be carefully dried at a temperature below 212° . When prepared for military purposes, it is found advisable to prolong the immersion in acid for 48 hours, and to continue the washing for several days. See Report on Gun Cotton, *Brit. Assoc. Report*, for 1863, p. 1.

As thus prepared, *pyroxylin* (so named from $\pi\upsilon\rho$ fire, $\xi\lambda\omicron\nu$, wood) scarcely differs from unchanged cotton in appearance; it is white and fibrous, rather harsh to the touch, and when examined by the microscope in a beam of polarized light it is found to have lost the property of depolarization which ordinary cotton

possesses. It is somewhat hygroscopic, but when dry it is an excellent insulator of electricity, and becomes highly electrical by the mere operation of pulling it out in the fingers. Pyroxylin is insoluble in water, alcohol, and dilute acids, but it is soluble in acetic ether and in methyl acetate. Ammonia, when mixed with ether, dissolves it, and leaves it by spontaneous evaporation in a pulverulent form. An aqueous solution of potash dissolves it freely, decomposing it at the same time; the solution contains a quantity of sugar, and a mixture of potassic nitrate, nitrite, and oxalate. The solution in potash also contains a peculiar acid (resembling the saccharic), which yields an insoluble precipitate with plumbic acetate. The alkaline solution of pyroxylin, when mixed with ammonia-nitrate of silver, and gently heated, reduces the silver in the form of a film upon the surface of the glass, producing a brilliant mirror-like deposit of the metal.

Strong sulphuric acid dissolves pyroxylin in the cold without the evolution of gas, and the liquid is not rendered turbid by dilution. If the pyroxylin be pure, the solution is colourless, but it is brown if any unaltered fibres of cotton remain in the mass. Nitric acid in the cold is without action upon it, but if the acid be heated it gradually dissolves the pyroxylin, and on dilution deposits it again. By boiling it with the acid it is decomposed, red fumes escape, and dilution then causes no precipitate. Pyroxylin, according to the observation of Hadow, may be reconverted into ordinary cotton, by digestion at ordinary temperatures in an alcoholic solution of hydric-potassic sulphide (KHS), whilst potassic nitrite is formed; and the change may be effected still more rapidly if the mixture be heated: the reaction may be indicated by the following equation:—



Béchamp states that a similar reduction takes place when the pyroxylin is acted upon by ferrous chloride.

The most remarkable property of pyroxylin is the facility with which it takes fire, and the rapid and complete manner of its combustion. In the open air it burns with a flash, but without either smoke or report; a temperature just below that of 302° (150° C.) is sufficient to inflame it, being more than 200° below that required to ignite gunpowder. In the open air, pyroxylin burns more rapidly than gunpowder, but if compressed so as to form a fuse, its rapidity of combustion may be reduced below that

of powder, and the more it is compressed the slower is the combustion. If it be fired in a confined space it produces violent explosive effects from the suddenness of its combustion, and from the large quantity of gaseous matter which it furnishes. The extreme suddenness of its inflammation, and the short space of time during which its propulsive force is exerted, produce both greater strain upon the gun-barrel and less effect upon the ball, than gunpowder exerts; but the rapidity of explosion may be regulated by proportioning not merely the weight of the cotton but the volume of the cartridge to the size of the chamber of the gun. In certain cases, such as in mining operations in hard and brittle rocks, it may be beneficially employed, as it may be driven into borings above the head of the miner; it produces much less fume and noxious gases than gunpowder; in addition to which it has the great advantage of leaving no 'train' by leakage from the vessels in which it is stored up. This compound may even be stored in water for indefinite periods, as indeed is commonly practised for keeping purposes, and when dried it is found not to have experienced any diminution of its explosive power. Carelessly prepared pyroxylin is liable to undergo spontaneous decomposition when kept in closed vessels; the presence of excess of acid, and of foreign impurities, such as oily or resinous matters in the original fibre being the principal agents in producing this instability (Abel).

During the combustion of pyroxylin in vacuo a large volume of steam is generated, mixed with a variable proportion of carbonic anhydride, carbonic oxide, nitrogen, marsh gas, and nitric oxide;* traces of cyanogen are also sometimes formed: but

* 100 parts of gun cotton yield, according to Karolyi (*Phil. Mag.*, Oct. 1863, p. 266), the following gases when burned in vacuo, and under pressure:—

Products of the Combustion of Gun Cotton.

| | In Vacuo. | | Under Pressure. | |
|------------------------------|--------------|---------------|-----------------|---------------|
| | By Vol. | By weight. | By Vol. | By Weight. |
| Carbonic oxide | 28'55 | 28'92 | 28'95 | 29'97 |
| Carbonic anhydride | 19'11 | 30'43 | 20'82 | 33'86 |
| Marsh gas | 11'17 | 6'47 | 7'24 | 4'28 |
| Nitric oxide | 8'83 | 9'59 | 0'00 | 0'00 |
| Hydrogen | 0'00 | 0'00 | 3'16 | 0'24 |
| Nitrogen | 8'56 | 8'71 | 12'67 | 13'16 |
| Carbon | | 1'60 | | 1'62 |
| Aqueous vapour | 21'93 | 14'28 | 25'34 | 16'87 |
| | <u>98'15</u> | <u>100'00</u> | <u>98'18</u> | <u>100'00</u> |

if fired under pressure, no nitric oxide, but a little free hydrogen is obtained in addition to the gases already enumerated. Considerable difference prevails in the statements of the earlier experimenters respecting its propulsive power as compared with that of gunpowder, but it is now ascertained that its power varies according to the circumstances in which it is exploded; so that it may be made to vary from three times to nearly six times that of an equal weight of the best musket powder.

The results of Hadow's experiments (*Q. J. Chem. Soc.* vii. 208), which have been in all their essential points confirmed by subsequent inquiries by a commission of chemists in Austria, and by Abel at Woolwich (*Phil. Trans.* 1866), serve to explain the conflicting statements relative to the properties and composition of this remarkable substance.* It appears from this inquiry that the composition of gun cotton differs according to the degree of concentration of the acids employed in its formation, and that at least four different and definite compounds, distinguished as A, B, C, and D, may be formed, having the following composition:—



When equal measures of the sulphuric and nitric acids are employed, each in the highest degree of concentration, the compound A is formed; it is highly explosive, soluble in acetic ether, and insoluble in any mixture of alcohol and ether. If the acids used be of a strength intermediate between $2 HNO_3 + 2 H_2SO_4 + 3 H_2O$ and $HNO_3 + H_2SO_4 + 2 H_2O$, the compound B is produced: it is less explosive than A, is insoluble in acetic acid, but soluble in a mixture of seven parts of ether and one part of alcohol. Mixed acids of the strength $HNO_3 + H_2SO_4 + 2 H_2O$, produce the compound C, which is largely soluble both in ether and in glacial acetic acid; it is highly combustible, but scarcely explosive. The compound D is formed when acids of the strength $2 HNO_3 + 2 H_2SO_4 + 5 H_2O$ are used; it is but sparingly soluble in alcohol and ether, and not soluble in boiling glacial acetic acid.

Collodion.—The solution of pyroxylin in a mixture of ether and alcohol is known under the name of *collodion*, from *κόλλα*, glue, in allusion to its glutinous character. Pure methylic

* An exhaustive inquiry into the processes of manufacture, and the causes which influence the stability of gun cotton, will be found in Abel's papers, *Phil. Trans.* 1866, 269; and 1867, 181.

alcohol may be used as a solvent without the addition of ether. When this solution is exposed to the air for a few moments in the form of a thin layer, the solvent evaporates, leaving the pyroxylin as a transparent membranous pellicle. Collodion has been applied to excoriated surfaces, for the purpose of forming an artificial skin in order to protect them from the action of the air; but its most important application is in the preparation of a sensitive transparent surface for the reception of photographic images (127 *h*), by diffusion over plates of glass, after it has been duly impregnated with a soluble iodide. On immersing the film in a solution of argentic nitrate, the whole surface becomes impregnated with argentic iodide in the most favourable condition for the reception of photographic impressions. According to Hadow, the compound B is that which is best fitted for the preparation of photographic collodion. The temperature at which the compound is formed has also a very material influence upon the mechanical qualities of the collodion. If the temperature be not raised to 122° (50° C.) or upwards, the solution is viscid and glairy, and does not diffuse itself readily over the glass. The successful preparation of good photographic collodion requires attention to a number of minute precautions, which are detailed in Hardwich's *Manual of Photography*.

(1105) *Nitrous Derivatives from Sugar, &c., allied to Pyroxylin*.—Other substances besides cellulose may be converted into bodies more or less analogous to pyroxylin, by the action of a mixture of nitric and sulphuric acids. Powdered cane sugar is converted by the same mixture of acids into a bitter yellowish mass of resinous appearance; it is very slightly soluble in water, and according to Sobrero contains $C_{12}H_{18}(NO_2)_4O_{11}$. A somewhat similar compound may be formed from gum arabic, and also from milk sugar. If starch be treated with concentrated nitric acid it is rapidly dissolved, and if the viscid solution thus obtained be immediately diluted with water, a white tasteless insoluble precipitate is occasioned, termed *xyloidin*, which appears to be a substitution product of starch and peroxide of nitrogen, $C_{12}H_{16}(NO_2)_4O_{10}$, analogous to the foregoing; this substance, by digestion in hydriopottassic sulphide (KHS), is reconverted into the soluble modification of starch, which becomes blue when mixed with iodine, whilst xyloidin does not yield a blue with iodine. But the most remarkable body belonging to this class is one which is produced when mannite is acted upon by the mixture of nitric and sulphuric acids. It is insoluble in water, but is readily dissolved by

boiling alcohol; the *nitromannite* $[C_6H_8(NO_2)_6O_6]$ crystallizes in fine needles as the solution cools. This compound explodes powerfully by a blow from a hammer. If gently heated it may be melted, but at a higher temperature than that required for its fusion it explodes, and produces red vapours.

In all these cases it will be observed that the derivative nitrous compounds are produced from the saccharine or amylaceous substance by the substitution of a variable number of atoms of hydrogen by an equal number of atoms of peroxide of nitrogen; each atom of nitric acid, when acted upon by an atom of hydrogen derived from the organic body, yielding one atom of water and one of peroxide of nitrogen; $HNO_3 + H$ becoming $NO_2 + H_2O$. The water is absorbed by the sulphuric acid contained in the mixture, which, after its action upon the organic compound, is found in all cases to have become diluted by the water thus removed from the body submitted to its influence. The addition of the sulphuric acid in these cases has two advantages, one being the removal of the water produced by the reaction; the other, the prevention of the solution of the new compound, and its further alteration by the nitric acid. A mixture of nitric and sulphuric acids is now frequently employed for the purpose of obtaining compounds in which NO_2 is substituted for hydrogen: nitroglycerin $C_3H_5(NO_2)_3O_3$, and various other compounds may be obtained in this manner with facility; the reaction however requires careful watching, as it is apt to become tumultuously violent, and sometimes, as in the case of nitroglycerin, the compounds which are formed are liable to explode during their preparation.

(1106) *Tunicin* $x(C_6H_{10}O_5)$ is the name given to a substance closely allied to cellulose, which is formed in the outer envelopes of the *Tunicata*, or *Ascidia* (*cynthia* or *phallusia*), from which it is prepared by treating them successively with concentrated hydrochloric acid, and with an aqueous solution of potash of sp. gr. 1.28, and then washing with water. It is coloured yellow by an alcoholic solution of iodine, dissolves slowly without blackening in concentrated sulphuric acid, and on boiling the solution with water it yields a fermentable sugar, which reduces the alkaline cupric tartrate. It is chiefly remarkable as being an animal product which has the same composition as vegetable fibre.

(1107) LIGNIN.—The incrusting matter contained within the cellular tissue, which gives hardness to wood, is most abundant in the heart-wood of trees, and in the hard shells of many varieties of nuts. This substance appears to be a mixture of several proximate principles; it contains a larger proportion of hydrogen than cellulose, the proportion of oxygen being insufficient to convert the whole of the hydrogen into water. This incrusting matter does

not appear to have a uniform composition in all woods. It is, however, always characterized by being soluble in alkaline liquids, though it is insoluble in water. Sulphuric acid chars it, and an aqueous solution of chlorine attacks and dissolves it. When submitted to distillation in closed vessels, it evolves acetic acid; and it is found that the harder the wood, and the larger the proportion of this incrusting substance which it contains, the greater is the proportion of acetic acid which is furnished when equal weights of different woods are subjected to destructive distillation. When ligneous fibre is moderately heated with solid caustic potash potassic oxalate and acetate are formed.

The ligneous matter is generally deposited in a state of mixture with a variable quantity of resinous matters, which colour the wood and increase its inflammability. The deposited fibre also contains a certain proportion of saline matter, as well as small quantities of compounds containing nitrogen.

The applications of cellulin and of ligneous fibre in the arts are numerous and of great importance. Besides its every-day use in the form of wood, the fibre constitutes the basis of all linen, cotton, and hempen goods; and after these substances have ceased to be serviceable as textile fabrics, they are still, in the hands of the paper-maker, converted into a material scarcely less valuable.

(1108) *Paper-making*.—The rags which are employed in the manufacture of paper are sorted, according to the material of which they consist, into linen, cotton, hempen, and woollen; and are afterwards further separated into white, coloured, and black. The seams and knots are cut out, and the rags are then well beaten to get rid of dust and dirt. Coloured rags can be employed in the preparation of writing-paper if they be first bleached by the action of chlorine, which is sometimes applied to them in the gaseous form. For this purpose the rags are moistened, and placed on perforated shelves in wooden or stone chambers into which the gas is transmitted. An excess of chlorine must be carefully avoided, because it is liable to enter into chemical combination with the fibre, and, by displacing a portion of the hydrogen, to form a substitution compound, which, being destitute of tenacity, furnishes a brittle paper. More frequently, however, the rags, after having been reduced to the form of pulp, are bleached by means of chloride of lime. In all cases it is necessary to ensure the removal of the last traces of chlorine, which would not only cause the paper to become brittle, but when the paper is used for manuscript purposes would gradually discharge the ink. The

removal of the chlorine is effected by the addition of a small quantity of sodic sulphite or hyposulphite; if the sulphite be used the chlorine is converted into sodic chloride, and the sulphite into sodic sulphate, whilst sulphurous anhydride is set free:—



The rags having been partially cleansed, either in their bleached or unbleached condition, are reduced by mechanical means into a fibrous paste, or smooth uniform pulp, with water. This pulp is then extended over wire strainers in a layer of uniform thickness, which when drained forms a film of paper. If this be simply dried and pressed it forms *blotting*, or *filtering* paper, and is too porous to be used as writing-paper. In order to fit it for the ink, it is *sized*, or coated with a mixture of weak fine glue and alum, by which means it is rendered less permeable to water. Many manufacturers mix the size with the pulp before it is made into sheets, but in this case it is necessary to employ a size of a description different from that which is applied to the finished sheets. The size which is to be mixed with the pulp usually consists of a mixture of three parts of a resinous soap and two parts of starch, to which a small quantity of alum is added.

Of all the numerous materials which have been tried as the basis of paper, none has been found so well adapted for the purpose as linen rags. Straw has been used to some extent as a material for paper, and it was at one time thought, owing to the abundance and cheapness of this substance, that it might be made a valuable substitute for rags, the supply of which is becoming inadequate to meet the demand; but the loss of material, from its brittle nature, during the process of manufacture, and other unforeseen circumstances, more than counterbalanced the advantage gained from the abundance of the supply. Within the last few years a species of grass (*Stipa tenacissima*), known as esparto grass, has been very largely imported from Spain to supply a portion of the necessary fibre. It requires boiling for several hours with one-tenth or more of its weight of caustic soda in solution to remove the resinous material in which it abounds; the yellow fibre is afterwards bleached with chloride of lime, and may be employed, when mixed with half its weight of pulp from rags, in the making of an inferior paper now largely consumed.

(1109) *General Remarks on Starch and Woody Fibre.*—The facts already mentioned show the ready convertibility of the organized bodies, starch and lignin, into others which, though of

organic origin, are yet devoid of structure, and therefore of a less complicated nature. In most cases great similarity exists in the ultimate composition of these bodies, many having identically the same composition as those from which they are derived: others, if not identical, differ among each other only in the presence or absence of the elements of water. It is, therefore, not surprising that a gradual transition should occur from the elaborate arrangement of the dense and compact tissue of the wood into the comparatively loose texture and low organization of starch; the ligneous tissue undergoing modifications of density, which gradually diminish from the compact structure of the *lignum vitæ* to the spongy cells of the fungus or lichen. The tissue of the Iceland moss, for example, presents a close analogy with starch; it is gradually disintegrated by boiling, it swells up into a gelatinous mass, and yields a magma colourable by iodine: thence we arrive at true starch, and gradually, as the organization of this body is broken up by the successive action of chemical agents, the addition of iodine produces a coloration less and less intense, until in the perfect formation of dextrin it disappears altogether; and at length in sugar, in place of the cellular structure, crystalline form becomes apparent.

(1110) *On the Decay of Woody Fibre and the Means of preventing it.*—When wood in a moist state is exposed to the air, it gradually undergoes decomposition; a species of fermentation is occasioned by the nitrogenized constituents, in consequence of which oxygen is absorbed, carbonic anhydride and water are exhaled, and the wood crumbles down into a blackish brown vegetable mould called *humus*, *ulmin*, or *gein*. This decay occurs most rapidly in young spongy wood, which admits the air more freely, and at the same time contains a proportionately larger quantity of the albuminous substance, than the harder and older portions.

The decomposition of this albuminous component favours the growth of lichens and fungi, and encourages the ravages of insects, to which the albuminous portions in particular afford the means of nutriment. It is obviously a matter of high importance to protect the wood, as far as possible, from these influences. A superficial coating of some substance impervious to air and moisture answers this object in great measure, so long as it can be maintained entire. Such a coating is usually supplied by the application of layers of resinous or oily matter, which, if needful, may be thickened with metallic oxides; as in the ordinary pro-

cesses of tarring and painting. But a more effectual method of preservation consists in steeping the wood, sail-cloth, cordage, or other similar materials, for a given time in crude coal tar kreasote. Various saline solutions have been employed, but they have been gradually abandoned. Kyan made use of a solution of corrosive sublimate, containing from $\frac{1}{60}$ to $\frac{1}{75}$ of its weight of the mercurial salt. Boucherie employed a solution which contained about 1 per cent. of raw acetate of iron, or more generally of cupric sulphate. This solution was forced into the recently felled wood, under the pressure of a column of the liquid of 20 or 30 feet in height, which enabled the metallic solution to displace the vegetable juices.

Products of the Decay of Woody Fibre.—When vegetable mould, or mouldered wood from the trunk of a decaying tree, is digested in a weak solution of potash or of soda, a brown liquid is formed, from which, on the addition of an acid, a blackish brown precipitate is obtained. This precipitate is readily soluble in alkalis, and always contains a considerable proportion of nitrogen. It is regarded by Mulder as a mixture of three substances, none of which is crystallizable, but which he considers as compounds of water, or of water and ammonia, with three different acids, viz., 1. *Geic acid*, $C_{20}H_{12}O_7$, (so called on account of its origin, from $\gamma\eta$, the earth); 2. *Humic acid*, $C_{20}H_{12}O_6$, (from *humus*, the ground); and 3. *Ulmic acid*, $C_{20}H_{14}O_6$, (from *ulmus*, an elm). These substances, whether or not they actually possess the composition above assigned to them, are obviously the product of vegetable matter in stages of decay more or less advanced. Mulder found the brown substances formed by the prolonged action of dilute acids at a boiling temperature upon sugar, to resemble the ulmic and humic acids from mould, both in composition and in properties. Besides these acids, Berzelius pointed out the existence of two other allied bodies, which have received the names of crenic and apocrenic acids (from $\kappa\rho\eta\nu\eta$, a spring); they have been found in many mineral waters, and accumulate in the ochry deposits that occur around the margin of ferruginous springs. *Crenic acid* ($H_6C_{24}H_{24}O_{19}$? Mulder) has also been found associated with ammonia, in vegetable mould. It forms a yellow solution, which retains ammonia with obstinacy, and absorbs oxygen rapidly, becoming converted into *Apocrenic acid* ($H_2C_{24}H_{12}O_{13}$? Mulder); the latter acid furnishes a brown solution in water, and also retains ammonia strongly. Indeed, this property of retaining ammonia with obstinacy is a characteristic of those imperfectly defined acid products which are formed

during the decay of ligneous matter, and it is connected in an important manner with the functions which they subserve in supplying nutriment to growing vegetables, towards the support of which they appear to contribute largely.

By the decay of herbaceous and aquatic plants in marshy soils, a material somewhat similar to humus is formed, which accumulates in beds, often of great depth and extent, constituting *peat bogs*. In Holland the peat is frequently 6 feet thick, and in the great central bogs in Ireland it even extends to a depth of 30 or 40 feet, or from 9 to 12 metres. Dried peat is found upon analysis to yield a larger proportion of carbon than woody fibre; it likewise contains an excess of hydrogen over the oxygen.

The process of decay in ligneous tissue is liable to considerable variation, according as it is allowed to take place with free access of air, or is effected under water with but a scanty supply of oxygen from without. When the atmosphere has free access, De Saussure found that the oxygen of the air is converted into an equal volume of carbonic anhydride, while at the same time a large quantity of water is evolved. According to Hermann, a small portion of nitrogen is absorbed during the process, and ammonia is generated. The water produced is at the expense of the oxygen and hydrogen contained in the ligneous tissue, so that the mouldered product contains a larger proportion of carbon than the wood upon which the experiment was conducted.

If the moistened wood be excluded from air, a small quantity of carbonic anhydride is evolved during its decay, accompanied, as in the former case, with the separation of water; and under certain circumstances marsh gas (CH_4) is liberated in considerable abundance. (See also p. 146.)

Coal and other Combustible Minerals.

(1111) The foregoing facts connected with the gradual decay of woody fibre and vegetable tissue, have a special interest, not only in their bearing upon the value of vegetable matter as a manure, but also in reference to the origin of the enormous masses of fossil fuel which are stored up in the bowels of the earth, and which are the result of complicated chemical changes under variable circumstances of temperature, moisture, and pressure—acting either upon plants which grew upon the spot, as in peat bogs now in process of formation, or upon the débris of trees or plants drifted from a distance, and accumulated in par-

ticular localities, as is now occurring in the deltas of the Mississippi, and other large rivers.

Most of the bituminous coal appears to have been formed from a cryptogamic vegetation, of which upwards of 500 species have been identified, including the ferns: *lepidodendra*, *calamites*, and *sigillariæ* are also abundant. The latter are especially interesting, as their roots, formerly mistaken for a distinct species of plant and termed *stigmara*, are found in nearly every bed of clay lying immediately below the coal and in contact with it, and the sigillaria has been found growing from them. This observation is one of high importance, as it proves that in most cases the plants actually grew upon the spot in which the coal is now found. In many instances the trunks of the sigillaria are found *in situ* traversing the seams of coal; the bark has in these cases been found converted into true pure coal, while the body of the tree appears to have decayed, and its internal cavity has been filled up with sandstone.

The deposits of fossil combustible matter may be subdivided into—1. Peat; 2. Fossil resins, and bitumen; 3. Lignites, or brown coal; 4. Bituminous, or eaking coal; 5. Steam, or 'free burning' coal; and 6. Anthracite.

1. *Peat*.—The vegetable origin of this substance is at once evident on inspection. Peat is formed only in the temperate regions of the globe; in tropical climates the decay of vegetable matter proceeds with too much rapidity to allow of the accumulation which occurs when the decomposition takes place slowly. The process of peat growth is comparatively rapid. Peat differs much in appearance and density; that taken near the surface of the bog is of a reddish brown colour, very porous, and preserves the fibrous structure of the plants. When dry its density often does not exceed 0·3; that from the deeper layers is much denser (0·7 or 0·8); it becomes much darker coloured as the depth increases, and then often exhibits little or no traces of its vegetable structure. The proportion of earthy matter is greater in the denser peat obtained from the deeper parts of the bog. In surface-peat the ash does not exceed 1 or 2 per cent.; whilst in the deeper layers, from 7 to 10 per cent. is a common proportion, and at the bottom of the bog it sometimes amounts to 30 per cent. upon the weight of the peat. Freshly cut peat often contains 40 or 50 per cent. of moisture; and the peat sold in Dublin, after being dried by exposure to the air for many months, still retains from 15 to 25 per cent. of water. In Bavaria, peat is dried extensively for use in the locomotive engines; and at Königsbrunn it has been for several years employed in the puddling furnaces in the conversion of cast into wrought iron.

2. *Fossil Resins, and Bitumen*.—These substances include *amber*, *retinite*, or *retinasphalt*, *asphalt*, and many other allied bodies such as *hatchetin*, *idrialin* (C_6H_8), and *ozocerite* or *fossil*

wax, which are chiefly contained in the tertiary strata. In many instances they are the products of the action of an elevated temperature upon vegetable bodies; and when this is the case, they form irregular deposits which impregnate the strata around: under these circumstances, masses of igneous rock, such as basalt or trap, are often found in their immediate neighbourhood. In other cases the bitumens occur in regular beds, which appear to have been formed in a manner similar to the deposits of true coal. Many lignites likewise contain the bitumens and resins disseminated through them in small quantities. They are more or less soluble in alcohol, ether, and the essential oils. Although combustible they are not consumed as fuel. Asphalt is largely used in the preparation of an artificial paving material, and the finer kinds are employed in the formation of a species of black varnish or enamel for leather. (1568.)

3. *Lignite or Brown Coal*.—This species of coal generally retains its woody lamellar structure to a considerable extent, though in this respect there are great differences; as its name implies, it has a brown colour. When first raised it contains a large proportion of moisture, amounting sometimes to 40 per cent., 15 or 20 per cent. of which is retained after exposure to the air for many months. When distilled in closed vessels it yields a coke which does not cake together, and in which the original form of the fragments is preserved; the ash is less abundant than in peat. The true lignites occur in the tertiary strata.

4. *Bituminous or Caking Coal*.—This is the most highly prized variety of coal, and is the most abundant product of the British coal fields. It occurs above the old red and beneath the new red sandstone, in what geologists have termed from its presence *the coal measures*. There are several varieties of bituminous coal; some, like the Scotch *parrot coal*, are of a brownish black colour, and of a slaty structure; when heated in closed vessels they emit a large quantity of gaseous matter, and leave a coke which is but incompletely fused and coherent. The Lancashire *cannel coal* is another form, which is characterized by its conchoidal fracture, and the waxy lustre which it exhibits. It is hard, and like jet it is often cut and polished for ornamental purposes; it is of a dull brownish black colour, yields a good deal of gas, and leaves an imperfectly fused hard lustrous coke; both these coals are highly prized as *gas coals*. *Newcastle coal* represents a third variety; it is of a full blue black colour; has a brilliant lustre, and a cubic fracture; it burns with a bright luminous flame, and is much valued as household fuel; it furnishes a coke

which is much swollen, caked together, and possessed of a high lustre.*

5. *Steam Coal*.—This is a coal intermediate in quality between the bituminous coals and the anthracites; it burns freely and with flame, giving out a steady heat, but it does not yield sufficient volatile matter to be advantageously employed in the preparation of coal gas. It is well fitted for use in the steam navy, since it does not crumble readily in the hold of a vessel during its rolling, and it emits but little smoke. It furnishes a coke which scarcely cakes together, and which possesses but little coherence or lustre. Much of the Welsh coal is of this description.

6. *Anthracite*.—The *stone coal*, or *culm*, as this variety is sometimes called, is found in the lowest portion of the carboniferous strata. It contains but a small portion of volatile matter, and burns almost without flame with a steady red glow. When heated, it splinters into small fragments, a circumstance which often occasions considerable inconvenience in its application as fuel. The most compact forms burn indeed with great difficulty. This coal is black; it has a high lustre, and often exhibits an iridescent play of colours; its fracture is lamellated parallel to the bed from which it was taken, but the cross fracture is oblique or conchoidal. The coke obtained from it differs little in appearance from the original coal either in bulk or in weight. Anthracite is extremely abundant over vast tracts of North America, but much of it is so compact that it is scarcely applicable as a fuel. A large quantity of excellent anthracite is obtained from the South Wales coal field.

The tables on the following page will give an idea of the composition of wood, and will illustrate the progress of its decay.

* Amongst the coal measures in the neighbourhood of Bathgate, near Edinburgh, occurs a remarkable bituminiferous deposit, which has been sold under the name of "Boghead Cannel Coal," and has been extensively employed to mix with inferior descriptions of coal in the manufacture of coal gas. It contains from 18 to 25 per cent. of an aluminous ash, which retains the form of the mineral when it is burned in the open fire; when distilled at a low temperature in closed vessels, the mineral gives off a very large proportion of liquid hydrocarbons, mixed with a certain quantity of dense gaseous hydrocarbons. The mass left after distillation is remarkable for the small proportion of carbon (from 6 to 10 per cent.) which is left behind in the ash. A singular lawsuit arose upon the question whether or not this substance was to be regarded as *coal*. The term *coal*, however, being one rather of popular than of scientific language, and not admitting of accurate definition, the opinions of the chemists, geologists, and histologists who were examined upon the question were divided, and the case was decided upon a collateral issue.

Composition of Wood and Coal.

| Variety . . | Sound Oak Wood. | Decayed Oak Wood. | Humus from Decayed Oak. | | Peat. | | Asphalt. Mexico. Regn't. | Lignite. | | Boghead. W.A.M. | |
|--|-----------------|-------------------|-------------------------|-------|--|---------------------|--------------------------|--|--------------|--|-------|
| | | | Meyer. | Will. | Dartmoor. Vaux. | Vulcaire. Regnault. | | Bovey. Vaux. | Dax. Regn't. | | |
| Locality, &c. | W.A.M. | Liebig. | | | | | | | | | |
| Authority . | W.A.M. | Liebig. | Meyer. | Will. | Vaux. | Regnault. | Regn't. | Vaux. | Regn't. | W.A.M. | |
| Sp. grav. . . | 0.81 | | | | 0.849 | | 1.063 | 1.129 | 1.272 | 1.196 | |
| Coke . . . | 21.3 | | | | 29.30 | | 9.0 | 30.8 | 49.1 | 30.23 | |
| Carbon . . . | 50.10 | 53.47 | 54.0 | 56.0 | 54.02 | 56.25 | 78.10 | 66.31 | 69.52 | 63.10 | |
| Hydrogen . . . | 6.07 | 5.16 | 5.1 | 4.9 | 5.21 | 5.63 | 9.30 | 5.62 | 5.59 | 8.91 | |
| Nitrogen . . . | } 43.68 | 41.37 | 40.9 | 39.1 | 2.30 | } 32.54 | 9.80 | 0.56 | } 19.90 | } 7.25 | |
| Oxygen . . . | | | | | 28.17 | | | 0.56 | | | 22.86 |
| Sulphur . . . | | | | | 0.56 | | | 2.36 | | | 0.96 |
| Ash . . . | 0.15 | | | | 9.73 | 5.58 | 2.80 | 2.27 | 4.99 | 19.78 | |
| <i>The same, Ash free.</i> | | | | | | | | | | | |
| Carbon . . . | 50.18 | | | | 59.73 | 59.57 | 80.34 | 67.85 | 73.18 | 78.67 | |
| Hydrogen . . . | } 6.08 | | | | 5.91 | 5.96 | 9.57 | 5.76 | 5.88 | 11.11 | |
| Nitrogen . . . | | | | | | 2.54 | 2.09 | } 10.09 | 0.58 | } 2.94 | |
| Oxygen . . . | 43.74 | | | | 31.82 | 32.38 | | | 23.39 | | |
| Empirical formula } C ₃₄ H ₄₈ O ₂₂ | | | | | C ₂₀ H ₂₂ O ₈ | | | C ₂₇ H ₂₈ O ₇ | | C ₂₂ H ₃₈ O ₂ | |

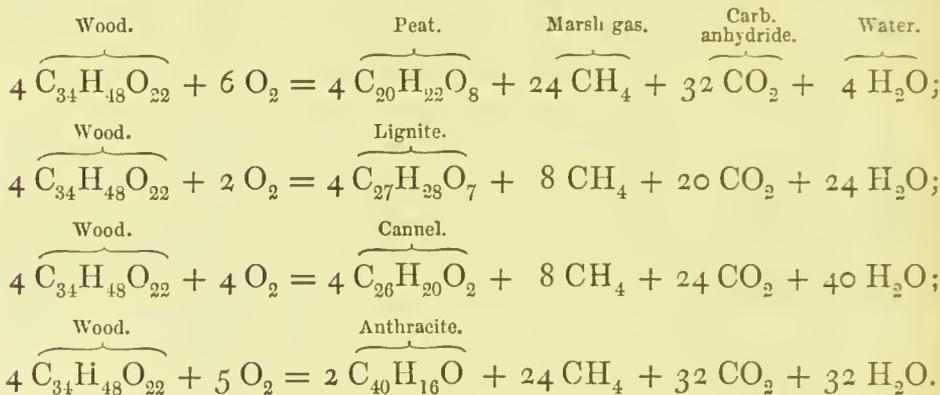
Composition of different Varieties of Coal—(continued).

| Variety | Parrot. | Canuel. | Caking. | Dry. | Dry. | Steam. | Anthracite. | |
|----------------------------|--|--|--|---------------------|--------------------|-----------------|-----------------------------------|-------------------------|
| | Lesmahagow. | Wigan. | Newcastle. | Wolverhampton Vaux. | St. Helen's. Vaux. | Newport. W.A.M. | S. Wales. Vaux. | Pennsylvania. Regnault. |
| Authority | W.A.M. | Vaux. | Richardson | Vaux. | Vaux. | W.A.M. | Vaux. | Regnault. |
| Specific gravity . . | 1.251 | 1.276 | 1.280 | 1.278 | 1.279 | 1.309 | 1.392 | 1.462 |
| Coke | 43.3 | 60.36 | | 57.21 | 65.5 | 75.1 | 92.1 | 89.5 |
| Carbon | 73.44 | 80.07 | 86.75 | 78.57 | 75.80 | 81.47 | 90.39 | 89.21 |
| Hydrogen | 7.62 | 5.53 | 5.24 | 5.29 | 5.22 | 4.97 | 3.28 | 2.43 |
| Nitrogen | } 11.761 | 2.12 | } 6.61 | 1.84 | 1.92 | 1.63 | 0.83 | } 3.69 |
| Oxygen | | 8.08 | | 12.88 | 10.99 | 5.32 | 2.98 | |
| Sulphur | | 1.145 | | 1.50 | 0.39 | 1.10 | 0.91 | |
| Ash | 6.034 | 2.70 | 1.40 | 1.03 | 5.17 | 5.51 | 1.61 | 4.67 |
| <i>The same, Ash free.</i> | | | | | | | | |
| Carbon | 78.16 | 82.29 | 87.97 | 79.38 | 79.93 | 86.27 | 91.87 | 93.59 |
| Hydrogen | 8.11 | 5.68 | 5.31 | 5.34 | 5.50 | 5.26 | 3.33 | 2.55 |
| Nitrogen | } 13.73 | 2.18 | } 6.72 | 1.86 | 2.03 | 1.73 | 0.84 | } 3.86 |
| Oxygen | | 8.31 | | 13.02 | 11.58 | 5.54 | 3.01 | |
| Empirical formula . | C ₂₅ H ₃₂ O ₃ | C ₂₆ H ₂₀ O ₂ | C ₄₅ H ₃₄ O ₂ | | | | C ₄₀ H ₁₆ O | |

They also furnish a synoptic view of the composition of some of the principal varieties of coal, in the order of their occurrence in successive geological stages. The proportion of oxygen, it will be seen, diminishes rapidly, and that of the hydrogen more slowly, as the coal passes from lignite towards anthracite, in which last form it consists of nearly pure carbon.

Observation has proved that during these changes oxygen in small amount is absorbed, whilst carbonic anhydride and carburetted hydrogen are evolved in

large quantities. It may be worth while to point out the simple mode in which we may from these facts theoretically explain the conversion of wood into coal under the influence of a very limited supply of oxygen, whilst the vegetable matter is submerged in water at a moderate temperature. If we assign to wood the empirical formula $C_{34}H_{48}O_{22}$, founded upon the analysis of oak given in the foregoing table, the approximative empirical formula for peat will be $C_{20}H_{22}O_8$; for Bovey lignite, $C_{27}H_{28}O_7$; for Wigan cannel, $C_{26}H_{20}O_2$; and for the Welsh anthracite, $C_{40}H_{16}O$. Now, if a small amount of oxygen, such as might be supplied by solution in water, be supposed to act upon the woody tissue, each of these varieties of fuel might be formed by the separation of marsh gas, carbonic anhydride, and water, in the following proportions:—



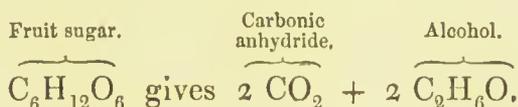
The amount of ash left by different kinds of coal is very variable. In the finest species of coals the fixed ash appears to be disseminated pretty evenly through the mass, but in the coarser varieties, thin seams of iron pyrites, and at other times, as in the Newport coal, crystallized laminae composed of the mixed calcie, magnesic, and ferrous carbonates are found. It is obvious that where these seams occur, their components must have been carried into the mass by infiltration. The ash of pure coal furnishes but minute quantities of the salts of the alkalis; it usually contains but little calcium or magnesium, the bulk of it consisting of aluminic silicate, with variable amounts of oxide of iron. Vaux also found traces of copper and lead in most of the coals which he analysed.

§ IV. ON FERMENTATION.

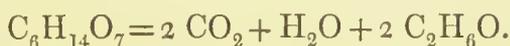
(1112) UNDER the term fermentation, frequent mention has been made of a particular change which saccharine bodies undergo, in consequence of which they become converted into carbonic anhydride and alcohol. Many other substances, however, besides sugar, are susceptible of an analogous change, and the term *fermentation* is now applied to various transformations which organic compounds experience under the influence of a small

quantity of organized matter, which is itself in a state of active alteration. This active substance is termed a *ferment*, and at the close of the operation appears neither to have imparted anything to, nor received anything from the substance which is undergoing fermentation. During this change, the body which is experiencing fermentation is gradually broken up into two or more substances of simpler composition; in certain cases, the elements of water are assimilated, in others they are separated, whilst in a third class of decompositions water is neither separated nor assimilated.

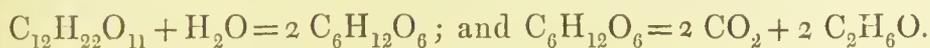
For example, when fruit sugar is placed in contact with ordinary yeast, the sugar is simply converted into carbonic anhydride and alcohol, the yeast acting as the ferment:—



No assimilation or separation of water occurs in this case. But when grape sugar, $\text{C}_6\text{H}_{14}\text{O}_7$, is subjected to fermentation, carbonic anhydride and alcohol are formed as before, and the elements of water are eliminated:—



Again, when cane sugar is submitted to fermentation, it assimilates the elements of water, first becoming changed into fruit sugar, and this substance is afterwards broken up into carbonic anhydride and alcohol as before:—



The different varieties of fermentation receive their distinctive name from the principal products which they furnish; for example, when spirit of wine is formed from sugar, the change is called the *alcoholic* or *vinous* fermentation; when lactic acid is converted into butyric acid, the process is termed the *butyric* fermentation, &c.

In all cases of fermentation the following conditions are essential:—1, the presence of water; 2, a temperature ranging between the extremes of 41° and 113° (5° and 45° C.); 3, a peculiar ferment (the nature of which varies in the different cases); 4, exposure for a longer or shorter period to the air; and 5, the body which is to undergo fermentation. It may be remarked that in most instances the compounds susceptible of fermentation are crystallizable products. It is especially to be observed, although the ferment does not contribute any of its components to the results

of fermentation, yet that it is itself destroyed during the operation; the products of its decomposition being generally discernible mixed with the results of the fermentation. This fact has an important bearing upon the theory of the process, but its significance will be best understood by tracing the operation through its different stages in the formation of alcohol.

(a) *Alcoholic Fermentation.*

(1113) When the juices of plants or of fruits containing sugar, such for instance as *must* (the juice of the grape), are kept at a temperature of about 68° (20° C.) for some hours, a change begins to show itself. The liquid becomes turbid, and small bubbles rise to the surface; or in popular language, it begins to *work* or to ferment. This change is due in the first instance to the alterations produced in the albuminous and azotised matters, which all such juices contain, under the combined influence of atmospheric oxygen, warmth, and moisture. This azotised matter is decomposed, and an intestine change commences, which after it has once begun, continues in vessels to which the further access of air is prevented. As the fermentation proceeds, a continual disengagement of heat is maintained, whilst a constant extrication of gas continues; this gas, if collected, is found to consist entirely of carbonic anhydride. After a time the escape of gas diminishes, and at length ceases; if the liquid be now examined, the sweet taste of the sugar will have disappeared, and the solution will have acquired a flavour more or less spirituous. If this liquid be distilled, the first portions that come over will be found to contain an inflammable product lighter than water, which is easily recognized as dilute spirit of wine or alcohol.

(1114) *Properties of Yeast.*—Upon examining the liquid which remains after fermentation is complete, it is found to contain a multitude of small oval organized bodies which do not exceed $\frac{1}{250}$ of an inch, or 0.1 millimetre, in diameter, and which when viewed under the microscope, are seen to consist of nucleated cells presenting the appearance shown in fig. 385, page 151. These cells form the essential constituent of *yeast*, a fungus to which the term *Torula cerevisiæ* has been applied, and which is obtained in great abundance during the fermentation of wort in the manufacture of beer.

Beer yeast is the substance which possesses, in the highest degree, the power of producing the alcoholic fermentation. Its efficacy in this respect is easily proved by the following experi-

ment:—Dissolve 4 parts of pure cane sugar in twenty parts of water, and add 1 part of fresh yeast; then expose the mixture to a temperature of about 77° (25° C.). In less than an hour fermentation will commence, and carbonic anhydride will be evolved in abundance.

Yeast, when in its active condition, always exhibits a slightly acid reaction; if thoroughly washed, the globules are much less active, but they again acquire activity by exposure for a few hours to the air, during which time the acidity is again developed. The addition of a minute quantity of some of the vegetable acids, such as the acetic or the tartaric acid, to washed yeast, immediately restores its activity, but if a larger quantity of the acid be employed the process of fermentation is arrested. The strong mineral acids, particularly the sulphuric acid, when present even in small quantity, immediately put a stop to the alcoholic fermentation; the same effect is also produced by solutions containing traces of sulphurous acid. It is also checked by the addition of a small quantity of free alkali. Many other circumstances likewise put an immediate stop to the process of fermentation. For example: a solution which contains more than one-fourth of its weight of sugar cannot be made to ferment; the presence of 20 per cent. of alcohol or upwards, also puts an end to the process; the addition of a strong solution of common salt, or the presence of many metallic salts in the liquid, such for instance as argentic nitrate, corrosive sublimate, and eupric sulphate or acetate, checks it immediately. The occurrence of fermentation is also prevented by the presence of small quantities either of black oxide of manganese, or of mercuric oxide, of strychnia, or of quinia. Small quantities of kreasote, of oil of turpentine, and of many other essential oils, have a similar effect. If, however, fermentation has once commenced, the vegetable bases have no specific power of arresting the process.

On the other hand, neither solution of arsenious acid, of plumbic acetate, nor of tartar emetic exerts any retarding effect upon the progress of fermentation. If yeast be boiled for a few minutes, it is deprived of its power of exciting vinous fermentation. Such yeast, however, effects the conversion of sugar into mucilage and mannite. Yeast may be dried at a low temperature or by pressure, and preserved in this condition without losing its activity.

The part which the globules of yeast perform in exciting fermentation is extremely obscure. The following experiment of Mitscherlich shows that the sugar ferments only in those points

which are in actual contact with the globules:—Over one extremity of a wide tube open at both ends, a piece of filtering paper is tied, and this covered extremity is plunged into a weak solution of pure cane sugar; the liquid quickly passes through the paper and rises in the tube, which may be supported so as not to touch the bottom of the jar of syrup; if a small quantity of yeast be now introduced into the tube, and the whole be set aside in a warm place, fermentation will be found to commence in an hour or two; but it will be confined to the portion of liquid within the tube;—that is, to those portions of syrup which are actually in contact with the yeast globules. The bibulous paper allows free communication between the liquid within and without the tube, but it prevents the globules from passing into the mass of syrup in the outer vessel. Berthelot indeed states that it is possible to effect the alcoholic fermentation without the presence of yeast globules, by exposing a solution of glucose or of cane sugar, mixed with gelatin and chalk, to a steady temperature of about 104° (40° C.), in vessels from which air is excluded. The solutions must be saturated with carbonic anhydride, and the experiments conducted over mercury. But the presence of yeast globules is by no means necessarily excluded under these circumstances, and the researches of Schröder as well as of Pasteur (see p. 121) show conclusively that no alcoholic fermentation occurs when due care is taken to exclude the spores of the yeast fungus. The experiments of Pouchet and others, in which the exploded notion of spontaneous generation is revived, are inconclusive. The more completely the air admitted to the vessels under experiment is sifted, so as to exclude organic germs, the more complete is the absence of the development of organic life.

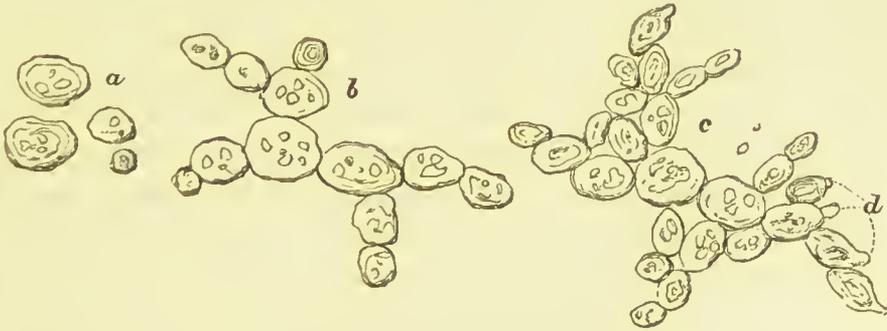
Varieties of Yeast.—According to the observations of Mitscherlich, who has carefully watched the development of the yeast plant under the microscope, there are two modifications of yeast: viz., *oberhefe* (surface yeast), and *unterhefe* (sediment yeast); these two varieties are propagated in different ways, and each produces specific results upon the fermenting liquid.

The *unterhefe* is the ferment of the Bavarian beer, which is allowed to ferment very slowly and at a low temperature; the formation of acid bodies, such as the lactic and acetic acids, is thus avoided, and the beer is more highly esteemed from their absence. The *unterhefe* consists of isolated globules of very varying dimensions. It appears to be propagated by spores thrown out from the larger cells, and not by buds and offshoots as is the

case with the surface yeast; the temperature must not be allowed to rise beyond 45° nor to fall below 32° F.

Surface yeast is developed rapidly at a temperature varying from about 70° to 80° , and is the more active of the two forms in producing the alcoholic fermentation. The development of the yeast globules may readily be watched under the microscope, by placing a drop of some saccharine infusion, such as wort, between two plates of glass, with a minute quantity of yeast. The granules will at first exhibit the appearance shown at *a*, fig. 385, where they can be seen to possess an outer cell wall, within which is a quantity of granular matter. In the course of a few hours some of these cells throw out buds such as are shown at *d*. The rapidity with which this development takes place, when it has once commenced, is often very great; *b* indicates a group of these bodies, probably all developed from the large central cell; *c d* shows the

FIG. 385.



same group three hours later: within nine hours after it was first observed an oval patch of cellules had been formed, containing between seventy and eighty separate cells, in which the original cell was distinctly visible in the centre, and around it were grouped the new cells, decreasing in size towards the circumference; each of these cells contained the granular matter above spoken of, and fresh buds continued to form upon the exterior margin of the outer cells. The yeast cells frequently assume a more elongated form, flattened at the sides, but they continue to be developed in the same manner; both varieties may often be seen side by side under the microscope at the same time. The walls of these cells consist of a thin membrane which has the same composition as cellulin (Mulder): and within this membrane is an azotised gelatinous mass which here and there exhibits a kind of granular nucleus. This granular matter is soluble in acetic acid, and may thus without difficulty be separated from the cell membrane in

which it is contained; it may then be precipitated for examination, by neutralizing the solution with ammoniac carbonate. The contents of the granules may also be extracted by means of a weak solution of potash, and can be precipitated by neutralizing it with acetic acid. When thus obtained, the precipitate has the properties and composition of protein.

Everything that destroys the vitality of these organized bodies destroys their power of exciting fermentation: for this reason too high a temperature, such as that of 122° (50° C.) stops the operation, and a depression of temperature also temporarily arrests it, though it is stated that even after exposure to a cold of 10° (-12° C.), the fermentation is renewed when the temperature is allowed to rise.

The globules of yeast do not increase in number in solutions of pure sugar: on the contrary, during the process of fermentation, the granules undergo a gradual disintegration, the new buds which are formed being produced at the expense of the material furnished by the decay of others. For the decomposition of 100 parts of sugar, about one part of yeast, calculating it in its dry state, is required. If the proportion of sugar to the yeast exceed this, the excess of sugar remains unaltered in the liquid; and if the cells be examined after fermentation has ceased, many of them will be seen to be ruptured and destroyed; and a certain quantity of ammoniac lactate and acetate, and other ammoniacal salts, will be found in the solution.

But although the yeast globules do not increase in quantity in a solution containing pure sugar only, they become rapidly developed in all saccharine vegetable infusions during fermentation, and multiply at the expense of the azotised matters which are always present in these liquids, and which form an essential part of the nutriment of the yeast plant. Owing to this cause the quantity of yeast is increased to at least six or eight times its original amount during the fermentation of beer.

Mitscherlich gives the following as the composition of ordinary washed yeast; first, when in a condition to excite fermentation; and secondly, in the partially exhausted state, after fermentation had ceased: in both cases the ashes have been deducted.

In this experiment the nitrogen in the spent portion was found to have become reduced to one-half of its former amount. This spent yeast, however, still contained an excess of active granules; when entirely exhausted, it would furnish scarcely any nitrogen on analysis:—

| | Entire cells. | Spent yeast. |
|------------------|---------------|--------------|
| Carbon | 47·0 | 47·6 |
| Hydrogen | 6·6 | 7·2 |
| Nitrogen | 10·0 | 5·0 |
| Sulphur | 0·6 | |
| Oxygen | 35·8 | |

The inorganic matter contained in yeast amounts to a considerable quantity, not less than about 7·5 per cent. of the dried yeast. It consists entirely of potassic, sodic, calcic, and magnesian phosphates (Mitscherlich).

Pasteur's experiments render it probable that in all cases alcoholic fermentation is connected with the assimilation of the sugar by the yeast plant during the development of the yeast globules: even when the globules are mixed with a solution of pure sugar, he considers that during the whole process of fermentation a development of fresh globules is taking place at the expense of those which are undergoing decomposition. The following is one of his experiments:—A quantity of washed beer yeast was divided into two equal portions, one of these was placed in a solution of pure sugar; the other portion was boiled with water, the decoction was filtered, and the filtrate added to a similar portion of pure syrup. A minute quantity of fresh yeast was now added to the second portion. In the first case 5 parts of yeast effected the transformation of 12·9 of sugar in six days, and then became exhausted; in the second case the liquid became turbid, fresh yeast was formed (at the expense of the azotised solution derived from the yeast globules), and 10 parts of sugar underwent fermentation in nine days. It appeared, therefore, that during the conversion of the soluble portion of yeast into organized globules, a quantity of sugar was decomposed nearly equal to that decomposed by an equivalent amount of yeast in its natural state. Pasteur considers that the essential condition of fermentation is the conversion of albuminoid matter into organized globules. The addition of a small proportion of ammoniacal salts to a solution of pure sugar was found by Leuchs to favour the development of fresh yeast cells, and to facilitate the process of fermentation.

The following analyses by Graham, Hofmann, and Redwood, show that during fermentation the azotised matters in the liquid are reduced in quantity, whilst the yeast plants are becoming developed:—Pale malt wort, of sp. gr. 1·088, which contained about 21 per cent. of solid matter before fermentation, yielded 0·217 per cent. of nitrogen, which would correspond to 3·43 per cent. of albumin; after full fermentation and removal of the yeast, the

nitrogen amounted only to 0.134 per cent. ; this existed, no doubt, partly in the form of ammoniacal salts ; but if all were calculated as albumin it would amount only to 2.11 of that substance.

The composition of the contents of the granules of yeast has already been stated to bear a close relation to that of albumin. This circumstance may afford some clue to the remarkable fact that yeast is never furnished except by the decomposition of albuminous matters. Various bodies which contain nitrogen furnish it when they have once begun to decay ; for example, in white of egg, muscular tissue, and cheese, during decomposition in the presence of saccharine solutions, these globules become developed, and true fermentation begins.

Berthelot has shown that by employing an azotised substance, such as the tissue of the pancreas, or, still better, a portion of casein obtained from poor cheese, and adding chalk to the liquid to prevent it from acquiring an acid reaction at any time, a number of substances not hitherto regarded as susceptible of the alcoholic fermentation may be made to furnish alcohol and carbonic anhydride, whilst a portion of calcic lactate or butyrate is formed. The temperature of 100° (37°·8 C.) is that most favourable for obtaining these results, and a period of several weeks is often requisite. The maintenance of the liquid in a neutral state by means of chalk or some corresponding substance, is an essential condition.* Not only do the ordinary sugars furnish a certain amount of alcohol when thus treated, but starch, sorbin, and gum give similar results. Even mannite, duleite, and glycerin may thus be made to yield alcohol, hydrogen in these cases being developed at the same time. During the progress of these fermentations it was not possible in any case to detect the conversion of the gum, the starch, the duleite, the sorbin, the mannite, or the glycerin into a fermentable variety of sugar as an intermediate step in the act of fermentation ; this, however, was most probably because the sugar was decomposed as fast as it was formed. A small quantity of gaseous nitrogen was commonly found amongst

* Béchamp (*Comptes Rendus*, lxiii. 451) states that chalk does not act merely by its neutralizing action on acids. He found that pure precipitated calcic carbonate does not produce the slow fermentations which occur when chalk is used, and chalk itself loses the power if previously heated to 572° (300° C.). This difference he attributes to the presence of organisms which, when viewed under the microscope, appear as numerous exceedingly minute points endowed with a tremulous motion ; and he states that the chalk itself contained about 0.8 per cent. of its weight of an organic azotised matter. The chalk examined was from the interior of a block taken from the chalk deposit at Sens.

the products, and was traced to the decomposition of the azotised matter which occurs simultaneously with the metamorphosis of the saccharine body.

(1115) *Progress of Fermentation*.—Much interesting information relative to the changes which solutions of sugar of various kinds undergo during fermentation may be obtained by examining them at intervals by means of a beam of polarized light. If a solution of starch sugar be mixed with yeast, the right-handed rotation which such sugar possesses in its natural state diminishes slowly, in a degree proportioned to the quantity of sugar which has undergone fermentation (Mitscherlich). But if a solution of *inverted* cane sugar (1086) be watched in like manner from time to time, the phenomena are more complicated; the left-handed rotation undergoes no decrease until about three-fifths of the sugar has been decomposed, after which the rotatory power rapidly diminishes as the fermentation proceeds, but there is *no inversion* of the rotation. Dubrunfaut, who made these observations, remarks that this uncrystallizable sugar must consist of a mixture of at least two, and possibly of more modifications of sugar; one of which is neutral, and is that which is first fermented, and the other is possessed of left-handed rotation, and does not undergo fermentation until the neutral sugar has all been decomposed.—(*Ann. de Chimie*, III. xxi. 172.)

It has been already mentioned that when cane sugar is subjected to the vinous fermentation, it undergoes a preliminary change in consequence of the necessity of assimilating the elements of water. Owing to this circumstance, a much larger quantity of yeast is required in order to produce the fermentation of sucrose or cane sugar than is needed by glucose. Berthelot states that the ferment by which this conversion of cane sugar into glucose is effected is contained in the soluble portion of ordinary yeast, and does not reside in the globules; and this is confirmed by Béchamp. It has been observed by Dubrunfaut, that if a solution of cane sugar which has been mixed with yeast be examined by polarized light before fermentation commences, the rotatory power upon polarized light will be inverted, and it will be found to have become left-handed, showing that the cane sugar has acquired the additional amount of water which it needed, and has thereby become altered into uncrystallizable sugar. The same change is also strikingly shown by the increase in density which a solution of cane sugar undergoes previous to entering into fermentation. This circumstance was pointed out by Graham, Hofmann, and Redwood, in their researches upon the decrease in density which

saccharine solutions undergo during fermentation. (See their "Report upon Original Gravities," *Q. J. Chem. Soc.* v. 232.)

It was ascertained by these chemists that when quantities of cane sugar, starch sugar, caramel, and dextrin, which contain equal quantities of carbon, are dissolved in water and diluted till the solutions are equal in *weight*, the density of these solutions varies greatly, as will be evident on inspecting the following table: from which it appears on comparing together quantities of the different solutions equal weights of which contain equal quantities of carbon, that starch sugar furnishes the densest solution; next to this comes malt wort, which owes its sweetness to starch sugar; then comes cane sugar; whilst dextrin gives a solution of smaller specific gravity; and caramel a solution the least dense of any of the substances compared together:—

| Parts of Cane Sugar in 1000 of Solution. | Specific Gravity of Solution of— | | | | |
|--|----------------------------------|-----------------|-------------|----------|----------|
| | Starch Sugar. | Pale Malt Wort. | Cane Sugar. | Dextrin. | Caramel. |
| 25 | 1'0104 | 1'0100 | 1'0101 | 1'0097 | 1'0087 |
| 50 | 1'0208 | 1'0203 | 1'0202 | 1'0193 | 1'0173 |
| 75 | 1'0313 | 1'0306 | 1'0302 | 1'0288 | 1'0262 |
| 100 | 1'0424 | 1'0412 | 1'0406 | 1'0383 | 1'0349 |
| 125 | 1'0535 | 1'0521 | 1'0510 | 1'0479 | 1'0438 |
| 150 | 1'0649 | 1'0630 | 1'0618 | 1'0573 | 1'0528 |
| 175 | 1'0760 | 1'0742 | 1'0729 | 1'0669 | 1'0623 |
| 200 | 1'0878 | 1'0855 | 1'0838 | 1'0776 | 1'0718 |
| 225 | 1'0994 | 1'0972 | 1'0952 | 1'0863 | 1'0813 |
| 250 | 1'1114 | 1'1090 | 1'1067 | 1'0958 | 1'0910 |

Suppose for instance that 175 grains of cane sugar were dissolved in water, and the solution diluted till it weighed 1000 grains; it would have a sp. gr. of 1'0729. This solution if converted into starch sugar would become increased in specific gravity: so that a solution of starch sugar which contained in 1000 grains of the liquid a quantity of this sugar which would be furnished by the amount of cane sugar contained in the first solution, would have, as is represented in the second column, a specific gravity of 1'076.

In a direct experiment made for the purpose of observing this effect, it was found that a solution of cane sugar, to which a sufficient quantity of yeast had been added to effect its fermentation, and which had at first had a sp. gr. of 1'055, became in the course of an hour of a sp. gr. of 1'058, though no fermentation had set in. In another experiment, a solution of a sp. gr. 1'055, containing $\frac{1}{300}$ of its weight of yeast, increased in specific gravity

in four days to a sp. gr. of 1.0579, although no appearance of fermentation, or of other change, was manifest, loss by evaporation being carefully prevented.

When sugar is fermented, it is assumed in theory to be wholly converted into carbonic anhydride and alcohol; but in practice this is never the case. It was found by the chemists just quoted, in three careful experiments on the fermentation of cane sugar, in which $1\frac{1}{2}$, 3, and 6 measures of yeast were respectively added to 100 measures of the syrup, that 4.4, 3.7, and 3.72 per cent. of the sugar were converted into a brown soluble substance resembling caramel, and at the same time a little free lactic acid was formed. Pasteur (*Ann. de Chimie*, III. lviii. 339) finds that, even under favourable circumstances, from 93 to 94 per cent. only of the sugar is converted into alcohol and carbonic anhydride, whilst from 5.6 to 6.5 per cent. is converted into other substances, among which is succinic acid, amounting to not less than 0.6 per cent. of the weight of the sugar employed. Glycerin was also found to the extent of 3.6 per cent. of the sugar employed, and from 1.2 to 1.5 per cent. of the sugar was expended in producing cellulin and fat in the newly developed yeast globules. These are obviously secondary results.

(b) *Fermentation of Bread.*

(1116) *Composition of Bread Stuffs.*—The fermentation which takes place during the manufacture of bread is merely a modification of the alcoholic fermentation, produced by the action of the yeast upon the saccharine matter, which is either naturally present in the flour, or is developed by the action of the ferment on the starch. The chemical process of baking, however, cannot be rightly understood without a knowledge of the ordinary composition of the principal varieties of flour employed in the preparation of bread.

When corn is ground in a mill, the grain is reduced to a powder separable by sifting into two principal portions—*flour* and *bran*. The bran is composed of the brownish coloured outer covering of the grain, which is tougher and harder than the internal portions, and consequently is not reduced by grinding to so fine a state of division: the flour is produced by the pulverization of the inner portion of the grain.

The most important constituents of the varieties of corn used as food are—1. starch; 2. gluten, a peculiar azotised substance allied to albumin, which confers the tenacity and toughness upon

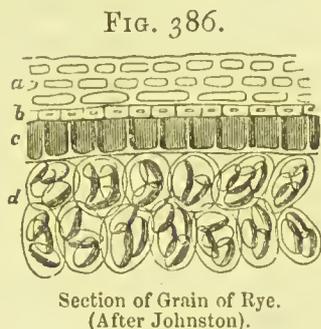
dough ; 3. a small portion of sugar,* or of dextrin ; 4. a little oily matter ; 5. a small quantity of saline matter ; and 6. a skeleton of ligneous tissue, which is the only portion of the seed not susceptible of digestion in the stomach. The proportions in which these ingredients are present in some of the principal varieties of grain used as food may be seen in the subjoined table. They vary, however, considerably in the same grain when grown in different climates. The proportion of gluten contained in wheat grown in the southern parts of Europe and in the north of Africa, is considerably higher than in the best English-grown wheat ; and the hard thin-skinned wheats furnish a larger proportion of gluten than the softer varieties of the grain.

| Components. | Whole wheat meal. | | | Maize. | Decorticated rice. | Rye. | Peas. | |
|-----------------------------|-------------------|--------------|-----------|---------------|--------------------|-------|--------|--------|
| | Polish. | Hardy white. | Algerian. | | | | | |
| | Péligot. | | | Boussingault. | | | | |
| Water | 15·2 | 13·6 | 13·6 | 17·1 | 7·3 | 14·7 | 8·6 | |
| Starch | 61·3 | 60·8 | 59·8 | 59·0 | 83·0 | 65·1 | 56·9 | |
| Dextrin and Sugar | } 6·3 | 10·5 | 6·4 | 1·5 | } 12·8 | } 7·5 | } 12·5 | } 25·0 |
| Azotised matter } soluble | | | | | | | | |
| } insol. | 12·7 | 10·5 | 14·4 | 7·0 | 0·7 | 2·0 | 2·2 | |
| Oily matter | 1·5 | 1·1 | 1·1 | 1·5 | 1·0 | 3·3 | 4·4 | |
| Fibre | | 1·5 | 1·4 | 1·1 | 0·5 | 2·4 | 3·1 | |
| Salts | 1·4 | | 1·7 | | | | | |
| | 100·0 | 100·0 | 100·0 | 100·0 | 100·0 | 100·0 | 100·2 | |

| Components. | Bran of soft French wheat. | Barley. (Fresenius.) | Hopetown oats. (Norton.) |
|-----------------------------|----------------------------|----------------------|--------------------------|
| Water | } 13·9 | 13·90 | 12·80 |
| Starch | | 48·06 | 56·89 |
| Dextrin and Sugar | } 51·0 | 3·87 | 1·83 |
| Gluten or its equivalent . | | 14·0 | 16·29 |
| Oily matter | 3·6 | 0·34 | 4·74 |
| Fibre | 9·7 | 13·34 | 1·03 |
| Salts | 5·7 | 3·56 | 2·49 |
| | 98·8 | 100·00 | 100·00 |

* Péligot considers that sugar does not exist ready formed in the grain, or in the freshly ground flour. He was unable to distinguish its presence when the aqueous solution of the flour was examined by optical means, and he did not find that lime was dissolved more freely by this solution than by pure water. If sugar were present, the lime should have been dissolved in proportion to the quantity of sugar in the liquid.

The principal portion of the woody fibre is accumulated in the bran; but this substance likewise contains a large proportion of nutritive matter, for both gluten and oily matter are deposited in its cells more abundantly than in any other part of the grain; as may be seen by the result of its analysis, given in the preceding table. Fig. 386 shows a section of part of a grain of rye, highly magnified; *a*, indicating the cells forming the outer coat of the seed; *b*, a single row of cells forming the inner seed coat; *c*, a layer of cells containing gluten (these three together form the bran); *d*, the white inner part of the seed filled with starch granules, lodged in the meshes of the cellular tissue.



(1117) GLUTEN.—This characteristic ingredient in the cereal seeds may be obtained in a separate form by mechanical means. The flour is made into a paste or dough, with water, and placed in a bag of fine linen, in which it is kneaded in a gentle stream of water so long as the washings have a milky appearance: the starch is by this means removed in suspension in the water, and the sugar and the dextrin are dissolved. Upon the cloth is left a grey, sticky, tenacious, tasteless substance, resembling bird-lime in appearance, consisting mainly of gluten, mixed with small quantities of bran and starch, and traces of oily matter. When dry it forms a hard, brownish, horny-looking mass. The gluten obtained from wheat and from rye possesses a peculiar tenacity, which is not observed, to anything like the same extent, in that obtained from the other cereals; and it is this tenacity of the gluten which especially fits the flour of wheat and rye for conversion into bread. Gluten is soluble in cold acetic acid, and in weak solutions of caustic potash or soda. It may be precipitated unchanged from either of these solvents by neutralizing them exactly with an acid. The diluted mineral acids combine with gluten and form a compound which is insoluble in excess of the acid. Gluten in its moist state putrefies rapidly, ammonia is formed, whilst hydrogen and carbonic anhydride are evolved, and the mass acquires the smell of decaying cheese. Gluten, however, cannot be regarded as a single definite body; it consists of at least two distinct substances, one of which is soluble in hot alcohol, whilst the other remains undissolved when treated with this menstruum. This insoluble portion is regarded by Liebig and by Dumas as vegetable fibrin. As the alcoholic solution cools, it deposits floeculi,

which have the composition and properties of casein. A third substance still remains in the alcoholic liquid, and gives to this solution a syrupy or gelatinous consistence. On the addition of water, a white substance resembling albumin is precipitated; Dumas and Cahours have termed it *glutin*: on treating it with ether a small quantity of fat is extracted, and the glutin is left in a state of purity: it may be dissolved by strong hydrochloric acid, and communicates to it a violet tint. It is, therefore, obvious that raw gluten contains several azotised principles, which differ considerably in chemical properties, though, as will be seen by the subjoined table, they are closely allied in ultimate composition:—

| Constituents. | Dumas and Cahours. | | | Bence Jones. |
|------------------------|--------------------|----------------|---------|---------------|
| | Gluten-Fibrin. | Gluten-Casein. | Glutin. | Crude Gluten. |
| Carbon | 53·23 | 53·46 | 53·27 | 55·22 |
| Hydrogen | 7·01 | 7·13 | 7·17 | 7·42 |
| Nitrogen | 16·41 | 16·04 | 15·94 | 15·98 |
| Oxygen and Sulphur . . | 23·35 | 23·37 | 23·62 | 21·38 |
| | 100·00 | 100·00 | 100·00 | 100·00 |

(1118) *Preparation of Bread.*—In the preparation of bread, the flour generally requires the addition of about half its weight of water, but the proportion varies with the quality of the flour. It is the usual practice to mix a certain quantity of the flour with yeast, salt, and lukewarm water; after which it is thoroughly kneaded into a stiff paste, or dough, and put aside, at a temperature of about 70° ($21^{\circ}\cdot 1$ C.), for an hour or two. The mass gradually swells up, or, as the baker terms it, the *sponge* rises; that is to say, the sugar in the dough is decomposed by the yeast; carbonic anhydride is set free at all points of the mixture, and, being imprisoned by the tenacious nature of the dough, the gas causes it to swell and become porous. When the sponge is in active fermentation it is thoroughly kneaded with the remainder of the flour, water, and salt, and set aside for a few hours. It is then kneaded a second time and cut into pieces of suitable size, after which it is put into an oven heated to a point between 455° and 554° (235° and 290° C.); the heat causes the imprisoned gas to expand still more, and gives the lightness of texture which characterizes good bread. During the process of baking, part of the water is expelled, 117 parts of dough, on the average, yielding 100 of bread; the granules of starch become converted into the pasty

or gelatinous condition: the temperature of the crumb never exceeds 212° , but the external surface of the loaf gradually becomes dry and hard, and losing a portion of its chemically combined water, is partially converted into a substance allied to caramel (1081), thus forming the *crust*. The bread is in this manner permanently fixed in the shape which it has acquired. During the baking, the alcohol formed by decomposition of the sugar, which corresponds in quantity to that of the carbonic anhydride, is expelled. Some years ago a company was formed, in whose operations the collection of this spirit formed an important object. This end was attained by performing the baking in closed ovens, furnished with a still-head for collecting and condensing the vapours. The project was, however, soon abandoned, and failed as a commercial speculation, owing in great measure to the dry unpalatable nature of the bread produced.

The French frequently employ *leaven* as a ferment instead of yeast. Leaven is dough kept from a previous batch for twenty-four hours in a warm place, till it has begun to undergo fermentation spontaneously. The decomposition which has commenced in the leaven spreads through the fresh mixture into which it is kneaded.

In England a species of unfermented bread has lately been manufactured to some extent; in this case also the sponginess is given to the dough by means of carbonic anhydride, but it is set free by the action of hydrochloric acid on sodic carbonate—common salt, a necessary ingredient in bread, being formed during the reaction; and a species of bread is obtained which, as might be expected, is sweeter than ordinary bread, but not so light. A good bread of this description may, according to Pereira, be obtained by mixing the materials in the following proportions:—Wheat flour 7 lb., sodic carbonate 350 to 500 grains, water $2\frac{3}{4}$ pints, hydrochloric acid 420 to 560 grains. The carbonate and flour are first intimately mingled, and then made into dough with the mixture of acid and water. If the carbonate be not equally and thoroughly distributed, it is detected after the baking, by the formation of a yellow spot around any portions of it that have escaped neutralization. An ingenious method of preparing unfermented bread was introduced by Dr. Daughlish. His plan is to force gaseous carbonic anhydride, at a pressure of 100 lb. upon the square inch, into the water which is to be used in preparing the dough, and to add the aerated water to the flour and salt, effecting their intermixture by machinery, whilst the whole is retained under pressure in a strong closed iron receiver. The dough is then drawn off into pans or moulding baskets, and baked in the

usual way. As soon as the pressure is removed, the dough rises owing to the expansion of the carbonic anhydride which has been thus intimately diffused through it.

Sponginess and lightness of texture are also sometimes given to pastry by the employment of ammoniac sesquicarbonate, which is mixed with the dough instead of yeast: on the application of heat, the salt is expelled in the gaseous state, and by its expansion it produces the desired effect mechanically.

In the latter case it is not improbable that the alkaline nature of the salt has an important influence upon the quality of the paste. Liebig has observed that in certain cases the employment of lime water in the manufacture of bread may be resorted to with great advantage. In order to understand the effect thus produced, it must be remembered that the peculiar toughness and elastic quality possessed by the dough furnished from the flour of certain of the cerealia, is dependent upon the gluten which they contain. Now it has been observed that when gluten is kept in a moist state, it undergoes a change in properties, in consequence of which it slowly loses its soft, elastic, insoluble condition, and becomes converted into a substance closely resembling diastase. In this state it acts, as Odling has shown, upon the starch of the flour, causing a considerable amount of it to pass into the form of dextrin and of sugar. Bread prepared from such flour is sticky, heavy, and sodden. The convertibility of good flour into dough, by the addition of water, depends upon the peculiar power which fresh gluten possesses of combining with water, and of forming with it a soft tenacious substance which does not yield its water to dry bodies placed in contact with it. Gluten, however, is a very hygroscopic substance, and when flour is kept exposed to the air for some time it gradually absorbs moisture; in consequence of which the gluten slowly undergoes the peculiar change above mentioned. This change in the qualities of the gluten occurs more rapidly in rye flour than in wheat flour.

It has been ascertained by Liebig, that flour in which the gluten has undergone this partial change, may have its original qualities restored by the substitution of lime water for common water in the preparation of bread: 100 parts of flour are to be mixed with 26 or 27 parts of saturated lime water, and a sufficiency of ordinary water must be added to furnish dough of the proper consistency. A given weight of flour, when treated with lime water, was found to yield 5 or 6 per cent. more bread than when made in the ordinary way, and the bread so obtained is stated to be more palatable than common bread.

It is to be hoped that this simple method will supersede the employment of alum, which is commonly resorted to by English bakers, to whiten the bread and to improve the tenacity of the dough of inferior flour. Even cupric sulphate, a still more deleterious ingredient, which in minute quantity exerts a similar effect upon the dough, has been employed in Belgium and elsewhere, for improving the appearance and sponginess of the loaf. Odling attributes the action both of lime water and of alum in improving the whiteness of bread, to its power of preventing the transforming influence of the altered gluten upon the starch. The brown colour of so-called 'brown' and 'seconds' bread has been shown not to be due, as is frequently supposed, to the presence of bran; for flour from which all the bran has been carefully removed will yield a brown bread if mixed with an infusion of malt, instead of with water. The change of colour appears, therefore, to be due to the partial conversion of starch into dextrin during the fermentation, and not to the presence of the colouring matter contained in the bran, which, indeed, is rather of an orange than a brown colour. An interesting report by Chevreul, upon the investigations of Mège Mouriès, and upon a new method of bread-making

which he has founded upon them, will be found in the *Comptes Rendus* for January, 1857.

New and Stale Bread.—Newly baked bread exhibits a well-known elastic appearance, and possesses a certain degree of moisture, which renders it more palatable to most persons than bread which has been kept for a day or two, and has become firmer and drier in appearance, and which is commonly said to have become *stale*. It is very generally supposed that this change in properties in bread which has been kept for a few days, is owing to the loss of water by keeping. This, however, is not the case. The crumb of newly baked bread when cold, contains about 45 per cent. of water, and that of stale bread contains almost exactly the same proportion. The difference in properties between the two depends simply upon difference in molecular arrangement. Boussingault found that a loaf which had been kept for six days, though it had become very stale, had not lost more than 1 per cent. of its weight when new. This same loaf was then placed in the oven for an hour, and at the end of that time it had acquired all the properties and appearance of new bread, although during the second baking it lost $3\frac{1}{2}$ per cent. of water. In another experiment a portion of bread was allowed to become stale when enclosed in a tight case, to prevent loss of water by evaporation; it was then heated, and was thus restored to the condition of new bread; these effects were produced alternately, many times in succession, upon the same piece of bread: a heat of about 131° (55° C.) was found to be sufficient to reconvert stale into new bread. Every person who has seen a thick slice of stale bread toasted, may have satisfied himself that the crumb has during this operation been converted into the same condition as that of new bread.

(c) *Lactic Fermentation.*

(1119) It has already been mentioned that sugar of milk does not undergo the vinous fermentation under ordinary circumstances. Milk, if it be kept in a warm temperature, may, notwithstanding, be converted into a spirituous liquor, which is in common use among the Tartars, who prepare it, under the name of *koumiss*, from mares' milk. More commonly, however, sugar of milk, when allowed to ferment, yields a product of a very different nature; *lactic* acid being formed, as may be seen in the common case of milk turning sour in warm weather. This acid ($C_3H_6O_3$) has the same centesimal composition as sugar of milk, its oxygen and hydrogen being in the proportion to form water, but the number of atoms contained in its molecule is fewer than

in that of sugar of milk ; and its formation furnishes a good instance of the reduction of a complex body into one of a simpler constitution, by the process of fermentation. In this case, the casein or curd of the milk, which is the basis of ordinary cheese, acts as the ferment. Casein is rendered insoluble by the presence of acids, and therefore it becomes separated in the form of insoluble floeculi, as soon as the milk turns sour. When all the curd has been thus rendered insoluble, the conversion of lactose into acid takes place very slowly ; but if the acid be neutralized by sodic carbonate, or by chalk, the curd is redissolved, and the fermentation or transformation is renewed in its former vigour. No extrication of gas nor absorption of oxygen occurs during the process ; the only perceptible change being the gradual disappearance of sugar of milk and the production of this acid, attended with the evolution of a peculiar offensive odour arising from the decay of the casein which accompanies the transformation. According to the observations of Pasteur, there is a special lactic ferment, consisting of microscopic vegetable cells, which are much smaller than those of beer yeast. These are developed during the decomposition of other animal matters, such as moistened bladder, and muscular and albuminous tissues, at a particular stage of their decomposition after exposure to the air for a certain time. Not only sugar of milk, but starch, dextrin, cane sugar, and gum pass readily into lactic acid under the influence of the ferment already mentioned.

The subject will be further examined under the head of lactic acid (1310).

(d) *Viscous Fermentation.*

(1120) Under certain circumstances, sugar becomes transformed into a mucilaginous substance, unattended by any evolution of gas ; the liquid loses its sweet taste, and acquires a *ropy* consistence, as is sometimes observed when sweet wines are kept for a time. This mucilaginous substance is insoluble in alcohol, and yields a precipitate with basic plumbic acetate, but it differs from ordinary gum in not yielding mucic acid when oxidized by nitric acid. A solution of tannic acid produces a precipitate when added to such a liquid, and checks the progress of the fermentation. This circumstance explains the fact, that red wines, which contain a good deal of astringent matter derived from the husk and stalks of the grape, are not liable to become ropy. The tendency of a sweet liquid to become ropy is also arrested by the presence of sulphurous acid or of alum in small quantities ; the alum causes the precipitation of the ferment in an insoluble form.

It has been found that various substances, such as boiled yeast, or the water in which flour or rice has been steeped, speedily cause sugar to undergo this transformation; and the sweet juice of the bect root, owing to the presence of an analogous substance, if left in a warm place for a few days, passes spontaneously into the viscous state. A quantity of mannite is usually formed at the same time in these cases.

CHAPTER III.

THE ALCOHOLS AND ETHERS.

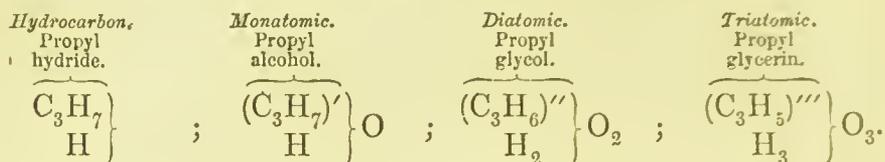
§ I. THE ALCOHOLS.

(1121) *General Characters of the Alcohols.*—The term alcohol is of Arabic origin, and was originally applied specifically to the volatile inflammable spirituous liquor, which is the characteristic product of the fermentation of sugar; but it has since been made generic, and has been extended to a class of bodies which possess chemical qualities analogous to those of wine alcohol, and which are homologues of that substance. Indeed, this class of compounds has already afforded us some striking illustrations of the existence of homologous groups (1059).

The term alcohol, however, has received a still further extension, and it is now applied to all neutral compounds of carbon hydrogen and oxygen, which react directly upon the acids in such a manner that water is eliminated whilst ethers are produced. The ethers so obtained are themselves neutral compounds of peculiar constitution, in which an atom of the typical hydrogen of the alcohol has been exchanged for the radicle of an acid. Recent researches have indeed led to the discovery of several distinct varieties of alcohols, including monatomic, diatomic, triatomic, and polyatomic groups, or groups formed upon the type of one molecule of water, $\left. \begin{array}{c} \text{H} \\ \text{H} \end{array} \right\} \text{O}$, two molecules $\left. \begin{array}{c} \text{H}_2 \\ \text{H}_2 \end{array} \right\} \text{O}_2$, three molecules of water $\left. \begin{array}{c} \text{H}_3 \\ \text{H}_3 \end{array} \right\} \text{O}_3$, and so on.

The alcohols which are best known are those which may be regarded as derivatives from the hydrocarbons of the marsh gas class ($\text{C}_n\text{H}_{2n+2}$), in which 1, 2, 3, . . . or n atoms of hydrogen

have been displaced by 1, 2, 3, . . . or n atoms of hydroxyl, HO; and they are monatomic, diatomic, or triatomic, according as 1, 2, or 3 atoms of hydrogen have thus been displaced by the corresponding number of atoms of hydroxyl:—



In the monatomic alcohols the remaining typical atom of hydrogen may be exchanged for a corresponding metal, or for a monobasic acid radicle; in the diatomic alcohols, one or both of the two remaining typical atoms of hydrogen may be exchanged similarly, and so on. The monatomic alcohols are those which have been longest known, and they are the most numerous and most important.

(1122) *Groups isologous with the Monobasic or Monatomic Alcohols and their Derivatives.*—The progress of research into the products of the decomposition of organic compounds, has disclosed the existence of a number of groups which bear a close relationship to the group of the ordinary monatomic alcohols. This relationship, however, is not one of homology: the groups of which we are now speaking are *isologous* (from *ἴσος*, equal, *λόγος*, a word) with the normal alcohols; and the compounds which constitute each of these groups are related to each other in a manner similar to that of the components of the alcohol group with which they are compared.

The following table contains a list of what are at present, for the most part, imaginary alcohols, which would illustrate the successive terms of an isologous series; the essential character of which is, that each succeeding term differs from the one that precedes it by two atoms of hydrogen, or by H_2 ; as for example:—

| | | | | |
|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|
| $\text{C}_{16}\text{H}_{32}\text{O}$ | $\text{C}_{15}\text{H}_{30}\text{O}$ | $\text{C}_{14}\text{H}_{28}\text{O}$ | $\text{C}_{13}\text{H}_{26}\text{O}$ | $\text{C}_{12}\text{H}_{24}\text{O}$ |
| $\text{C}_{16}\text{H}_{30}\text{O}$ | $\text{C}_{15}\text{H}_{28}\text{O}$ | $\text{C}_{14}\text{H}_{26}\text{O}$ | $\text{C}_{13}\text{H}_{24}\text{O}$ | $\text{C}_{12}\text{H}_{22}\text{O}$ |
| $\text{C}_{16}\text{H}_{28}\text{O}$ | $\text{C}_{15}\text{H}_{26}\text{O}$ | $\text{C}_{14}\text{H}_{24}\text{O}$ | $\text{C}_{13}\text{H}_{22}\text{O}$ | $\text{C}_{12}\text{H}_{20}\text{O}$ |
| $\text{C}_{16}\text{H}_{26}\text{O}$ | $\text{C}_{16}\text{H}_{24}\text{O}$ | $\text{C}_{14}\text{H}_{22}\text{O}$ | $\text{C}_{13}\text{H}_{20}\text{O}$ | $\text{C}_{12}\text{H}_{18}\text{O}$ |
| $\text{C}_{16}\text{H}_{24}\text{O}$ | $\text{C}_{15}\text{H}_{22}\text{O}$ | $\text{C}_{14}\text{H}_{20}\text{O}$ | $\text{C}_{13}\text{H}_{18}\text{O}$ | $\text{C}_{12}\text{H}_{16}\text{O}$ |
| $\text{C}_{16}\text{H}_{22}\text{O}$ | $\text{C}_{15}\text{H}_{20}\text{O}$ | $\text{C}_{14}\text{H}_{18}\text{O}$ | $\text{C}_{13}\text{H}_{16}\text{O}$ | $\text{C}_{12}\text{H}_{14}\text{O}$ |
| $\text{C}_{16}\text{H}_{20}\text{O}$ | $\text{C}_{15}\text{H}_{18}\text{O}$ | $\text{C}_{14}\text{H}_{16}\text{O}$ | $\text{C}_{13}\text{H}_{14}\text{O}$ | $\text{C}_{12}\text{H}_{12}\text{O}$ |
| &c. | &c. | &c. | &c. | &c. |

Each of the vertical columns displays an isologous series, while each of the horizontal lines exhibits a series in homologous succession.

The number of isologous groups actually known and studied is comparatively small. Amongst these is a class of compounds derived from the essential oil of garlic (*allium sativum*), and constituting what has been termed the *allylic* series. Another class, related to the fragrant acid contained in gum benzoin, is known as the *aromatic* or *benzoic* series; and a third class, related to oil of cinnamon, has been termed the *cinnamic* series. Now, upon comparing together the relations of the different heterologous compounds composing each of these three groups, it has been found that certain of them bear to each other relations similar to those observed between the heterologous compounds derived from ethyl alcohol. For example, in each of the groups just mentioned there is a compound indicated as the *alcohol* of the series; there is another which contains two atoms of hydrogen less than this body; it has the power of forming a crystalline compound with the hydric-potassic sulphite (KHSO_3), and corresponds in properties with the *aldehyds*. These aldehyds constitute a particular variety of the essential oils. It has further been observed that these new aldehyds, by combining with an additional atom of oxygen, furnish *volatile acids*, which contain two atoms of oxygen, and correspond to the series of volatile fatty acids. The alcohols of these three groups are not homologous with ethyl-alcohol; for the semi-molecule of *diallyl* (the hydrocarbon of the allylic series, corresponding to diethyl) contains one atom of hydrogen less than twice the number of atoms of carbon, whereas the semi-molecule of diethyl contains one atom of hydrogen more than twice the number of atoms of carbon. The semi-molecule of the hydrocarbon of the benzoic series, contains seven atoms of hydrogen less than twice the number of atoms of carbon; and in the cinnamic hydrocarbon the disproportion is still greater, the number of atoms of hydrogen falling short by nine, of that of twice the proportion of carbon. Yet, all these bodies in their derivatives present an analogy with the corresponding derivatives of ethyl alcohol. The allylic, the benzoic, and the cinnamic series, are *isologous* with that of alcohol and with each other.

In the benzoic series the existence of three homologous terms is already indicated more or less fully; namely, the benzoic, the toluic, and the cuminic series. In the allylic and cinnamic group only a single series is in each case as yet known; but it can scarcely be doubted that other homologous series of each of these varieties of alcohol will be found.

The following table will serve to elucidate the general relations of these groups to each other; and it will also indicate the

analogy of the compounds which they form with corresponding compounds in the comprehensive family to which ethylic alcohol belongs:—

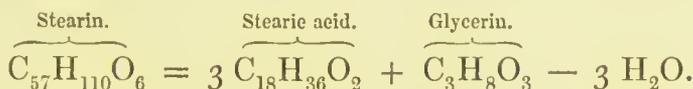
Table of Isologous Groups.

| (a) <i>Compounds of the Ethylic Series.</i> | | | | | |
|---|--------------------------------|--------------------------------|--------------------------------------|---------------------------------------|------------------------------------|
| Hydrocarbon. | Oxide. | Chloride. | Alcohol. | Aldehyd. | Volatile acid. |
| $(C_nH_{2n+1})_2$ | $(C_nH_{2n+1})_2O$ | $C_nH_{2n+1}Cl$ | $C_nH_{2n+1}HO$ | $C_nH_{2n-1}O,H$ | $C_nH_{2n}O_2$ |
| Diethyl. $(C_2H_5)_2$ | Ether. $(C_2H_5)_2O$ | Ethyl chloride. C_2H_5Cl | Alcohol. C_2H_5HO | Acetic aldehyd. C_2H_3O,H | Acetic acid. $C_2H_4O_2$ |
| (b) <i>Compounds of the Allylic Series.</i> | | | | | |
| $(C_nH_{2n-1})_2$ | $(C_nH_{2n-1})_2O$ | $C_nH_{2n-1}Cl$ | $C_nH_{2n-1}HO$ | $C_nH_{2n-2}O,H$ | $C_nH_{2n-2}O_2$ |
| Diallyl. $(C_3H_5)_2$ | Allyl oxide. $(C_3H_5)_2O$ | Allyl chloride. C_3H_5Cl | Allyl alcohol. C_3H_5HO | Acrolein. C_3H_3O,H | Acrylic acid. $C_3H_4O_2$ |
| (c) <i>Compounds of the Aromatic or Benzoic Series.</i> | | | | | |
| $(C_nH_{2n-7})_2$ | $(C_nH_{2n-7})_2O$ | $C_nH_{2n-7}Cl$ | $C_nH_{2n-7}HO$ | $C_nH_{2n-9}O,H$ | $C_nH_{2n-8}O_2$ |
| Dibenzyl. (1) $(C_7H_7)_2$ | Benzyl ether. $(C_7H_7)_2O$ | Benzyl chloride. C_7H_7Cl | Benzyl alcohol. C_7H_7HO | Oil of bitter almonds. C_7H_5O,H | Benzoic acid. $C_7H_6O_2$ |
| (2) | | | Tolyl alcohol. C_8H_9HO | Tolnic aldehyd. C_8H_7O,H | Tolnic acid. $C_8H_8O_2$ |
| (4) | | | Cuminic alcohol. $C_{10}H_{13}HO$ | Oil of cummin. $C_{10}H_{11}O,H$ | Cuminic acid. $C_{10}H_{12}O_2$ |
| (d) <i>Compounds of the Cinnamic Series.</i> | | | | | |
| $(C_nH_{2n-9})_2$ | $(C_nH_{2n-9})_2O$ | $C_nH_{2n-9}Cl$ | $C_nH_{2n-9}HO$ | $C_nH_{2n-11}O,H$ | $C_nH_{2n-10}O_2$ |
| | | | Styrone. C_9H_9HO | Oil of cinnamon. C_9H_7O,H | Cinnamic acid. $C_9H_8O_2$ |

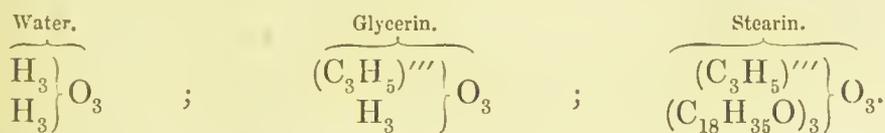
(1123) *Polybasic or Polyatomic Alcohols.*—In addition to the various alcohols of which we have spoken, and which are all monatomic, and formed upon the type $\left. \begin{matrix} H \\ H \end{matrix} \right\} O$, we meet with others of more complicated constitution, formed upon the types of $\left. \begin{matrix} H_2 \\ H_2 \end{matrix} \right\} O_2$, and $\left. \begin{matrix} H_3 \\ H_5 \end{matrix} \right\} O_3$, and of some higher multiples of H_2O . Chevreul, when he published his masterly researches upon the fatty bodies, pointed out the analogy between the fixed oils and

fats, and the compound ethers: when under the influence of bases the fats undergo saponification, they are decomposed, with the assimilation of the elements of water, into a fatty acid, and into glycerin, a body which in this respect presents an analogy with alcohol: but he did not see the precise difference between the fats and fixed oils and the compound ethers; and the completeness of the parallel has only recently been established, and the distinction between the two pointed out. Berthelot, by synthetic experiments (1240) has shown that the neutral fats are derived from three molecules of a monobasic acid, and one molecule of glycerin; glycerin being in fact a *triatomic alcohol*, and presenting a constitution which has its representative among the acids, in the tribasic phosphoric acid.

The formation of stearin ($C_3H_5, 3C_{18}H_{35}O_2$), for instance, may be thus illustrated:—

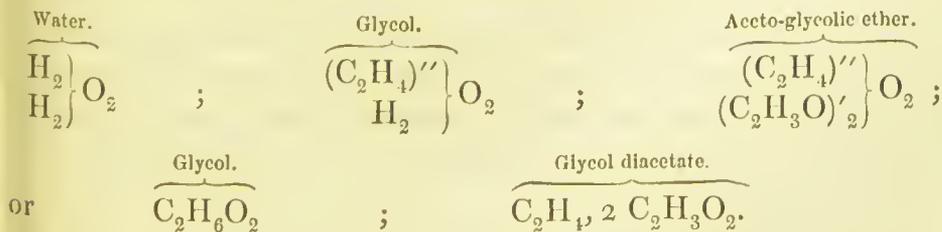


And if glycerin be a triatomic alcohol, the composition of glycerin and that of stearin may be represented as follows, on the type of 3 molecules of water:—



Intermediate between ordinary alcohol and glycerin, which is the representative of the group of triatomic alcohols, is a series of diatomic alcohols, the glycols, the existence of which was inferred by Wurtz, and which by synthetic operations he succeeded in discovering. They are purely artificial bodies obtained from the hydrocarbons of the olefiant gas series (1213).

The glycols yield compound ethers which are derived from two atoms of a monobasic acid and one of the glycol, so that they may be represented as formed on the type of two molecules of water—



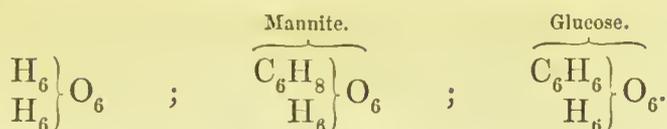
In the case of glycerin, the triad radicle (C_3H_5)''' which it contains impresses its character upon the compound; whilst in

the glycols the dyad hydrocarbon $(C_2H_4)''$ or one of its homologues imparts a dibasic constitution to the body.

| Type $\left. \begin{matrix} H \\ H \end{matrix} \right\} O$ <i>Monatomic Alcohols and Derivatives.</i> | | | | | |
|--|---|---|-------------------------------------|---|---|
| Hydrocarbon. | Alcohol. | Ether. | Aldehyd. | Acid. | Compound ether. |
| (2) $\overbrace{(C_2H_5)_2}$ | $\overbrace{C_2H_6O}$ Ethylic. | $\overbrace{(C_2H_5)'_2O}$ Ethyl ether. | $\overbrace{C_2H_4O}$ Acetic. | $\overbrace{C_2H_4O_2}$ Acetic. | $\overbrace{C_2H_5, C_2H_5O_2}$ Acetic ether. |
| (3) $\overbrace{(C_3H_7)_2}$ | $\overbrace{C_3H_8O}$ Propylic. | $\overbrace{(C_3H_7)'_2O}$ Propyl ether. | $\overbrace{C_3H_6O}$ Propionic. | $\overbrace{C_3H_6O_2}$ Propionic. | $\overbrace{C_2H_5, C_2H_5O_2}$ Ethyl propionate. |
| Type $\left. \begin{matrix} H_2 \\ H_2 \end{matrix} \right\} O_2$ <i>Diatomic Alcohols and Derivatives.</i> | | | | | |
| (2) $\overbrace{C_2H_4}$ Ethylene. | $\overbrace{C_2H_6O_2}$ Glycol. | $\overbrace{(C_2H_4)''O}$ Ethylene oxide. Hydro-ethyl-glycol. $\overbrace{HC_2H_5O, C_2H_4O}$ Diethyl-glycol. $\overbrace{(C_2H_5)_2O, C_2H_4O}$ | $\overbrace{C_2H_2O_2}$ Glyoxal. | $\overbrace{C_2H_4O_4}$ Glyoxylic. Oxalic. $\overbrace{C_2H_2O_4}$ | $\overbrace{H, C_2H_4O, C_2H_5O_2}$ Glycol hydroacetate. $\overbrace{C_2H_4, 2 C_2H_5O_2}$ Glycol diacetate. |
| (3) $\overbrace{C_3H_6}$ Propylene. | $\overbrace{C_3H_8O_2}$ Propyl-glycol. | | Not yet formed. | Laetic. $\overbrace{C_3H_6O_3}$ Wanting. Malonic. $\overbrace{C_3H_4O_4}$ | $\overbrace{H, C_3H_6O, C_2H_5O_2}$ Propyl-glycol hydroacet. $\overbrace{C_3H_6, 2 C_2H_5O_2}$ Propyl-glycol diacet. |
| Type $\left. \begin{matrix} H_3 \\ H_3 \end{matrix} \right\} O_3$ <i>Triatomic Alcohols and Derivatives.</i> | | | | | |
| (3) $\overbrace{(C_3H_8)_2}$? | $\overbrace{C_3H_8O_3}$ Glycerin. | $\overbrace{(C_3H_8)'''_2O_3}$ Glyceric ether. Ethylin. $\overbrace{H_2, C_2H_5, C_3H_5O_2}$ Diethylin. $\overbrace{H(C_2H_5)_2, C_3H_5O_3}$ | Not yet formed. | Glyceric. $\overbrace{C_3H_6O_4}$ Tartronic. $\overbrace{C_3H_4O_5}$ | $\overbrace{H_2C_3H_5O_2, C_2H_5O_2}$ Monoacetin. Diacetin. $\overbrace{H, C_3H_5O, 2 C_2H_5O_2}$ Triacetin. $\overbrace{C_3H_5, 3 C_2H_5O_2}$ |

The active study of the compounds of which glycerin and glycol are the representatives, is daily bringing to light a multitude of new bodies, and rapidly extending our views upon the constitution of many organic bodies of very complicated composition.

For example, it appears to be very probable that mannite and the sugars are polyatomic alcohols,—mannite, and possibly glucose, being hexatomic (1244):—

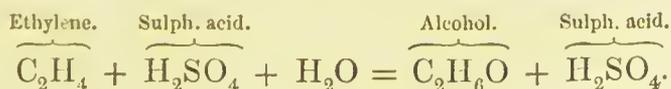


Each polyatomic alcohol has its hydrocarbon radicle, its corresponding ethers, its aldehyds, and its acids; and all these heterologous derivatives from the alcohol are themselves, like it, polyatomic. A general idea of the very numerous bodies which are correlated by this view may be formed from an examination of the table on the foregoing page.

Although many of these polyatomic alcohols are artificial bodies, yet the study of this class of compounds presents high attractions to the chemist, as it is amongst these substances that many of the most interesting and extensively diffused natural compounds occur, as, for instance, the sugars, the different forms of mannite, glycerin and all its compounds in the natural fats and fixed oils.

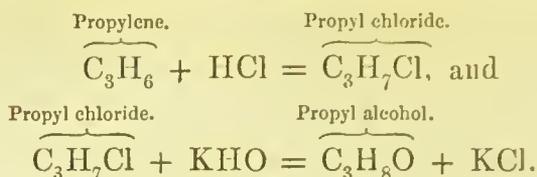
(A.) MONATOMIC ALCOHOLS.

(1124) *General Methods of Preparation.*—1. The monatomic alcohols homologous with ordinary alcohol are usually formed by a process of fermentation from sugar, as occurs with ethylic, tri-tylic, tetrylic, amylic, and hexylic alcohol. 2. Some, however, are procured by destructive distillation, as in the preparation of wood spirit. 3. Others are obtained by treating certain fatty bodies with caustic potash, as in the process of obtaining octylic, laurylic, cetylic, cerylic, and melissylic alcohols. 4. Certain of the alcohols may also be formed synthetically by dissolving the dyad hydrocarbons, such as ethylene and propylene, in oil of vitriol, diluting the liquid and then distilling. For example:—

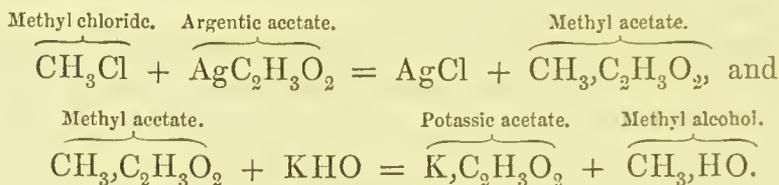


5. They may also be obtained by causing a hydrocarbon of the ethylene series (1209), to combine with a hydracid, and then decomposing the compound so obtained by long continued exposure to the action of caustic potash. Berthelot has in this way obtained propyl, amyl, octyl, and cetyl alcohol, by the reaction indicated in the equations which follow :*—

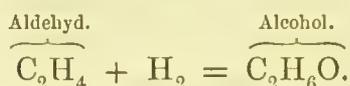
* Wurtz has shown that the higher terms of the alcohols obtained by these methods are not identical with the alcohols obtained by fermentation, but only isomeric with them.



A more perfect reaction may be effected by subjecting the alcohol chloride to the action of potassic or argentic acetate, and then distilling with caustic potash the acetic ether so obtained; for example:—



6. Another method practised by Wurtz consists in treating the aldehyds with nascent hydrogen, by acting upon them in the presence of water with an amalgam of sodium; direct union between two atoms (one molecule) of hydrogen and one molecule of aldehyd then occurs; as for instance:—



7. It has also been found that it is possible to decompose one of the alcoholic derivatives of ammonia (1373) by nitrous acid. If ammonia be gently warmed with nitrous acid, two atoms of water are liberated and two of nitrogen—



Hofmann ascertained that if instead of ammonia an atom of an alcohol base in which one of the atoms of hydrogen in the molecule of ammonia is displaced by an alcohol radicle, such as ethyl, the atom of hydrogen in one of the two atoms of water formed in the reaction will be displaced by ethyl, and consequently an atom of alcohol will be formed in its place: *e. g.*—



The method also answers with aniline, which is thus converted into carboic acid.

Properties.—The monatomic alcohols present themselves in the form of liquids or solids which are lighter than water. The lower terms of the series are freely soluble in water, but they become less soluble as the proportion of carbon and hydrogen

increases, the higher terms becoming successively more viscid and oily, whilst those which are solid at ordinary temperatures are insoluble in water, and resemble the fats in appearance. The lower terms may be volatilized without experiencing decomposition. The boiling point of each alcohol is about 72° (40° C.) lower than that of the fatty acid which it yields by oxidation.

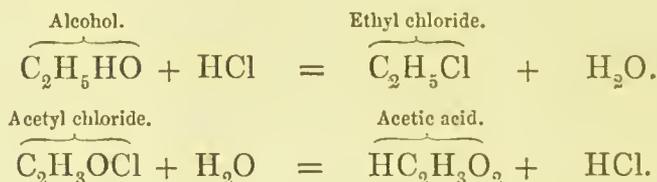
The following table contains most of the bodies at present known, which belong to the class of substances homologous with ethyl alcohol; but there can be no doubt that as science progresses this list will be extended, and that ultimately an alcohol will be found corresponding to each term of the series of the volatile acids represented by the general formula, $C_nH_{2n}O_2$.

| Alcohols. | Formula. $C_nH_{2n+2}O$ | Specific gravity. | | Vapour. Rel. wt. H = 1. | Boiling Point. | |
|---|----------------------------|-------------------|---------|-------------------------------|----------------|---------------|
| | | Liquid. | Vapour. | | $^{\circ}$ F. | $^{\circ}$ C. |
| 1. Wood spirit, or methyl alcohol } | C_1H_4O | 0.798 | 1.12 | 16 | 149.9 | 65.5 |
| 2. Spirit of wine, or ethyl alcohol . . } | C_2H_6O | 0.7938 | 1.6133 | 23 | 173 | 78.3 |
| 3. Trityl, or propyl do. | C_3H_8O | 0.817 | 2.02 | 30 | 206 | 96.7 |
| 4. Tetryl or butyl do. | $C_4H_{10}O$ | 0.8032 | 2.589 | 37 | 233 | 111.7 |
| 5. Fousel oil, or amyl alcohol . . . } | $C_5H_{12}O$ | 0.8184 | 3.147 | 44 | 269.6 | 132.0 |
| 6. Hexyl, or caproic do. | $C_6H_{14}O$ | 0.833 | 3.53 | 51 | 299-309 | 148-154 |
| 7. Heptyl alcohol . . | $C_7H_{16}O$ | 0.819 | | 58 | 351 | 176.7 |
| 8. Octyl, or capryl do. | $C_8H_{18}O$ | 0.823 | 4.5 | 65 | 356 | 180.0 |
| 12. Lauryl alcohol . . | $C_{12}H_{26}O$ | | | | | |
| 16. Ethal, or cetyl do. | $C_{16}H_{34}O$ | | | | | |
| 27. Cerotin, or ceryl do. | $C_{27}H_{56}O$ | | | | | |
| 30. Melissin, or melissyl alcohol . . . } | $C_{30}H_{62}O$ | | | | | |

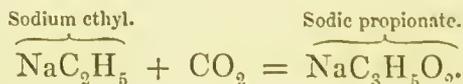
The formula of each of these substances, it will be seen, contains one atom of oxygen, combined with quantities of carbon and hydrogen in which the number of atoms of hydrogen always exceeds by two twice the number of atoms of carbon. The monoatomic alcohols may all be regarded as compound oxides of hydrogen and of a peculiar hydrocarbon, of which the general formula is

C_nH_{2n+1} ; or as formed from a molecule of water $\left. \begin{matrix} H \\ H \end{matrix} \right\} O$ in which one-half of the hydrogen has been displaced by an equivalent of a hydrocarbon: they retain therefore but a single atom of typical hydrogen; ordinary alcohol being represented upon this view as $\left. \begin{matrix} C_2H_5 \\ H \end{matrix} \right\} O$. The typical atom of hydrogen admits of being displaced by potassium, sodium, and other metallic bodies: under certain

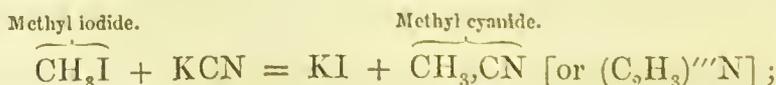
circumstances the displacement may be effected by a second equivalent of a hydrocarbon either identical with or analogous to the first, thus giving rise either to a simple or to a mixed ether (1139); or it may be displaced by an acid radicle, in which case a compound ether is formed. The general formula of an alcohol, therefore, may be represented as $C_nH_{2n+2}O$, or $(C_nH_{2n+1})HO$. Notwithstanding the possibility of thus displacing hydrogen in definite quantity from the molecule of alcohol by sodium or potassium, the alcohols are not to be regarded as acids, from which class of compounds they differ in a marked manner. One of the most characteristic differences between an alcohol and an acid consists in the fact that an alcohol is convertible by the action of hydrochloric acid into a hydrochloric ether, with elimination of water: whilst a reaction exactly the reverse takes place in the case of the acids; for the chlorides of the acid radicles are decomposed by water into the free acid and hydrochloric acid; as for example:—



The reactions by which a passage is effected from one series to a higher or lower term by the addition or removal of an atom of carbon are particularly interesting: for example, the addition of carbon, as in the passage from the ethylic to the propylic series, may be effected as follows, by acting on sodium ethyl with carbonic anhydride (1184):—



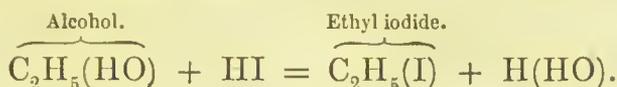
Methyl iodide, by exchange of cyanogen for iodine, furnishes methyl cyanide, which is identical with acetonitrile:—



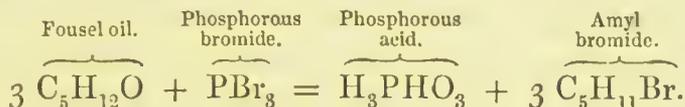
and acetonitrile, by the process of Mendius, digesting it with zinc and an alcoholic solution of hydrochloric acid, furnishes ethylia hydrochlorate, from which, by distillation with caustic potash, the base ethylia is isolable.

A similar reaction takes place with other halogens, and this characteristic of the alcohols has been represented by the state-

ment that the alcohols have the power of exchanging hydroxyl for one of the halogens ; as for instance :—



It is not necessary in order to produce such reactions always to employ the hydracid itself. Indeed in most cases it is more convenient to act upon the alcohol with the chloride, bromide, or iodide of phosphorus ; as for example :—



The researches of Kolbe (*Liebig's Annal.* cxxxii. 102), of Butlerow (*Lieb. Ann.* cxliv. 1), and others, have rendered it probable that the homologous terms of the alcohols and their derivatives are all referable to the methyl alcohol ; ordinary alcohol being wood spirit containing an atom of methyl in the place of one of the atoms of hydrogen in methyl : and each successive term being produced by the substitution successively for the same atom of hydrogen of an atom of ethyl, propyl, butyl, &c., in the original molecule of wood spirit :*—

| | |
|--------------------------|---|
| Methyl alcohol | C(H)H ₂ ,HO |
| Ethyl alcohol | C(CH ₃)H ₂ ,HO |
| Propyl alcohol | C(C ₂ H ₅)H ₂ ,HO |
| Butyl alcohol | C(C ₃ H ₇)H ₂ ,HO |
| Amyl alcohol | C(C ₄ H ₉)H ₂ ,HO |

Alcohols formed on this type Kolbe terms *primary* alcohols, these being the ordinary or true alcohols.

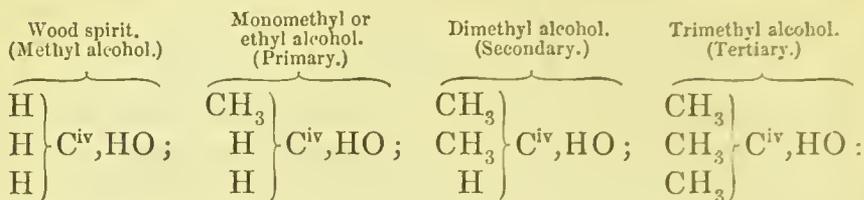
By the substitution of another atom of an alcohol radicle for a second atom of hydrogen in the original atom of methyl, a new set of alcohols, termed by Kolbe *secondary* alcohols, may be obtained ; and by a substitution of the third atom of hydrogen in

* The homology of the normal alcohols is explained by Kolbe and by Butlerow on the hypothesis that the radicles ethyl, propyl, butyl, amyl, &c., are each formed from methyl, by successive substitutions of methyl (CH₃) for an atom of hydrogen within the methyl group ; as for instance—

| | | |
|--------|---|---|
| Methyl | = | C(H)H ₂ |
| Ethyl | = | C(CH ₃)H ₂ |
| Propyl | = | C[C(CH ₃)H ₂]H ₂ |
| Butyl | = | C[C[C(CH ₃)H ₂]H ₂]H ₂ |
| Amyl | = | C[C[C[C(CH ₃)H ₂]H ₂]H ₂]H ₂ |

each successive group of methyl which is introduced becoming methylated by successive substitution of a fresh atom of methyl for an atom of hydrogen.

methyl by an alcohol radicle, tertiary alcohols are procured, as may be illustrated by the following formulæ:—



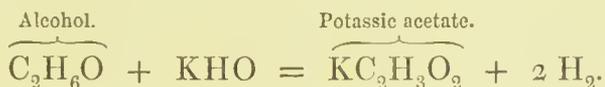
One of the secondary alcohols best known, isopropyl alcohol, is isomeric with propyl alcohol, and was obtained by Friedel by acting upon acetone (1259) with nascent hydrogen; and among the tertiary alcohols is one isomeric with butyl alcohol, obtained by Butlerow by acting upon the product of zinc-methyl (1182) on acetyl chloride (1266) with water. Corresponding secondary and tertiary dibasic and polybasic alcohols also exist, to which class the pseudo-glycols of Wurtz belong: see also Lieben (*Lieb. Ann.* cxli. 236). A large number of isomeric alcohols have been obtained by pursuing these ideas experimentally; and a particular nomenclature has been proposed by Kolbe, to enable these different bodies to be distinguished from each other. The starting point is methyl alcohol, which he terms *carbinol*; for example:—

1. Methyl alcohol . . . *Carbinol* . . . $(\text{CH}_2, \text{H})\text{HO}$
2. Ethyl alcohol . . . *Methyl carbinol* $(\text{CH}_2, \text{CH}_3)\text{HO}$
3. $\left\{ \begin{array}{l} \text{Propyl alcohol . . . } \\ \text{Isopropyl alcohol (sec-} \\ \quad \text{condary) . . .} \end{array} \right. \left. \begin{array}{l} \textit{Ethyl carbinol} . \\ \textit{Dimethyl carbinol} \end{array} \right. \left. \begin{array}{l} (\text{CH}_2, \text{C}_2\text{H}_5)\text{HO} \\ [\text{CH}(\text{CH}_3)_2]\text{HO} \end{array} \right.$
4. $\left\{ \begin{array}{l} \text{Butyl alcohol . . .} \\ \text{(primary) . . .} \\ \text{(secondary) . . .} \\ \text{(tertiary) . . .} \end{array} \right. \left. \begin{array}{l} \left\{ \begin{array}{l} \textit{Propyl Carbinol} \\ \textit{Isopropyl carbinol} \end{array} \right\} \\ \left. \begin{array}{l} \textit{Methyl ethyl} \\ \textit{carbinol} \end{array} \right\} \\ \textit{Trimethyl carbinol} \end{array} \right. \left. \begin{array}{l} (\text{CH}_2, \text{C}_3\text{H}_7)\text{HO} \\ [\text{CH}_2, \text{C}(\text{CH}_3)_2\text{H}]\text{HO} \\ (\text{CH}, \text{CH}_3, \text{C}_2\text{H}_5)\text{HO} \\ (\text{C}[\text{CH}_3]_3)\text{HO}; \end{array} \right.$

and so on.

A number of secondary alcohols have been formed by Wurtz, and described by him under the name of *pseudo-alcohols*, (*Ann. de Chimie*, IV., iii. 129). They boil at temperatures considerably below those of the primary alcohols, and break up readily by simply heating them for some hours in sealed tubes to a temperature ranging from 392° to 482° (200° to 250°C .). The products of decomposition in this case are a hydrocarbon of the form C_nH_{2n} , and water. The amylic compound ($\text{C}_5\text{H}_{10}, \text{H}_2\text{O}$) thus splits into amylene C_5H_{10} , and water H_2O .

The primary alcohols by partial oxidation lose two atoms of hydrogen, and then furnish *aldehyds*; and these bodies by the further absorption of oxygen, yield *acids*; these acids contain the same number of atoms of carbon as the alcohol from which they were procured, but two atoms less of hydrogen and one atom more of oxygen than the alcohol; (*vide* table, page 38). The potassium salts of these fatty acids may be obtained by heating the alcohol with caustic potash: ethyl alcohol, for instance, yields an acetate of the basyl whilst hydrogen escapes:—



The alcohols are further characterized by yielding, when treated with sulphuric acid and other dehydrating compounds, a class of substances termed *ethers*, which formerly were regarded as alcohols minus $\frac{1}{2} \text{H}_2\text{O}$; though, as will hereafter be explained (1139), there can be no doubt that this does not truly represent the mode of their formation. By a still more complete dehydration the alcohols give rise to the hydrocarbons of the olefinic series (C_nH_{2n}).

(1125) I. WOOD SPIRIT; *Methyl Alcohol*, or *Pyroxylic Spirit* ($\text{CH}_4\text{O} = 32$). *Sp. gr. of liq. at 32° (0° C.)*, 0·8179; *of vap.* 1·12; *Rel. wt.* 16; *Boil. pt.* 149°·9 (65°·5 C.).—Wood spirit is the alcohol of the *methylic* series, which derives its name, not very appropriately, from $\mu\acute{\epsilon}\theta\upsilon$, wine. This alcohol has not as yet been procured by any process of fermentation; it is found amongst the volatile products obtained by the destructive distillation of wood at a high temperature in closed vessels, accompanied by a large quantity of impure acetic acid, ammoniac acetate, methyl acetate, tarry matter, and various hydrocarbons. It has also been obtained artificially by Berthelot, by acting upon marsh gas by chlorine, and decomposing the chloride thus obtained by means of a solution of potash; $\text{CII}_3\text{Cl} + \text{KHO}$ becoming $\text{CH}_4\text{O} + \text{KCl}$.

Purification.—In order to isolate methyl alcohol, the crude products of the distillation of wood are rectified by the heat of a water bath, and the product is distilled from quicklime, which retains the acetic acid, the water, and tarry matter. The wood naphtha of commerce is simply rectified from chalk: as thus prepared it is a mixture consisting chiefly of methyl alcohol and methyl acetate, with certain oily hydrocarbons insoluble in water, and which may be separated from it by admixture with water.

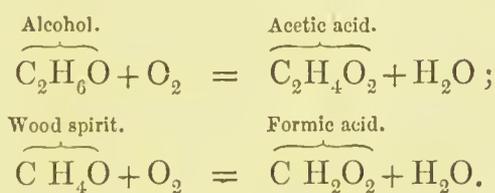
In order to free it from these impurities it is mixed with an equal volume of concentrated solution of potash, and allowed to stand for some hours; any oily matters which may have risen to the surface are removed, and it is then distilled: the alkali decomposes the methyl acetate, usually present in large quantity, and forms potassic acetate, whilst wood spirit is produced; after this it may be in great measure deprived of water by adding potassic carbonate as long as it is dissolved; the upper stratum of liquid is then decanted and may be saturated with calcic chloride, which forms with pyroxylic spirit a compound not decomposable at the temperature of boiling water; the mixture is subjected in a retort to the heat of a steam-bath, and the volatile portions, containing acetone and methylic acetal, are thus expelled. The residue, which retains the wood spirit, is mixed with an equal weight of water, by which the spirit is displaced from its combination with the chloride; and on renewing the application of heat, methyl alcohol, mixed with a little water, passes over; a second rectification from quicklime furnishes it in a state of purity.

Wöhler obtains wood spirit in a pure state more readily by converting it first into methyl-oxalic ether (1169) which being a solid may be purified by crystallization. When this ether is simply distilled with water it is converted into oxalic acid and wood spirit: the latter may then be rectified from quicklime, by which means it is obtained pure and in the anhydrous form.

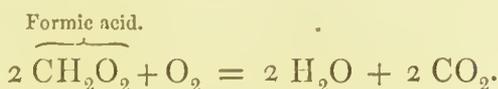
Properties.—Wood spirit is a limpid inflammable, colourless liquid, of a penetrating spirituous odour, and a disagreeable burning taste: the empyreumatic smell commonly observed is due to impurities in the product; most of which may be removed by prolonged digestion upon charcoal, and methodical filtration through it as practised by Mr. Esehwege. It has a sp. gr. of 0.798 at 68° (20° C.). It is soluble in water, alcohol, and ether, in all proportions. After it has been mixed with water the two liquids occupy less bulk than when separate. It is very inflammable, and burns with a pale flame, furnishing carbonic anhydride and water. When pure it does not reduce mercurous nitrate if mixed with its solution. Methyl alcohol mixes readily with the essential oils, and dissolves many fatty bodies and resins with facility. Its principal application in the arts, as crude wood naphtha, is founded upon its power of dissolving the resins, which, when thus dissolved, are employed as varnishes. A solution of shell-lac and other resins in wood naphtha, is extensively used for stiffening the basis of silk hats. The hydrates of the alkalies are soluble in wood spirit, but they immue-

diately colour it brown. Ure used this reaction as a means of discovering small quantities of pyroxylic spirit when mixed with alcohol, since alcohol is not thus altered in colour until after a considerable lapse of time. Caustic baryta is soluble in wood spirit, forming with it a crystallizable compound, $\text{BaO}, 2 \text{CH}_4\text{O}$. Many salts also form definite compounds with it; that with calcic chloride ($\text{CaCl}_2, 4 \text{CH}_4\text{O}$) crystallizes in six-sided tables.

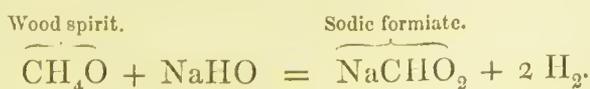
It has already been mentioned that when wine alcohol is submitted to a gradual and incomplete oxidation, one of the products of the operation is aldehyd (1249), which passes, by further oxidation, into acetic acid. Now, wood spirit may in like manner be subjected to partial oxidation, under the influence of finely divided platinum; and though the different stages of the process have been less satisfactorily investigated than those which occur with ordinary alcohol, it appears that an intermediate substance is formed, which, like aldehyd, has the power of reducing the salts of silver; and finally, a strong solution of formic acid is produced. This acid stands in the same relation to the methylic series that the acetic does to the ethylic series:—



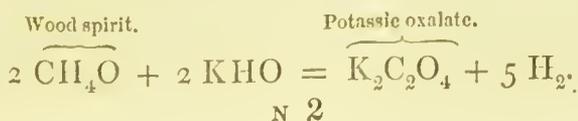
This method, however, is not an advantageous one for the preparation of formic acid, since it is difficult to prevent the oxidation from going a stage further, and converting the formic acid into carbonic anhydride and water:—



When wood spirit is heated moderately with soda-lime, formiate of the basyl is produced, and hydrogen is liberated:—



If caustic potash be employed instead of soda-lime, potassic oxalate is formed, whilst a large evolution of hydrogen occurs:—



(1126) 2. ALCOHOL; *Vinic or Ethyl Alcohol; Spirit of Wine* ($C_2H_6O=46$). *Sp. gr. of liq. at 32°*, 0·815; *of vap.* 1·6133; *Rel. wt.* 23; *Boil. pt.* 173° (78°·3 C.)—Alcohol is a colourless volatile inflammable liquid, of an agreeable well-known spirituous odour, and an acrid burning taste. When pure it has a specific gravity of 0·7938 at 60°. It has never been frozen, though at a temperature of $-166°$ ($-110°$ C.) it becomes viscid. When taken in small quantities in a diluted form it furnishes a useful and well-known stimulant, and it forms the basis of all fermented liquors. In large quantities it produces intoxication, and acts as a powerful narcotic poison, frequently occasioning fatal results when taken in a concentrated state and in excess.

Alcohol furnishes a cleanly and valuable fuel to the chemist: it emits a high temperature during its combustion, and deposits no soot upon cold bodies which are introduced into its flame. When burned in air it emits but little light, and is wholly converted into carbonic anhydride and water: two volumes, or one molecule, of alcohol vapour, for complete combustion requires three times its bulk, or six volumes, of oxygen; $C_2H_6O + 3O_2 = 2CO_2 + 3H_2O$. When the vapour of alcohol is transmitted through red-hot tubes it is decomposed. The products vary according to the temperature employed: at low temperatures, olefiant gas, marsh gas, water, carbonic oxide, and acetylene are formed; and at higher temperatures naphthalin; whilst at a bright-red heat carbon is deposited, and free hydrogen produced. By gradual oxidation alcohol yields amongst other bodies, aldehyd and acetic acid (1250). With nitric acid it furnishes nitrous ether, glyoxal, glyoxylic acid (1299 *note*), with glycolic (1308) and oxalic acids.

When alcohol is exposed in its concentrated form to the atmosphere it attracts moisture like sulphuric acid; and like this compound, when mixed with water, it emits heat and contracts in bulk, though to a considerably less extent: the observed density of the mixture of alcohol and water is therefore greater than its calculated mean density. According to Rudberg, the condensation is greatest when 53·739 measures of alcohol and 49·836 of water are mixed at 59° (15° C.): these proportions correspond to $C_2H_6O + 3H_2O$; when cooled again to 39°, this mixture occupies only 100 measures instead of 103·575, and has a sp. gr. of 0·927. From the importance of alcohol as an excisable article, great labour has been bestowed upon the means for readily determining its percentage in spirituous liquors. The method in common use for distilled spirits consists in determining the specific gravity by

means of a sensitive hydrometer ; and tables have been constructed for showing the percentage of alcohol in mixtures of various densities. In these cases great attention must be paid to the temperature, since slight differences in this particular make a material variation in the density. The term *proof spirit*, in constant use among the excise, is defined by an Act of Parliament (58 George III.), to be "such as shall at the temperature of 51° F. (10°·5 C.) weigh exactly twelve thirteenth parts of an equal measure of distilled water." It consists of water 50·76, alcohol 49·24 by weight, and indicates alcohol of sp. gr. 0·920 at 60° (0·91984; Drinkwater). The term derives its origin from the rude method of proof formerly in use, in which gunpowder was moistened with the spirit of wine to be tried, and the alcohol ignited ; if it fired the powder it was said to be *over proof*, but if the spirit burned off and left the powder damp, it was considered to be *under proof*; the weakest spirit capable of thus firing powder had a sp. gr. of about 0·920.* Every additional 0·5 per cent. of absolute alcohol above 0·920 is said to be one degree over proof.

Alcohol is a solvent of great value to the chemist. It usually exerts but little chemical action upon the bodies which it dissolves, and owing to its volatility it is easily expelled by a gentle heat, leaving the substances which it previously held in solution, in a pure state. Alcohol dissolves many of the gases freely ; some of them, as for instance, nitrous oxide, carbonic anhydride, phosphuretted hydrogen and cyanogen, and the hydrocarbons, are dissolved by it more readily than by water. Iodine and bromine are also readily soluble in it, but their solutions gradually undergo decomposition, in consequence of the reaction of iodine and bromine upon the alcohol. Absolute alcohol dissolves small quantities of phosphorus and of sulphur. The alkaline sulphides, as well as caustic potash and soda, are soluble in it to a very large extent ; and ammoniacal gas is absorbed by it nearly as readily as by water ; but it does not dissolve the carbonates of these alkalies. Alcoholic solutions of caustic potash and soda act powerfully as reducing agents upon many metallic solutions, such as those of platinum ; they gradually absorb oxygen from the air, and become brown, owing to the formation of a resinoid substance, the resin of aldehyd. When dropped upon fused caustic potash, alcohol is decomposed, hydrogen is evolved, and

* In the Appendix two tables of the strength of alcohol at different specific gravities will be found.

potassic acetate is produced; $C_2H_6O + KHO = 2 H_2 + KC_2H_3O_2$. Sodium or potassium dissolves readily in alcohol with evolution of hydrogen, and considerable rise of temperature, forming a powerfully alkaline substance, sodic or potassic ethylate; $2 C_2H_6O + Na_2 = 2 C_2H_5NaO + H_2$. When heated with sulphuric acid, alcohol yields ethyl-sulphuric acid, ether, or olefiant gas, according to the temperature employed and the proportions used.

The results of the action of chlorine (1174) and of sulphuric and other acids (1133), as well as of sodium and other metals (1181 *et seq.*) upon alcohol, will be further alluded to hereafter.

Most of the deliquescent salts are soluble in alcohol, but the efflorescent salts, and those which are sparingly soluble in water, are not dissolved by it. Anhydrous alcohol combines with many anhydrous saline bodies in definite proportions, and forms with them crystallizable compounds, in which the alcohol, according to Graham, occupies the place of water of crystallization. The chlorides and the nitrates offer the best examples of the formation of these *alcoates*. The compound with calcium chloride ($CaCl_2, 4 C_2H_6O$), crystallizes readily; and analogous compounds may be obtained with the chlorides of zinc and manganese, and with the calcium and magnesium nitrates.

Alcohol likewise dissolves freely many organic bodies, such as the resins, the essential oils, the vegetable alkaloids, and many of the vegetable acids. It also dissolves, more sparingly, sugar, and the soaps of potash, soda, and ammonia; but the fats and fixed oils, with the exception of castor oil, are dissolved by it in but small quantities.

A characteristic reaction of alcohol is its power of forming argentic fulminate; when 0.1 grm. of silver is dissolved in 2 grms. of nitric acid, and about 5 of alcohol are added, crystals of argentic fulminate are gradually deposited.

Preparation.—Alcohol may be obtained in a state of purity by subjecting to distillation any saccharine solution that has undergone fermentation; for being more volatile than water it passes over in the first part of the distillation, accompanied with more or less water. By repeated rectifications, or by a single operation in Coffey's still (188), it may be concentrated till it contains about 10 per cent. of water. Beyond this point the water adheres to it so strongly that it requires a different process for the complete separation of the last portions:—it is first rectified from charcoal, with a view of retaining all essential oils to which the peculiar odour and flavour of different spirits are mainly owing, and is then mixed with about half its weight of quicklime,

and allowed to stand for three or four days: the lime gradually slakes and falls to powder in consequence of its conversion into a hydrate, at the expense of the water in the alcohol; then, on applying heat by means of a bath of calcic chloride, the pure spirit may be distilled off, the calcic hydrate retaining the water at temperatures far above 302° (150° C.). Any traces of water which it may still retain are removed by a second distillation from quicklime, or from caustic baryta. The alcohol thus obtained is anhydrous, or as it is often termed, *absolute alcohol*.

The methylated spirit of commerce consists of a mixture of alcohol of sp. gr. 0.830 with 10 per cent. of common wood spirit. This addition of wood spirit scarcely interferes with the employment of the spirit as a solvent, though it renders it unfit for use afterwards as a stimulant drink; it was added to facilitate the use of spirit in the arts without inflicting injury on the revenue; amongst other advantages, the aid it has afforded in facilitating researches in organic chemistry in this country is very considerable. The offensive odour may be removed by prolonged contact with charcoal, as has been shown by Mr. Eschwege.

Berthelot (*Ann. de Chimie*, III. xliii. 388) has pointed out a means of obtaining alcohol synthetically, by forming a solution of olefiant gas in oil of vitriol, which dissolves about 120 times its bulk of the gas, then diluting the mixture with water, and submitting it to distillation. Small quantities of dilute alcohol are thus obtained with facility.

Triyl alcohol has been obtained by acting on tritylene in a similar manner; but the denser hydrocarbons of this series, such as octylene, become charred when thus treated.

(1127) *Wines, Fermented Liquors, and Spirits*.—The various kinds of spirits in use derive their names from accidental circumstances,—often from the flavour which they possess. For instance, *gin* is spirit flavoured by distilling it with juniper berries; *peppermint* owes its aroma to the essential oil of the plant after which it is named; *whisky* is spirit distilled from wort prepared from malt which has been dried over a peat fire, to which its peculiar flavour is due; *arrack* is a spirit distilled from fermented rice; and *rum*, a West Indian product from molasses; *brandy* is really the ‘spirit of wine,’ being obtained from wines by distillation, and coloured more or less deeply with burnt sugar. In all these cases the characteristic flavour depends upon a small quantity of some volatile oil or compound ether, which passes over with the spirit during the process of distillation.

The varieties of spirits are very numerous, and those of fermented liquors which are used without subjecting them to distillation, are still greater. To this class belong all the different kinds of wine, which owe their peculiarities of flavour partly to the different varieties of grape, of which 500 or 600 are cultivated, and partly to the different flavour which even the same variety of grape* possesses in different climates, according as the saccharine, the aromatic, the acidulous, or the astringent principle of the fruit predominates. The grapes grown in the hottest climates furnish the sweetest juice, but not the wines of finest quality; the flavour is also materially influenced by the manner in which the wine is prepared. For example, when fermentation is allowed to proceed until all the sugar is transformed into spirit, a dry wine is produced; when checked before this term is reached, the result is a rich fruity wine: and when bottled whilst the fermentation is still proceeding, a brisk effervescent wine like champagne is the result. It is the usual practice to add cane sugar to champagne before bottling. According to the experiments of Bence Jones, claret, Burgundy, and the wines of the Rhine and the Moselle, contain no sensible quantity of sugar; sherry, yields from 1 to 5 per cent., port from 3 to 7 per cent., and Tokay as much as 17 per cent. of sugar. The change of flavour consequent on the ageing of wine, depends partly upon the gradual fermentation of sugar still retained in rich wines, and partly upon the slow separation of saline matter, principally in the form of hydric-potassic tartrate ($\text{KHC}_4\text{H}_4\text{O}_6$), which becomes less soluble as the proportion of spirit increases, and is deposited, particularly from port wines, as a crust of tartar, upon the sides of the bottle. An important part of the change of flavour appears also to be owing to the slow formation of minute quantities of fragrant and aromatic ethers, which are gradually produced by the reaction of the vegetable acids upon the alcoholic portion of the wine. It has been observed that the presence of a considerable amount of acidity favours the development of the 'bouquet' or aroma which is especially characteristic of the acidulous wines of the Rhine and the Moselle.

Some wines, instead of improving, become ropy by keeping. This occurs only with sweet wines, and is due to a peculiar species

* A certain variety of grape when grown upon the Rhine furnishes a species of Hoek; the same grape when raised in the valley of the Tagus yields Bucellas; whilst in the island of Madeira it produces the wine known as Sercial, which has a flavour quite different from either of the others.

of fermentation in which the sugar passes into the uncrystallizable form of mueilage (1101, 1120).

The colour of the wine is dependent upon the mode in which the fermentation is effected. Red grapes may be made to yield a 'white' wine, if the husks of the grape be removed from the must before the fermentation begins, as in the preparation of champagne and sherry; but if the skins be left in the fermenting mass, the alcohol, as it is formed, dissolves the colouring matter, producing the different shades of 'red' wine. During the preparation of red wines the skins and stalks rise to the surface of the fermenting mass and form the *chapeau*, which is removed from the fermenting juice at an earlier stage in the making of clarets than in the preparation of ports, and this is one reason why port is the more astringent wine of the two.

The process of fermentation in making wine is much more gradual and protracted than in the preparation of malt liquors. After the grapes have been trodden in the press, the juice passes to the fermenting vessels: no addition of yeast is necessary, and after a short time a copious deposit of ferment granules or yeast occurs spontaneously. The fermenting vats are so constructed that when the active stage of the fermentation is over, they can be loosely closed by a bung. As soon as the winter frost sets in, the wine is decanted from the lees into casks, which are completely filled, and then closed with care. In order to supply the loss from leakage or evaporation, the casks are carefully filled up at intervals. Here a secondary very gradual fermentation occurs. It requires careful watching, exclusion of the air at this stage being indispensable in order to prevent the wine from becoming sour, owing to the formation of acetic acid by the oxidation of the alcohol.

Sometimes a wine acquires a peculiar flavour known as the 'taste of the cask.' This is attributed to the development of a peculiar essential oil during the growth of fungi, or 'mould,' upon the surface of the wine. It is said that it may be removed by adding to each pipe about a quart of olive oil, which dissolves the obnoxious flavouring matter, and carries it with it to the surface.

It is obvious that in wines and other fermented liquors which have not been submitted to distillation, all the soluble matter of the fruit is present in the beverage. Other saccharine juices, besides that of the grape, admit of being fermented, and thus a great variety of drinks may be produced. Beer and ale, for example, consist of an infusion of malt, flavoured by the aromatic bitter of the hop, and subsequently fermented. The different kinds of porter are similarly prepared, and owe their dark colour to the use of high-dried malt; *cider* is the fermented juice of the apple: *perry* is a similar liquid obtained from the pear; and nearly every fruit may be made to yield its own peculiar liquor. Even savage nations evince a knowledge of this fact. The natives of the islands in the Pacific, when discovered by Cook, not only knew how to prepare an intoxicating liquor from the juice of the cocoa-nut, but they were accustomed to rectify it by a rude process of distillation.

Since foreign matters are present in all fermented liquors, the

specific gravity would, except in special cases,* be no guide to the quantity of spirit contained in them. A simple means of overcoming this difficulty was successfully practised by Brande;—Potassic carbonate is soluble in water, but insoluble in alcohol: when perfectly dry potassic carbonate in powder is added to a mixture of alcohol and water until it ceases to become dissolved on agitation, the water becomes saturated with the salt, and the liquid separates into two layers, the upper of which consists of alcohol of sp. gr. 0·825. By employing a graduated tube for the experiment, the volume of alcohol which is contained in a known bulk of any wine or liquor may be read off at once by inspection.

Christison submitted different wines to distillation, in order to determine their percentage of alcohol; he thus obtained a series of results, the most important of which are embodied in the following table. The numbers represent the weight of absolute alcohol contained in 100 parts of each variety of wine or fermented liquor:—

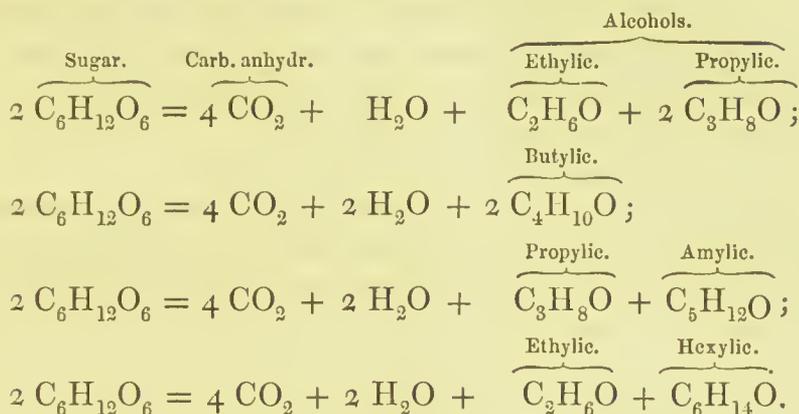
| | | | |
|---------------|---------------------|-------------------|-------------------|
| Port . . . | from 14·97 to 17·10 | Amontillado . . . | 12·63 |
| Dry Lisbon | 16·14 | Claret . . . | from 7·72 to 8·99 |
| Madeira . . | from 14·09 to 16·90 | Hambacher . . . | 7·35 |
| Sherry . . . | „ 13·98 „ 16·17 | Rudesheimer . . | from 6·90 to 8·40 |
| Teneriffe . . | 13·64 | Edinburgh ale . . | „ 5·70 „ 6·06 |
| Shiraz . . . | 12·95 | Best London { | 5·36 |
| Malmsey . . | 12·86 | porter . } | |

(1128) 3. *Trityl* (or *Propyl*) *Alcohol* ($C_3H_5O=60$). *Sp. gr. of liq.* 0·817; *of vap.* 2·02; *Rel. wt.* 30; *Boil. pt.* about 206° (97° C.)—Although, during the ordinary process of the fermentation of fruit or grape sugar, the products are carbonic anhydride and ordinary (ethyl) alcohol, it usually happens that minute quantities of other homologous bodies are formed. This is particularly the case when masses of the lusk of the grape, from which the juice has been expressed (technically termed the *marc* of the grape), are thrown aside, and allowed to ferment. The saccharine matter which they still retain undergoes decomposition, and when the fermented liquor furnished by them is submitted to distillation, a mixture of propyl, butyl, amyl, and hexyl alcohols is obtained.

These different modes of fermentation admit of explanation by means of the following equations, in which it is assumed that

* See "Report on Original Gravities" by Graham, Hofmann, and Redwood (*Q. J. Chem. Soc.* v. 229).

in addition to the separation of carbonic anhydride, a certain quantity of water is eliminated at the same time:—



Propyl alcohol, the third term of the series of alcohols, is obtained only in small quantity from the fermented marc. It is a limpid, colourless liquid, lighter than water, with an agreeable fruity odour. Although freely soluble in water, it does not mix with it in all proportions. One of its isomerides may be prepared by Berthelot's process of absorbing propylene by oil of vitriol, diluting the solution with 5 or 6 times its bulk of water and distilling. An isomeric alcohol, boiling below 194° (90° C.), *isopropyl alcohol* [$\text{C}(\text{CH}_3)_2\text{H}_2\text{O}$], perhaps identical with Berthelot's, has also been obtained, by acting upon acetone with sodium amalgam in the presence of water; the acetone ($\text{C}_3\text{H}_6\text{O}$), by combining with 2 atoms of hydrogen, furnishes this secondary alcohol (p. 176). Its characteristic reaction is its reproducing acetone when oxidized by diluted chromic acid.

(1129) 4. *Tetryl* or *Butyl Alcohol* ($\text{C}_4\text{H}_{10}\text{O} \doteq 74$). *Sp. Gr. of liq.* 0.8032 ; *of vap.* 2.589 ; *Rel. wt.* 37; *Boil. pt.* 233° (112° C.).—Wurtz procured this fourth term of the alcohols during the rectification of fousel oil obtained from beet-root spirit: it is contained in that portion which boils below 266° (130° C.) By fractional distillation, this portion may be made to yield a liquid, the boiling point of which remains steady at 233° , and which is the desired alcohol. Butyl alcohol is a colourless liquid of high refracting power, lighter than water, and only partially soluble in water. It has an odour resembling that of fousel oil, but less oppressive. When heated with caustic potash, it is readily converted into potassic butyrate, with evolution of hydrogen; and when mixed with concentrated sulphuric acid, it forms *butylsulphuric* (or *sulphobutylic*) acid ($\text{H},\text{C}_4\text{H}_7\text{SO}_4$) without difficulty.

Butlerow has obtained an isomeric tertiary butyl alcohol $\text{C}(\text{CH}_3)_3\text{HO}$, by decomposing a mixture of zinc methyl and acetyl chloride with water.

(1130) 5. *AMYL ALCOHOL*, *Fousel Oil*, or *Potato Spirit* ($\text{C}_5\text{H}_{12}\text{O} = 88$). *Sp. gr. of liq. at* 32° . 0.827 ; *of vap.* 3.147 ; *Rel. wt.* 44; *Boil. pt.* 269.6 (132° C.; Kopp).—This substance, which constitutes the fifth term of the alcohol series, is a frequent impurity in brandies distilled from fermented potatoes,* barley, rye,

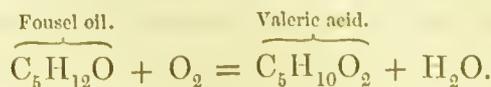
* The *amylic* series has been so named from *amyllum*, starch, the most abundant constituent of the potato.

and the marc of grapes, to which it communicates a peculiar offensive odour and taste. Since it is considerably less volatile than either alcohol or water, it accumulates in the last portions of the liquid when such brandies are submitted to distillation. Crude fousel oil is usually mixed with a variable amount of different ethers of the acids of the acetic series.

According to Liebig (*Familiar Letters*, 4th ed. p. 217), fousel oil is formed principally in the fermentation of alkaline or neutral liquids, and its production in the potato mash may be prevented, in great measure, by adding crude tartar to the fermenting liquid. Its formation, he says, never occurs in acidulous fermenting liquids which contain tartaric, racemic, or citric acid. The addition of hops to the liquid has a similar effect in checking the development of fousel oil.

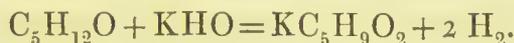
Amyl alcohol is a colourless, limpid liquid, which has a persistent, penetrating, and oppressive odour, and a burning taste. It is but sparingly soluble in water, though it may be mixed with alcohol, ether, and the essential oils, in all proportions. Its vapour is very irritating when respired; it burns with difficulty with a bluish flame. The specific gravity of fousel oil at 59° (15° C.) is 0.8184. At about -4° (-20° C.) it congeals into crystalline plates. Amyl alcohol causes a left-handed rotation of the plane of polarization in a ray of polarized light, but the extent of this rotation varies greatly in different specimens. According to Pasteur, ordinary amyl alcohol consists of a mixture of two metameric bodies, one of which is inactive on polarized light, but the other produces left-handed rotation of a polarized ray. The two modifications can be separated by converting the alcohol into amylsulphuric acid and combining this with baryta. Both the baric amylsulphates crystallize in the same form, but the inactive variety requires $2\frac{1}{2}$ times as much water for its solution as the active one. The active alcohol has a sp. gr. about $\frac{1}{106}$ greater than the inactive variety, and it boils between $260^{\circ}.6$ and $262^{\circ}.4$. The inactive alcohol boils at $264^{\circ}.2$.

Under the influence of spongy platinum, amyl alcohol gradually absorbs oxygen, whilst hydrogen is eliminated in the form of water, and valeric acid is produced: this acid bears the same relation to amyl alcohol that acetic acid does to ordinary alcohol:—



The action of nitric acid upon amyl alcohol varies with the degree

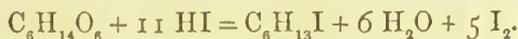
of its concentration and the temperature of the mixture, as it may be made to yield either amyl nitrate, valeric acid, amyl valerate, or valeric aldehyd. Caustic potash is freely soluble in fousel oil. If fousel oil be heated on a mixture of hydrates of potash and lime to 428° (220° C.), potassic valerate is formed whilst hydrogen is liberated:—



When heated with phosphoric acid, or with zincic chloride, fousel oil yields hydrocarbons homologous with olefiant gas. When mixed with half its bulk of sulphuric acid, the mixture becomes hot, assumes a red colour and a viscid consistence, a large quantity of *amylsulphuric* acid being formed, the amount of which increases if the mixture be allowed to stand for 24 or 48 hours. The amyl-sulphates crystallize with difficulty, and form syrupy solutions. When a mixture of sulphuric acid with amyl alcohol is heated, it does not yield an ether or a homologue of olefiant gas, but blackens and is charred. Besides the amyl alcohol produced by fermentation, three isomeric forms are known,—two secondary alcohols, viz., *Amylene hydrate* (C_5H_{10}, H_2O), and *Ethyl allyl alcohol* (C_2H_5, C_3H_5, H_2O), and an imperfectly studied tertiary alcohol.

(1131) 6. *Caproic* or *Hexyl Alcohol* ($C_6H_{14}O$). *Sp. gr. at 32° , 0.833 ; of vap. 3.53 ; Rel. wt. 51° .*—This compound has also been obtained from the fermented marc of the grape. Pelouze and Cahours have likewise formed this alcohol from hexyl hydride, one of the constituents of American petroleum. It is a limpid, aromatic liquid, which is insoluble in water and boils between $298^{\circ}.4$ and $309^{\circ}.2$ (148° and 154° C.). It yields potassic caproate, with disengagement of hydrogen, when heated with caustic potash; caproic acid standing in the same relation to hexyl alcohol that acetic acid does to ordinary alcohol.

By distilling mannite with hydriodic acid Erlenmeyer and Wanklyn obtained free iodine and a volatile compound ($C_6H_{13}I$), which they termed β hexyl iodide:—

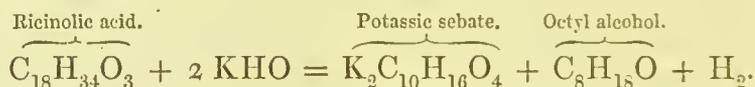


From this iodide, β *hexyl alcohol* ($C_6H_{14}O$) isomeric with the alcohol from the marc of grapes, may be obtained by treating the iodide with hydrated argentic oxide. This β alcohol boils at $278^{\circ}.6$ (137° C.). The special peculiarity of the β hexyl iodide is that it tends to split it up into the olefine (C_6H_{12}) and hydriodic acid, whilst the ordinary iodide would assimilate the elements of water and become converted into the alcohol and hydriodic acid. (*Jour. Chem. Soc.* 1863, 221.) Two other isomeric tertiary alcohols have been obtained: one, $C(CH_3)(C_2H_5)_2HO$, methyl-diethyl carbinol, by treating zinc ethyl and acetyl chloride with water; the second [$C(C_3H_7)(CH_3)_2HO$], propyl-dimethyl carbinol, by decomposing a mixture of zinc methyl and butyryl chloride with water.

7. *Heptyl* or *Cenanthyl Alcohol* ($C_7H_{16}O$), *Sp. gr. of liq. 0.819 , Rel. wt. 58 , Boil. pt. $350^{\circ}.6$ (177° C.),* is obtained, according to Stædelcr, mixed with other products, by distilling a mixture of sodic hydrate with sodic ricinolate in

a copper retort. Sodie sebate is left in the retort, and the distillate is treated with hydric-sodie sulphite (HNaSO_3) to separate the aldehyds; the liquid portion is removed by pressure, and after standing over calcic chloride is rectified; the greater portion distils between 350° and 352° . It is a transparent, rather viscous liquid, which smells like œnanthol.

(1132) *Octyl* or *Capryl Alcohol* ($\text{C}_8\text{H}_{18}\text{O} = 130$). *Sp. gr. of liq.* 0.823 at 62° ; *of vap.* 4.5; *Rel. wt.* 65; *Boil. pt.* 356° (180°C.)—This substance occurs in small quantity in the fermented marc of the grape; but it has been as yet but little examined. Its better known isomeric secondary alcohol was obtained from castor oil by Bouis (*Ann. de Chimie*, III. xlv. 100). Castor oil consists principally of the glycerin compound of a peculiar acid *ricinolic acid* (1223), the formula for the latter being ($\text{C}_{18}\text{H}_{34}\text{O}_3$). This acid, when heated with an excess of caustic potash to about 482° (250°C.) undergoes decomposition; potassic sebate being formed, whilst octyl alcohol [methyl-hexyl carbinol, $\text{C}(\text{C}_6\text{H}_{13})(\text{CH}_3)\text{H}_2\text{HO}$] and hydrogen are liberated, as shown by the following equation:—



In order to isolate the alcohol, the castor oil is saponified by means of caustic potash or soda, and afterwards an excess of the hydrated alkali, amounting to about half the weight of the oil operated upon, is added. The mass is heated moderately in a copper retort. It froths up at first considerably; but the foam gradually subsides, and a fragrant oily liquid distils over, which collects in the receiver above the water by which it is accompanied. The residue in the retort may be employed for the preparation of sebatic acid (1306). This distilled oil, which usually amounts to from a fourth to a fifth of the weight of the oil operated upon, must be purified by repeated rectifications from caustic potash, until the residue no longer has a brown colour.

Octyl alcohol is a colourless liquid, of a powerful, persistent, aromatic odour: it leaves a greasy stain upon paper, is insoluble in water, but freely soluble in alcohol and ether, as well as in acetic acid. It dissolves fatty and resinous bodies with facility. It undergoes no change when exposed to the air; but, when heated sufficiently, takes fire and burns with a white luminous flame.

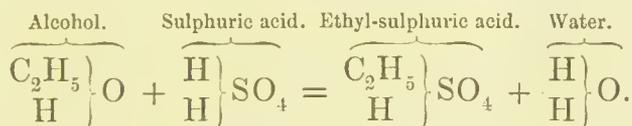
Sulphuric acid combines with the alcohol, and forms *sulphocaprylic* or *octyl-sulphuric acid*, which yields crystallizable salts. Bouis has obtained a large number of compound and double ethers with this alcohol; some of them are very fragrant and aromatic. When oxidized by means of a mixture of sulphuric acid and potassic dichromate, methyl-hexyl carbinol yields the corresponding ketone ($\text{C}_6\text{H}_{12}\text{O}, \text{C}_2\text{H}_5$), and this by prolonged oxidation furnishes caproic and acetic acids. From this reaction it has been concluded that this is a true secondary alcohol.

Other monatomic alcohols will be alluded to in speaking of the fats (1225, 1226), under the heads of ethal, and of ceryl and melissyl alcohols.

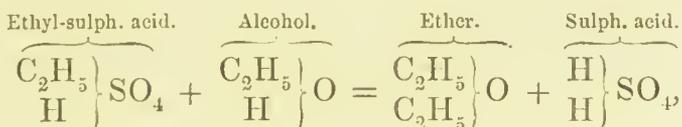
§ II. ACTION OF THE ACIDS UPON THE ALCOHOLS.

(1133) WHEN a powerful acid is mixed with one of the alcohols several cases may arise, dependent on the nature of the acid, the proportions in which it is added, and the temperature applied to the mixture.

1st. If a polybasic acid which has a strong attraction for water, such as the sulphuric, the phosphoric, or the arsenic, be added to one of the alcohols, the elements of the acid and of the alcohol enter into combination, and form a new compound acid, while water is liberated; a *vinic acid* being produced, in quantity varying with the temperature and relative proportions of the acid and the alcohol; for instance:—

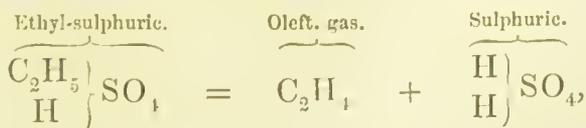


2nd. If such a mixture be submitted to distillation, the alcohol is decomposed, and a quantity of ether and water is formed and volatilized, *e.g.*:—



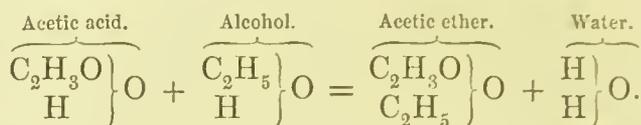
while the residue in the retort is capable of effecting the etherification of fresh portions of alcohol.

3rd. If the proportion of acid to the alcohol exceed a certain amount, so as to cause the temperature at which the distillation is effected to rise beyond a certain point, the vinic acid which had been formed becomes decomposed, the original acid is separated, and one of the olefines (hydrocarbons homologous with olefiant gas) is formed; for instance:—



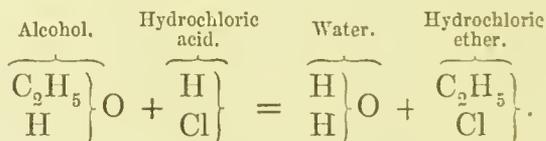
whilst at still higher temperatures the acid originally used begins to undergo decomposition, and the products are still more complicated.

4th. When an organic acid is submitted to distillation with one of the alcohols, a double decomposition occurs, and a compound ether is produced, whilst the elements of water are separated; for example:—



It is generally found advisable in such cases to use a salt of the organic acid, and after this salt has been mixed with a due proportion of alcohol, to decompose it by the addition of sulphuric acid.

5th. If a hydracid, such as the hydrochloric, hydrobromic, or hydriodic, be made to act upon an alcohol, double decomposition occurs, and an ether is formed by the substitution of the radicle of the alcohol for the hydrogen of the hydracid; for instance, when hydrochloric acid acts upon alcohol, water and hydrochloric ether are the result:—



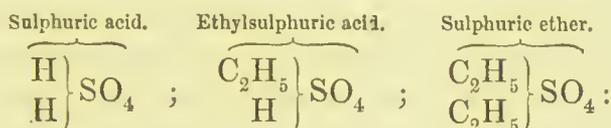
The Vinic Acids.

(1134) When a mixture of concentrated sulphuric acid with any of the alcohols is heated to about 212° , portions of the two compounds enter into combination, and the result is the formation of a new coupled acid in which the elements of 1 molecule of the alcohol and 1 of sulphuric anhydride (SO_3) are present. In these compounds the existence of sulphuric acid is no longer indicated by the formation of the insoluble baric sulphate on the addition of baric chloride; the barium salts of these acids being readily soluble in water.

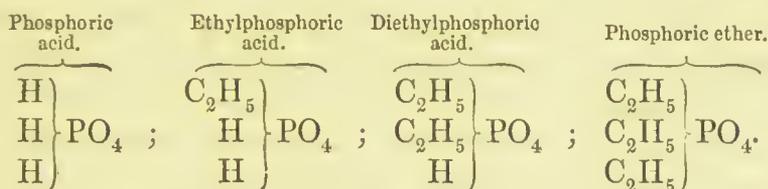
The following may be taken as examples of a few of the compound acids thus obtained:—

| Name of acid. | Formula of acid. | Potassic salt. |
|--|---|---|
| Methylsulphuric . . . | $\text{H}_3\text{C H}_3 \text{SO}_4$ | $2 (\text{KC H}_3 \text{SO}_4) \cdot \text{H}_2\text{O}$ |
| Ethylsulphuric, or sulphovinic | $\text{H}_2\text{C}_2\text{H}_5 \text{SO}_4$ | $\text{KC}_2\text{H}_5 \text{SO}_4$ |
| Tritylsulphuric | $\text{H}_3\text{C}_3\text{H}_7 \text{SO}_4$ | $\text{KC}_3\text{H}_7 \text{SO}_4$ |
| Tetrylsulphuric | $\text{H}_4\text{C}_4\text{H}_9 \text{SO}_4$ | $\text{KC}_4\text{H}_9 \text{SO}_4$ |
| Amylsulphuric | $\text{H}_5\text{C}_5\text{H}_{11} \text{SO}_4$ | $2 (\text{KC}_5\text{H}_{11} \text{SO}_4) \cdot \text{H}_2\text{O}$ |
| Octylsulphuric | $\text{H}_8\text{C}_8\text{H}_{17} \text{SO}_4$ | $2 (\text{KC}_8\text{H}_{17} \text{SO}_4) \cdot \text{H}_2\text{O}$ |

The vinic acids may, in fact, be looked upon as compound ethers, in which the basylous hydrogen of the polybasic acid has been only partially displaced by an alcohol radicle. With a dibasic acid two stages of such substitution are possible, an acid ether being the result of the first stage, and a neutral ether that of the second; with a tribasic acid there are three such stages: for example, in dibasic sulphuric acid we may have—

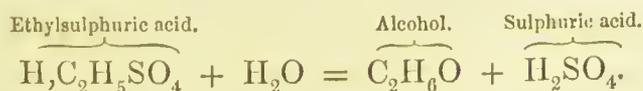


whilst in tribasic phosphoric acid we may have the following steps:—



These acids furnish crystallizable salts with potassium, as well as with calcium, barium, and many other basyls; the salts thus formed have a peculiar pearly lustre, but they are unstable, and sometimes undergo spontaneous decomposition. It is important to remark, that although the acid contains the elements of one molecule or two equivalents of sulphuric acid, the salts are monobasic, and contain only one atom of a metallic monad, as may be seen by inspecting the column headed 'potassic salt.'

These sulpho-acids are more unstable than their metallic salts; they cannot be distilled without undergoing decomposition, and they then break up into the ether corresponding to the alcohol which furnishes them, and sulphuric acid. If diluted with water and heated, the solution becomes rapidly converted into a mixture of diluted sulphuric acid and the alcohol from which the compound was originally obtained: for instance,



The most interesting of these acids is the ethylsulphuric, and it is necessary to examine its properties on account of the prominence which has been assigned to it in the theory of etherification.

(1135) *Ethylsulphuric, Sulphethylic, or Sulphovinic Acid* ($\text{H}_2\text{C}_2\text{H}_5\text{SO}_4$).—When alcohol is mixed with an equal measure of

oil of vitriol, great heat is evolved, and the two bodies enter partially into combination.* The sulphuric acid thus combined with the elements of alcohol, loses half its saturating power, and the compound acid, when diluted with 5 or 6 times its bulk of water, may be neutralized by the gradual addition of baryta, lime, or plumbic oxide. The base should be mixed with water till of the consistence of a thin cream: the salts thus formed are soluble in water. By adding sulphuric acid gradually to a solution of the barium salt, until no further precipitate of baric sulphate is produced, the acid is set at liberty in a state of purity. It was originally called the *sulphovinic acid*, but the term *ethylsulphuric*, by which it is now frequently described, is better, as it forms one of a numerous class of analogous acids. Ethylsulphuric acid may also be formed by gradually adding ether, perfectly free from alcohol, to concentrated sulphuric acid; the temperature rises rapidly, but must not be allowed to exceed 248° (120° C.); on diluting the mixture with water it will be found that much of the ether has been converted into ethylsulphuric acid. It is worthy of notice in connexion with the theory of etherification (1142), that when alcohol is mixed with sulphuric acid, diluted till of sp. gr. 1.53 ($=\text{H}_2\text{SO}_4 + 3\text{H}_2\text{O}$), no ethylsulphuric acid is formed at ordinary temperatures, but this acid is produced if the temperature be raised to 212° .

Ethylsulphuric acid is very unstable. If diluted with water and distilled, alcohol passes over, and sulphuric acid is left in the retort; but the diluted acid may be concentrated over sulphuric acid *in vacuo*, when it forms a colourless syrupy liquid, of a sharp acid taste; it is not soluble in ether. It gradually undergoes spontaneous decomposition. When heated in the presence of an excess of alcohol, it experiences a remarkable decomposition, to which it will be necessary to give particular attention (1142), owing to its connexion with the formation of ether.

All the ethylsulphates are freely soluble in water; many of them are likewise dissolved by alcohol; most of these salts crys-

* In order to produce the largest amount of the compound acid, the mixture should be heated to about 266° (130° C.) for a short time, and then allowed to stand for 24 hours. But the alcohol is never wholly converted into the new acid, for even if anhydrous alcohol be mixed in the above proportions with concentrated sulphuric acid, not more than half the alcohol becomes converted into the vinic acid, since, in the act of combination, a portion of water is formed; and on applying a heat of 212° , diluted alcohol gradually passes over, though the liquid does not boil at this temperature.

tallize with facility in pearly scales which feel greasy to the touch. When subjected to dry distillation, they yield olefant gas, heavy oil of wine, and sulphurous and carbonic anhydrides, leaving a residue of sulphate of the basyl, mixed with chareoal. If distilled with caustic potash they yield alcohol. When in solution they are decomposed at a boiling temperature, the solution, if neutral, becoming acid during the ebullition; but this change is prevented in the case of the potassic and sodic ethylsulphates, by the addition of a few drops of a solution of the hydrates of these alkalies.

Potassic ethylsulphate is anhydrous and somewhat deliquescent, but insoluble in alcohol and in ether. It crystallizes readily in large tables. *Baric ethylsulphate* $[\text{Ba}(\text{C}_2\text{H}_5)_2 \cdot 2 \text{SO}_4, 2 \text{H}_2\text{O}]$ crystallizes in rhombic prisms, which are soluble in water and in alcohol. *Calcic ethylsulphate* $[\text{Ca}(\text{C}_2\text{H}_5)_2 \cdot 2 \text{SO}_4, 2 \text{H}_2\text{O}]$ crystallizes in thin six-sided tables, very soluble in water, but not in ether: it sometimes undergoes spontaneous decomposition. The normal *plumbic ethylsulphate* $[\text{Pb}(\text{C}_2\text{H}_5)_2, 2 \text{SO}_4, 2 \text{H}_2\text{O}]$ forms colourless tables which are soluble in water and in alcohol; they also are liable to spontaneous decomposition. If digested upon an excess of plumbic oxide, a soluble uncrystallizable basic salt $[\text{Pb}(\text{C}_2\text{H}_5)_2 \cdot 2 \text{SO}_4, \text{PbO}]$ is formed.

(1136) *Acids isomeric with the Ethylsulphuric.*—Besides ethylsulphuric (sulphovinic) acid, there appear to be three other isomeric sulpho-acids formed by the action of oil of vitriol upon alcohol, viz.: the *isethionic*, *parethionic* and *althionic* acids.

Isethionic Acid $(\text{H}, \text{C}_2\text{H}_5\text{SO}_4)$.—This acid is at once distinguished from the ethylsulphuric by the greater stability of its salts, which may generally be heated to 401° (205°C.) without experiencing decomposition. It derives its name from the erroneous idea of its isomerism with ethionic acid. Isethionic acid is formed readily by boiling a strong solution of ethionic acid (1137) for some time. On neutralizing the solution by means of baric carbonate, baric isethionate $(\text{Ba} \cdot 2 \text{C}_2\text{H}_5\text{SO}_4)$ is obtained, and may be procured in hexagonal tables, which when heated to 608° (320°C.) fuse without undergoing decomposition. By a stronger heat they are decomposed, and blacken, swelling up very considerably. *Potassic isethionate* crystallizes in anhydrous rhomboidal prisms, which are soluble in alcohol. *Ammonic isethionate* forms transparent octahedra. The isethionates, when heated with caustic potash, evolve hydrogen, whilst a mixture of carbonate, oxalate, sulphate, and sulphite of the basyl is formed. Isethionic acid is also formed during the prolonged action of sulphuric acid upon alcohol or ether, in consequence of which it is found in the residue obtained from the preparation of ether (1141).

Parethionic Acid.—This acid is only known in combination with barium. If the solution of baric ethylsulphate be boiled for some time, it becomes acid, and deposits baric sulphate; on neutralizing the filtered liquid with baric carbonate, a crystallizable baric parethionate is obtained, which is not altered by

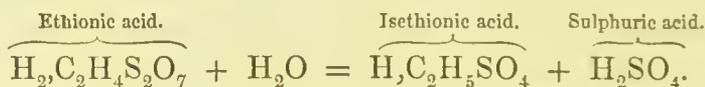
boiling. When calcined it does not froth up like the isethionate, but yields vapours of heavy oil of wine, and burns steadily (Gerhardt).

Another isomeric modification, termed by Regnault *althionic acid*, was procured by him from the residue of the preparation of ether by neutralizing it with baryta. A dilute solution of baric althionate may be boiled without undergoing decomposition. By spontaneous evaporation the salt is obtained in radiated groups of delicate prisms.

(1137) Olefiant gas combines readily with sulphuric anhydride, producing a compound which may be regarded as *ethionic anhydride*, the term ethionic having been given to indicate the union of the elements of *ether* with those of sulphuric acid, from *θεῖον*, sulphur. This compound is converted by water into ethionic acid; and the solution, when boiled, becomes decomposed, isethionic and sulphuric acids being produced. These decompositions may be readily traced, since the composition of these different compounds is the following:—



Consequently the change which occurs when ethionic acid is diluted with water and boiled, is the following:—



Ethionic Anhydride (C₂H₄ 2 SO₃) was termed by Magnus, its discoverer, *Sulphate of Carbyle*. It is prepared in the form of a white crystalline solid, by allowing the vapours of sulphuric anhydride to come into contact with dry olefiant gas in a bent tube kept cool. The same compound is obtained when a tube charged with anhydrous alcohol is placed in a bottle fitted with an accurately ground stopper, and containing sulphuric anhydride. In the course of a few days white silky crystals of ethionic anhydride are formed in the tube. These crystals melt at 176° (80° C.), and deliquesce rapidly on exposure to the air. They are soluble in water and in alcohol with great elevation of temperature, and cannot be recovered by evaporating the liquid, for each atom of the anhydride assimilates an atom of water, and becomes converted into the acid. The acid thus obtained, however, is not pure, since owing to the elevation of temperature a portion of ethionic is converted into isethionic acid. If the solution be neutralized by means of baric carbonate, and evaporated at a temperature below 212° until precipitation commences, baric ethionate is formed, and may be obtained by adding absolute alcohol until the density of the solution is reduced to 0.900; the salt thus precipitated is impure baric ethionate: it must be redissolved in water, and again precipitated by the addition of alcohol. The ethionates are soluble in water, but insoluble in alcohol; they are decomposed by a temperature of 212°. If baric ethionate be heated strongly in a tube, it yields sulphuric acid and a sublimate of sulphur, the residuc containing baric sulphate and sulphide. The ethionates of potassium, sodium, and ammonium may be readily obtained in crystals; they are prepared by decomposing a solution of baric ethionate by means of a solution of the respective sulphates of the different basyls.

(1138) *Other Vinic Acids*.—Sulpho-acids may be obtained from the methylic, tritylic, tetrylic, amylic, and other alcohols, by treating them in a manner similar to that directed for procuring ethylsulphuric acid. *Methylsulphuric acid* may be obtained in

crystals by evaporating its solution *in vacuo*. But the sulphuric is not the only acid which gives rise to these compound acids with the alcohols. The polybasic acids in general exhibit this power, even though their acid character may be but feeble. Carbonic, oxalic, and tartaric acids, for instance, may be made to yield compound acids analogous to the ethylsulphuric; and the same thing has been observed with sulphocarbonic acid (carbon disulphide). The tribasic acids, such as the phosphoric, even form two acid compounds. The formulæ of some of these coupled acids in the ethylic series and of their salts are exhibited in the following table:—

| Vinic acid. | Hydrate. | Metallic salt. |
|--|----------------------|----------------------------|
| Ethylcarbonic | $H, C_2H_5CO_3$ | $KC_2H_5CO_3$ |
| Xanthic, or ethylsulpho-carbonic | H, C_2H_5O, CS_2 | $KC_2H_5OCS_2$ |
| Ethylloxalic | $H, C_2H_5C_2O_4$ | $KC_2H_5C_2O_4$ |
| Ethyltartaric | $H, C_2H_5C_4H_4O_6$ | $2 (KC_2H_5C_4H_4O_6)H_2O$ |
| Ethylsulphurous | $H, C_2H_5SO_3$ | $KC_2H_5SO_3, H_2O$ |
| Ethylphosphoric | $H_2, C_2H_5PO_4$ | $BaC_2H_5PO_4, 6 H_2O$ |
| Diethylphosphoric | $H, (C_2H_5)_2PO_4$ | $Pb, (C_2H_5)_2PO_4$ |

Similar compounds may be formed with the other alcohols.

Ethylcarbonic or *Carbovinic acid* cannot be isolated, but potassic ethylcarbonate is obtained by transmitting a current of carbonic anhydride through a solution of caustic potash in absolute alcohol. It is soluble in alcohol, and forms pearly scales which are decomposed by water into hydric-potassic carbonate ($KHCO_3$) and alcohol.

Xanthic or *Ethylsulphocarbonic Acid*.—Potassic xanthate, or ethylsulphocarbonate, is a salt which crystallizes in needles. It is easily obtained by adding to an alcoholic solution of potash a quantity of carbon disulphide, until the alkaline reaction has disappeared: on exposing the solution to a cold of 32° , the salt is deposited in needles; and the ethylsulphocarbonic acid may be obtained from this salt by decomposing a concentrated solution of it with hydrochloric acid, when it separates as a heavy oily liquid.

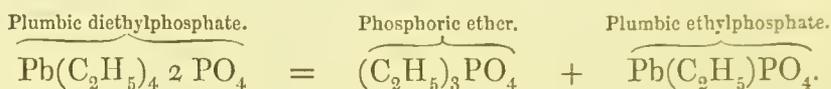
Ethylloxalic Acid.—Potassic ethylxalate (oxalovinate) is obtained by decomposing oxalic ether dissolved in alcohol by means of a quantity of an alcoholic solution of potash sufficient to neutralize one-half of the oxalic acid which it contains. The alcoholic solution yields pearly scales of the salt, which, when decomposed with hydro-fluosilicic acid, furnishes free ethylloxalic acid.

Ethylsulphurous or *Sulphoethylolic Acid* is obtained by acting upon mercaptan (C_2H_6S ; 1147) with nitric acid of sp. gr. 1.23, so long as decomposition continues to take place: a violent reaction occurs, attended with the escape of nitrous fumes. The excess of nitric acid is expelled by evaporating the liquid over the water bath, and the residue, after dilution, is saturated with plumbic carbonate; the filtered liquid is evaporated, and the plumbic ethylsulphite is allowed to crystallize. If this salt be decomposed by means of sulphuretted hydrogen, the acid is set at liberty, and by concentration over the water bath it may be obtained in transparent crystals, which have an acid disagreeable taste.

Ethylphosphoric or *Phoshovinic Acid*.—When equal parts of alcohol and

syrupy phosphoric acid are heated together, combination takes place; baric ethylphosphate ($\text{BaC}_2\text{H}_5\text{PO}_4, 6\text{H}_2\text{O}$) may be obtained by saturating the liquid with baric carbonate, distilling off the excess of alcohol, and then filtering the solution and allowing it to crystallize. On decomposing this salt cautiously by the addition of sulphuric acid, the ethylphosphoric acid is liberated.

Diethylphosphoric Acid.—By adding phosphoric anhydride gradually to absolute alcohol, a mixture of ethylphosphoric and diethylphosphoric acid is formed. On the addition of plumbic carbonate, the ethylphosphoric acid and the excess of phosphoric acid are removed, whilst plumbic diethylphosphate remains in solution, and may be obtained in crystals by evaporation; if the acid be required in a separate form, it may be procured by passing sulphuretted hydrogen through a solution of the lead salt. When plumbic diethylphosphate is subjected to a heat of about 374° (190° C.) it is decomposed, and phosphoric ether distils over:—

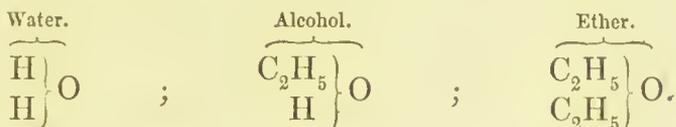


§ III. THE ETHERS—SIMPLE, DOUBLE, AND COMPOUND.

(1139) *General Remarks on the Ethers.*—The ethers admit of being conveniently subdivided into three classes, viz., *a.* The *simple ethers*, of which ordinary ether ($\text{C}_2\text{H}_5, \text{C}_2\text{H}_5, \text{O}$) is the best representative. *b.* The *double or mixed ethers*, discovered by Williamson, such as the methyl-amylie ($\text{CH}_3, \text{C}_5\text{H}_{11}, \text{O}$), and the ethyloctylic ($\text{C}_2\text{H}_5, \text{C}_8\text{H}_{17}, \text{O}$). *c.* The *compound ethers*, which may either contain the elements of an alcohol radicle and of an oxy-acid oxion, such as nitric ether ($\text{C}_2\text{H}_5, \text{NO}_3$), amyl acetate ($\text{C}_5\text{H}_{11}, \text{C}_2\text{H}_3\text{O}_2$), and methyl formiate ($\text{CH}_3, \text{CHO}_2$): or they may be produced by the action of a hydraacid, such as the hydrochloric, upon one of the alcohols; hydrochloric ether ($\text{C}_2\text{H}_5, \text{Cl}$) and hydriodic ether ($\text{C}_2\text{H}_5, \text{I}$) affording examples of this kind.

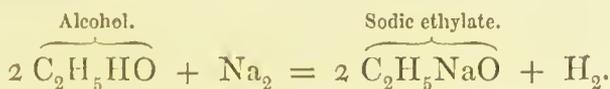
a. The *simple ethers* all contain oxygen, and are usually formed by the distillation of the alcohol with sulphuric acid: the distilled liquid so obtained was at one time viewed as a compound derived from alcohol by the removal of water. There are, however, reasons for thinking that the true relation between the alcohol and the ether is of a different nature: but, supposing this hypothesis to be correct, the simple ethers might be considered to consist of oxides of particular hydrocarbons which form the radicles of the ethers, whilst the alcohols would be hydrated oxides of the same bodies. Thus, adopting the small atomic weight for carbon and for oxygen, Liebig represented ordinary (ethyl) ether as oxide of ethyl ($\text{C}_4\text{H}_5\text{O}$), and ordinary alcohol as hydrated oxide of ethyl ($\text{C}_4\text{H}_5\text{O}, \text{HO}$). Berzelius suggested, on the other hand, that ether and alcohol might each be

formed upon a similar plan, and later researches, particularly those of Williamson, have demonstrated that the molecular constitution of alcohol is similar to that of ether; so that both may be regarded as compounds formed upon the type of water $\left. \begin{array}{c} \text{H} \\ \text{H} \end{array} \right\} \text{O}$, in which case alcohol would be water in which one-half of the hydrogen has been displaced by ethyl; and ether would be water in which both halves of the hydrogen have been displaced by ethyl; for instance;—

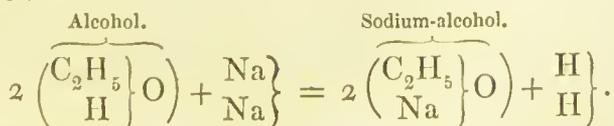


This doubling of Liebig's formula for ether has become necessary if the atomic weight of oxygen be taken as 16 instead of 8. It is also a logical consequence of Williamson's discovery of the existence of double ethers, the general properties of which we proceed to examine.

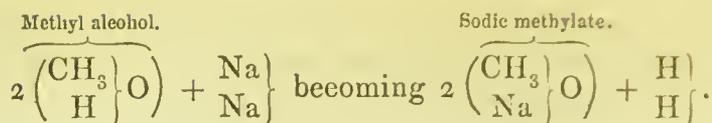
b. Double or Mixed Ethers.—When sodium or potassium is added gradually to anhydrous alcohol, a brisk action occurs; the temperature rises rapidly, and the metal is dissolved, whilst an extrication of pure hydrogen gas takes place, and a fusible, crystallizable, deliquescent compound is formed, which has received the name of *sodium-alcohol* (or potassium-alcohol), or of *sodic* (or potassic) *ethylate*. The composition of these bodies is such that it may be regarded as alcohol in which its typical atom of hydrogen has been displaced by an atom of sodium or of potassium (Williamson, *Q. J. Chem. Soc.*, iv 106, 229); for example, if sodium be used:—



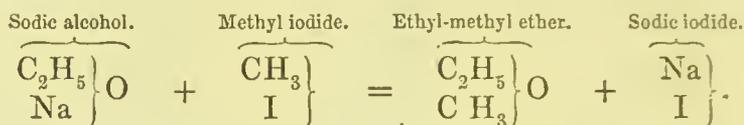
This and the subsequent reactions may, perhaps, be more readily traced by throwing the equations into a form similar to the one which follows:—



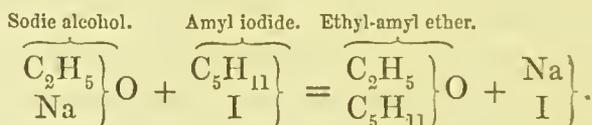
The action of sodium or potassium upon the other alcohols is of an analogous nature; for example, a similar result is obtained when wood spirit is treated with sodium:—



Now, if sodie ethylate be scaled up in a tube with an equivalent amount of methyl iodide, and heat be applied, mutual decomposition occurs; sodie iodide being formed, whilst the methyl takes the place of the sodium in the alcohol, and thus a double or *mixed* ether, the ethyl-methylie, is formed:—



A reaction of a similar kind is obtained if amyl iodide be made to act upon sodie alcohol; amyl-ethyl ether being formed in this case, as follows:—

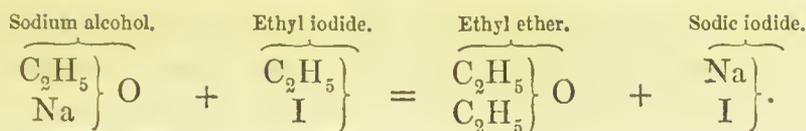


Several other double ethers have been formed by analogous methods. The uncombined molecule of each of these ethers yields two volumes of vapour, as may be seen by comparing the theoretical with the experimental numbers:—

| Mixed ether. | Formula. □ □ | Boiling Point. | | Specific gravity. | |
|-------------------------|--|----------------|------|-------------------|-------------|
| | | ° F. | ° C. | Theory. | Experiment. |
| Methyl-ethyl ether. . . | C H ₃ , C ₂ H ₅ , O | 51·8 | 11 | 2·084 | 2·158 |
| Methyl-amyl ether. . . | C H ₃ , C ₅ H ₁₁ , O | 197·6 | 92 | 3·546 | 3·74 |
| Ethyl-amyl ether. . . . | C ₂ H ₅ , C ₅ H ₁₁ , O | 233·6 | 112 | 4·031 | 4·042 |

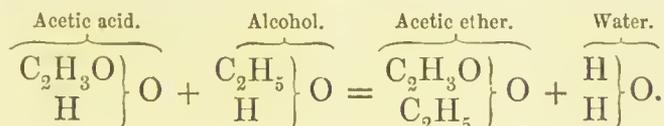
It is certain that these bodies are truly compounds, and not mere mixtures of the two ethers; the constancy of their boiling points alone would be sufficient to prove this fact; for example, methyl ether is gaseous at ordinary temperatures, and ethyl ether boils at 95° (35° C.), but the double ether resulting from their union has a fixed boiling point at 51°·8.

Now, if ethyl iodide be substituted for amyl iodide or methyl iodide in the foregoing experiment, the ethyl iodide also is decomposed by the sodium-alcohol, and ordinary ether is produced;—



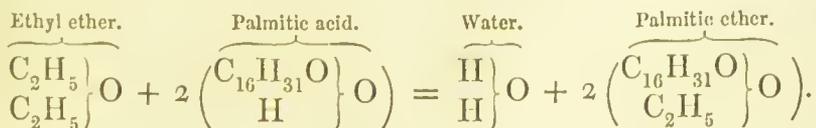
The conclusion, therefore, appears to be inevitable, that the molecule of common ether must likewise be analogous in its construction to the molecules of the double ethers. Moreover, if the uncombined molecule of ether be regarded as composed ($C=6$ and $O=8$) only of C_4H_5O , it yields only one volume of vapour; whereas, if the molecule be taken as (C_4H_5O, C_4H_5O) , it yields two volumes of vapour, like alcohol and the other organic compounds.

c. Compound Ethers.—1. When one of the alcohols is brought into contact with a monobasic acid, the two bodies react upon each other, in the proportion of one atom of each; one atom of water is eliminated, and a compound ether is formed. When acetic acid, for instance, is subjected to distillation with ordinary alcohol, water is eliminated and acetic ether is produced:—



A double decomposition occurs in this case, as in the foregoing, the basylous hydrogen of the acetic acid changing places with the ethyl contained in the alcohol.

Many compound ethers, such as the butyric, the benzoic, and the palmitic, may, according to Berthelot (*Ann. de Chimie*, III. xli. 432), be obtained by sealing up a mixture of the pure monobasic acid with the simple oxygen ether in a tube, and exposing it to a temperature of about 752° (400° C.): much of the ether remains unconverted, however great the excess of acid employed. In this case water and the compound ether are the sole products, no alcohol being formed, one molecule of water (H_2O) being separated from two molecules of the acid, whilst two molecules of the compound ether are obtained; as for example:—

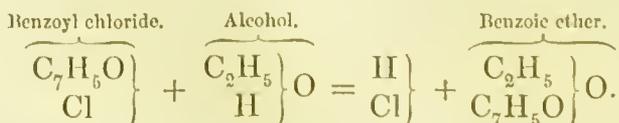


2. When the chemical activity of the acid is not very strong, the reaction is facilitated by mixing one of the salts of the acid with the alcohol, and then liberating the acid by the agency of sulphuric acid. In this manner formic ether is readily obtained by

distilling a mixture of dry sodic formiate, alcohol, and concentrated sulphuric acid; although formic acid (hydric formiate) and alcohol, when distilled together under the ordinary atmospheric pressure, have but a comparatively small action upon each other.

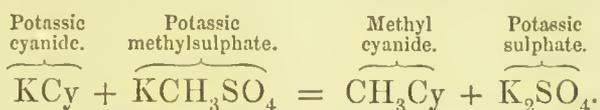
An elaborate investigation of the mutual action of the alcohols and acids, both when mixed in the presence of water, and when water is absent, has been made by Berthelot and Pean de St. Gilles (*Ann. de Chimie*, III. lxx. 385, lxxi. 5, and lxxiii. 225). They found that all the compound ethers when heated in contact with water, gradually become decomposed into the alcohol and the acid from which they were derived; but the decomposition is never complete, although in proportion as the quantity of water is increased it approaches more and more to completion. When on the contrary an anhydrous alcohol is treated with the pure hydrogen salt of any acid, combination occurs more or less rapidly, a compound ether being formed, whilst a corresponding amount of water is liberated. But in proportion as the amount of the water and the compound ether increases during the progress of the experiment, at the expense of the original materials, so the rapidity with which the chemical action occurs is seen to slacken, and at length it reaches a limit. The proportion of compound ether ultimately formed varies in each case, according to the nature of the acid and alcohol employed; it also varies with different mixtures of the same acid and alcohol, according to the proportion of acid to the alcohol. However large the proportion of acid employed, the amount of alcohol is never wholly transformed into the compound ether, though as the amount of acid is increased it continually approaches this point; but the presence of water, which is produced during the reaction, prevents the change from being absolutely complete.

3. Other modes may be adopted for obtaining the compound ethers. When the chlorides of the monobasic acid radicles are heated with alcohol, a compound ether of the corresponding monobasic acid is obtained: for instance, benzoyl chloride, when heated with anhydrous alcohol, yields benzoic ether and hydrochloric acid:—



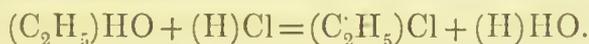
4. The distillation of the concentrated aqueous solution of a vinic salt—such as potassic or calcic methylsulphate or ethylsulphate, with a concentrated solution of potassic sulphide, selenide,

telluride, or cyanide,—furnishes an easy method of obtaining the corresponding ether with sulphur, selenium, tellurium, or cyanogen. For instance, if methyl cyanide were required, the reaction would be the following :—

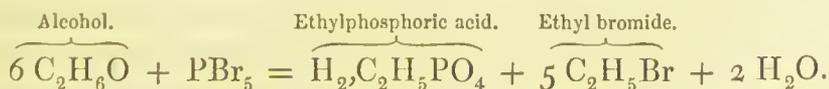


Other modes of preparing particular ethers are adopted ; these will be noticed when the ethers to which they apply are described.

5. The ethers of the hydracids are readily formed by the direct action of these acids upon the alcohols ; hydrochloric ether, for instance, may be formed by saturating alcohol with hydrochloric acid gas, and submitting the mixture to distillation : the atom of ethyl in the alcohol and that of hydrogen in the acid change places, and hydrochloric ether and water are produced by double decomposition. The reaction may also be expressed by saying,—in the formation of the ethers of the hydracids the alcohols lose hydroxyl (HO), and receive in its place an atom of chlorine, bromine, or iodine,—the hydracid ether and water being produced ; as for example :—



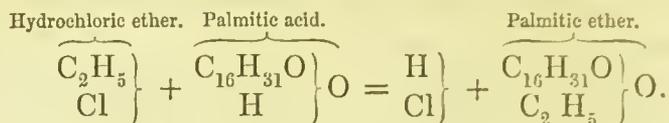
In other cases it is found advantageous to act upon the alcohol with the corresponding compound of phosphorus, which is prepared at the moment by reaction in the presence of the alcohol ; as for instance, in the preparation of hydrobromic ether :—



In many instances it is best to act upon the anhydrous alcohol with the tribromide or triiodide of phosphorus, and simply to wash the product with water.

Advantage is taken of the facility with which the hydracids act upon the alcohols, in order to prepare compound ethers with acids of comparatively feeble chemical activity. If, for example, it be desired to obtain ethers of the fatty acids, such as palmitic ether, the palmitic acid is dissolved in alcohol, and a current of hydrochloric acid is transmitted, whilst the alcohol is gently heated. After the reaction has terminated, the product is washed with hot water, and the palmitic ether being insoluble in water, is readily separated from the mixture. It appears that hydrochloric

ether is first formed, and this afterwards undergoes double decomposition when heated with the fatty acid:—



The ethers of the dibasic acids, when converted into vapour, yield only one volume of vapour for each atom of ethyl (C_2H_5) which they contain: so that if two volumes of vapour be taken as the representative of the molecule of those compounds, the molecular formula of the oxalic, carbonic, and succinic ethers must be taken as containing one atom of the dibasic acid and two atoms of ethyl; the formula of carbonic ether being written $[(\text{C}_2\text{H}_5)_2\text{CO}_3]$.

(1140) *Chemical Properties of the Ethers.*—The simple ethers, and the compound ethers of the monobasic acids, may generally be volatilized without undergoing decomposition; but their boiling point rises about 39° ($21^\circ\cdot6$ C.) for each addition of the hydrocarbon (CH_2). A similar observation may be applied to the boiling point of compound ethers of different alcohols derived from the same acid, as well as to that of ethers derived from the same alcohol, though containing different but homologous acids. The ethers are generally sparingly soluble in water, but they are readily dissolved by alcohol and by ordinary ether. None of the simple ethers have as yet been detected ready formed in the vegetable kingdom, but the compound ethers appear to be not unfrequently present in fruits and some other parts of plants, which occasionally owe their fragrance to these bodies. The *oil of winter-green* is a methyl salicylate ($\text{CH}_3, \text{C}_7\text{H}_5\text{O}_3$), and as Cahours has shown, it may be artificially produced by the reaction of methyl oxide upon salicylic acid. Many of the artificial essences sold by the perfumers and confectioners consist of compound ethers dissolved in alcohol: for it is a remarkable circumstance, that the pure ethers often have a repulsive odour, which is very different from that which they possess when largely diluted with alcohol. The so-called *pear oil*, or *essence of Jargonelle pear*, is an alcoholic solution of amyl acetate, $\text{C}_5\text{H}_{11}, \text{C}_2\text{H}_3\text{O}_2$. *Apple oil* is a similar preparation of amyl valerate, $\text{C}_5\text{H}_{11}, \text{C}_5\text{H}_9\text{O}_2$. *Pine-apple oil* is simply butyric ether ($\text{C}_2\text{H}_5, \text{C}_4\text{H}_7\text{O}_2$), diluted with alcohol (Hofman, *Ann. de Chimie*, III. xxxiv. 325). *Essence of melons* is the ethyl compound of one of the acids of cocoa-nut oil. *Essence of quinces* is dilute pelargonic ether, $\text{C}_2\text{H}_5, \text{C}_9\text{H}_{17}\text{O}_2$; and the peculiar odour of wine is found to be due to an ether, termed by Liebig

and Pelouze, who discovered it, *œnanthic ether* (from οἶνος, wine), and which, according to Fischer, is a mixture of rutie and caprylic ethers. This ether is stated to be the basis of *Hungarian wine oil*, which has been sold at a very high price for flavouring brandy.

(a) *Ordinary Ether—Theory of Etherification.*

(1141) ETHER: *Ethylic* or *Vinic Ether*, sometimes improperly called *Sulphuric Ether*, $(C_2H_5)_2O=74$: *Sp. gr. of liq. at 32°*, 0.7365; *of vap.* 2.586; *Rel. wt.* 37; *Boil. pt.* 95° (35° C.).

Preparation.—Formerly ether was prepared by mixing two measures of alcohol and one measure of sulphuric acid, and distilling until it began to blacken; then a quantity of alcohol, equal to half that originally used, was added to the residue in the retort, and the distillation was again proceeded with until the ether ceased to come over. The method at present in general use for the preparation of ether is that known as the ‘continuous process’ of Boullay. It consists in mixing together two measures of alcohol (sp. gr. 0.830) and one measure of concentrated sulphuric acid; the mixture is submitted to distillation in a capacious retort, which must be connected with an efficient condenser. Through the tubulure of the retort a tube is introduced, which is in communication with a reservoir of alcohol, designed to furnish a supply of spirit sufficient to keep the amount of liquid at a uniform level in the retort, during the course of the subsequent distillation. The temperature is then raised rapidly so as to maintain the mixture in a steady ebullition. The liquid which passes over consists almost entirely of ether and water, mixed with a small portion of alcohol, which has distilled over unchanged.

This process may go on without interruption until a quantity of alcohol, about 30 times as great as that originally taken, has become converted into ether. Isethionic acid is gradually formed in the residue.

Mitscherlich distilled a mixture of one part of absolute alcohol with two parts of sulphuric acid, consisting of five parts of oil of vitriol diluted with one part of water ($H_2SO_4 + H_2O$; sp. gr. 1.78 nearly), the original volume of liquid in the retort being maintained by a gradual supply of absolute alcohol. He found that for every 100 parts of alcohol consumed, about 65 of ether, 17 of water, and 18 of undecomposed alcohol were obtained: the quantity of alcohol which distils depends upon the rapidity with which the operation is conducted; the more quickly it is performed the larger being the quantity of alcohol. When absolute alcohol is

used, for every 65 parts of ether obtained, 15.4 of water should be produced, the slight excess observed depending upon the presence of a little water in the alcohol. With a more dilute alcohol the proportion of water which passes over is greater, the excess corresponding with the amount present in the alcohol. The temperature most favourable to the formation of ether is from 28.4° to 29.0° (14.0° to 14.3° C.) At a temperature of 32.0° (16.0° C.) the disengagement of sulphurous anhydride mixed with olefiant gas and oil of wine commences. If a sulphuric acid much more dilute than one of sp. gr. 1.632 ($\text{H}_2\text{SO}_4 + 2 \text{H}_2\text{O}$) be employed, the excess of water gradually distils over with the alcohol, which undergoes little change until the liquid has become sufficiently concentrated to allow the boiling point to rise to 28.4° , after which ether is formed as usual.

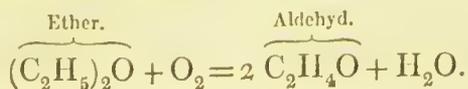
Alcohol may also be converted into ether by heating it with phosphoric, arsenic, and perchloric acids, as well as by means of stannic chloride, zincic chloride, boric fluoride, and by several other processes which will be further considered when the theory of etherification is passed under review (1142).

In order to purify the crude ether, it should be agitated with an equal bulk of water, containing $\frac{1}{40}$ of its weight of caustic soda in solution; the water combines with the alcohol, and the soda neutralizes any sulphurous acid that may have distilled over; the liquid separates into two layers, the upper one of which consists of ether holding a little water in solution. The ether may be freed from water by allowing it to stand for a day or two upon quicklime, or upon calcic chloride: it is then to be rectified by the heat of a water-bath, and condensed in vessels kept cool with ice-cold water.

Properties.—Pure ether is a very limpid, colourless, transparent, volatile liquid, of high refracting power; it possesses a powerful, penetrating, and peculiar odour, and a taste at first fiery but afterwards cooling: if taken internally it produces stimulating and intoxicating effects. Its vapour, when inhaled, at first occasions exhilaration, speedily followed by complete insensibility to pain; owing to this property it was at one time extensively administered during surgical operations, to diminish the sufferings of the patient; but its employment for this purpose has been nearly superseded by the use of chloroform, the effects of which are more speedy and certain, and are attended with less excitement to the system. Ether has a sp. gr. of 0.724 at 55° , and it is usually stated to freeze at -24° (-31° C.). It is probable, however, that the specimen which gave this result was not pure, as, ac-

ording to Mitchell, it may be exposed to a cold of -146° ($-98^{\circ}.9$ C.) without becoming solid. It boils at 95° (35° C.). From its great volatility, and the consequent depression of temperature furnished by its rapid evaporation, it is frequently employed for producing cold artificially. Ether is dissolved freely by alcohol, but sparingly by water. When agitated with an equal bulk of water, it dissolves about $\frac{1}{36}$ of its volume of water, while the water takes $\frac{1}{8}$ of its bulk of ether. Ether is employed to some extent as a solvent for fatty bodies, and is used in the proximate analysis of organic matters, for separating the fats or oils which they contain, from other substances which are not soluble in ether. Iodine, sulphur, and phosphorus are dissolved by ether. Ammoniacal gas, and nitric oxide, are also freely absorbed by it. Certain metallic salts are likewise dissolved by it; among these are platinic chloride, and ferric chloride: with stannic chloride it forms a volatile crystalline compound $2[(C_2H_5)_2O], SnCl_4$; and a similar compound containing titanium may likewise be procured. Mercuric and auric chloride are also freely soluble in ether; these two compounds may be separated from their solutions in water, by agitation with ether, and they rise with it to the surface when left at rest.

Ether is highly inflammable, and as it is also very volatile and furnishes a vapour of considerable density, care must be taken not to pour it out in the vicinity of a flame; many serious accidents have arisen from a neglect of this precaution. In certain proportions its vapour forms an explosive mixture with air or oxygen. When burned with a sufficient supply of oxygen it produces only water and carbonic anhydride. Its flame is more luminous than that of alcohol, and it deposits charcoal on cold bodies which are introduced into it. When passed through ignited porcelain tubes filled with fragments of porcelain it is decomposed; charcoal is deposited, and aldehyd is found among the products. If the temperature be not too high, a large quantity of acetylene (C_2H_2 ; 1208) is obtained, mixed with olefiant gas. If burned at a lower heat with insufficient access of air, it yields a mixture of aldehyd with acetic acid and acetal; but aldehyd is the predominating ingredient. This formation of aldehyd is easily explained, since the substitution of one atom of oxygen for two of hydrogen in one molecule of ether, furnishes the elements of two molecules of aldehyd, the hydrogen combining with another atom of oxygen, and being eliminated in the form of water:—



If ether be kept in vessels partially filled with air, it absorbs oxygen gradually, and acetic acid is formed. When treated with concentrated sulphuric acid, ordinary ether becomes converted into ethylsulphuric acid; and if this liquid be boiled, sweet oil of wine mingled with sulphurous anhydride passes over; the mixture blackens considerably, and ethionic and isethionic acids are formed in the retort.

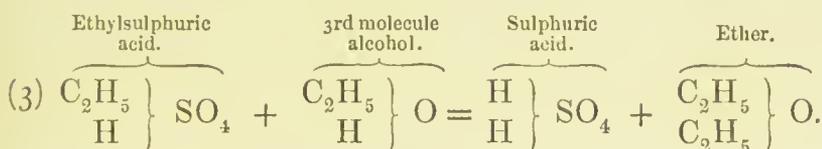
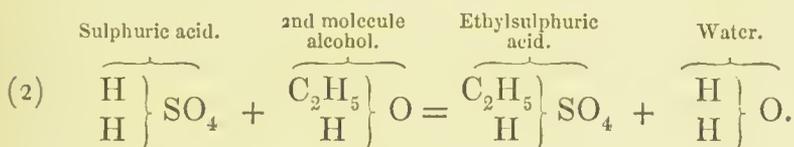
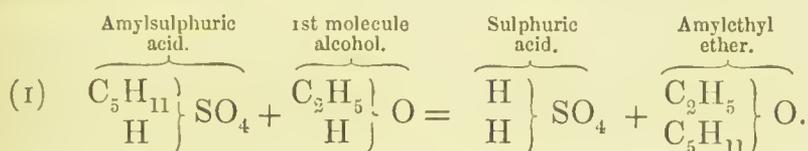
Nitric acid acts powerfully upon ether with the aid of heat, forming carbonic, acetic, and oxalic acids.

If ether be saturated with hydrochloric acid and distilled, hydrochloric ether is the product; and the effects of hydrobromic and hydriodic acid are analogous, though the bromide and iodide of ethyl are less easily produced. Chlorine acts violently upon ether, converting it into various substitution compounds (1174), and producing aldehyd, chloral, and hydrochloric ether, whilst hydrochloric acid is evolved in abundance.

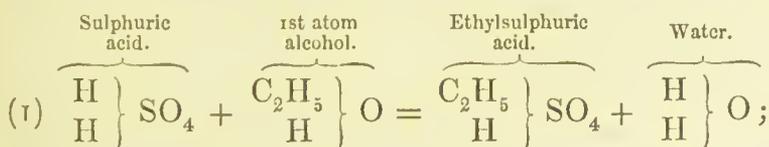
Potassium and sodium decompose ether slowly, and liberate hydrogen gas.

(1142) *Theory of Etherification.*—In the process of preparing ether from alcohol by the agency of sulphuric acid, it will be observed that a small quantity of this acid converts an indefinite quantity of alcohol into ether and water. The explanations which have been offered to account for the formation of ether by the action of sulphuric acid are numerous. Most chemists, however, now admit with Liebig, that the essential change may be divided into two stages, the first of which consists in the formation of ethylsulphuric acid, and the second in the decomposition of this acid into sulphuric acid, water, and ether. When fresh alcohol is added to the mixture, a new quantity of ethylsulphuric acid is formed with the sulphuric acid liberated during the previous distillation; this ethylsulphuric acid in its turn undergoes decomposition into ether, water, and sulphuric acid, and thus the same portion of sulphuric acid continues the etherification for an indefinite period. The following ingenious experiment by Williamson goes far towards proving the occurrence of this successive formation and decomposition of ethylsulphuric acid during the process of etherification. A mixture of sulphuric acid and amyl alcohol was prepared, so as to obtain amylsulphuric acid ($\text{HC}_5\text{H}_{11}\text{SO}_4$, one of the homologues of ethylsulphuric acid); this mixture was placed in a retort and then submitted to distillation, supplying it with ordinary alcohol, as in the continuous process of making ether already described. The distillation was continued until the liquid

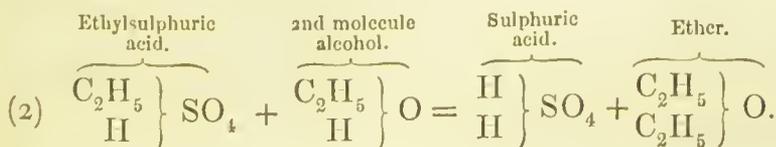
which passed over contained only ordinary ether, without any compound of fousel oil. On examining the residuc in the retort it was found to contain ethylsulphuric acid only, the amylsulphuric acid having entirely disappeared, a double ether (amylethyl ether, C_2H_5, C_5H_{11}, O) being found in the first portions of the distilled liquid. The successive stages of this action may be traced as follows:—



Now, since two successive stages have been proved to occur during the formation of this double ether, and since they have been also traced with other double ethers, it appears to be highly probable that similar steps attend the formation of common ether by the continuous process, in which it may be supposed that the first reaction takes place between one molecule of sulphuric acid and one of alcohol; one of the atoms of basylous hydrogen in the acid exchanging places with the ethyl of the alcohol, thus forming one molecule of ethylsulphuric acid and one of water, as follows:—



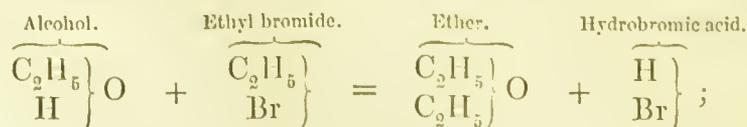
but in the second stage of the reaction the newly-formed ethylsulphuric acid, and a new molecule of alcohol undergo double decomposition, the typical hydrogen of the alcohol being substituted for the atom of ethyl contained in the ethylsulphuric acid; a molecule of ether being produced, whilst the molecule of sulphuric acid is again set at liberty to perform a similar round with fresh portions of alcohol:—



Alcohol, even when mixed with very small proportions of ethylsulphuric acid, was found by Reynoso to be etherized by prolonged heating under pressure; the more diluted the acid, the higher was the temperature, and the longer the time required. Reynoso (*Ann. de Chimie*, III. xlviii. 390) finds that the hydrochloric, hydrobromic, and hydriodic acids act similarly when heated for several hours to 464° (240° C.) in sealed tubes with an excess of alcohol.

Various salts are also capable of etherifying alcohol, if heated strongly with it under pressure. Reynoso states that the several crystallized neutral sulphates isomorphous with magnesian sulphate, when sealed up with the alcohol in tubes and heated to 464° (240° C.), effect a partial etherification of the alcohol: whilst the sulphates themselves, with the exception of those of nickel and copper, experience no change beyond the loss of their water of crystallization. Normal aluminic sulphate etherizes alcohol between 392° and 464° (200° and 240° C.), with but little formation of basic aluminic sulphate, and without any liberation of gas; when alum is used the results are similar, but the alcohol is etherified at a lower temperature. Both iodide and bromide of cadmium, and the chlorides of cobalt, cadmium, manganese, and copper, under similar circumstances, effect the etherification of alcohol, but undergo no change themselves. With stannous and cupric chloride, the production of ether is sufficient to furnish a considerable stratum of ether, but a certain amount of permanent gas is also formed. Corrosive sublimate blackens the alcohol, ether is formed, and much gas is liberated. Chlorides of zinc and ammonium effect a similar change; ferric chloride and the chlorides of aluminum and antimony yield a mixture of ether and hydrochloric ether.

Ethyl chloride, as well as ethyl bromide and iodide, when heated with an excess of alcohol in sealed tubes to 392° (200° C.) for 8 hours, converts the alcohol into a mixture of ether and water, whilst hydrochloric, hydrobromic, or hydriodic acid is liberated, owing to the successive formation of hydrochloric, hydrobromic, or hydriodic acid, and the conversion of the acid into chloride, bromide, or iodide of ethyl, with liberation of water; the reaction with ethyl bromide may be represented as follows:—



And again:—



the hydrobromic ether thus formed, going through the same series of changes with successive portions of alcohol.

The metallic chlorides act upon the alcohol in some manner as yet unexplained, in consequence of which the alcohol becomes more or less completely resolved into ether and water. This effect cannot be produced by the action of heat alone; and it must be admitted, that the theory of etherification is still incomplete, notwithstanding the numerous researches of which it has been the subject.

The oxygen in ordinary ether may be displaced by other bodies analogous to it, such as sulphur, selenium, and tellurium, as well as by chlorine, bromine, and iodine. The compounds thus formed are sometimes described under the names of hydrosulphuric, hydrochloric, hydrobromic, and hydriodic ethers.

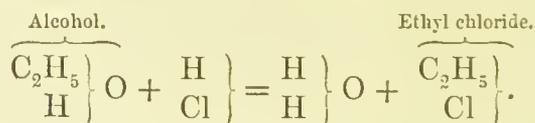
Ethylic Ethers.

| Name of Ether. | Formula. Mol. Vol. □ □ | Boiling Point. | | Specific Gravity. | | Rel. wt. of Vapour. H=1. |
|---|--|----------------|-------|-------------------|---------|--------------------------------|
| | | ° F. | ° C. | Liquid. | Vapour. | |
| Ethyl oxide . . | (C ₂ H ₅) ₂ O | 95 | 35 | 0·7365* | 2·586 | 37 |
| „ sulphide . | (C ₂ H ₅) ₂ S | 163·4 | 73 | 0·825 | 3·1 | 45 |
| „ disulphide. | (C ₂ H ₅) ₂ S ₂ | 303·8 | 151 | 1·0 | 4·27 | 61 |
| „ chloride . | C ₂ H ₅ Cl | 51·9 | 11 | 0·921* | 2·219 | 32·2 |
| „ bromide . | C ₂ H ₅ Br | 105·8 | 41 | 1·4733* | 3·754 | 54·5 |
| „ iodide . | C ₂ H ₅ I | 158·5 | 70·3 | 1·9755* | 5·475 | 78 |
| „ cyanide . | C ₂ H ₅ CN | 190·4 | 88 | 0·787 | 1·928 | 27·5 |
| „ sulphate . | (C ₂ H ₅) ₂ SO ₄ | | | 1·120 | | |
| „ sulphite . | (C ₂ H ₅) ₂ SO ₃ | 320 | 160 | 1·1063* | 4·78 | 69 |
| „ nitrate . | C ₂ H ₅ NO ₃ | 185 | 85 | 1·112 | | |
| „ nitrite . | C ₂ H ₅ NO ₂ | 62 | 16·6 | 0·947 | 2·627 | 37·5 |
| „ phosphate | (C ₂ H ₅) ₃ PO ₄ | | | 1·086 | | |
| „ carbonate | (C ₂ H ₅) ₂ CO ₃ | 257 | 125 | 0·975 | 4·09 | 59 |
| „ borate . | (C ₂ H ₅) ₃ BO ₃ | 246·2 | 119 | 0·8849* | 5·31 | 73 |
| „ tetrabasic silicate } „ dibasic si- licate } „ formiate . | (C ₂ H ₅) ₄ SiO ₄ | 330 | 165·5 | 0·933 | 7·32 | 104 |
| „ acetate . | (C ₂ H ₅) ₂ SiO ₃ | 662 | 350 | 1·079 | | |
| „ butyrate . | C ₂ H ₅ CHO ₂ | 127·4 | 53 | 0·9357* | 2·573 | 37 |
| „ valerate . | C ₂ H ₅ C ₂ H ₃ O ₂ | 165·2 | 74 | 0·9069* | 3·067 | 44 |
| „ cyanate . | C ₂ H ₅ C ₄ H ₇ O ₂ | 239·0 | 115 | 0·9041* | 4·04 | 58 |
| „ cyanurate | C ₂ H ₅ C ₅ H ₉ O ₂ | 272·3 | 133·5 | 0·894 | 4·558 | 65 |
| „ benzoate. | C ₂ H ₅ CNO | 140 | 60 | 0·8981 | 2·475 | 35·5 |
| „ lactate . | (C ₂ H ₅) ₃ C ₃ N ₃ O ₃ | 487·4 | 253 | | 7·4 | 106·5 |
| „ oxalate . | C ₂ H ₅ C ₇ H ₅ O ₂ | 408·2 | 209 | 1·053 | 5·407 | 75 |
| „ succinate | C ₂ H ₅ C ₃ H ₅ O ₃ | | | 1·08 | 4·75 | 59 |
| „ citrate . | (C ₂ H ₅) ₂ C ₂ O ₄ | 365 | 185 | 1·0929 | 5·087 | 73 |
| | (C ₂ H ₅) ₂ C ₄ H ₄ O ₄ | 417·2 | 214 | 1·036 | 6·22 | 87 |
| | (C ₂ H ₅) ₃ C ₆ H ₅ O ₇ | 541·4 | 283 | 1·142 | | |

(1143). The preceding table exhibits the composition of a few of the principal compound ethylic ethers. It would be useless to attempt to enumerate them all, since every acid forms at least one ether, and some, such as the silicic and boracic, furnish more than one. The specific gravities to which an asterisk is affixed were taken at 32° F.

(b) *Hydracid Ethylic Ethers.*

(1144) *Ethyl Chloride, Chloride of Ethyl, or Hydrochloric Ether* (C_2H_5Cl). *Sp. gr. of vap.* 2.219; *of liq. at 32°*, 0.921; *Rel. wt.* 32.25; *Boil. pt.* 51°.9 (11° C.)—This compound is obtained easily, either by saturating alcohol with hydrochloric acid gas, and then distilling at a gentle heat, or by distilling a mixture of 3 parts of oil of vitriol, 2 of alcohol, and 4 of fused sodic chloride; the retort is in either case connected with a tubulated receiver surrounded by water at a temperature of about 68° (20° C.), where most of the alcohol and water which pass over during the operation are condensed, while the ether escapes in the form of vapour, through a bent tube which is inserted into the tubulure of the receiver, and passes to the bottom of a flask kept cool with ice. The liquid which is condensed in this flask must be rectified from calcic chloride.



Another mode in which it may be formed consists in heating anhydrous ether with phosphorous chloride to 383° (195° C.) in a sealed tube, ethyl chloride and phosphorous acid being formed, 3 molecules of ether reacting upon 2 of the trichloride, $3 [(C_2H_5)_2O] + 2 PCl_3 = 6 C_2H_5Cl + P_2O_3$.

Ethyl chloride is also formed by the action of other chlorides, such as chloride of sulphur, antimony, tin, or zinc, upon alcohol.

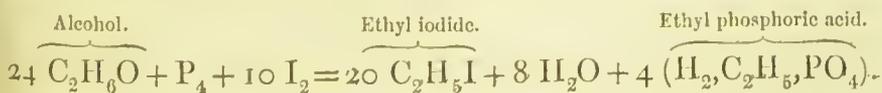
Ethyl chloride is a colourless liquid, of a penetrating, ethereal, and somewhat alliaceous odour. It burns with a brilliant flame edged with green, emitting fumes of hydrochloric acid. If passed through red-hot tubes, it is decomposed into equal measures of hydrochloric acid and olefant gas, $C_2H_5Cl = C_2H_4 + HCl$. It is sparingly soluble in water, but is freely dissolved by alcohol. These solutions give no precipitate with a solution of argentic nitrate. If an alcoholic solution of potash be enclosed in a sealed

tube with hydrochloric ether and heated to 212° , potassic chloride and ordinary ether are formed; $2 \text{C}_2\text{H}_5\text{Cl} + 2 \text{KHO} = (\text{C}_2\text{H}_5)_2\text{O} + 2 \text{KCl} + \text{H}_2\text{O}$ (Balard); but if the vapour of the ether be passed over heated caustic potash, water and pure olefiant gas are evolved; $\text{C}_2\text{H}_5\text{Cl} + \text{KHO} = \text{C}_2\text{H}_4 + \text{H}_2\text{O} + \text{KCl}$.

(1145) *Ethyl Bromide, Bromide of Ethyl, or Hydrobromic Ether* ($\text{C}_2\text{H}_5\text{Br}$). *Sp. gr. of liq.* 1.4733 at 32° ; *of vap.* 3.754 ; *Rel. wt.* 54.5 ; *Boil. pt.* $105^{\circ}.8$ (41°C.)—This compound is usually prepared by adding, by degrees, 12 parts of bromine to 40 parts of alcohol (sp. gr. 0.827) and 1 part of phosphorus, contained in a retort, which must be kept cool by immersing it from time to time in cold water; the reaction of bromine and phosphorus upon each other in the presence of the water contained in the alcohol produces hydrobromic ether and ethylphosphoric acid; and on subjecting the mixture to distillation, hydrobromic ether comes over. It may be purified by agitation with a weak solution of potash, after which it is left to subside; it is then decanted, digested on calcic chloride, and redistilled.

Ethyl bromide is a colourless liquid of a peculiar ethereal odour and taste. It boils at $105^{\circ}.8$, though it requires to be heated to 120° before ebullition commences. It remains liquid at -24° (-31°C.). It burns with difficulty, producing a green flame and emitting fumes of hydrobromic acid.

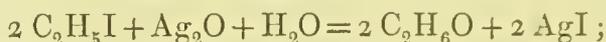
(1146) *Ethyl Iodide, Iodide of Ethyl, or Hydriodic Ether* ($\text{C}_2\text{H}_5\text{I}$). *Sp. gr. of liq. at* 32° , 1.9755 ; *of vap.* 5.475 ; *Rel. wt.* 78 ; *Boil. pt.* $158^{\circ}.5$ ($70^{\circ}.3 \text{C.}$)—In order to prepare this ether, 100 parts of alcohol are placed in a retort, and a small amount of iodine is introduced; phosphorus is added in small quantities at a time until the liquid becomes colourless; a fresh portion of iodine is then added, and then a fresh quantity of phosphorus; this may be continued until about 200 parts of iodine and 9 or 10 parts of phosphorus have been added. The mixture thus obtained must be cooled by immersing the bulb of the retort after each addition, in cold water to moderate the action. After the reaction has terminated, the liquid is distilled by the heat of a water-bath, taking care that the iodine (as shown by its brown colour) is in slight excess. The distillate should be washed with water, digested on calcic chloride, and redistilled. The reaction which occurs during this operation may be thus represented:—



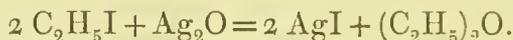
Hofmann finds it advantageous to place the alcohol and phos-

phorus in the retort, and to dissolve the iodine in ethyl iodide; this liquid is allowed to flow gradually into the retort during the distillation, and the operation is thus rendered continuous.

Ethyl iodide is a colourless liquid, which, if kept in half-closed bottles, soon undergoes a partial decomposition, and becomes brown from the liberation of iodine. When heated with water to 302° (150° C.), in a sealed tube, it becomes decomposed into ordinary ether and hydriodic acid (Frankland); according to Hofmann, if boiled with water and argentic oxide, alcohol and argentic iodide are produced:—



and Wurtz finds that when the anhydrous iodide is heated in a sealed tube with argentic oxide, argentic iodide and ordinary ether are formed with facility:—



If a mixture of equivalent quantities of methyl iodide and ethyl iodide be treated with oxide of silver, methyl-ethyl ether ($\text{CH}_3, \text{C}_2\text{H}_5, \text{O}$) is produced.

Both the bromide and the iodide of ethyl have been extensively employed for the preparation of substitution-compounds containing ethyl; and it was by decomposing ethyl iodide in a sealed tube by means of zinc, that Frankland succeeded in isolating the hydrocarbon diethyl, originally known as ethyl.

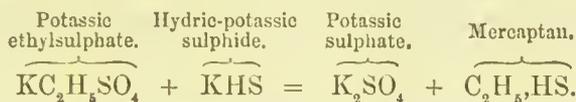
(1147) **SULPHIDES OF ETHYL.**—Alcohol furnishes not less than three remarkable compounds which contain sulphur. One of these, $(\text{C}_2\text{H}_5)_2\text{S}$, corresponds in composition to the oxide, or ordinary ether; the second is the so called *ethyl disulphide* $(\text{C}_2\text{H}_5\text{S})_2$ —no oxidized representative of this body is known; and the third is *mercaptan* $(\text{C}_2\text{H}_5\text{HS})$, a compound which corresponds with alcohol in which the oxygen is displaced by sulphur. All these bodies are distinguished by a disgusting alliaceous odour, which is extremely powerful and persistent.

Diethyl Sulphide, Hydrosulphuric Ether, or Sulphide of Ethyl $(\text{C}_2\text{H}_5)_2\text{S}$. *Sp. gr. of liq.* 0.825; *of vap.* 3.1; *Rel. wt.* 45; *Boil. pt.* $163^{\circ}.4$ (73° C.).—This compound is easily prepared by decomposing an alcoholic solution of dipotassic sulphide K_2S (563), by transmitting into it the vapour of ethyl chloride, and submitting it to distillation: the distilled liquid is to be well washed with water, and rectified from calcic chloride. It is a colourless liquid with an intensely powerful odour of garlic. It forms crystalline compounds with some of the metallic chlorides; its compound with corrosive sublimate contains $[(\text{C}_2\text{H}_5)_2\text{S}, \text{HgCl}_2]$.

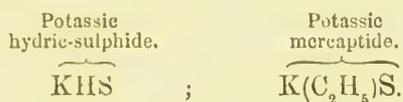
Diethyl Disulphide or Disulphide of Ethyl $[(\text{C}_2\text{H}_5\text{S})_2, \text{or } (\text{C}_2\text{H}_5)_2\text{S}_2]$. *Sp. gr.*

of liq. 1.0; of vap. 4.27; Rel. wt. 61; Boil. pt. 303°.8 (151° C.).—This ether is obtained by distilling three parts of potassic ethylsulphate dissolved in its own weight of water, with two parts of dipotassic pentasulphide, K_2S_5 . The alcoholic solution of this compound gives a yellow precipitate with plumbic acetate, and a white with corrosive sublimate. There appears to be ground for supposing that higher sulphides of ethyl may be obtained.

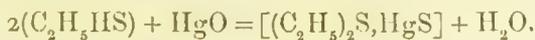
Ethylhydric Sulphide, or *Mercaptan* (C_2H_5HS). *Sp. gr. of liq.* 0.835; *of vap.* 2.14; *Rel. wt.* 31; *Boil. pt.* 96°.8 (36° C.).—This compound may be obtained by distilling a mixture of equal parts of an aqueous solution of potassic ethylsulphate, of sp. gr. 1.28, with a solution of potash of the same density, previously saturated by sulphuretted hydrogen:—



A better plan, according to Regnault, is to saturate an alcoholic solution of potash completely with sulphuretted hydrogen, and then to distil it with hydrochloric ether. Mercaptan is a colourless, transparent, very mobile liquid, with a most intense and repulsive odour of garlic; it is very inflammable, and burns with a blue flame. It is sparingly soluble in water, but is dissolved freely by alcohol and by ether. The solution is neutral to test papers, but mercaptan nevertheless presents the characters of a feeble acid. It dissolves sulphur, phosphorus, and iodine, with facility. Mercaptan becomes solid at $-7°.6$ ($-22°$ C.): if a glass rod be moistened with this compound and moved quickly through the air, the cold produced by the evaporation is sufficient to freeze a portion of the remainder. With the metals mercaptan forms compounds which correspond to the double sulphides of the metals with hydrogen, but they contain ethyl instead of hydrogen, as may be seen by comparing their respective formulæ:—



Potassic mercaptide is obtained by acting on pure mercaptan with potassium, hydrogen gas being liberated: but it is more particularly on the oxides of the noble metals that the action of mercaptan is remarkable. The name mercaptan (*mercurium captans*) is derived from the energy with which the body attacks mercuric oxide. Mercuric mercaptide [$(C_2H_5)_2S, HgS$] is a white crystalline compound, destitute of odour, and fusible at $185°$ ($85°$ C.). It is insoluble in water, but soluble in alcohol: it is easily obtained by digesting mercuric oxide in an alcoholic solution of mercaptan, water being formed, whilst the odour of mercaptan disappears:—



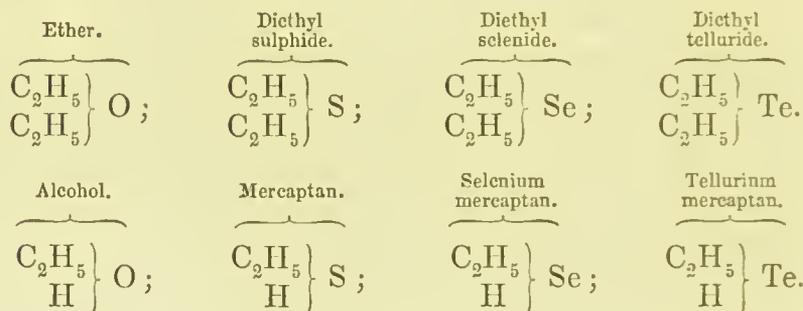
The corresponding compound of gold is white and gelatinous; that of platinum is bright yellow, and that of lead [$(C_2H_5)_2S, PbS$] is yellow and crystalline.

(1148) Selenium and tellurium each form compounds with ethyl, corresponding to diethyl sulphide; they may be obtained by distilling potassic selenide or telluride with potassic ethylsulphate. It is, however, to be remarked that both the selenide and the telluride of ethyl combine with chlorine, bromine, and iodine; and they become oxidized, and form salts with the oxyacids, just as though they were metallic bodies. In fact, they

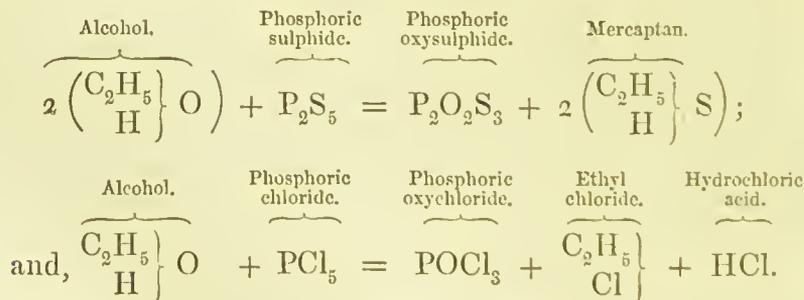
present many chemical analogies with the compounds which arsenicum, antimony, bismuth, and other metals form with ethyl (1191 *et seq.*)

A compound of selenium (C_2H_5HSe), corresponding in composition and properties to mercaptan, is formed during the operation of preparing diethyl selenide.

These compounds of sulphur and selenium with ethyl are analogous to the alcohols and ethers, or oxygen compounds of ethyl. Each sulphur compound furnishes a volume of vapour equal to that of the molecule of the corresponding oxygen compound:—

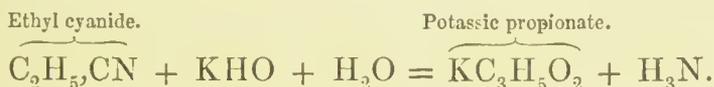


Each molecule of alcohol, when decomposed by phosphoric sulphide, yields a single molecule of mercaptan, an atom of sulphur changing places with the atom of oxygen in the alcohol; but if the molecule of alcohol be decomposed by phosphoric chloride, the atom of oxygen is displaced by two atoms of chlorine, and a molecule of ethyl chloride with one of hydrochloric acid is formed:—

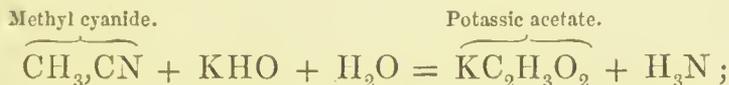


(1149) *Ethyl Cyanide, Cyanide of Ethyl, Hydrocyanic Ether, or Propionitrile* ($C_2H_5Cy = C_3H_5N$). *Sp. gr. of liq.* 0.787; *of vap.* 1.928; *Rel. wt.* 27.5; *Boil. pt.* 190°.4 (88° C.).—This compound is obtained in a manner analogous to that directed for the preparation of the foregoing bodies, viz., by the distillation of well-dried potassic ethylsulphate with two-thirds of its weight of potassic cyanide. A still better method consists in heating a solution of 2 parts of ethyl iodide in 8 of alcohol with 1

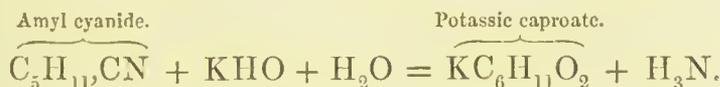
part of potassic cyanide, condensing the vapours, and allowing them to fall back into the retort as long as they show any sign of iodine. The product is washed with water, and rectified by the heat of the water bath. It is a colourless, very poisonous liquid, of an alliaceous odour. When ethyl cyanide is treated with a boiling solution of potash, the elements of water are assimilated, ammonia is evolved, and potassic propionate is formed:—



A similar mode of decomposition is observed to occur with all the hydrocyanic ethers of this class when treated with caustic potash: they all combine with the elements of water, and yield a salt of one of the acids homologous with formic acid, the acid so formed containing 1 atom more of carbon than the alcohol which furnished the hydrocyanic ether; methyl cyanide thus yields potassic acetate:—

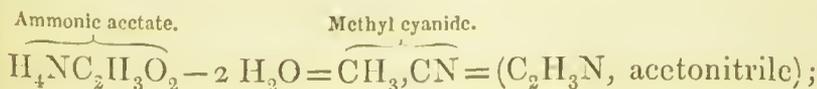
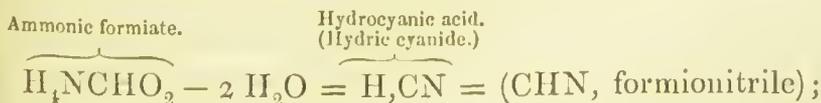


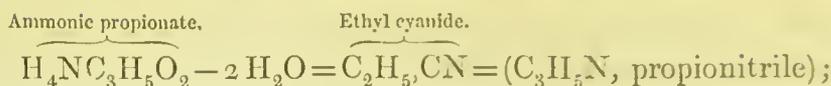
and amyl cyanide in like manner furnishes potassic caproate:—



This method of forming the higher terms of the homologous series from those below them is one of considerable interest.

It is interesting to observe in connexion with the discovery of the isomeric cyanides of Hofmann, to be noticed immediately (1149 a) that this form of the hydrocyanic ethers (the *nitriles* of some chemists), as a class, may also be obtained by a process of dehydration, from the acids to which they correspond; that is to say, if the ammoniacal salts of the acids homologous with the formic, be distilled with phosphoric anhydride, or be otherwise treated in such a manner as to deprive one molecule of the salt of two molecules of water, they yield one molecule of the corresponding hydrocyanic ether (1340, 1351), thus:—



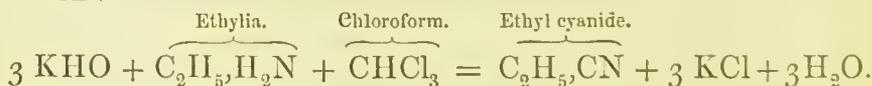


and in this manner the hydrocyanic ethers of several series of alcohols have been obtained, although the corresponding alcohols are at present unknown.

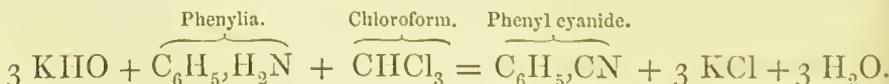
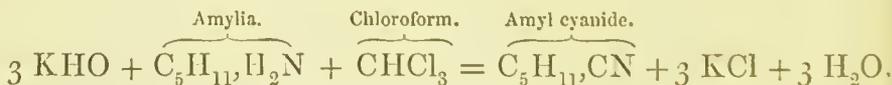
The action of potassium upon hydrocyanic ether is remarkable. If the ether be allowed to fall drop by drop upon potassium contained in a flask fitted to a vertical condenser, so as to cause any part of the ether which escapes decomposition to fall back upon the potassium, ethyl hydride ($\text{C}_2\text{H}_5, \text{H}$) is formed, whilst potassic cyanide is produced, and an alkaline base termed *cyanethine* ($\text{C}_9\text{H}_{15}\text{N}_3$) remains in the flask (Frankland and Kolbe). This base is polymeric with hydrocyanic ether. It crystallizes from boiling water in pearly scales, and forms salts with the acids. The nitrate ($\text{C}_9\text{H}_{15}\text{N}_3, \text{HNO}_3$) crystallizes in large colourless prisms, which are neutral in their reactions.

The hydrocyanic ethers of the other alcohols when treated with potassium appear to furnish compounds homologous with cyanethine.

(1149 a) *Isomeric Hydrocyanic Ethers.*—Hofmann has lately prepared a series of compounds isomeric with these hydrocyanic ethers, but differing from them entirely in properties (*Proceed. Roy. Soc.* xvi. 144), by acting with chloroform and potash upon the primary ammonia bases of the alcohols. The reaction is attended with elimination of 3 molecules of hydrochloric acid, and may be represented in the case of ethylia by the following equation:—



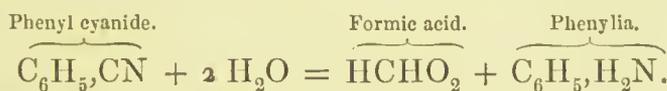
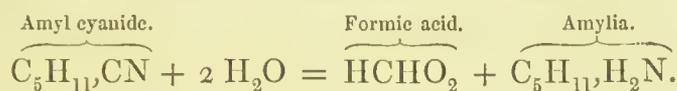
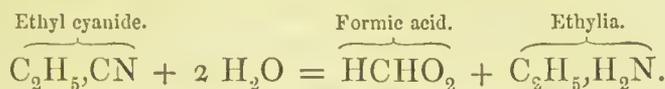
With amyliia, and with phenylia (aniline), corresponding reactions occur:—



In preparing these compounds, an alcoholic solution of the base is mixed with chloroform, and the mixture is gradually introduced into a retort containing powdered potassic hydrate; the mixture enters into ebullition, and the cyanide passes over mixed with portions of the base employed, alcohol, chloroform, and water, from which the cyanide must be freed by rectification.

These cyanides possess an exceedingly penetrating odour, recalling that of hydrocyanic acid, with a peculiar bitter taste. They are but little affected by treatment with alkalis, but it is characteristic of this series of bodies, that when submitted to the action of concentrated acids, they are rapidly decomposed; the

base being separated, while formic acid is liberated, and the elements of water are assimilated ; for example :—



Amyl Cyanide [(C₅H₁₁,CN) ; *Boil. pt.* 278°·6 (137° C.),] may be taken as the representative of the class. It is a transparent, colourless liquid, lighter than water, in which it is insoluble. It is soluble in alcohol and in ether. Its vapour has an oppressive odour, resembling that of amyl alcohol and hydrocyanic acid, with an insupportably bitter taste, and producing a sensation of choking. It may be distilled unaltered, but is decomposed by concentrated acids with violence.

(c.) *Ethyl Ethers of the Oxyacids.*

(1150) *Diethyl sulphate, Sulphate of Ethyl, or true Sulphuric Ether* [(C₂H₅)₂SO₄]. *Sp. gr. of liq.* 1·120.—This compound was first obtained by Wetherill, by the direct combination of ether with sulphuric anhydride. The vapours of the anhydride are transmitted into a flask containing ether, which is kept cool by ice ; the syrupy liquid thus produced is agitated with its own volume of ether and with four times its bulk of water ; when left at rest the ethyl sulphate rises to the surface ; it is purified by agitation with milk of lime, washed, filtered, and dried *in vacuo*. Sulphuric ether is an oily liquid, of burning taste and ethereal odour, resembling that of peppermint. It is scarcely possible to distil it without occasioning its decomposition, as a temperature of 266° or 284° (130° or 140°C.) resolves it into alcohol, sulphurous acid, and olefiant gas.

Sweet or heavy oil of wine appears to be a mixture of the foregoing compound with some hydrocarbons polymeric with olefiant gas ; it is obtained during the latter stages of the distillation of ether. If this oil be treated with a solution of potash, it is decomposed ; potassic ethylsulphate, and a hydrocarbon, termed *etherol* (C₁₆H₃₂ ?) rises to the surface. This hydrocarbon, known also as *light oil of wine*, is polymeric with olefiant gas, and forms a colourless liquid which has a *sp. gr.* of 0·917 ;

it boils at 536° (280° C.), and is readily soluble in ether and in absolute alcohol. When exposed to a temperature of -30° ($-34^{\circ}5$ C.), it usually deposits semitransparent, friable, colourless prisms of an isomeric hydrocarbon named *etherin*, which fuses at 230° (110° C.), and boils at 500° (260° C.); it is lighter than water, in which it is insoluble, but it is dissolved freely by alcohol and by ether.

(1151) *Ethyl Nitrate*, or *Nitric Ether* ($C_2H_5NO_3$). *Sp. gr. of liq.* 1.112; *Boil. pt.* 185° (85° C.).—Millon obtains this substance by gently heating a mixture of one volume of nitric acid, of sp. gr. 1.40 (to which a few grains of urea nitrate have been added in order to prevent the formation of nitrous acid), and two volumes of alcohol, of sp. gr. 0.842; the quantity of the mixture operated on should not exceed a quarter of a pint, or about 150 cubic centimetres; under these circumstances the operation proceeds quietly. The first portions of the distillate contain little except alcohol, but as soon as the liquid which distils over becomes turbid on the addition of water, the receiver must be changed, and the nitric ether collected separately: the distillation must be stopped when about three-fourths of the liquid have passed over, in order to prevent the ether from becoming mixed with secondary products, which cannot be removed without difficulty. The distillate is purified by agitation with a weak solution of alkali, and rectified from calcic chloride. Nitric ether is a colourless liquid of an agreeable odour, and a taste at first very sweet, but followed by a bitterish after-taste. Its vapour burns with a white luminous flame, and if heated to a little beyond its boiling point, it is decomposed with explosion, on the approach of a light.

(1152) *Ethyl Nitrite*, or *Nitrous Ether* ($C_2H_5NO_2$). *Sp. gr. of liq.* 0.947; *of vap.* 2.627; *Rel. wt.* 37.5; *Boil. pt.* 62° ($16^{\circ}6$ C.).—The *Spiritus Etheris Nitrosi* of the Pharmacopœia consists of a solution of this ether in alcohol; it has long been used as a therapeutic agent. The safest method of preparing the pure ether consists in introducing into a retort containing copper filings, one measure of alcohol sp. gr. 0.83, to which one measure of nitric acid of sp. gr. 1.36 is gradually added. The reaction of nitric acid upon alcohol begins at a very moderate heat, and is apt to become extremely violent, therefore no external heat should be applied during the distillation, after the reaction has once commenced. The vapours which are evolved contain hydrocyanic acid; they should be transmitted through a washing bottle containing water, then through a long bent tube filled with calcic chloride,

and finally should be condensed in a flask cooled by ice. Nitrous ether is of a pale yellow colour; it has an agreeable odour of apples. When this ether is kept in contact with water, it speedily becomes decomposed, and an acid is formed which was formerly supposed to be the malic. Debus has, however, shown that the result is a complicated one, nitric, formic, acetic, oxalic, glycolic, and glyoxylic acid ($C_2H_4O_4$?) being formed, whilst glyoxal ($C_2H_2O_2$), the aldehyd of glycol, is liberated, together with other aldehyds. (*Phil. Mag.* Nov. 1856.) A solution of ferrous sulphate becomes blackened when mixed with nitrous ether.

Nitrous ether is decomposed by transmitting its vapours through a red-hot tube, when it gives rise to a variety of products, among which are ammonic cyanide and carbonate, derived from the reactions of the nitrogen upon the carbon and hydrogen.

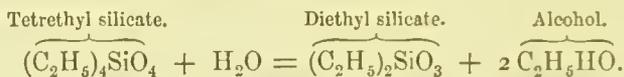
(1153) *Ethyl Perchlorate*, or *Perchloric Ether* ($C_2H_5ClO_4$).—This singular compound cannot be prepared without considerable danger, since it explodes with extraordinary violence when heated to a little beyond 212° ; a similar result is produced by friction or by a sudden blow, and sometimes it explodes by merely lifting the vessel which contains it, or even without any assignable cause. In order to obtain it, a few grains of crystallized baric ethylsulphate are placed in a tube retort with an equal weight of baric perchlorate, and are cautiously distilled by the heat of an oil bath, which must not be allowed to exceed 338° (170° C.). The ether is heavier than water, and has a sweetish pungent taste, somewhat resembling that of cinnamon. Its boiling point is not known with accuracy, but it is above 212° . The explosive character of the compound depends upon the large proportion of oxygen which it contains in union with chlorine, for which the attraction of oxygen is very small, whilst hydrogen has a powerful attraction for both chlorine and oxygen; the chlorine forms hydrochloric acid with 1 atom of hydrogen, and the oxygen is sufficient to convert the carbon into the form of carbonic oxide and the remaining hydrogen into water; $C_2H_5ClO_4 = 2CO + 2H_2O + HCl$.

(1154) SILICIC ETHERS.—Few of the ethers are more remarkable than those obtained by Ebelmen with silica. In these compounds the polybasic character of the acid is preserved.

Tetrethyl Silicate [$(C_2H_5)_4SiO_4$], formerly *Dibasic Silicate of Ethyl*. *Sp. gr. of liq* 0.933; *of vap.* 7.32; *Rel. wt.* 104; *Boil. pt.* 330° ($165^\circ.5$ C.).—When absolute alcohol is added gradually to silicon tetrachloride, a powerful reaction occurs; hydrochloric acid is evolved in abundance, and a colourless liquid is obtained, which, when submitted to distillation, at first evolves hydrochloric acid, but the boiling point rises rapidly until it reaches 330° , at which temperature pure tetrethyl silicate distils over. It is a limpid liquid, of a pleasant ethereal odour, and a hot taste resembling that of pepper. It is combustible, and burns with a flame of dazzling whiteness, depositing pulverulent silica. The

molecular volume of this body affords a good illustration of the tetrad character of silieon. This ether is not miscible with water, but is decomposed by it with the separation of gelatinous silicic hydrate. If this decomposition be allowed to take place slowly, by placing an imperfectly closed vessel containing the ether in a moist atmosphere, the silica is gradually deposited in the form of a hard transparent solid, resembling quartz in appearance.

Diethyl Silicate, or *Silicic Ether* $[(C_2H_5)_2SiO_3]$?—A second ether, containing only half the quantity of ethyl oxide present in the foregoing compound, may be procured by acting upon alcohol of sp. gr. 0.838 with silicon tetrachloride, and distilling; tetrethyl silicate is formed at the same time, and the first portions of the distillate consist entirely of this compound; but by degrees the boiling point becomes higher, and when it reaches 662° (350° C.) the diethyl silicate passes over. The tetrethyl silicate is in fact transformed into the diethyl silicate by the action of the water present in the dilute alcohol, whilst alcohol is set free:—



If more water be added, a viscous compound is obtained, which, according to Ebelmen, contains a third ether, with twice as much silica as the foregoing one.

(1155) *Triethyl Borate* $[(C_2H_5)_3BO_3]$ or *Tribasic Boracic Ether*. Sp. gr. of liq. 0.8849; of vap. 5.31; Rel. wt. 73; Boil. pt. $246^\circ.2$ (119° C.).—This ether is obtained by the action of boron trichloride upon anhydrous alcohol; it is immediately decomposed by water. Boracic acid is readily soluble in anhydrous alcohol with evolution of heat. Ebelmen considers that under these circumstances a second ether is formed, which when pure is solid at ordinary temperatures. It softens at about 104° (40° C.), and can be drawn out into long threads. Its composition is not certainly known, but it has been represented as $[(C_2H_5)_2O, 2B_2O_3]$ analogous to ordinary borax.

(1156) *Ethyl Formiate*, or *Formic Ether* (C_2H_5, CHO_2) . Sp. gr. of liq. 0.915 at 64° ; of vap. 2.573; Rel. wt. 37; Boil. pt. $127^\circ.3$ (53° C.).—This ether is readily obtained by distilling 7 parts of dry sodic formiate with 10 of oil of vitriol, and 9 of alcohol of sp. gr. 0.825. Wöhler prepares it from a mixture of 10 parts of starch, with 37 of finely powdered black oxide of manganese, and 15 parts of alcohol, 15 of water, and 30 of oil of vitriol: the whole is distilled by a gentle heat in a capacious retort. The formic acid generated by the oxidation of the starch, reacts upon the alcohol at the moment of its formation. Formic ether does not mix with the water which accompanies it; and is purified by washing with water, and rectification from calcic chloride. Formic ether is also a secondary product of the reaction of nitric acid upon alcohol. When pure it is colourless, and has an agreeable odour and taste, recalling that of peach kernels. If left in contact with water, it becomes readily resolved into formic acid and alcohol.

(1157) *Ethyl Acetate*, or *Acetic Ether* $(C_2H_5, C_2H_3O_2)$. Sp. gr.

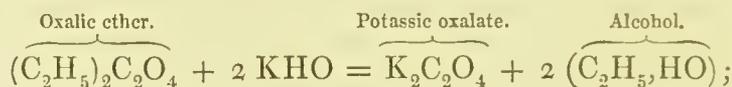
of liq. 0.89; of vap. 3.067; Rel. wt. 44; Boil. pt. 165°·2 (74° C.).—Acetic acid, if repeatedly distilled with alcohol, gives rise to the formation of acetic ether, but the effect is much hastened by the addition of sulphuric acid to the liquid. A mixture of 6 parts of alcohol, 4 of glacial acetic acid, and 1 part of oil of vitriol, yields the ether with facility. When a volume of liquid equal to that of the alcohol employed has come over, the process is stopped; the distillate is washed twice with its own bulk of water, and rectified from calcic chloride. Sodie or plumbic acetate may be substituted for acetic acid in the foregoing process, but then a larger quantity of oil of vitriol is needed. If 6 parts of alcohol be employed, 100 of sodie acetate and 15 of oil of vitriol may be used; or 24 parts of plumbic acetate (dried) and 9 of oil of vitriol.

Acetic ether has a burning taste and an agreeable odour, remotely resembling that of apples; a small quantity of it appears to be contained in several varieties of wine. Water dissolves about one-seventh of its bulk of it. Acetic ether is a good solvent for the essential oils, for the resins, and for pyroxylin. A mixture of this ether with an alcoholic solution of caustic potash, is immediately decomposed into potassic acetate and alcohol. Acetic ether dissolves calcic chloride readily, and forms with it a crystallizable compound, which yields the ether unchanged on the application of heat.

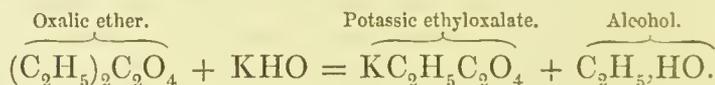
(1158) *Ethyl Butyrate*, or *Butyric Ether* ($C_2H_5, C_4H_7O_2$). *Sp. gr. of liq.* 0.9041; *of vap.* 4.04; *Rel. wt.* 58; *Boil. pt.* 239° (115° C.).—This ether may be formed with great facility. If a mixture of 2 parts of alcohol and 2 of butyric acid be agitated with 1 part of oil of vitriol, which may even be diluted with an equal bulk of water, the liquid, on standing, separates into two layers, the upper of which is butyric ether. It is nearly insoluble in water, and when diluted with alcohol, has the odour of pine-apple, constituting, indeed, what is sold as *pine-apple oil*. It appears to be present in old rum, and is used for heightening the flavour of this spirit. The melon and strawberry are supposed to owe a portion of their flavour to the presence of this compound. In order to purify the ether, it must be agitated with water, and rectified after standing upon calcic chloride.

(1159) *Cenanthic Ether* (probably a mixture of rutic and caprylic ethers). *Sp. gr. of liq.* 0.872; *of vap.* 7.042 (Delffs).—This ether is a fragrant liquid of a stupefying, extremely powerful odour, which is the cause of the peculiar smell that characterizes grape wine, and which adheres so tenaciously to vessels in which wine has been kept; hence its name, from *οἶνος*, wine. When large quantities of wine, or the lees of wine, are distilled, this ether passes over, mixed with free rutic and caprylic acids (Fischer, *Lieb. Ann.* cxviii. 307), in the form of an oily layer; the crude product is gently heated with a solution of sodie carbonate, which removes the free acid, whilst the ether floats as an oily layer upon the surface. It boils at from 435°·2 to 446° (224° to 230° C.), and emits a very dense and highly inflammable vapour. The quantity of this ether appears to increase with the age of the wine.

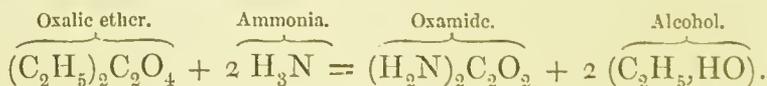
(1160) *Diethyl Oxalate*, or *Oxalic Ether* $[(C_2H_5)_2C_2O_4]$. *Sp. gr. of liq.* 1·0929; *of vap.* 5·087; *Rel. wt.* 73; *Boil. pt.* $363^{\circ}2$ (184° C.).—This is one of the most interesting of the numerous ethers which are formed with the organic acids. It is obtained by distilling rapidly a mixture of 4 parts of alcohol (sp. gr. 0·825), 5 of oil of vitriol, and 4 of hydrie-potassic oxalate (HKC_2O_4, H_2O). The distillate should be washed with water, and rectified from litharge to keep back any traces of free oxalic acid. Oxalic ether is heavier than water. It is colourless, and has an agreeable ethereal odour and taste. If pure it may be kept unchanged in contact with water, but if it retain any acid it is slowly decomposed into oxalic acid and alcohol; an excess of caustic potash decomposes it with rapidity into normal potassic oxalate and alcohol; but if the quantity of potash be small, alcohol and potassic ethyloxalate (oxalovinate) are formed; the reaction in the first case being:—



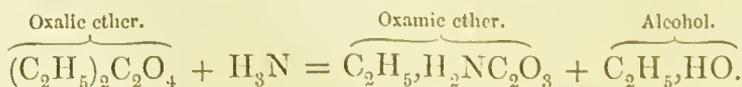
and in the second case:—



When an aqueous or an alcoholic solution of ammonia is added to oxalic ether, a somewhat analogous decomposition is effected, an excess of ammonia giving rise to the formation of oxamide and alcohol. Indeed, this reaction furnishes one of the best methods of procuring oxamide:—



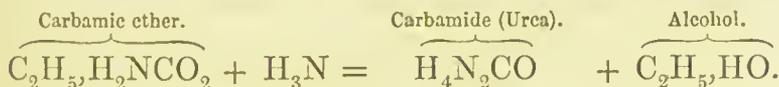
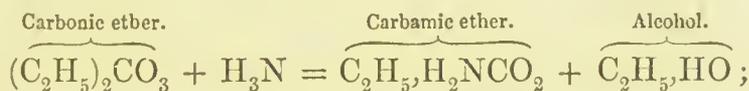
If the ether be in excess, the decomposition is different; alcohol, and a substance soluble in alcohol but insoluble in water, crystallizing in beautiful pearly tables, is formed: this body was originally termed *oxamethane*, but it is now admitted to be *oxamic ether*, or the ether of amidated oxalic acid (1356):—



If equal parts of potassic ethyloxalate and potassic methylsulphate be thoroughly dried, then mixed, and submitted to distillation, a curious double ether (*methyl-ethyl oxalate*, CH_3, C_2H_5, C_2O_4) is obtained. It forms a yellowish oil, heavier than

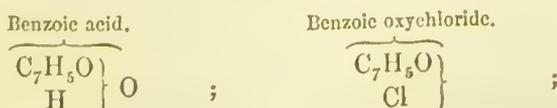
water, of sp. gr. 1.127, boiling at about 329° (165° C.) and emitting a vapour of sp. gr. 4.67.

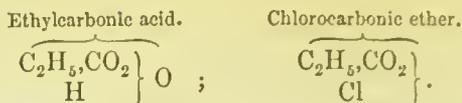
(1161) *Diethyl Carbonate*, or *Carbonic Ether* [(C₂H₅)₂CO₃]. *Sp. gr.* 0.975; *of vap.* 4.09; *Rel. wt.* 59; *Boil. pt.* 257° (125° C.).—This ether cannot be obtained by the ordinary mode of preparing these compounds. It may be formed by heating argentic carbonate with ethyl iodide in a closed tube; but it is generally procured by heating sodium or potassium with oxalic ether, in which case carbonic oxide is disengaged abundantly, whilst carbonic ether distils over, and oxalate of the alkali-metal remains in the retort. This reaction does not admit of a simple expression by an equation. Carbonic ether is a very mobile liquid, of a sweet aromatic odour; it is not very inflammable; but it is readily decomposed by an alcoholic solution of potash. When heated in a sealed tube with an alcoholic solution of ammonia, alcohol, and carbamic ether (urethane) are formed; and if the temperature be raised to about 356° (180° C.), the excess of ammonia slowly converts the carbonic ether into alcohol and urea, or carbamide (Natanon); both decompositions being analogous to those which oxalic ether undergoes with greater facility by the same reagents:—



Urethane, or *Carbamic Ether* (C₂H₅,H₂NCO₂). *Sp. gr. of vap.* 3.14; *Rel. wt.* 44.5; *Boil. pt.* 356° (180° C.).—This is a substance which resembles spermaceti in appearance; it evinces a remarkable disposition to crystallize, and forms large transparent leaflets, which are fusible below 212°, and very soluble in alcohol and in ether. If distilled in a moist state it gives off large quantities of ammonia.

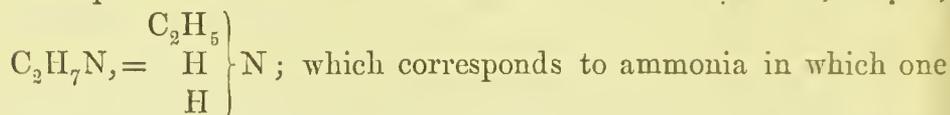
(1162) *Chlorocarbonic Ether* (C₂H₅,CClO₂). *Sp. gr. of liq.* 1.133; *of vap.* 3.823; *Rel. wt.* 54.2; *Boil. pt.* 201° 2 (94° C.).—This compound is obtained by absorbing phosgene gas (388) with absolute alcohol, and rectifying the product from powdered litharge and calcic chloride. It is a colourless, very limpid liquid, which emits a suffocating odour, and irritates the eyes powerfully. Its vapour burns with a green flame. It is not soluble in cold water, but is decomposed by boiling water. Gerhardt represents this compound as an oxychloride, which bears the same relation to ethylcarbonic acid that benzoic oxychloride (chloride of benzoyl) does to benzoic acid:—



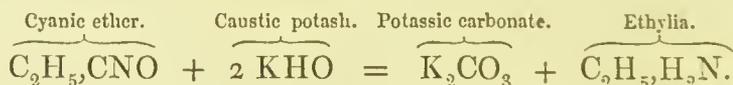


(1163) *Triethyl Citrate*, or *Tribasic Citric Ether* $[(\text{C}_2\text{H}_5)_3\text{C}_6\text{H}_5\text{O}_7]$, may be obtained by saturating an alcoholic solution of citric acid with hydrochloric acid, neutralizing with sodic carbonate, and agitating the liquid with ordinary ether. The ethereal solution rises to the surface on standing; and if the ordinary ether be expelled by the heat of a water bath, citric ether is left as a colourless oily liquid.

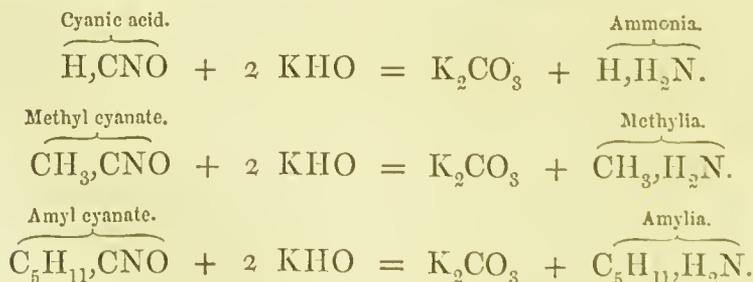
(1164) *Ethyl Cyanate*, or *Cyanic Ether* $(\text{C}_2\text{H}_5, \text{CNO})$. *Sp. gr. of liq.* 0.898; *of vap.* 2.475; *Rel. wt.* 35.5; *Boil. pt.* $140^\circ (60^\circ \text{C.})$.—This ether may be prepared by distilling potassic cyanate with potassic ethylsulphate. It is an extremely pungent volatile liquid of high refracting power. Ethyl cyanate, when decomposed by caustic potash, undergoes a remarkable transformation, in consequence of which it is converted into a new base, ethylia,



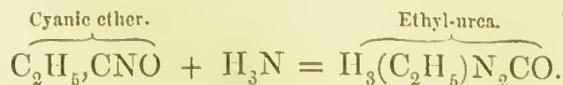
atom of hydrogen has been displaced by ethyl (C_2H_5) , the organic radicle of alcohol (Wurtz, *Ann. de Chimie*, III. xxx. 447).



A similar decomposition ensues when the cyanic ethers of the other alcohols are treated with caustic potash, a series of alkalies homologous with ethylia being formed. For instance, starting with cyanic acid, which contains hydrogen instead of one of the radicles of the alcohols:—

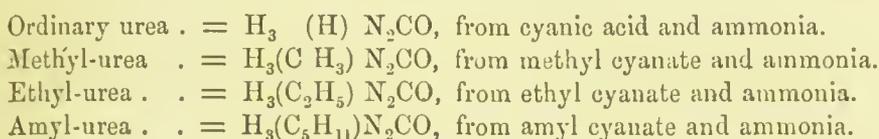


When cyanic ether is treated with ammonia, combination occurs between the two bodies, and a body homologous with urea, *ethyl-urea* $(\text{C}_3\text{H}_8\text{N}_2\text{O})$, is formed (1604):—

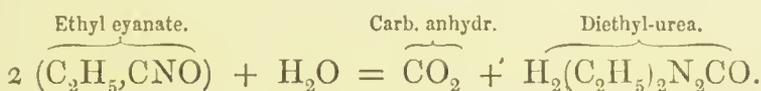


The cyanic ethers of the other monobasic alcohols, when treated

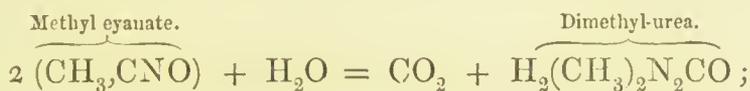
with ammonia, form homologous bodies, or ureas, in which the place of one atom of hydrogen has been supplied by one equivalent of the radicles of the various alcohols: for instance,



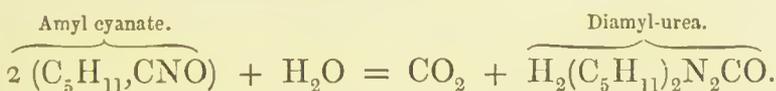
The various cyanic ethers when placed in contact with water undergo decomposition; they evolve carbonic acid, and the members of another series of ureas are produced, in which two atoms of the hydrogen contained in ordinary urea have been displaced by two equivalents of the alcohol radicle; for example:—



Methyl cyanate yields under like circumstances dimethyl-urea;



and amyl cyanate yields diamyl-urea;



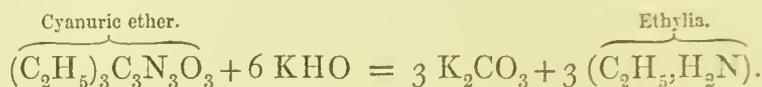
It may be observed that dimethyl-urea is metameric with ethyl-urea, though not identical with it; for



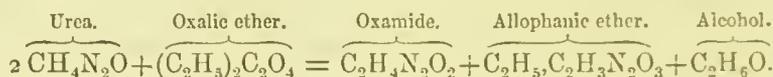
Methyl cyanate undergoes a singular spontaneous change even when sealed up in a tube, in consequence of which in the course of a few hours it becomes converted into a crystalline mass of methyl cyanurate.

(1165) *Triethyl Cyanurate*, or *Cyanuric Ether* $[(C_2H_5)_3C_3N_3O_3]$.
Sp. gr. of vap. 7.4; *Rel. wt.* 105.5; *Freez. pt.* $204^{\circ}.8$ (96° C.);
Boil. pt. $487^{\circ}.4$ (253° C.).—This compound is obtained by distilling a mixture of potassic ethylsulphate and cyanurate, by the heat of an oil-bath. It is polymeric with cyanic ether; but it is solid at ordinary temperatures, and may be obtained from its solution in ether in brilliant crystals, which melt at 205° , forming a liquid heavier than water, which may be distilled unaltered. When treated with caustic potash, it yields ethylia as the ultimate result. The cyanuric ethers of the other alcohols yield the cor-

responding alkalis when similarly treated, the final products being identical with those which are furnished when the cyanic ethers of the same series are similarly decomposed:—



Allophanic Ether ($\text{C}_2\text{H}_5, \text{C}_2\text{H}_3\text{N}_2\text{O}_3$).—This compound was long mistaken for cyanuric ether. It is obtained by transmitting the vapours of cyanic acid into alcohol. Allophanic ether may also be obtained by heating for several hours in a sealed glass tube a mixture of urea and oxalic ether, when a reaction takes place which may be represented by the following equation (Hlasiwetz):—



It is a solid crystalline, colourless, tasteless, inodorous body, which is insoluble in cold water, but is soluble in boiling water, in ether, and in boiling alcohol. It is soluble in cold baryta water, which converts it into alcohol, and a new salt, baric allophanate ($\text{Ba } 2 \text{C}_2\text{H}_3\text{N}_2\text{O}_3$). Allophanic acid is not known except in combination (1605).

(d) *Ethers not derived from Ethyl Alcohol.*

(1166) METHYL OXIDE, or *Methyl Ether* [$(\text{CH}_3)_2\text{O}$]. *Sp. gr. of vap.* 1.617; *Rel. wt.* 23.—By distilling 1 part of pyroxylic spirit and 4 parts of oil of vitriol, a colourless gas, homologous with ethyl ether, is disengaged. It is accompanied by carbonic and sulphurous acids, which may be removed by allowing the gaseous mixture to stand for twenty-four hours in contact with slaked lime. Gaseous methyl ether has a peculiar oppressive ethereal odour; it is freely soluble in water, which dissolves about 37 times its bulk of the gas, and acquires its odour and pungent ethereal taste. It is still more soluble in alcohol. This gas is very inflammable, and burns with a pale flame; it is liquefiable at a temperature of -32.8 (-36°C.) and boils at -5.8 (-21°C.) (Berthelot). This substance, it should be observed, is metameric with alcohol, with which it corresponds, both in its molecular weight and in the density of its vapour.

Compounds of methyl may be obtained with chlorine, bromine, iodine, and sulphur, forming chloride, bromide, iodide, and sulphide of methyl: all these bodies are inflammable: the chloride is gaseous at ordinary temperatures; the bromide and the iodide are volatile liquids of considerable density. All these compounds are prepared like the corresponding compounds of ethyl. Combinations of methyl with the radicles of the oxyacids also exist, forming a class of compounds parallel with the ethylic oxyacid

ethers: thus we have sulphate, nitrate, oxalate, acetate of methyl, and so on.

(1167) *Dimethyl Sulphate, Sulphate of Methyl, or Methyl-Sulphuric Ether* $[(\text{CH}_3)_2\text{SO}]$. *Sp. gr. of liq.* 1.324; *of vap.* 4.565; *Rel. wt.* 63; *Boil. pt.* $370^{\circ}\cdot 4$ (188° C.)—is procured by transmitting dry methyl ether over sulphuric anhydride, or by distilling 1 part of pyroxylic spirit with 8 or 10 parts of oil of vitriol; in the latter process the ether passes over as a tasteless oily liquid, and collects in the receiver. It must be washed with cold water, digested on quick-lime to free it from sulphurous acid and water, and then rectified. It is thus obtained as a colourless liquid which is slowly decomposed by water in the cold, but is quickly resolved by it at the boiling point, into wood spirit and methyl-sulphuric acid.

(1168) *Methyl Acetate, Acetate of Methyl, or Methyl-Acetic Ether* $(\text{CH}_3\text{C}_2\text{H}_3\text{O}_2)$. *Sp. gr. of liq.* 0.9562; *of vap.* 2.563; *Rel. wt.* 37; *Boil. pt.* $133^{\circ}\cdot 3$ ($56^{\circ}\cdot 3\text{ C.}$).—This compound is formed abundantly during the destructive distillation of wood, and enters largely into the composition of crude wood spirit. It is a colourless liquid, of an agreeable ethereal odour, and is freely soluble in water. The hydrated alkalis decompose it into acetic acid and wood spirit. It may be obtained by distilling 2 parts of wood spirit with 1 part of concentrated acetic acid, and 1 of oil of vitriol; the crude product is rectified from calcic chloride, which retains the unchanged wood spirit.

(1169) *Dimethyl Oxalate, Oxalate of Methyl, or Methyl-Oxalic Ether* $[(\text{CH}_3)_2\text{C}_2\text{O}_4]$. *Rel. wt.* 59; *Boil. pt.* $321^{\circ}\cdot 8$ (161° C.); *Sp. gr. of liq. at* 122° , 1.1566.—This compound is solid at ordinary temperatures, and may be sublimed without difficulty. It may be obtained by mixing 1 part of crude wood spirit with one of oil of vitriol, and distilling the mixture with 2 parts of hydric-potassic oxalate $(\text{HKC}_2\text{O}_4\cdot\text{H}_2\text{O})$. The materials should be allowed to remain in contact for 24 hours before the distillation is proceeded with. A volatile liquid first passes over, followed by crystals of the ether. When these crystals begin to appear in the neck of the retort, the receiver must be changed, and the distillation carried on as long as the crystals continue to be formed. The crystals must be purified by strong pressure between folds of blotting-paper, and must afterwards be maintained for some time in a melted state by gentle heat, in order to drive off adhering volatile matters.

(1170) A compound of methyl with one of the organic acids has been discovered ready formed in the vegetable kingdom, con-

stituting, in combination with salicylic acid, *methyl salicylate* ($\text{CH}_3\text{C}_7\text{H}_5\text{O}_3$), the essential oil procured from the *Betula lenta*, a species of birch, and from the *winter green* (*Gaultheria procumbens*): a compound exactly resembling the natural oil is obtained by distilling a mixture of wood spirit with salicylic and sulphuric acids. This compound possesses the power of uniting with bases like an acid (1458).

(1171) The following table shows the composition and some of the physical properties of the more important methylic ethers. The densities to which an asterisk is affixed were taken at 32°F .

| Methyl= (CH_3) . | Formula. $\boxed{\quad}$ | Boiling Point. | | Specific Gravity. | | Rel. Wt. of Vapour. H=1. |
|---------------------------|---|--------------------|--------------------|-------------------|---------|-----------------------------|
| | | $^\circ\text{F}$. | $^\circ\text{C}$. | Liquid. | Vapour. | |
| Methyl oxide . . | $(\text{CH}_3)_2\text{O}$ | -5.8 | -21 | | 1.617 | 23 |
| „ sulphide . | $(\text{CH}_3)_2\text{S}$ | 105.8 | 41 | 0.845 | 2.115 | 31 |
| „ disulphide | $(\text{CH}_3\text{S})_2$ | about 240 | 116 | 1.048 | 3.310 | 47 |
| „ chloride . | CH_3Cl | -7.6 | -22 | | 1.731 | 25.2 |
| „ bromide . | CH_3Br | 55.4 | 13 | 1.644* | | |
| „ iodide . | CH_3I | 111.2 | 44 | 2.1992* | 4.883 | 71 |
| „ cyanide . | CH_3CN | 170.6 | 77 | | 1.45 | 20.5 |
| „ sulphate . | $(\text{CH}_3)_2\text{SO}_4$ | 370.4 | 188 | 1.324 | 4.565 | 63 |
| „ nitrate . | CH_3NO_3 | 150.8 | 66 | 1.182 | 2.640 | 38.5 |
| „ borate . | $(\text{CH}_3)_3\text{BO}_3$ | 161.6 | 72 | 0.955 | 3.66 | 52 |
| „ formiate . | CH_3CHO_2 | 92.3 | 33.5 | 0.9984* | 2.084 | 30 |
| „ acetate . | $\text{CH}_3\text{C}_2\text{H}_3\text{O}_2$ | 133.3 | 56.3 | 0.9562* | 2.563 | 37 |
| „ butyrate . | $\text{CH}_3\text{C}_4\text{H}_7\text{O}_2$ | 203.2 | 95 | 0.9209* | 3.52 | 51 |
| „ valerate . | $\text{CH}_3\text{C}_5\text{H}_9\text{O}_2$ | 241.1 | 116.2 | 0.9015* | | 58 |
| „ cyanate . | CH_3CNO | about 104 | 40 | | | 28.5 |
| „ cyanurate | $(\text{CH}_3)_3\text{C}_3\text{N}_3\text{O}_3$ | 525.2 | 274 | | 5.98 | 85.5 |
| „ benzoate . | $\text{CH}_3\text{C}_7\text{H}_5\text{O}_2$ | 389.3 | 198.5 | | 4.717 | 68 |
| „ oxalate . | $(\text{CH}_3)_2\text{C}_2\text{O}_4$ | 321.8 | 161 | 1.1566 | | 59 |
| „ salicylate | $\text{CH}_3\text{C}_7\text{H}_5\text{O}_3$ | 431.6 | 222 | 1.18 | 5.42 | 76 |

(1172) *Propylic, Butylic, Amylic, and Octylic Ethers*.—1. *Propylic Ether* was obtained by Chancel, but it is little known, and its derivatives have scarcely been investigated. Isopropyl alcohol also may be made to yield ethers, such as isopropyl iodide, bromide, and acetate.

2. *Tetryl, or Butyl Ether*, was first described by Kolbe as one of the products of the voltaic decomposition of potassic valerate. Since that time, Wurtz has published a memoir on the ethers of the butylic series, to which the reader is referred for a description of their properties (*Ann. de Chimie*, III. xlii. 129).

3. *Amyl Oxide, or Amyl Ether* [$(\text{C}_5\text{H}_{11})_2\text{O}$], *Boil. pt.* 348.8 (176°C).—This compound is obtained only in small quantity by the distillation of fousel oil with sulphuric acid, since by this method the greater part of the alcohol is converted into hydrocarbons polymerie with olefiant gas. Balard states that he also procured it by decomposing amyl chloride ($\text{C}_5\text{H}_{11}\text{Cl}$) by means of a concentrated solution of potash: the mixture is to be sealed up in a tube and heated for some time to 212° . The liquid which floats upon the surface has a fragrant odour, and boils at about 233.6 (112°C). It is, however, doubtful, according to Williamson, whether this be not amyl-ethyl ether. No analysis of it has been made. It is probable that some of the compound ethers of the amylic

series are the bodies to which the odour and flavour of certain fruits belong (1140), but they present no special points of interest, and therefore need no detailed description. They may be procured by methods analogous to those which were described when treating of the different ethylic ethers. The amylic series was carefully investigated by Cahours (*Ann. de Chimie*, II. lxx. and lxxv.).

The following table contains the principal ethers of the tetrylic and amylic groups:—

Butylic or Tetrylic Ethers.

| Tetryl=C ₄ H ₉ . | Formula. | Boiling Point. | | Sp. Gravity. | | Rel. Wt. H=1. |
|--|--|----------------|------|--------------|---------|------------------|
| | | ° F. | ° C. | Liquid. | Vapour. | |
| Tetryl chloride . | C ₄ H ₉ Cl | 160 | 71·1 | | | 46·2 |
| „ bromide . | C ₄ H ₉ Br | 192·2 | 89 | 1·274 | 4·72 | 68·5 |
| „ iodide . | C ₄ H ₉ I | 249·8 | 121 | 1·604 | 6·217 | 92 |
| „ cyanide . | C ₄ H ₉ Cy | 257 | 125 | 0·810 | 2·892 | 41·5 |
| „ nitrate . | C ₄ H ₉ NO ₃ | 266 | 130 | | | 59·5 |
| „ acetate . | C ₄ H ₉ ·C ₂ H ₃ O ₂ | 237·2 | 114 | 0·884 | 4·073 | 58 |
| „ carbonate | (C ₄ H ₉) ₂ CO ₃ | 374 | 190 | | | 87 |

Amylic Ethers.

| Amyl=C ₅ H ₁₁ . | | | | | | |
|---------------------------------------|--|-------|------|-------|-------|------|
| Amyl oxide . . | (C ₅ H ₁₁) ₂ O | 348·8 | 176 | | | 79 |
| „ sulphide . | (C ₅ H ₁₁) ₂ S | 420·8 | 216 | | 6·3 | 87 |
| „ disulphide | (C ₅ H ₁₁) ₂ S ₂ | 480? | 249? | 0·918 | | |
| „ chloride . | C ₅ H ₁₁ Cl | 215·6 | 102 | | 3·77 | 53·2 |
| „ bromide . | C ₅ H ₁₁ Br | 246·2 | 119 | 1·137 | | 75·5 |
| „ iodide . . | C ₅ H ₁₁ I | 294·8 | 146 | 1·511 | 6·675 | 99 |
| „ cyanide . | C ₅ H ₁₁ Cy | 294·8 | 146 | 0·806 | 3·335 | 48·5 |
| „ nitrate . . | C ₅ H ₁₁ NO ₃ | 298·4 | 148 | 0·994 | | 66·5 |
| „ formiate . | C ₅ H ₁₁ ·CHO ₂ | 237·2 | 114 | 0·884 | | 58 |
| „ acetate . | C ₅ H ₁₁ ·C ₂ H ₃ O ₂ | 271·4 | 133 | 0·869 | 4·458 | 65 |
| „ valerate . | C ₅ H ₁₁ ·C ₅ H ₉ O ₂ | 368·6 | 187 | 0·864 | 6·17 | 86 |
| „ carbonate | (C ₅ H ₁₁) ₂ CO ₃ | 435·2 | 224 | 0·914 | | 101 |
| „ oxalate . | (C ₅ H ₁₁) ₂ C ₂ O ₄ | 503·6 | 262 | | 8·4 | 115 |
| „ silicate . | (C ₅ H ₁₁) ₄ SiO ₄ | 517 | 325 | 0·868 | 11·7 | 188 |

4. Bouis has examined (*Ann. de Chimie*, III. xlv. 128) several of the ethers of the *octylic* (caprylic) series: many of them possess a very agreeable and fragrant odour, which may possibly lead to their employment as perfumes; but they do not present sufficient importance to require further notice in this work. These ethers may generally be obtained by methods analogous to those directed to be used for the preparation of the corresponding methylic and ethylic ethers.

§ IV. ACTION OF CHLORINE ON THE ETHERS AND ALCOHOLS.

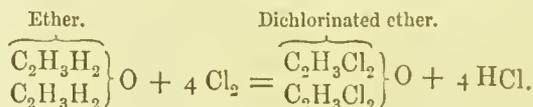
(1173) Chlorine exerts a powerful action upon the alcohols, the first effect being to remove hydrogen which is not replaced, and thus to form aldehyds. If the action is continued, hydrogen

continues to be removed, but a substitution of a corresponding number of atoms of chlorine occurs.

Chlorine also acts upon the ethers energetically, forming by substitution numerous compounds, in which a certain number of atoms of hydrogen are displaced by a corresponding number of atoms of chlorine. Similar effects are produced by bromine and by iodine, though the action of these elements is less energetic. Solar light greatly increases the facility with which these reactions are effected. The general law which regulates these substitutions will be best understood by the description of a few of the most important compounds thus formed.

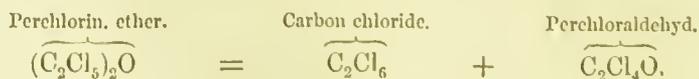
(a) *Chlorinated Derivatives from Ethyl Alcohol.*

(1174) *Dichlorinated Ether* $[(C_2H_3Cl_2)_2O]$. *Sp. gr.* 1.5008.—When dry chlorine is passed into anhydrous ether, abundance of hydrochloric acid is formed; two of the five atoms of hydrogen in each half of the molecule of ether are displaced, and in their stead two atoms of chlorine enter into the compound. Four molecules of chlorine, and one molecule of ether, thus produce four molecules of hydrochloric acid, and one molecule of this new body.



It forms a heavy, colourless, oily liquid, neutral to litmus paper, with an odour and taste resembling that of fennel; at 28.4° (14.0° C.) it undergoes decomposition before it begins to boil, and by contact with water it is gradually converted into acetic and hydrochloric acids; $(C_2H_3Cl_2)_2O + 3 H_2O = 2 C_2H_4O_2 + 4 HCl$. An alcoholic solution of potash immediately produces a similar decomposition, potassic chloride and acetate being formed.

Perchlorinated Ether $[(C_2Cl_5)_2O]$. *Sp. gr. of solid* 1.9; *Fusing pt.* $156^\circ.2$ (69° C.).—If ether, saturated with chlorine, be exposed in a vessel with excess of the gas, to the direct rays of the sun, a crystalline body is formed, which is soluble in hot alcohol, and crystallizes on cooling in octahedra with a square base. This substance represents ether, in which the whole of the hydrogen has been displaced by chlorine. Under certain circumstances the perchlorinated ether, at the moment of its formation, is resolved into Faraday's solid chloride of carbon, and into a body corresponding to aldehyd, but in which all the hydrogen has been displaced by chlorine: and a similar transformation occurs when the vapour of perchlorinated ether is exposed to a temperature of about 590° (310° C.).



An alcoholic solution of potash decomposes perchlorinated ether, but the reaction is complicated, owing to the presence of compounds derived from the alcohol employed.

The action of chlorine upon ethyl chloride is more regular; with suitable care it is possible to obtain from it compounds in which each atom of hydrogen

is successively removed, and its place supplied by chlorine, as shown in the table given at page 78.

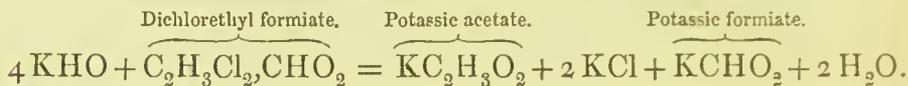
(1175) *Action of Chlorine upon Compound Ethers.*—The foregoing examples are true cases of substitution; but in some rare instances the chlorine unites directly with the compound, producing a new chlorinated body, without separation of hydrogen or formation of hydrochloric acid; a case of this kind is presented in pyromucic ether ($C_2H_5, C_5H_3O_3$), each molecule of which absorbs four atoms, or rather more than its own weight of chlorine, and from a crystalline solid, it becomes converted into a colourless syrupy liquid, $C_2H_5, C_5H_3Cl_4O_3$. A more familiar example is offered in the direct union of chlorine and olefiant gas; these two gases, when mingled in equal measures, combine to form the oily liquid discovered by the Dutch chemists, and which, by the continued action of chlorine, yields a series of compounds (488), the last member of which is Faraday's chloride of carbon, (C_2Cl_6).

The following table exhibits in one view the effect of chlorine in its successive stages, upon alcohol and ether, and on some of the compound ethers.

| | Normal Ethers. | Diechlorinated. | Perchlorinated. | Various Stages. |
|-------------------|----------------------|-------------------------|-----------------------|-------------------------|
| Alcohol . . . | C_2H_5, HO | | C_2Cl_5, HO | |
| Ether . . . | $(C_2H_5)_2O$ | $(C_2H_3Cl_2)_2O$ | $(C_2Cl_5)_2O$ | |
| Carbonic ether . | $(C_2H_5)_2CO_3$ | $(C_2H_3Cl_2)_2, CO_3$ | $(C_2Cl_5)_2CO_3$ | |
| Oxalic „ . | $(C_2H_5)_2C_2O_4$ | | $(C_2Cl_5)_2C_2O_4$ | |
| Formic „ . | C_2H_5, CHO_2 | $C_2H_3Cl_2, CHO_2$ | C_2Cl_5, CHO_2 | |
| Acetic „ . | $C_2H_5, C_2H_3O_2$ | $C_2H_3Cl_2, C_2H_3O_2$ | $C_2Cl_5, C_2H_3O_2$ | |
| Trichloroacetic . | $C_2H_5, C_2Cl_3O_2$ | | $C_2Cl_5, C_2Cl_3O_2$ | $C_2HCl_4, C_2Cl_3O_2$ |
| Benzoic „ . | $C_2H_5, C_7H_5O_2$ | | | |
| Pyromucic „ . | $C_2H_5, C_5H_3O_3$ | | | $C_2H_5, C_5H_3Cl_4O_3$ |

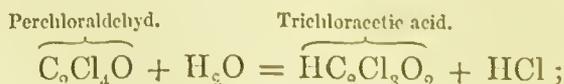
Experiment shows that, whether ether be free or in combination, the first two atoms of hydrogen are more readily removed from the atom of ethyl than the others, as indeed might be expected from the facility with which alcohol loses two atoms of hydrogen by oxidation, in the manufacture of acetic acid. All the compounds indicated in the third column of the table are represented as containing $(C_2H_3Cl_2)$; and when any one of these is submitted to the action of an alcoholic solution of caustic potash, it is decomposed; whilst potassic acetate and potassic chloride are found among the products. This circumstance can only be explained by supposing that, whenever the compound ethers of an organic acid into the composition of which hydrogen enters are submitted to the action of chlorine, the hydrogen is in

the first instance displaced from the ethyl; and subsequently, by prolonged continuance of the action, the displacement extends to the hydrogen contained in the acid radiæ of the compound. The mode in which the new bodies undergo decomposition, in many instances affords proof that the displacement is effected in this order. When, for example, chlorinated formic ether is decomposed, by an alcoholic solution of potash, potassic chloride with potassic acetate and formiate are the results.

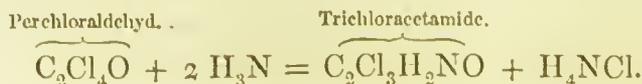


Now the compound $(\text{C}_2\text{H}_3\text{Cl}_2)_2\text{O}$, when decomposed by potash, yields potassic acetate and chloride (1174), so that the formiate is evidently derived from the undecomposed formic acid radiæ.

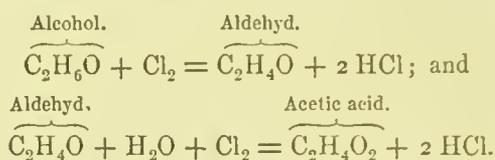
When chlorine is made to act upon the ethers under the combined influence of the sun's ray and of a high temperature, the whole of the hydrogen, both of the ethyl and of the acid combined with it, is displaced. These perchlorinated compound ethers, such as the perchloroacetic ether $(\text{C}_2\text{Cl}_5, \text{C}_2\text{Cl}_3\text{O}_2)$ and perchloroformic ether $(\text{C}_2\text{Cl}_5, \text{CClO}_2)$, are very unstable. They are readily decomposed by elevation of temperature and by alcohol, as well as by solutions of ammonia and of the fixed alkalies. When the perchlorinated ethyl ethers are subjected to a high temperature, the products obtained vary with the nature of the acid combined with the ether: but amongst these products perchloraldehyd $(\text{C}_2\text{Cl}_4\text{O})$ is always present. This body is doubtless derived from the compound $(\text{C}_2\text{Cl}_5)_2\text{O}$, which all those bodies contain, and which, at an elevated temperature (1174) splits into the carbon chloride, C_2Cl_6 and perchloraldehyd $\text{C}_2\text{Cl}_4\text{O}$. When the decomposition is effected by alcohol, or by an alcoholic solution of potash, amongst other bodies trichloroacetic acid $(\text{H}, \text{C}_2\text{Cl}_3\text{O}_2)$, or some product of its decomposition, is always found. This substance is the result of the action of water upon perchloraldehyd, hydrochloric acid being liberated, as is shown thus:—



and when ammonia is made to act upon one of these perchlorinated ethers, trichloroacetamide, which is always one of the products, is obtained by the following reaction upon perchloraldehyd:—



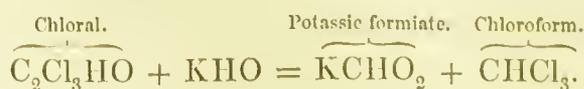
If chlorine be passed into dilute instead of into anhydrous alcohol, no chloral is formed; but instead of it, aldehyd, acetic acid, and hydrochloric acid are produced. In this case aldehyd appears to be the compound formed; and by a secondary reaction of aldehyd upon water at the moment of its formation, it appropriates an atom of oxygen from the water, whilst the chlorine removes the corresponding quantity of hydrogen:—



In order to obtain chloral in a state of purity, the alcohol is subjected for many hours to a current of chlorine, which is transmitted so long as it is absorbed. It is necessary at first to keep the alcohol cool, but afterwards the temperature must be gradually raised until the liquid boils. The crude product is mixed with three times its bulk of oil of vitriol, and distilled at a gentle heat. This operation must be repeated, and the product finally distilled over quicklime. Stædelcr finds that chloral may also be formed by distilling a mixture of one part of starch (or sugar) with 7 parts of hydrochloric acid, and 3 of peroxide of manganese; formic and carbonic acids, and other bodies accompany it.

Chloral is in many respects a remarkable body. It is a colourless, oily-looking fluid, of a peculiar penetrating odour, which produces a flow of tears; when dropped upon paper it leaves a transient greasy stain. It is soluble in water, alcohol, and ether. If mixed with a small quantity of water, much heat is extricated, and a crystalline hydrate is formed. One of its most singular properties is the change which it undergoes spontaneously when kept; in a few days anhydrous chloral becomes converted into a tough white porcellanous-looking mass, isomeric with the liquid form, into which, by distillation, it can be again converted. This white substance is insoluble in alcohol, in ether, and in water; but by contact with water it is gradually converted into crystallized hydrated chloral. The facility of thus effecting its transformation into isomeric modifications indicates a certain resemblance to aldehyd in the instability of its molecular arrangement.

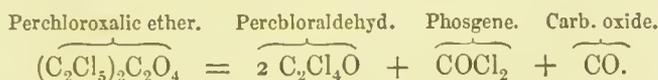
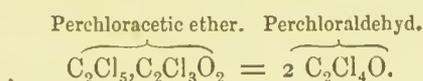
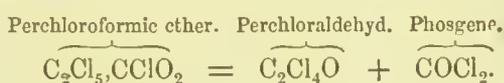
An alcoholic solution of potash converts chloral immediately into potassic formiate and chloroform:—



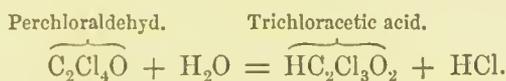
This fact cannot, however, be supposed to indicate much respect-

ing the grouping of the component elements of chloral, the unstable equilibrium of which is evidenced by the facility with which chloral spontaneously passes from the liquid to the solid condition. There is no doubt that the constitution of the body is very different in these two forms; and if thus, whilst unsolicited by any extraneous chemical forces, its molecular arrangement is so readily altered, it is obvious that the results of its decomposition under the influence of powerful chemical agents will throw but little light upon the probable grouping of its constituent elements.

(1177) *Perchloraldehyd* (C_2Cl_4O). *Sp. gr. of liq.* 1.603; *of vap.* 6.32; *Rel. wt.* 91; *Boil. pt.* $244^{\circ}.4$ ($118^{\circ}C.$).—This body is obtained by transmitting the vapour of perchlorinated ether (C_2Cl_5O) through heated tubes (1174), a mixture of solid carbon chloride and perchloraldehyd being the result. The two compounds may be separated by distillation, since the carbon chloride is the less volatile of the two. Perchloraldehyd is also always one of the products of the decomposition of the compound chlorinated ethylic ethers by heat (1175) of which the following may be taken as examples:—



It is a transparent, fuming, volatile liquid, which emits a suffocating odour, and turns the skin white if allowed to fall upon it. Water decomposes it gradually into hydrochloric and trichloroacetic acids:—

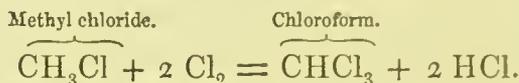


(1178) Bromine resembles chlorine in its action upon alcohol, forming *bromal* (C_2Br_3HO), which is a colourless oil of sp. gr. 3.34, boiling above 212° .

(b) *Chlorinated Derivatives from other Alcohols and their Ethers.*

(1179) It will be unnecessary to enter into any detailed description of the innumerable compounds which may be formed from the simple and compound ethers of the other alcohols, by the substitution of chlorine, bromine, and iodine for hydrogen; for, with one exception, which occurs in the case of chloroform, they present but little to arrest the attention of the chemist. They have been minutely studied by Malaguti, Cahours, and Cloez, to whose various papers in the *Annales de Chimie*, the reader is referred for further information on the subject.

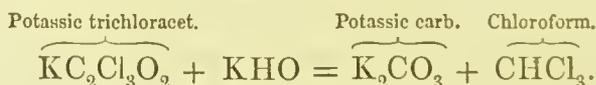
(1180) CHLOROFORM (CHCl_3). *Sp. gr. of liq.* 1.497; *of vap.* 4.2; *Rel. wt.* 59.7; *Boil. pt.* 142° ($61^\circ.1$ C.).—This interesting compound is produced by a variety of reactions: 1. when chlorine is made to act upon methyl chloride, the following change occurs:—



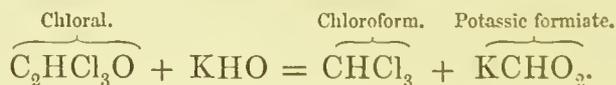
2. Another remarkable mode of its formation has been pointed out by Dumas, who finds that an oily liquid, consisting of chloroform and carbon tetrachloride, is slowly produced by mixing together in diffused daylight 4 measures of chlorine with 1 measure of marsh gas, which latter must be diluted with an equal bulk of carbonic anhydride in order to prevent the danger of spontaneous explosion. The relative amounts of chloroform and the tetrachloride vary in different experiments, but the mode of their formation may be illustrated by the subjoined equation:—



3. Chloroform is also produced during the decomposition of the trichloroacetates by the hydrated alkalies:—



4. Also by the action of the hydrated alkalies upon chloral:—



5. But it is most economically obtained by acting upon diluted alcohol with chloride of lime (bleaching powder). Wood spirit, acetone, oil of turpentine, and many essential oils yield it likewise, under the influence of chloride of lime. Chloroform is readily procured in a state of purity by the following process:—6 parts of chloride of lime, 24 parts of water, and 1 part of alcohol, are to be mixed in a capacious still, and the temperature raised as rapidly as possible till it reaches 180° ($82^\circ.2$ C.). The distillation is then to be continued until about one part and a half have passed over; the products, consisting chiefly of chloroform, accompanied by water, collect in two layers in the receiver—the chloroform constituting the lower layer. It should be decanted from the aqueous portion, and agitated with oil of vitriol in order to destroy traces of volatile oils which accompany it: by another rectification it is obtained in a state of purity.

Chloroform is a colourless, volatile liquid, of high refracting

power. It has a powerful agreeable ethereal odour, and a sweet penetrating taste. Alcohol and ether dissolve it in every proportion, but it is very sparingly soluble in water. Concentrated sulphuric acid has no action upon it, and even potassium does not occasion its decomposition. It is inflamed with difficulty, and burns with a greenish somewhat smoky flame, producing hydrochloric acid as well as carbonic anhydride and water. By admixture with an alcoholic solution of potash it is decomposed, potassic chloride and formiate being produced:—



Aqueous solution of potash does not produce this change, owing to the sparing solubility of chloroform in water.

The vapour of chloroform possesses the remarkable power of producing, in the person who has respired it, complete temporary insensibility to pain. It may be readily inhaled for this purpose by placing a small quantity of the liquid upon a sponge or a handkerchief which is to be held before the mouth and nostrils; and it is now commonly employed for rendering patients insensible to pain during severe surgical operations.

It is of great importance that the chloroform used for this purpose should be quite pure. In some cases it has been found after exposure to a strong light to have undergone spontaneous decomposition. It ought to communicate no colour to oil of vitriol when agitated with it. The liquid itself should be free from colour, and it should be perfectly destitute of any chlorous odour. When a few drops are allowed to evaporate on the hand no unpleasant odour should be left.

Chloroform was at first regarded as formic anhydride, in which the whole of its oxygen is displaced by its equivalent amount of chlorine, and hence its name: but the mode in which it is obtained by substitution from methyl chloride shows that this cannot be its true constitution; it probably is the analogue of methylic ether, in which 2 of the atoms of hydrogen are displaced by chlorine; CH_3Cl , becoming CCl_2HCl . If distilled in a current of dry chlorine, chloroform is wholly deprived of hydrogen, and yields carbon tetrachloride (387) and hydrochloric acid, $\text{CHCl}_3 + \text{Cl}_2 = \text{CCl}_4 + \text{HCl}$.

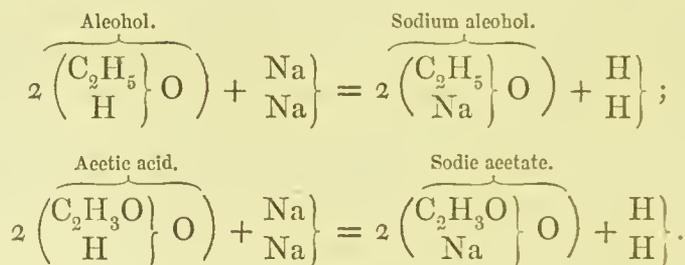
Chloroform freely dissolves sulphur, phosphorus, and iodine. It is also a good solvent for fatty and resinous bodies. No other liquid is so perfect a solvent for caoutchouc, which is left unaltered by it on evaporation.

Iodoform (CHI_3) is a solid, of a yellow colour, in which 3 atoms of iodine occupy the place of the chlorine in chloroform.

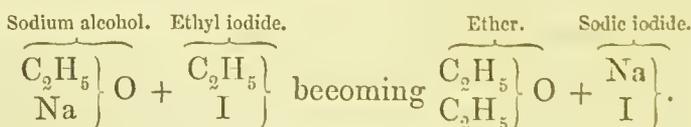
Bromoform (CHBr_3), the corresponding compound with bromine, may be formed by the distillation of bromide of lime with dilute alcohol. It is a liquid of sp. gr. 2.9, boiling at 305.6 (152°C .), and emitting a vapour of a density of 8.632; *Rel. wt.* 126.5.

§ V. METALLIC DERIVATIVES OF THE MONATOMIC ALCOHOLS.

(1181) It has been already stated (1139) that when sodium or potassium is made to act upon one of the alcohols* the typical hydrogen of the alcohol is eliminated, and a compound is formed, which presents a certain analogy with the ordinary salts of sodium or of potassium; if we compare the action of sodium upon alcohol, and upon acetic acid, the results of the reaction may be thus represented:—



We have seen that when the compound formed by the action of one of the alcohols upon sodium or potassium is acted upon by one of the ethers of the hydracids, either a simple or a double ether is produced, by a process of substitution or double decomposition:—



Within the last few years, however, a series of compounds has been obtained in which a metallic element enters still more intimately into combination with the hydro-carbon of the alcohol. The

* Thallium furnishes compounds by acting upon the alcohols similar to those produced by potassium and sodium—*e.g.*, *thallium ethylate*, $\text{C}_2\text{H}_5\text{TlO}$, may be obtained by suspending thin sheets of thallium in an exhausted receiver, over anhydrous alcohol, and gradually admitting dry oxygen gas. After the lapse of 24 hours a heavy oily liquid is obtained in the dish, from which, by a heat of 212° , the unchanged alcohol may be expelled: by exposure *in vacuo* a liquid is obtained of sp. gr. 3.685. It solidifies a few degrees below the freezing point of water. It is soluble in anhydrous alcohol and ether. Traces of water when present decompose it with separation of thallic oxide.

first substance of this class that was carefully investigated was kakodyl (AsC_2H_6); and this body was shown, by the masterly researches of Bunsen, to perform the part of a compound metal. The subsequent researches of Frankland proved the possibility of obtaining a number of new bodies more or less analogous to kakodyl; and the field thus opened has since been successfully cultivated by many distinguished chemists. These investigations have led to the discovery of a number of metallic substitution-derivatives of alcohol which are more or less closely allied to the compound ammonias. These bodies, however, are not all formed upon the type of ammonia. In some instances each atom of the metal is combined with one atom of the alcohol radicle, whilst in others 2 atoms of the alcohol radicle, in others, 3, and in some even 4 atoms of the alcohol radicle, are combined with 1 atom of the metal.

The explanation of the mode in which these compounds are formed now generally admitted was first suggested by Frankland (*Phil. Trans.*, 1852, 440), who regards them as derivatives from the inorganic compounds of the various metals: and he considers that the number of atoms of the alcohol radicles which combine with any given metal, is regulated by the atomic proportion in which that metal tends to combine with the elements, hydrogen, sulphur, oxygen, &c., or by what has since been termed the equivalency of the element. For example:—The monad sodium forms with ethyl a compound containing one atom of ethyl $\text{Na}(\text{C}_2\text{H}_5)$ corresponding with its chloride (NaCl): zinc, as a dyad, forms compounds which correspond in composition to zincic chloride ZnCl_2 ; the methyl and other alcohol derivatives of zinc containing 2 atoms of the monad alcohol radicle, such as:—

| | | |
|-------------------|-------------------|--|
| Zincic chloride, | Zinc-methyl . . . | $\text{Zn}(\text{CH}_3)_2$ |
| ZnCl_2 ; | Zinc-ethyl . . . | $\text{Zn}(\text{C}_2\text{H}_5)_2$ |
| | Zinc-amyl . . . | $\text{Zn}(\text{C}_5\text{H}_{11})_2$ |

Cadmium, which forms a chloride corresponding to that of zinc, yields compounds of analogous composition, cadmium-ethyl containing $\text{Cd}(\text{C}_2\text{H}_5)_2$; and the composition of magnesium-ethyl, $\text{Mg}(\text{C}_2\text{H}_5)_2$ is similar. Aluminum forms compounds $[\text{Al}_2(\text{C}_2\text{H}_5)_6]$ corresponding to its chloride, Al_2Cl_6 .

The tendency of arsenicum is to the formation of compounds which contain 2, 3, or 5 atoms of some other monad element, or group, the bodies thus produced corresponding to realgar, to arseniuretted hydrogen, and to arsenic anhydride:—

| | | | |
|---|--|---|--|
| Realgar (As_2S_2) | { | Kakodyl | $[\text{As}(\text{CH}_2)_2]_2$ |
| | | Arseniodiethyl | $[\text{As}(\text{C}_2\text{H}_5)_2]_2$ |
| { | Arseniuretted hydrogen | Arseniotriethyl | $\text{As}(\text{C}_2\text{H}_5)_3$ |
| | | (AsH_3) | |
| { | Arsenious chloride (AsCl_3) | Kakodyl oxide | $[\text{As}(\text{CH}_2)_2]_2\text{O}$ |
| | | Kakodyl chloride | $\text{As}(\text{CH}_3)_2\text{Cl}$ |
| | | Arsenio-methyl oxide | AsCH_3O |
| Arsenic anhydride (As_2O_5) | { | Arsenio-tetrethylum chloride | $\text{As}(\text{C}_2\text{H}_5)_4\text{Cl}$ |
| | | Arsenio-triethyl dichloride | $\text{As}(\text{C}_2\text{H}_5)_3\text{Cl}_2$ |
| | | Kakodyl trichloride | $\text{As}(\text{CH}_3)_2\text{Cl}_3$ |
| | | Arsenio-methyl tetra-chloride | AsCH_3Cl_4 |

Antimony does not form any compound corresponding to realgar, but it yields bodies which contain 3 or 5 atoms of some other element; and the alcohol compounds of this metal correspond to antimoniuuretted hydrogen, and to antimony pentachloride:—

| | | | |
|--|---|--|--|
| Antimoniuuretted hydrogen (SbH_3) | { | Stibiotriethyl | $\text{Sb}(\text{C}_2\text{H}_5)_3$ |
| Antimony pentachloride (SbCl_5) | { | Hydrated stibiotetrethylum oxide | $\text{Sb}(\text{C}_2\text{H}_5)_4\text{HO}$ |
| | | Stibiotriethyl oxide | $\text{Sb}(\text{C}_2\text{H}_5)_3\text{O}$ |

The triad bismuth presents compounds which correspond to its trichloride:—

| | | | |
|--------------------------------------|---|--------------------------|---|
| Bismuth trichloride, BiCl_3 | { | Bistriethyl | $\text{Bi}(\text{C}_2\text{H}_5)_3$ |
| | | Bisethyl oxide | $\text{Bi}(\text{C}_2\text{H}_5)_2\text{O}$ |

Mercury, which is a dyad, yields compounds corresponding in composition to the dichloride of the metal:—

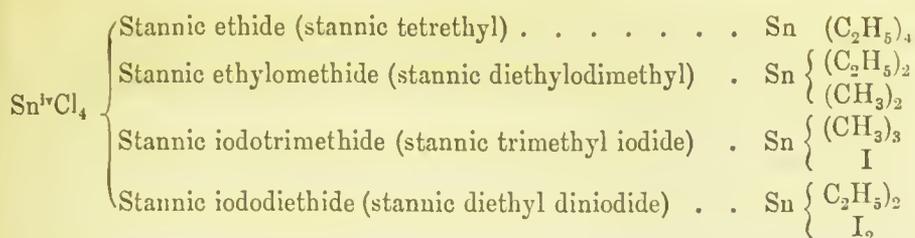
| | | | |
|-------------------------------------|---|---------------------------------|---|
| Mercuric chloride . HgCl_2 | { | Mercuric ethyl iodide | $\text{Hg}[(\text{C}_2\text{H}_5)\text{I}]$ |
| | | Mercuric dimethyl | $\text{Hg}(\text{CH}_3)_2$ |

The tetrad element lead yields compounds corresponding to lead dioxide (PbO_2):—

| | | | |
|---|---|-------------------------------------|--|
| Lead dioxide (PbO_2) | { | Plumbic tetrethyl | $\text{Pb}(\text{C}_2\text{H}_5)_4$ |
| | | Plumbic triethyl chloride | $\text{Pb}(\text{C}_2\text{H}_5)_3\text{Cl}$ |

The compounds of tin, though a tetrad also, are more numerous, but they are all formed upon the three following types, $\text{Sn}''\text{Cl}_2$; Sn_2O_3 ; $\text{Sn}^{\text{iv}}\text{Cl}_4$, as, for example:—

| | | | | | |
|--------------------------|---|---|-------------|------------------------|-------------------|
| $\text{Sn}''\text{Cl}_2$ | Stannous ethide (stannodiethyl) | Sn | { | C_2H_5 | |
| | | | | C_2H_5 | |
| Sn_2O_3 | { | Sesquimethide of tin (stannotrimethyl) | Sn | CH_3 | |
| | | | | CH_3 | |
| | | | | CH_3 | |
| | | Dimethiodide of tin (stannodimethyl iodide) | Sn | { | $(\text{CH}_3)_2$ |
| | | | | | I |



The compounds of selenium and tellurium with the alcohol radicles are closely allied to the class of bodies which we are now considering, although they present some analogy with the ethers, and they have already been alluded to (1148) when speaking of these substances. The intermediate position occupied by selenium and tellurium between the metallic and non-metallic elements, explains why their compounds with the alcohol radicles should exhibit properties intermediate between those of the true ethers and of these metallic derivatives of the alcohols. The tellurium and selenium ethers differ from the ordinary ethers in the tendency to combine with oxygen which they exhibit, thus forming bodies which by interaction with acids yield definite salts. Tellurethyl $(\text{C}_2\text{H}_5)_2\text{Te}$, for instance, becomes oxidized, and forms the body $(\text{C}_2\text{H}_5)_2\text{TeO}$, and this compound, by its reaction with oxalic acid, yields a crystalline salt, $2[(\text{C}_2\text{H}_5)_2\text{TeO}]\text{C}_2\text{O}_3, \text{H}_2\text{O}$.

These *organo-metallic* compounds, as they have been termed, are, as a class, distinguished by the extraordinary energy of their chemical attractions. Their disposition to unite with the electro-negative elements increases with the positive character of the metal, and with the smallness of the atomic weight of the alcohol radicle. For example, the potassium and sodium compounds are more energetic than those of zinc, and these than the compounds of tin, of lead, or of bismuth; and the methylic compounds of each metal are more active than the ethylic, and these again than the amylic compounds.

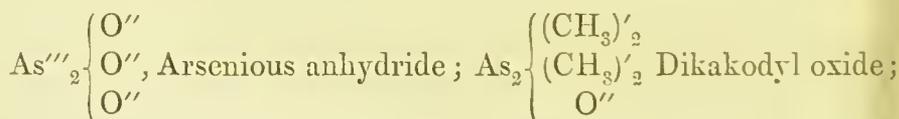
Many of the compounds of the alcohol radicles with the metals, such for example as zinc-methyl, kakodyl, stibiotriethyl, and bistrichethyl, have an attraction for oxygen so powerful that they take fire by simple contact with it, or with atmospheric air: but it is important to remark, that the results of such oxidation are very different in different cases. In some instances, when the operation is conducted slowly and with due care, organo-metallic oxides are procured, into the composition of which the alcohol radicle enters; they thus furnish bases which, like kakodyl oxide, by their action upon acids, form well-defined neutral crystallizable compounds. In other instances no such basic organo-metallic oxides can be obtained: for example, zinc-methyl

and zinc-ethyl, although their attraction for oxygen is very intense, do not yield any organo-metallie base by the gradual action of oxygen upon them.

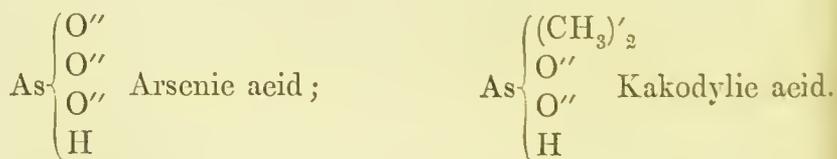
Kakodyl and arseniodiethyl (the kakodyl of the ethylic series) both unite with oxygen in two proportions: the lower oxide, in the case of kakodyl, exerting the properties of a powerful base, neutralizing acids, and forming with them crystallizable salts; whilst the higher oxide furnishes a strong monobasic acid. For instance:—



Frankland accounts for the difference between the results of the oxidation of kakodyl and of zinc-methyl from the circumstance that in the case of zinc no dioxide is known, and as zinc-methyl is formed upon the type of zincic oxide, there should, therefore, be no tendency to the formation of an oxide of zinc methyl, the zinc-methyl itself forming a *saturated* molecule. In the case of kakodyl, the addition of an atom of oxygen produces a compound corresponding, in a certain degree, with arsenious anhydride:—



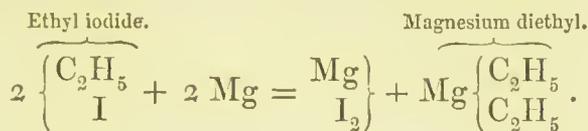
whilst kakodylic acid corresponds to the monohydrated arsenic acid (HAsO_3):—



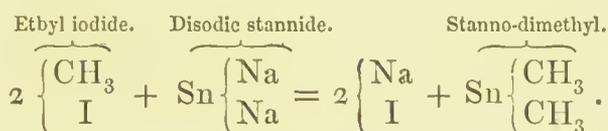
The organo-metallie compounds, to use Frankland's words, when "in a state of partial saturation, play the part of compound radicles: they are uniatomic, biatomic, teratomic, or quadratomic, according to the number of molecules requisite to complete their saturation. On the other hand, organo-metallie bodies in a state of saturation, never perform radical functions; they never undergo chemical change without decomposition." (See *Q. J. Chem. Soc.*, xiii. 192, which contains a recent digest, by Frankland, of the principal facts bearing upon this subject.)

Organo-metallie compounds may be formed by various processes, the most important of which are the following:—

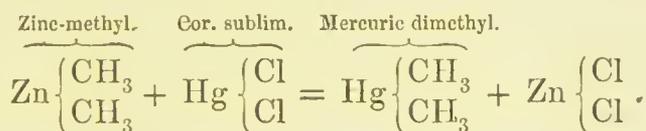
1. Combination of the organic radicle in the nascent state with the metal, as in the preparation of magnesium-ethyl:—



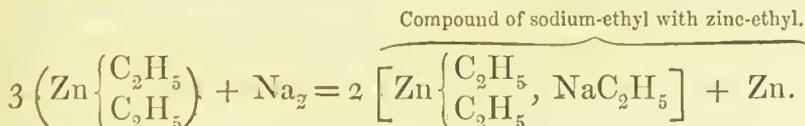
2. Decomposition of the iodides of the alcohol radicles by an alloy of the metal with potassium or sodium, as when stannodimethyl is formed by the action of disodic stannide on methyl iodide:—



3. Action of organo-zinc compounds upon the haloid compounds of the metals, as in the preparation of mercuric-dimethyl by the action of zinc-methyl upon corrosive sublimate:—



4. Displacement of the metal in the organo-metallie compound by another more positive metal, as when sodium-ethyl is formed from zinc-ethyl by the action of sodium upon the zinc compound:—



In order to illustrate the properties and mode of formation of these singular compounds, a description will now be given of a few of the organo-metallie bodies into the formation of which zinc, mercury, arsenium, and antimony enter.

(α) *Compounds of Zinc with the Alcohol Radicles.*

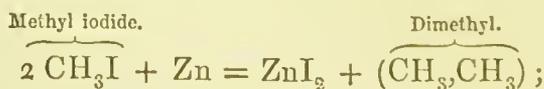
(1182) The properties of the compounds formed by zinc with the alcohol radicles are very remarkable; they furnish a good illustration of the organo-metallie compounds of a dyad metal, and these substances are further interesting in connexion with the process of isolating the so-called alcohol radicles themselves.

ZINC-METHYL $[\text{Zn}(\text{CH}_3)_2]$. *Sp. gr. of vap.* 3.291; *Rel. wt.* 47.5] is a very volatile, colourless, transparent, and highly mobile liquid, with a penetrating, peculiar and insupportable

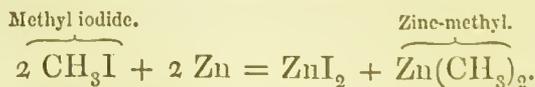
odour, and boiling between 122° and 140° (50° and 60° C.). It is immediately decomposed by oxygen, chlorine, and iodine. If placed in contact with atmospheric air, it takes fire instantaneously, burning with a beautiful greenish-blue flame, and forming white clouds of zincic oxide; in contact with pure oxygen it burns with explosion, and the presence of a small quantity of its vapour in combustible gases gives them the property of spontaneous inflammability on admixture with oxygen. When thrown into water, zinc-methyl decomposes this liquid with explosive violence, attended with flame; and if the mixture of the two liquids be effected very gradually, so as to prevent any intense elevation of temperature, the sole products of the decomposition are zincic oxide and methyl hydride (marsh gas); $\text{Zn}(\text{CH}_3)_2 + 2 \text{H}_2\text{O} = 2 (\text{CH}_3, \text{H}) + \text{ZnO}, \text{H}_2\text{O}$. Ether dissolves zinc-methyl freely.

Frankland has shown that, owing to the intense attraction of zinc-methyl for oxygen and chlorine, it is possible in certain cases to employ it for effecting the substitution of methyl for oxygen and for chlorine.

In order to obtain zinc-methyl in a state of purity, methyl iodide is sealed up with an excess of dry granulated zinc, in a strong glass tube, drawn out to a capillary end, and exposed to a temperature of from 302° to 320° (150° to 160° C.) in an oil-bath, until all the methyl iodide has disappeared. A mass of white crystals, consisting of a compound of zinc-methyl with zincic iodide, and a colourless, mobile liquid, which is zinc-methyl, are thus formed, and at the same time a considerable quantity of gaseous dimethyl is produced and confined. One portion of the methyl iodide is converted into zincic iodide and dimethyl,



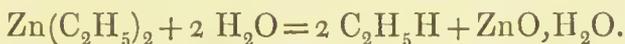
whilst another portion yields zincic iodide and zinc-methyl,



The zinc-methyl may be obtained by breaking off the capillary extremity, and allowing the included gaseous dimethyl to escape, and the liquid contents are separated from the solid ones by distillation at a gentle heat in an atmosphere of dry hydrogen.

(1183) ZINC-ETHYL [$\text{Zn}(\text{C}_2\text{H}_5)_2$]. *Sp. gr. of vap.* 4.259; *of liq.* 1.182 at $64^{\circ}.4$ (18° C.); *Rel. wt.* 61.7; *Boil. pt.* $244^{\circ}.4$ (118° C.). Frankland, *Phil. Trans.* 1855.—This compound is a

colourless, transparent, mobile liquid, which refracts light strongly, and is possessed of a peculiar, powerful, but not disagreeable odour. It is not solidified by a cold of $-7^{\circ}6$ (-22° C.). It may be distilled without change in vessels filled with carbonic anhydride, or with hydrogen. Zinc-ethyl is less inflammable than zinc-methyl, but its attraction for oxygen is sufficiently intense to cause it to take fire as soon as the liquid is brought into contact with that gas, or with atmospheric air, when it burns with a brilliant blue flame, fringed with green, and forms dense white clouds of zincic oxide. If a cold piece of glass, or of porcelain, be held in the flame, it becomes coated with a deposit of metallic zinc, surrounded by a white ring of the oxide of this metal. If the oxidation be allowed to take place more slowly, zinc-alcohol (zinc-ethylate) $\text{Zn}(\text{C}_2\text{H}_5)_2\text{O}_2$, is the principal product; and this mode of the formation of zinc-alcohol by the direct combination of zinc-ethyl with oxygen, is certainly very remarkable. Ether dissolves zinc-ethyl freely without change, but water immediately decomposes it; hydrated zincic oxide and the gaseous ethyl hydride ($\text{C}_2\text{H}_5\text{H}$), being the result:—



Iodine, bromine, and chlorine, decompose zinc-ethyl with great violence; if the action be moderated, iodide, bromide, or chloride of zinc is formed, whilst the corresponding compound of ethyl with the halogen is produced; in the case of iodine, the reaction may be thus represented:—



A similar effect is produced if zinc-ethyl be heated with powdered sulphur, the double sulphide of zinc and ethyl being formed.

Preparation.—Zinc-ethyl is obtained by heating anhydrous ethyl iodide (diluted with an equal volume of anhydrous ether* to regulate the reaction) with twice its weight of well-dried granulated zinc. The mixture is introduced into a sealed glass tube, and heated in a closed vessel to about 266° (130° C.) for twelve or eighteen hours. When large quantities are required, a convenient plan is to conduct the operation in a strong metallic vessel, or species of digester. A full description of this apparatus is given by Frankland in his paper. Pebal, however, conducts the operation in ordinary glass retorts filled with carbonic anhy-

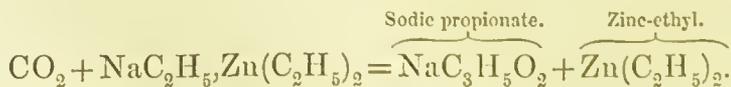
* In order to deprive this mixture completely of moisture, it is agitated with about one-twentieth of its weight of phosphoric anhydride.

dride. If the materials employed for the preparation of the zinc-ethyl are really anhydrous, very little permanent gas is produced, but if moisture be present, a quantity of ethyl hydride is formed. After the apparatus has become cool, the permanent gas, if any, is allowed to escape; and the zinc-ethyl is distilled from the materials employed in its preparation, in vessels filled with carbonic anhydride, or hydrogen. Particular modes of manipulation are required during the distillation and purification of the product, in order to prevent the access of air, which would oxidize and destroy the compound. For details upon these points, the reader is referred to the memoir already cited.

(1184) *Sodium-ethyl*.—Wanklyn found that if a piece of sodium be sealed up in a tube (previously filled with coal gas) with about 10 times its weight of zinc-ethyl, in the course of a few days the sodium is dissolved, a deposit of metallic zinc takes place, and a viscid liquid is formed:—



This liquid consists of a solution of a compound of sodium-ethyl and zinc-ethyl $[\text{NaC}_2\text{H}_5, \text{Zn}(\text{C}_2\text{H}_5)_2]$ dissolved in an excess of zinc-ethyl, and when exposed to a temperature of 32° beautiful crystals of this compound are deposited; they fuse at about $80^\circ.6$ (27° C.). Attempts to procure sodium-ethyl in an isolated state were unsuccessful. When the foregoing double compound is heated, an evolution of gas occurs, and an alloy of sodium and zinc, free from carbonaceous residue, is left. When exposed to the air the crystals instantly take fire, burning explosively with a yellow flame. Water decomposes them with evolution of pure ethyl hydride. The reaction with carbonic anhydride is especially remarkable, sodic propionate being formed, which combines with the zinc-ethyl, and may be obtained in a separate form by decomposing the compound with water. The reaction which gives rise to the formation of the propionate appears to be the following:—

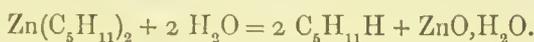


This reaction is extremely interesting, since it points out a method of forming the fatty acids by substitution from carbonic acid. Sodium-methyl has been found in like manner to yield sodic acetate, and sodium-amyl would probably furnish sodic caproate. It is remarkable that a series of monobasic acids are thus obtained from the dibasic carbonic acid.

A compound of zinc-ethyl with potassium-ethyl may be obtained by means

analogous to those adopted for procuring the sodium compound; and there can be no doubt that corresponding compounds of the other alcohol radicles could be procured.

(1185) *Zinc-amyl* [$\text{Zn}(\text{C}_5\text{H}_{11})_2$].—This body is obtained by decomposing amyl iodide with zinc in a sealed tube, at a temperature of 350° (180° C.). It forms a colourless, transparent liquid, which emits fumes, and absorbs oxygen rapidly when exposed to the air; but it does not take fire spontaneously. Water decomposes it into hydrated zincic oxide and amyl hydride:—

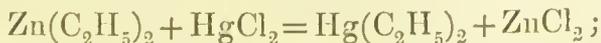


(b) *Compounds of Mercury with the Alcohol Radicles.*

(1186) This series is also furnished by a dyad metal. All its members may be compared in constitution with corrosive sublimate; as for instance:—

| | | | |
|---|----|---|--|
| Mercuric chloride | Hg | { | Cl Cl |
| Mercuric-dimethyl | Hg | { | CH ₃ CH ₃ |
| (Mercuric methiodide) mercuric-methyl iodide | Hg | { | CH ₃ I |
| (Mercuric methhydrate) hydrated mercuric- methyl oxide | Hg | { | CH ₃ HO |
| (Mercuric metho-nitrate) mercuric-methyl nitrate | Hg | { | CH ₃ NO ₃ |
| Mercuric-diamyl | Hg | { | C ₅ H ₁₁ C ₅ H ₁₁ |
| Mercuric-amyl chloride | Hg | { | C ₅ H ₁₁ Cl |

The organo-mercurial compounds, when first discovered, were obtained either by acting upon the iodide of the alcohol radicle by means of mercury in sunlight, when direct combination takes place, $\text{Hg} + \text{CH}_3\text{I}$, for instance, becoming HgCH_3I ; or by acting by means of corrosive sublimate upon the zinc compound of the alcohol radicle, as for instance:—



simple exchange of the two metals taking place if the compounds are presented to each other in equivalent proportions; but if the mercuric chloride be in excess the reaction takes the following form; $\text{Zn}(\text{C}_2\text{H}_5)_2 + 2 \text{HgCl}_2 = 2(\text{Hg}, \text{C}_2\text{H}_5\text{Cl}) + \text{ZnCl}_2$.

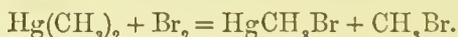
Frankland and Duppa have since (*J. Chem. Soc.*, 1863, 415) found that mercuric dimethyl, diethyl, or diamyl, may be obtained

in quantity by the easier method of decomposing the iodide of the corresponding alcohol radicle by means of sodium amalgam in the presence of acetic ether; and the mercury compounds thus obtained can be employed as sources whence zinc-ethyl, aluminum-ethyl, and other inflammable compounds of this class may be procured more easily than by methods hitherto used. Inhalation of the vapour of these compounds cannot be too carefully avoided. It acts as a cumulative poison, which gradually and completely destroys the powers of thought by a specific action on the brain.

(1187) *Mercuric Dimethyl (Mercuric Methide)*, $[\text{Hg}(\text{CH}_3)_2]$. *Sp. gr. of liq.* 3.069; *of vap.* 8.29; *Rel. wt.* 115; *Boil. pt.* 200° – 205° (about 96° C).—In order to prepare this compound ten parts of methyl iodide and one part of acetic ether are agitated with sodium amalgam (1 part sodium, 500 mercury), in a flask, which is occasionally plunged into cold water to moderate the action. The methyl iodide is to be condensed in a Liebig's coudeuser as it rises in vapour. When the quantity of sodic iodide deposited becomes considerable, the more volatile portions are to be distilled off, and treated with fresh amalgam. The residues in the flasks, when the decomposition is complete, are mixed with water, and submitted to distillation in an oil bath, the temperature of which need not exceed 230° (110° C.).

The distillate is separated from the water, agitated with alcoholic solution of potash to remove acetic ether, and then well washed with water and redistilled.

Mercuric dimethyl is a colourless easily inflammable liquid, and except thallium ethylate, the densest transparent liquid known. It is readily soluble in alcohol and in ether. It has no tendency to enter into combination. Bromine and iodine decompose it, forming mercuric-methyl bromide or iodide, with bromide or iodide of methyl:—



With hydrochloric or sulphuric acids, mercuric-methyl chloride or sulphate, and methyl hydride are formed:—



A hydrated mercuric-methyl oxide $[\text{HgCH}_2\text{HO}]$ may be obtained by decomposing the chloride with argentic oxide.

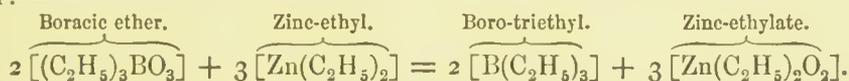
(1188) *Mercuric Diethyl* $[\text{Hg}(\text{C}_2\text{H}_5)_2]$. *Sp. gr. of liq.* 2.44; *of vap.* 9.97; *Rel. wt.* 129; *Boil. pt.* 318° (159° C).—This is a heavy, transparent, colourless, inflammable liquid, very like the methylic compound. It may be obtained by an analogous process, in which ethyl iodide mixed with acetic ether is treated with sodium amalgam; and it shows a similar indifference to combination: but it is decomposed with loss of an atom of ethyl by treatment with acids, with the halogens, or with corrosive sublimate: the reactions are similar to those which occur with the methyl compound.

(1189) *Mercuric Diamyl* $[\text{Hg}(\text{C}_6\text{H}_{11})_2]$. *Rel. wt.* 171; *Sp. gr.* 1.6663 at 32° .—This compound is a colourless, transparent, mobile liquid, with a very faint amylic odour, and a peculiar persistent taste. It cannot be distilled alone, even *in vacuo*, without undergoing decomposition; but its vapour passes over unaltered when distilled with water. Mercuric diamyl is prepared by a process corresponding to that adopted for the foregoing compounds that are analogous to it, but it is still more easily procured. 5 parts of amyl iodide are mixed with 1 of acetic ether, and digested with the amalgam of sodium. It forms mercuric

amylic salts when treated with bromine, with iodine, or with acids, attended with the formation of compounds corresponding with those formed by mercuric dimethyl.

(1190) BORIC ETHIDE, or *Borotriethyl* $[B(C_2H_5)_3]$. *Sp. gr. of liq.* 0.696; *of vap.* 3.4; *Rel. wt.* 49; *Boil. pt.* 203° (95° C.).—Frankland and Duppa have described (*Phil. Trans.* 1862, 167) an interesting addition to this class of bodies in a compound corresponding to boric chloride, in which the three atoms of chlorine are displaced by ethyl. It is a colourless liquid, which takes fire spontaneously when exposed to the air, and burns with a beautiful green flame.

It is formed by decomposing boracic ether by means of zinc-ethyl, and is purified by distillation from the accompanying zinc ethylate and unaltered zinc-ethyl:—



If allowed to oxidize slowly by the gradual admission of air into a flask, it forms a colourless liquid $[B(C_2H_5)_3O_2]$ which is decomposed by distillation. This new body is immediately dissolved by water, and is converted into alcohol, and a white volatile crystallized compound with an intensely sweet taste:—



The anomalous oxidized body $B(C_2H_5)_3O_2$, is regarded by Frankland as $B''' \left\{ \begin{array}{l} (C_2H_5)' \\ (C_2H_5O)' \end{array} \right\}_2$ or *boric dioxyethide*. Its composition, however, does not agree with the theory of these bodies given above; for no oxidized body of this composition is known.

(c) Compounds of Arsenicum with the Alcohol Radicles.

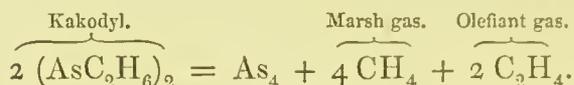
(1191) Arsenicum forms with the alcohol radicles four classes of compounds, three of which have been minutely examined in the methyl, and less completely in the ethyl series. The methylic series is as follows:—

1. Arsenio-methyl . . . $As(CH_3)$, a tetrad or a dyad radicle, not known in the free state.
2. Arsenio-dimethyl . . . $As(CH_3)_2$, a monad or a triad radicle.
3. Arsenio-trimethyl . . . $As(CH_3)_3$, a dyad radicle.
4. Arsenio-tetramethylum . $As(CH_3)_4$, a monad radicle, not known in the isolated form.

The most important and best known of these is arsenio-dimethyl, or kakodyl, which formed the starting point of the inquiries into the organo-metallic compounds.

(1192) KAKODYL, or *Arseniodimethyl* $[As(CH_3)_2]_2$; *Mol. vol.* $\square\square$; *Sp. gr. of vap.* 7.1; *Rel. wt.* 105; *Fusing pt.* $21^\circ.2$ (-6° C.); *Boil. pt. about* 338° (170° C.).—This body in its isolated form is more properly regarded as kakodylide of kakodyl. It is an extremely poisonous, colourless, viscous liquid, heavier

than water; it emits fumes, and takes fire spontaneously when exposed to the air. Its vapours have a disgusting arsenical odour, and hence the origin of the name (from *κακός*, bad, *ὄσμη*, odour). At 21° it becomes solid, and crystallizes in square prisms. It is only slightly soluble in water, but is readily dissolved by alcohol and by ether. When heated to about 752° (400° C.) it is entirely decomposed into arsenic and a gaseous mixture consisting of 2 volumes of marsh gas and 1 volume of olefiant gas:—



Kakodyl burns in oxygen with a pale blue flame, producing water, with carbonic and arsenious anhydrides: but if atmospheric air be admitted bubble by bubble into kakodyl, white fumes are formed, and kakodyl oxide, $(\text{AsC}_2\text{H}_6)_2\text{O}$, is the result: an excess of oxygen in the presence of water converts it into kakodylic acid $\text{H}(\text{AsC}_2\text{H}_6)\text{O}_2$; but if the supply of oxygen be insufficient to complete this change, kakodyl kakodylate $(\text{AsC}_2\text{H}_6)_2\text{O}_2$ (dikakodyl dioxide) is produced.

The remarkable peculiarity of kakodyl is its power of thus uniting directly with oxygen; and it exhibits a similar tendency to combine with sulphur, chlorine, &c.; in this manner it performs the part of a simple metallic body, since the group AsC_2H_6 (which may be represented by the abbreviated symbol *Kd*) admits of being substituted for hydrogen. The discovery of this compound in an isolated form exercised an important influence upon the development of the theory of organic chemistry, as it furnished the first instance of what was then regarded as the isolation of an organo-metallic base; although other bodies more or less analogous to it in this respect are now known. Chemists, however, have now agreed to double the formula for free kakodyl, so that it loses its importance as a radical, the progress of research having rendered it nearly certain that all the compounds formerly viewed as isolated monad radicals are combinations of those radicals with themselves (1061).

Kakodyl was obtained by Bunsen from its chloride, which, when treated with fragments of granulated zinc, is decomposed; zinc chloride being formed, whilst pure kakodyl is liberated. The chloride employed for this purpose (p. 255) must be quite anhydrous, and free from kakodyl oxide. To obtain it in this state, the chloride, after digestion with concentrated hydrochloric acid, is allowed to stand for several days upon fragments of quicklime and calcic chloride. This purification of the chloride must be

effected in a bulb-tube of the form shown in fig. 387, the quicklime and calcic chloride being first introduced into the bulb.

A current of dry carbonic anhydride is next transmitted through the bulb tube in order to displace the atmospheric air completely, and the capillary extremities are then sealed: when the kakodyl chloride is to be introduced, the point of the capillary tube *a* is cut off, and by means of a caoutchouc tube it is connected with a hand syringe; the tube *b* is then opened, and made to dip into the liquid chloride, which by the movement of the piston is drawn into the bulb.

The decomposition must be effected in an apparatus similar to that shown in fig. 388. The zinc having first been placed in the bulb *a*, the apparatus is to be filled with carbonic anhydride, and a portion of the kakodyl chloride is admitted. The capillary tubes are then sealed, and the heat is applied to the bulb *a*, which acts as a retort, *b* serving as the receiver. The zinc gradually becomes

FIG. 387.

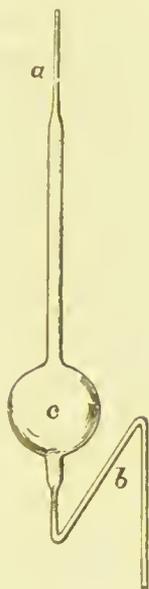
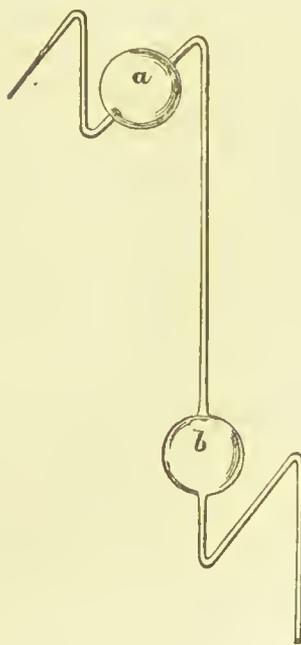


FIG. 388.



dissolved without any evolution of gas; when the action has ceased, the apparatus is allowed to cool, and the capillary tube at *b* is opened under boiled water: the bulb is next heated gently to expel a portion of the carbonic anhydride, and water enters as the apparatus cools, after which the capillary tube is again sealed: by inclining the tube, the water is made to act upon the crystallized mass in the bulb *a*; it thus dissolves the zinc chloride, leaving the excess of metallic zinc, and liberating kakodylide of kakodyl in the form of an oily fluid, which is transferred to a bulb-tube of the form of fig. 387, the bulb having been previously filled with calcic chloride, and the air displaced by means of carbonic anhydride, in the manner already described: here it is dried, then transferred to the bulb apparatus (fig. 388), and rectified from a fresh portion of zinc. Dikakodyl may also be obtained by the action of mercury upon dikakodyl sulphide.

(1193) *Compounds derived from Kakodyl.*—Bunsen has described a large number of compounds of kakodyl; some of those of most importance are the following:—

| | | |
|--|--------------------------------|--|
| Kakodyl (kakodylide of kakodyl) | $(AsC_2H_6)_2$ | Kd ₂ |
| Dikakodyl oxide (kakodyl oxide) | $(AsC_2H_6)_2O$ | Kd ₂ O |
| Dikakodyl dioxide (kakodylate of kakodyl) } | $(AsC_2H_6)_2O_2$ | Kd ₂ O ₂ |
| Kakodyl sulphate | $(AsC_2H_6)_2SO_4$ | Kd ₂ SO ₄ |
| Kakodylic acid | $H(AsC_2H_6)O_2$ | HKdO ₂ |
| Argentick kakodylate | $Ag(AsC_2H_6)O_2$ | AgKdO ₂ |
| Dikakodyl sulphide | $(AsC_2H_6)_2S$ | Kd ₂ S |
| Dikakodyl disulphide | $(AsC_2H_6)_2S_2$ | Kd ₂ S ₂ |
| Sulphokakodylic acid | $H(AsC_2H_6)S_2$ | HKdS ₂ |
| Argentick sulphokakodylate | $Ag(AsC_2H_6)S_2$ | AgKdS ₂ |
| Kakodyl chloride | $(AsC_2H_6)Cl$ | KdCl |
| Kakodyl trichloride | $(AsC_2H_6)Cl_3$ | KdCl ₃ |
| Kakodyl oxychloride | $(AsC_2H_6)_2O, 6(AsC_2H_6Cl)$ | Kd ₂ O, 6 KdCl |
| Kakodyl hydrargo-oxychloride | $(AsC_2H_6)_2O, 2 HgCl_2$ | Kd ₂ O, 2 HgCl ₂ |

Kakodyl Oxide ($[As(CH_3)_2]_2O$), or Kd₂O. *Sp. gr. of vap.* 7.55; *Rel. wt.* 113; *Boil. pt.* about 248° (120° C.).—The preparation of the compounds of kakodyl, owing to the inflammability of many of them, and their highly poisonous character, is both difficult and dangerous. Kakodyl oxide in an impure form constitutes the horribly fœtid, spontaneously inflammable liquid, formerly known as *Cadet's fuming liquor*, or *alkarsin*, which is obtained by the distillation of a mixture of equal parts of dried potassic acetate and arsenious anhydride. The receiver must be fitted to the neck of the retort, and furnished with a tube for carrying off the gaseous products into the chimney; the retort is then to be heated by a sand bath, the temperature of which is gradually raised to dull redness. The distilled liquid separates into three layers; the lower one consists of arsenicum; above this is a brown oily liquid, composed chiefly of a mixture of impure kakodyl and kakodyl oxide; and above this is a mixture of water, acetone, and acetic acid. A copious disengagement of carbonic acid and of marsh gas accompanies the operation. The stratum of alkarsin (kakodyl oxide) is drawn off, by means of a syphon filled with boiled water, into a flask also filled with the same liquid, into which the longer limb of the syphon is plunged, with a view of preventing the contact of the air with the inflammable alkarsin. It is washed with boiled water, and then rectified from caustic potash in a current of hydrogen; air is afterwards gradually admitted to the distillate, sufficiently slowly to prevent it from taking fire. The liquid thus obtained consists of a mixture of kakodyl oxide and kakodylic acid; it is dissolved in water and distilled. At first a quantity of water having the odour of kakodyl passes over, and when the temperature rises to 248°, the oily liquid which distils is nearly pure kakodyl oxide. A second rectification from anhydrous baryta in

vessels from which air is excluded, furnishes the compound in a state of purity. All these operations must be conducted with the greatest possible care, and with the adoption of special precautions, on account of the deadly nature of the vapours. Full particulars upon all these points are given by Bunsen in the interesting and remarkable series of memoirs which he has published upon the compounds of kakodyl and its derivatives. These papers are worthy of careful study, as models of ingenuity and precision in the prosecution of a research beset with unusual difficulty and danger (*Liebig's Ann.*, xxxvii. 1; xlii. 14; and xlvi. 1). Kakodyl oxide is a colourless, limpid, ethereal liquid, endowed with a penetrating odour; it is insoluble in water, but soluble in alcohol. It absorbs oxygen slowly from the air, and combines with acids to form salts: the sulphate crystallizes in radiating tufts of needles.

Kakodyl oxide also combines with the electro-negative chlorides with facility. If an alcoholic solution of corrosive sublimate be mixed with a dilute solution of Cadet's liquor in alcohol, an abundant white precipitate is formed, and the intolerable odour of kakodyl disappears completely. The precipitate, if collected, pressed, to remove the adhering mother-liquor, and redissolved in boiling water, is deposited in well-defined crystals, $(\text{AsC}_2\text{H}_6)\text{O}_2, 2\text{HgCl}_2$. The ready formation of this crystalline compound offers one of the best means of purifying the crude compounds of kakodyl.

When this mercurial compound is distilled with concentrated hydrochloric acid it furnishes *kakodyl chloride* [$\text{As}(\text{CH}_3)_2\text{Cl}$, or KdCl ; *Sp. gr. of vap.* 4.56; *Rel. wt.* 70.2; *Boil. pt.* about 212°] in the form of a colourless liquid, which remains liquid at a temperature of -49° (-45° C.). It takes fire spontaneously in the air, and in an atmosphere of chlorine; in the latter case depositing carbon abundantly. Its vapour is still more deleterious than that of the oxide: kakodyl chloride is insoluble in water and in ether, but very soluble in alcohol. If it be dissolved in carbon disulphide and a current of chlorine be transmitted over its surface, the chlorine is absorbed, and crystalline plates of the trichloride, $\text{As}(\text{CH}_3)_2\text{Cl}_3$, are deposited: this compound becomes gradually decomposed at ordinary temperatures, and when heated it is rapidly resolved into methyl chloride and arsenio-methyl dichloride.



An *iodide* and a *bromide of kakodyl* may be obtained by treating the mercurial compound with hydriodic or with hydrobromic acid.

Kakodyl Cyanide [$\text{As}(\text{CH}_3)_2\text{CN}$; or KdCy .] *Sp. gr. of vap.* 4.63; *Rel. wt.* 65.5; *Fusing pt.* $91^\circ.4$ (33° C.); *Boil. pt.* 284° (140° C.).—This compound shows a remarkable tendency to crystallization; it appears to be the most deadly compound of the whole series, a single grain diffused in vapour through a room being sufficient to produce numbness of the hands and feet, vertigo, and even syncope, in those exposed to its effects. It may be obtained in brilliant

prisms by decomposing a concentrated solution of mercuric cyanide with kakodyl oxide, and rectifying the crystals over caustic baryta.

Sulphur combines with kakodyl in three proportions. The *dikakodyl sulphide* $[(Kd_2S)]$; *Sp. gr. of vap.* 7·81; *Rel. wt.* 121; *Boil. pt. above* 212° is a colourless, very fœtid liquid, which absorbs oxygen rapidly from the air. It may be obtained by distilling Cadet's liquor with barie sulphide. This sulphide is readily soluble in alcohol and in ether: it combines easily with an additional quantity of sulphur, and then becomes converted into the solid *disulphide* (Kd_2S_2) . *Dikakodyl trisulphide* (Kd_2S_3) possesses the properties of a sulphur acid. If an alcoholic solution of the sulphide (Kd_2S) be mixed with an alcoholic solution of euprie nitrate, octahedral crystals of adamantine lustre are deposited; they are permanent in the air, and consist of a double sulphide of kakodyl and copper $[As(CH_3)_2CuS_2]$.

Kakodylic acid $[HAs(CH_3)_2O_2]$ crystallizes in oblique equilateral prisms which are soluble in water and in alcohol. It is remarkable that it appears to possess little or no poisonous action upon the animal system, seven grains of it having been injected into the blood of the rabbit without producing any marked effect. It is a weak acid, and decomposes the carbonates slowly. Its salts, with the exception of the silver salt, crystallize with difficulty. The acid is easily obtained by treating kakodyl oxide with mercuric oxide: metallic mercury is reduced, whilst the acid is dissolved.

(1194) COMPOUNDS OF ARSENIO-METHYL.—Arsenio-methyl (*arsenio-monomethyl*) is not known in the isolated state, but compounds are obtainable in which one atom of arsenicum and one of methyl are found united with two or with four atoms of some monad, such as chlorine or iodine. They are chiefly interesting as showing the persistence of the triad and pentad type in the compound of arsenicum, $As(CH_3)$ requiring either two atoms of chlorine, as in the dichloride $[As(CH_3)]''Cl_2$, or four atoms, as in the tetrachloride $[As(CH_3)]''''Cl_4$. (See table, page 242.)

Arsenio-methyl dichloride $[(AsCH_3)''Cl_2]$. *Boil. pt.* 271°·4 (133° C.).—This is a liquid of disgusting odour, and it exerts a terribly irritating effect on the mucous membranes. It is one of the products of the distillation of kakodyl trichloride. An *oxide* $[(AsCH_3)''O]$ may be obtained by decomposing the dichloride with potassic carbonate, treating with alcohol, evaporating to dryness, and dissolving the residue in carbon disulphide; it forms fine crystals, which are at first transparent, but gradually become white and opaque. A corresponding *sulphide* $[As(CH_3)S]$ and *diiodide* may also be obtained.

Arsenio-methyllic acid $[H_2As(CH_3)O_2]$, is a dibasic crystallizable acid, obtained by treating the dichloride with argentic oxide, whilst argentic chloride and metallic silver are separated.

Arsenio-methyl tetrachloride $[As(CH_3)Cl_4]$, is an unstable compound, which is obtained in large crystals from a mixture of carbon disulphide and the arsenio-methyl dichloride, which must be cooled by a freezing mixture, and submitted to the action of chlorine. As soon as the temperature rises to near the

freezing point, the compound becomes gradually decomposed into methyl chloride and arsenious chloride.

(1195) ARSENIODIETHYL $[\text{As}(\text{C}_2\text{H}_5)_2]_2$, forms a series of compounds parallel to those of kakodyl, but it does not so instantaneously burst into flame on exposure to air, and generally its chemical activity is somewhat less powerful.

(1196) ARSENIOTRIMETHYL $[\text{As}(\text{CH}_3)_3]$; *Boil. pt.* 248° (120° C.)] corresponds in composition with the analogous compound of the ethyl series, which has been more completely examined.

ARSENIOTRIETHYL $[\text{As}(\text{C}_2\text{H}_5)_3]$. *Sp. gr. of liq.* 1.151; *of vap.* 5.278; *Rel. wt.* 81; *Boil. pt.* 356° (180° C.).—This is a fuming, colourless, mobile liquid, of high refracting power, with the oppressive odour of arseniuretted hydrogen. It is soluble in alcohol and in ether, but not in water. It begins to boil at 284° ; but it undergoes partial decomposition during distillation. It does not usually take fire by exposure to the air unless gently heated, though it absorbs oxygen rapidly. It also becomes gradually oxidized if its solution in ether be exposed to the air; and it then produces a base $[\text{As}(\text{C}_2\text{H}_5)_3\text{O}]$, each atom of which requires two atoms of a monobasic acid for its saturation: no hydrochlorate of arseniotrimethyl corresponding to hydrochlorate of ammonia can be obtained. A chloride, bromide, and iodide may be obtained, each of which contains two atoms of the electro-negative body to one of arseniotriethyl; the formula of the iodide being $\text{As}(\text{C}_2\text{H}_5)_3\text{I}_2$: that of the sulphide is $\text{As}(\text{C}_2\text{H}_5)_3\text{S}$. Arseniotriethyl is obtained by the action of ethyl iodide upon an alloy of arsenicum and sodium: under these circumstances it is accompanied by arseniodiethyl, from which it is separated by distillation; the latter compound being the less volatile, remains in the retort. These operations must be performed in vessels filled with carbonic anhydride. The compounds of arseniotriethyl have the closest analogy with those of stibiotriethyl (1199).

(1197) HYDRATED ARSENIOTETRETHYLUM OXIDE $[\text{As}(\text{C}_2\text{H}_5)_4\text{HO}]$.—If arseniotriethyl be treated with ethyl iodide it combines with it and forms a new compound, which has been termed arseniotetrethylum iodide $[\text{As}(\text{C}_2\text{H}_5)_4\text{I}]$. It may be crystallized from water or from alcohol, and when its aqueous solution is treated with silver oxide, silver iodide is formed, while hydrated arseniotetrethylum oxide is obtained in solution. It may be procured in the form of a white hydrated solid by evaporation *in vacuo*, and like the ordinary ammonium bases, it presents the properties of a powerful and caustic alkali. It forms crystallizable salts, which when neutral contain 1 atom of the radicle of a monobasic acid.

By treating kakodyl with ethyl iodide *arseniodimethyl-diethylum iodide* $[\text{As}(\text{C}_2\text{H}_5)_2(\text{CH}_3)_2\text{I}]$ is formed, from which the hydrated oxide $[\text{As}(\text{C}_2\text{H}_5)_2(\text{CH}_3)_2\text{HO}]$ may be obtained by the action of argentic oxide. A corresponding compound containing amyl $[\text{As}(\text{C}_5\text{H}_{11})_2(\text{CH}_3)_2\text{I}]$ may be obtained by substituting amyl iodide for ethyl iodide, when acting upon kakodyl. The attempts to isolate the unoxidized compound metals of the form of arseniotetrethylum $[\text{As}(\text{C}_2\text{H}_5)_4]$ have as yet been fruitless.

(d) *Compounds of Antimony with the Alcohol Radicles.*

(1198) The alcohol derivatives of antimony have been carefully examined by Löwig and Schweizer (Liebig's *Annalen*, lxxv. 315) and by Landolt (*ib.* lxxviii. 91, and lxxxiv. 44). No compounds of antimony corresponding to the kakodyl series have been discovered, but those analogous to the third and fourth class

of the arsenical compounds have been studied. The following are the principal compounds with methyl and with ethyl which correspond to the third series of the arsenical compounds:—

| | |
|---------------------------------|--|
| Stibiotrimethyl | $\text{Sb}(\text{CH}_3)_3$ |
| Stibiotrimethyl oxide | $\text{Sb}(\text{CH}_3)_3\text{O}$ |
| „ sulphide | $\text{Sb}(\text{CH}_3)_3\text{S}$ |
| „ chloride | $\text{Sb}(\text{CH}_3)_3\text{Cl}_2$ |
| „ sulphate | $\text{Sb}(\text{CH}_3)_3\text{SO}_4$ |
| „ nitrate | $\text{Sb}(\text{CH}_3)_3 \cdot 2\text{NO}_3$ |
| <hr/> | |
| Stibiotriethyl | $\text{Sb}(\text{C}_2\text{H}_5)_3$ |
| Stibiotriethyl oxide | $\text{Sb}(\text{C}_2\text{H}_5)_3\text{O}$ |
| „ sulphide | $\text{Sb}(\text{C}_2\text{H}_5)_3\text{S}$ |
| „ chloride | $\text{Sb}(\text{C}_2\text{H}_5)_3\text{Cl}_2$ |
| „ sulphate | $\text{Sb}(\text{C}_2\text{H}_5)_3\text{SO}_4$ |
| „ nitrate | $\text{Sb}(\text{C}_2\text{H}_5)_3 \cdot 2\text{NO}_3$ |

The radicles stibiotrimethyl and stibiotriethyl at the first glance seem to resemble ammonia in composition, since they correspond to antimoniu-retted hydrogen in which the three atoms of hydrogen have been displaced by methyl or by ethyl, but they differ entirely from ammonia in their mode of combination; they are dyad in function, each of these bodies forms an oxide with one atom of oxygen; and this oxide requires two atoms of hydrochloric or of nitric acid for its saturation.

Antimony also forms a second class of organo-metallic compounds, the methyl series of which is represented as follows:—

| | |
|---|---|
| Stibiotetramethylium hydrated oxide | $\text{Sb}(\text{CH}_3)_4\text{HO}$ |
| „ sulphide | $[\text{Sb}(\text{CH}_3)_4]_2\text{S}$ |
| „ chloride | $\text{Sb}(\text{CH}_3)_4\text{Cl}$ |
| „ sulphate | $[\text{Sb}(\text{CH}_3)_4]_2\text{SO}_4$ |
| „ hydric sulphate | $\text{Sb}(\text{CH}_3)_4\text{HSO}_4$ |
| „ nitrate | $\text{Sb}(\text{CH}_3)_4\text{NO}_3$ |

This group acts as a monad basyl, and corresponds exactly with the ammonium series, with which indeed it presents the most striking analogies.

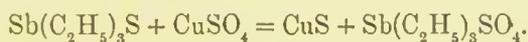
(1199) STIBETHYL, or *Stibiotriethyl* $[\text{Sb}(\text{C}_2\text{H}_5)_3]'$. *Sp. gr. of liq.* 1.324; *of vap.* 7.438; *Rel. wt.* 104.5; *Boil. pt.* 316°.4 (158° C.).—In order to procure stibiotriethyl, an alloy of antimony with potassium must be prepared by heating a mixture of 4 parts of powdered antimony and 4 of crude tartar in a covered crucible. This alloy, after being reduced to powder, is to be mixed with three times its weight of siliceous sand, and placed in a retort with ethyl iodide.

The operation must be conducted upon small quantities at a time, and in an atmosphere of carbonic anhydride: it requires a number of minute precautions (Löwig and Schweizer, *loc. cit.*). Stibiotriethyl is a heavy, limpid liquid, with an insupportable odour of onions. It is insoluble in water, but very soluble in alcohol and in ether. When a glass rod is dipped into pure stibiotriethyl and exposed to the air, the liquid emits dense white fumes, and takes fire in a few moments, burning with a white luminous flame.

Stibiotriethyl decomposes concentrated hydrochloric acid; hydrogen being liberated, whilst stibiotriethyl dichloride is formed as a heavy insoluble oil.

The *oxide* is obtained by acting on stibiotriethyl with mercuric oxide. It forms a viscous transparent liquid, soluble in water and in alcohol. The solution has a very bitter taste, but it does not appear to be poisonous. It is not volatile, and forms salts which crystallize with difficulty, except the nitrate, which forms beautiful rhomboidal, readily soluble crystals; they melt at $143^{\circ} 6$ (62°C.) into a colourless liquid, and are decomposed with deflagration on raising the heat.

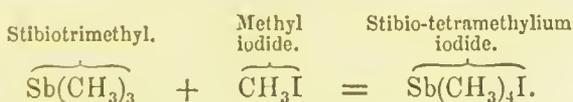
Stibiotriethyl Sulphide $[\text{Sb}(\text{C}_2\text{H}_5)_3\text{S}]$.—If stibiotriethyl and sulphur be mixed under water, they enter directly into combination, and great heat is evolved during the reaction: the compound is soluble in water, and may be obtained in crystals on evaporation. This solution, when mixed with solutions of the metallic salts, precipitates the metallic sulphides (just as sulphide of potassium would do), while a salt of stibiotriethyl remains dissolved;—for instance, if cupric sulphate be mixed with a solution of stibiotriethyl sulphide, stibiotriethyl sulphate and cupric sulphide are formed:—



Stibiotriethyl Diniodide $[\text{Sb}(\text{C}_2\text{H}_5)_3\text{I}_2]$ is soluble in alcohol, from which it crystallizes in long transparent colourless needles. It is also soluble in ether and in hot water.

STIBIOTRIMETHYL $[\text{Sb}(\text{CH}_3)_3]''$ may be formed in a manner similar to that directed for stibiotriethyl, which in properties it greatly resembles.

(1200) *Hydrated Stibiotetramethylium Oxide* $[\text{Sb}(\text{CH}_3)_4\text{HO}]$.—When stibiotrimethyl is brought into contact with methyl iodide, the two bodies combine, and a crystalline stibiotetramethylium iodide is the result:—



This compound is soluble in boiling water and in alcohol, from either of which solutions it may be obtained in crystals. When treated with argentic oxide, hydrated stibiotetramethylium oxide is separated, whilst argentic iodide is formed. This oxide is freely soluble in water and in alcohol. Its solution is very caustic, and absorbs carbonic acid from the air, presenting most of the usual characters of an ammonium base, and precipitating many of the metallic oxides from their salts. Upon evaporating its aqueous solution *in vacuo*, the hydrated oxide may be obtained in crystals, which if heated with due care in a tube, may be volatilized without undergoing decomposition. Its salts are very stable and are readily soluble; they have a bitter taste, but are not poisonous: they present great similarity in appearance to those of potassium and ammonium. On the addition of caustic soda or potash to their solutions, hydrated stibiotetramethylium oxide is liberated.*

* In addition to the papers already cited on the organo-metallic compounds, the reader may consult Cahours, *Ann. de Chimie*, III. lviii. 5; Buckton, *Phil.*

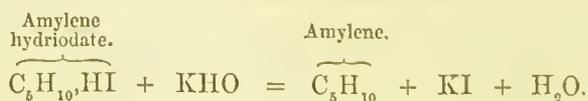
§ VI. PSEUDO-ALCOHOLS.

(1201) Synthetic experiments upon the formation of the monatomic alcohols have led to the discovery of a class of compounds, the members of which are isomeric with the true alcohols, but which differ from them in certain important particulars (p. 176). Several of these compounds, examined by Wurtz (*Ann. de Chimie*, IV. iii. 129), comport themselves as hydrates of the olefines of the true alcohols. Some of the compounds of this class are the following:—

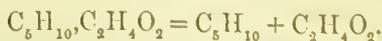
| | | Boiling Point. | |
|-----------------------------|-------------------|----------------|------|
| | | ° F. | ° C. |
| Isopropyl alcohol | C_3H_6, H_2O | 188·6 | 87 |
| Tetryl pseudo do. | C_4H_8, H_2O | 226·4 | 108 |
| Amyl pseudo do. | C_5H_{10}, H_2O | 221 | 105 |
| | | about | |
| Hexyl do. | C_6H_{12}, H_2O | 257 | 125 |

These pseudo-alcohols boil at temperatures considerably below the boiling point of the true alcohols isomeric with them. Simply heating them from 392° to 482° (200° to 250° C.) for some hours in closed vessels effects their decomposition into the olefine and water. When mixed with sulphuric acid they do not yield vinic acids, but give rise to the olefine, or to a compound polymeric with it, with separation of water. Bromine decomposes them into a dibromide of the olefine with liberation of water. Even in the cold, hydrochloric, hydrobromic, and hydriodic acids form hydrochlorate, hydrobromate, or hydriodate of the olefine, with separation of water; and these hydracid compounds all have a lower boiling point than the hydracid ethers of the true alcohols, with which they are metameric.

The hydriodates are readily decomposed by argentic oxide without the application of more than a very gentle heat, whilst argentic iodide and the secondary alcohol are formed. These hydriodates are easily decomposed by heat alone into hydriodic acid and free hydrocarbon. If heated with an alcoholic solution of caustic potash, they furnish the olefine, water, and potassic iodide; as for example:—



These secondary alcohols furnish compound ethers with the acids, such as the acetic and benzoic, but the oxyacid ethers thus obtained are not more stable than the corresponding hydracid ethers; amyleno acetate, for example, partially breaks up by mere distillation, into amyleno and acetic acid:—



Oxidizing agents do not convert these secondary alcohols into either aldehyds or acids, but first furnish a ketone (1258), and then attack the hydrocarbon itself, decomposing it with evolution of carbonic anhydride.

The formation of the secondary alcohols of this form occurs when the higher olefines (1203), from tetrylene upwards, are treated with one of the hydracids.

Trans., 1859, for organo-metallic compounds of tin, mercury, and lead; Breed, *Liebig's Annal.* lxxxii. 106; and Dunhaupt. *ib.* xcii. 371, for the compounds of bismuth; Odling and Buckton, for aluminum ethide, and methide (*Proceed. Roy. Soc.* 1865, xiv. 19).

Direct combination between the hydrocarbon and the acid occurs, and an isomeride of the corresponding true hydracid ether is obtained ($C_4H_8 + HBr = C_4H_7HBr$) from which the secondary alcohol is easily obtained by the action of hydrated argentic oxide; $C_4H_7HBr + AgHO = C_4H_7H_2O + AgBr$.

§ VII. ON THE HYDROCARBONS DERIVABLE FROM THE ALCOHOLS.

(1202) *Isologous Hydrocarbons*.—Allusion has already been made to the olefines, a series of hydrocarbons homologous with olefiant gas, which are derivable from the alcohols, and the process of preparing olefiant gas itself has been described (487). But besides the olefines other hydrocarbons may be obtained from the alcohols, to which they present equally definite relations. One series of these bodies (C_nH_{2n+1}) corresponds to the radicle of the alcohol, the other ($C_nH_{2n+1}H$) to the hydride of that radicle. Another series of the form (C_nH_{2n-2}) is represented by acetylene, a gaseous compound recently studied by Berthelot. There are also other hydrocarbons derived from the turpentine and from the distillation of resinous and carbonaceous substances. Indeed the hydrocarbons may be regarded as the starting-point whence the various classes of organic compounds take their origin. Hence a general view of these bodies will afford the student important aid in tracing the relations of the different groups of organic compounds to each other.

In the table on the following page the principal hydrocarbons are enumerated. It will be seen that all the hydrocarbons in the same horizontal line of the table (except the last, which contains some terms of series which are very incomplete) belong to the same isologous series: that is, they differ by successive decrements of H_2 , while the compounds mentioned in each vertical line constitute the successive terms of a homologous series.

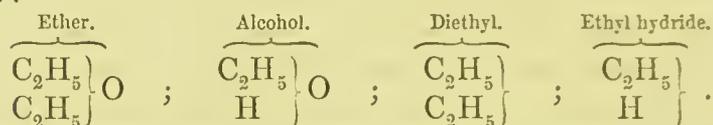
(1202 a) *Synthesis of Hydrocarbons*.—The researches of Berthelot (*Comptes Rendus*, lxi. 624), have shown that many of the hydrocarbons undergo condensation when heated, acetylene becoming condensed to benzol ($3C_2H_2 = C_6H_6$), by mere heating for some hours to dull redness, and marsh gas yielding acetylene and hydrogen; $2CH_4 = C_2H_2 + 3H_2$. Many of the hydrocarbons appear to unite directly with each other under the influence of a high temperature. Naphthalin, for example, by combining with acetylene, furnishes accenaphthene ($C_{10}H_8 + C_2H_2 = C_{12}H_{10}$), and benzol with acetylene furnishes styrolene ($C_6H_6 + C_2H_2 = C_8H_8$).

(a) *On the Hydrocarbon Radicles of the Alcohols* $(C_nH_{2n+1})_2$.

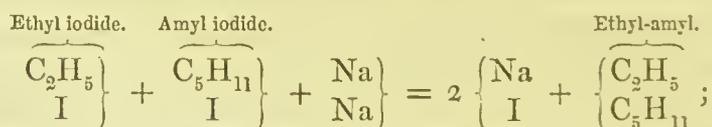
(1203) The first substance of this class which was obtained in an isolated form, corresponds in composition to the radicle of butyl alcohol; this was procured by Kolbe during the electrolysis of potassic valerate, and was by him termed valyl $(C_4H_9)_2$; other hydrocarbons homologous with dibutyl have been obtained by the electrolytic decomposition of the salts of the volatile fatty acids (289, 1274); and subsequently a general method of obtaining these bodies was contrived by Frankland, who decomposes the hydriodic ether of the alcohol by means of zinc, at a high temperature in sealed tubes. Greville Williams subsequently succeeded in isolating valyl or dibutyl $(C_4H_9)_2$, and several other hydrocarbons of this class, from the products of the destructive distillation of Boghead cannel at low temperatures.

The hydrocarbons of this group have not hitherto been made to combine directly with chlorine, bromine, or iodine, so as to reproduce the corresponding hydrochloric, hydrobromic, or hydriodic ether; no action occurs between these bodies and chlorine, or the other halogens, so long as light is excluded, but if light be admitted various substitution compounds are produced. Some chemists, including Hofmann and Gerhardt, when Frankland first announced the isolation of these bodies, considered the non-occurrence of direct combination with chlorine as a strong argument against the admission of the view that they were truly alcohol radicles, and they proposed to regard them as homologues of marsh gas: but the subsequent isolation of the true homologues of marsh gas which constitute the hydrides of the alcohol radicles (1207) has neutralized this objection. The bodies which have been termed alcohol radicles, may very consistently be regarded as analogues of hydrogen gas, which, when in its free state, seems not to be a simple body, but a compound of hydrogen with itself,—in short, hydrogen hydride, or dihydrogen $\left. \begin{array}{c} H \\ H \end{array} \right\}$, and the so-called radicle of alcohol may in like manner be considered as ethyl ethylide, or diethyl, $\left. \begin{array}{c} C_2H_5 \\ C_2H_5 \end{array} \right\}$, a view, the correctness of which the discovery of the double radicles of Wurtz (to which we shall presently refer) may be said to have proved. The semi-molecule (C_nH_{2n+1}) of the hydrocarbons of this class performs in combination the functions of a basylous monad radicle. The hydrocarbons of this group are not absorbed by sulphuric anhydride or by oil of vitriol, but are completely soluble in alcohol.

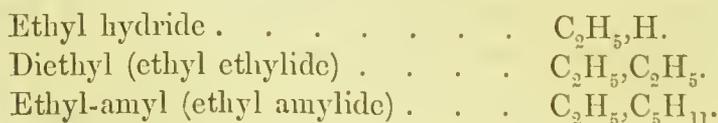
These hydrocarbons appear to belong to the hydrogen or metallic type $\left. \begin{matrix} \text{H} \\ \text{H} \end{matrix} \right\}$, and are represented by the formula $\left. \begin{matrix} \text{C}_n\text{H}_{2n+1} \\ \text{C}_n\text{H}_{2n+1} \end{matrix} \right\}$ a molecule of the compound $(\text{C}_n\text{H}_{2n+1})_2$ yielding 2 volumes of vapour. They would therefore stand to the third series of hydrocarbons $(\text{C}_n\text{H}_{2n+2})$, the hydrides which are to be described shortly (1206), in a relation somewhat similar to that of ether to alcohol, *e.g.* :—



Wurtz (*Ann. de Chimie*, III. xlv. 275), following up the ideas of Williamson and of Brodie upon the double ethers, has succeeded in obtaining compounds in which the second semi-molecule of the hydrocarbon is displaced by the semi-molecule of the hydrocarbon of a different alcohol, thus forming a series of double radicles corresponding with Williamson's double ethers. If a mixture of the hydriodic ethers of the two alcohols in equivalent proportions be decomposed by means of sodium, the two radicles combine at the moment of their liberation, and form a new double radicle. For example, in the preparation of ethyl-amyl, the following reaction occurs :—



Wurtz's double radicles are therefore merely compounds in which the place of the semi-molecule of hydrogen, or of the ethyl, is supplied by a different hydrocarbon :—



It is interesting to remark, that the boiling point of these double radicles rises gradually as the number of atoms of carbon and hydrogen increases in the molecule, and that this regular progression is observed in the simple alcohol radicles when compared with them, as in the following table; the boiling point and vapour density of the simple alcohol radicles being such as would theoretically be assigned to them upon the view above given; showing that both the simple and the double radicles are formed upon a similar molecular plan :—

| Double Radicles. | Formulæ. Mol. Vol. = <input type="text"/> | Boiling Point. | | Rel. Wt. H=1 | Specific Gravity. | | |
|----------------------------|--|----------------|------|--------------------|-------------------|---------|---------|
| | | ° F. | ° C. | | Vapour. | | Liquid. |
| | | | | | Expt. | Theory. | |
| Diethyl (ethyl ethylide) . | $C_4H_{10} = C_2H_5, C_2H_5$ | -9.4 | -23 | 29 | 2.046 | 2.004 | |
| Ethyl-butyl | $C_6H_{14} = C_2H_5, C_4H_9$ | 143.6 | 62 | 43 | 3.053 | 2.972 | 0.7011 |
| Ethyl-amyl | $C_7H_{16} = C_2H_5, C_5H_{11}$ | 190.4 | 88 | 50 | 3.522 | 3.455 | 0.7069 |
| Methyl-hexyl | $C_7H_{16} = C_2H_5, C_6H_{13}$ | 179.6 ? | 82 | 50 | 3.426 | 3.455 | |
| Dibutyl (butyl butylide) . | $C_8H_{18} = C_4H_9, C_4H_9$ | 222.8 | 106 | 57 | 4.070 | 3.939 | 0.7057 |
| Butyl-amyl | $C_9H_{20} = C_4H_9, C_5H_{11}$ | 269.6 | 132 | 64 | 4.405 | 4.423 | 0.7247 |
| Diamyl (amyl amylide) . | $C_{10}H_{22} = C_5H_{11}, C_5H_{11}$ | 311 | 155 | 71 | 4.899 | 4.907 | 0.7413 |
| Butyl-hexyl | $C_{10}H_{22} = C_4H_9, C_6H_{13}$ | 311 | 155 | 71 | 4.917 | 4.907 | |
| Dihexyl (hexyl hexylide) | $C_{12}H_{26} = C_6H_{13}, C_6H_{13}$ | 395.6 | 202 | 85 | 5.983 | 5.874 | 0.7574 |

It may further be remarked, in illustration of the persistence of the original molecular arrangement of the component groups of these compound bodies, that Wurtz finds that amyl preserves its rotatory action on a ray of polarized light when it passes into these compounds, ethyl-amyl displaying the power of causing the rotation of a polarized ray to the right; whilst amylene, valeric acid, and other derivatives of amyl alcohol, in which there is reason to suppose that the molecule of amyl is destroyed, exert no rotatory power.

(1204) 1. *Dimethyl, Methyl Methylide, or Methyl* $[(CH_3)_2]$. *Sp. gr.* 1.0365; *Rel. wt.* 15] is a gaseous body which burns with a bluish feebly luminous flame: it is not liquefied by a cold of 0° F. Dimethyl is obtained by acting upon methyl iodide with zinc, exactly in the manner directed for the preparation of ethyl. When mixed with twice its bulk of chlorine in the dark, and afterwards brought into diffused daylight, no change of volume takes place, but a mixture of 2 volumes of hydrochloric acid, and 1 volume of a chlorinated compound $(CH_2Cl)_2$ is formed.*

2. *Diethyl, Ethyl Ethylide, or Ethyl* $(C_2H_5)_2$. *Sp. gr. of gas* 2.046; *Rel. wt.* 29.—When a mixture of granulated zinc and ethyl iodide is sealed up in a strong glass tube from which air has been exhausted, and exposed for two hours in an oil bath to a temperature of 302° (150° C.), the ethyl iodide is gradually decomposed; the sides of the tube become coated with a white crystalline substance, and a colourless mobile liquid, equal in bulk to about half that of the ethyl iodide employed, is formed. This liquid is a mixture of diethyl, with other hydrocarbons (olefiant gas, and ethyl-hydride, the product of a secondary decomposition), the hydrocarbons having been liquefied by the pressure of their own vapour, whilst the crystals consist of a compound of zinc-ethyl with zincic iodide. On breaking off the capillary extremity of the tube under water, the whole of the liquid portion disap-

* Schorlemmer, however, considers dimethyl to be really ethyl hydride, and not merely isomeric with it; and he has extended this view to others of the so-called alcohol radicles. (*Proceed. Roy. Soc.* xiv. 164, 464, and xvi. 34, 367, 372.)

pears rapidly and escapes in the gaseous form. By collecting the portions which pass off last, the diethyl, which is the least volatile of these gases, is obtained nearly in a state of purity (Frankland, *Q. J. Chem. Soc.*, ii. 281). Diethyl may also be obtained, mixed with ethylene and ethyl hydride, when ethyl iodide is exposed over mercury to the sun's rays, mercuric iodide being produced.

Diethyl is a colourless gas with a slight ethereal smell; it burns with a highly luminous flame. At a temperature of 0° it remains gaseous under the ordinary atmospheric pressure, but it becomes liquefied at 38° ($3^{\circ}3$ C.) under a pressure of $2\frac{1}{2}$ atmospheres. Frankland estimates its boiling point at about $-9^{\circ}4$ (-23° C.), when the barometer stands at 29.92 inches (760 millim.). Diethyl is insoluble in water, but freely soluble in alcohol, which dissolves about 18 times its bulk of the gas, and gives it off when diluted with water. Chlorine has no action upon diethyl in the dark, but in diffused daylight it immediately combines with it and forms a colourless liquid.

3. *Propyl Propylide*, or *Ditrityl* (C_3H_7)₂.—The properties of this compound have not been minutely examined; but it formed one of the hydrocarbons separated by Williams from the lighter portion of the distillate from Boghead canal at low temperatures.

4. *Diteryl*, *Butyl*, or *Valyl* (C_4H_9)₂. *Sp. gr. of liq.* 0.7057 at 32° ; *of vap.* 4.070; *Rel. wt.* 57; *Boil. pt.* $222^{\circ}8$ (106° C.).—This compound is one of the products of the distillation of coal at low temperatures, and it may likewise be obtained during the electrolysis of potassic valerate (289). It may also be prepared by the action of sodium upon butyl iodide, in a flask connected with a vertical condenser, so arranged that the volatilized products shall return constantly into the flask as fast as they are volatilized and condensed. When the reaction has terminated, the dibutyl may be distilled off by a temperature not exceeding 302° (150° C.).

5. *Diamyl*, *Amyl Amylide*, or *Amyl* (C_5H_{11})₂. *Sp. Gr. at* 32° , 0.7413; *of vap.* 4.899; *Rel. wt.* 71; *Boil. pt.* 311° (155° C.).—Frankland obtained this hydrocarbon by heating amyl iodide with an amalgam of zinc in sealed tubes for some hours at a temperature of from 320° to 356° (160° to 180° C.). It is one of the products of the distillation of coal, and may also be procured by the electrolysis of potassic caproate, or still more easily as devised by Wurtz, by the action of sodium on amyl iodide. It is a colourless liquid, with a somewhat aromatic odour. It exerts a right-handed rotatory action on a ray of polarized light, the degree of which appears to vary in different specimens, being connected with the power exerted by that of the fousel oil from which the hydrocarbon was prepared, some samples of fousel oil having a greater rotatory power than others.

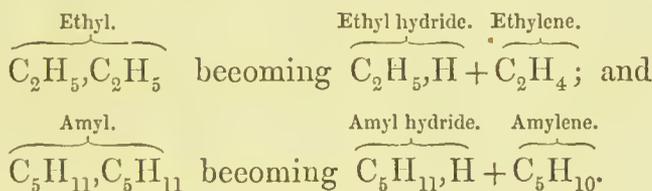
6. *Diheryl*, or *Caproyl* (C_6H_{13})₂, was obtained by the voltaic decomposition of potassic cœnanthylate. It is a liquid of an agreeable aromatic odour: its boiling point is about $395^{\circ}6$ (202° C.).

(1205) DOUBLE OR MIXED HYDROCARBON RADICLES.—*Ethylbutyl* (C_2H_5, C_4H_9). *Sp. gr. of liq. at* 32° , 0.7011; *of vap.* 3.053; *Rel. wt.* 43.—This compound was obtained by decomposing a mixture of 40 parts of butyl iodide, and 34 of ethyl iodide, with

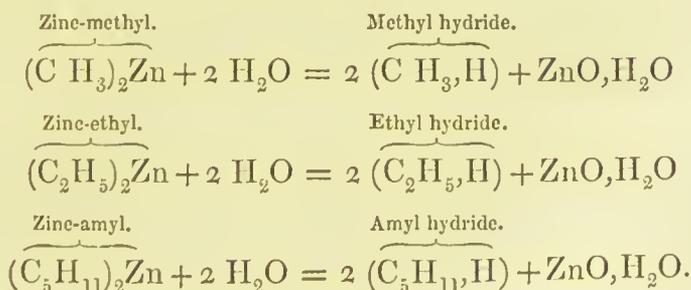
11 of sodium, in the manner already described for procuring dibutyl: by distillation of the product, collecting the portion which passes over between 140° and 158° (60° and 70° C.), and again rectifying it, a mobile liquid is obtained, the boiling point of which when pure is stationary at $143^{\circ}6$ (62° C.). By a similar method, employing mixtures of the corresponding hydriodic ethers, Wurtz succeeded in obtaining other analogous compounds, which are enumerated in the table, page 265.

(b) *Hydrocarbons homologous with Marsh Gas* (C_nH_{2n+2}) $^{\circ}$.

(1206) 1. When the hydriodic ethers are submitted to the action of zinc at a high temperature, other hydrocarbons are formed in addition to the radieles already described; the alcohol radiele itself undergoing a secondary decomposition into two hydrocarbons, which are complementary to each other. Ethyl, for example, breaks up into ethyl hydride and ethylene (olefiant gas); and amyl, in like manner, yields amyl hydride, and a corresponding hydrocarbon:—



2. These hydrocarbons may also be formed by the regulated action of water upon the metallic compounds of zinc with the alcohol radieles. For example:—



3. Berthelot procures the homologues of marsh gas by decomposing the bromide of the corresponding hydrocarbon in the ethylene series, by heating it in a sealed tube to 482° (250° C.) with water and potassie iodide. Propylene bromide ($C_3H_6Br_2$) thus yields propyl hydride.

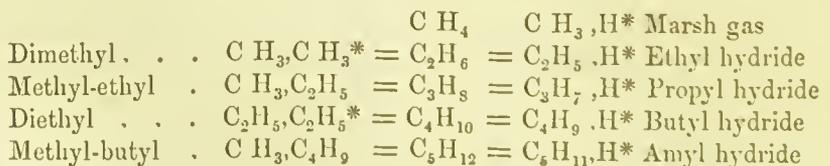
4. In addition to marsh gas, many of these hydrocarbons are found as natural products, and according to the researches of

Pelouze and Cahours (*Ann. de Chimie*, IV. i. 5), the American petroleum consists of a mixture of the homologues of marsh gas; these chemists consider that they have isolated thirteen consecutive terms of the series from trityl hydride to palmityl hydride inclusive, and they believe other higher terms also exist in the heavier portions of the oil. It appears, indeed, that the solid fats to which the term *paraffin* has been applied are really the higher terms of this series, though they were for a long time regarded as members of the group of olefines (1209, 1537).

The following table embodies the chief numerical results of the experiments of Pelouze and Cahours:—

| Hydrocarbons. | Formula Mol. = <input type="text"/> <input type="text"/> | Boiling Point. | | Specific Gravity. | | Rel. Wt. H = 1. |
|---------------------|---|-----------------|------|-------------------|---------|--------------------|
| | | ° F. | ° C. | Liquid. | Vapour. | |
| Butyl hydride . . . | C ₄ H ₁₀ | 32 ^p | 0 | 0·600 | | 29 |
| Amyl " . . . | C ₅ H ₁₂ | 86 | 30 | 0·628 | 2·557 | 36 |
| Hexyl " . . . | C ₆ H ₁₄ | 154 | 68 | 0·669 | 3·055 | 43 |
| Heptyl " . . . | C ₇ H ₁₆ | 200 | 93 | 0·699 | 3·600 | 50 |
| Octyl " . . . | C ₈ H ₁₈ | 243 | 117 | 0·726 | 4·010 | 57 |
| Nonyl " . . . | C ₉ H ₂₀ | 279 | 137 | 0·741 | 4·541 | 64 |
| Rutyl " . . . | C ₁₀ H ₂₂ | 320 | 160 | 0·757 | 5·040 | 71 |
| Endecyl " . . . | C ₁₁ H ₂₄ | 358 | 181 | 0·766 | 5·458 | 78 |
| Lauryl " . . . | C ₁₂ H ₂₆ | 390 | 199 | 0·778 | 5·972 | 85 |
| Cocynyl " . . . | C ₁₃ H ₂₈ | 426 | 219 | 0·796 | 6·569 | 92 |
| Myristyl " . . . | C ₁₄ H ₃₀ | 460 | 238 | 0·809 | 7·019 | 99 |
| Benyl " . . . | C ₁₅ H ₃₂ | 511 | 266 | 0·825 | 7·526 | 106 |
| Palmityl " . . . | C ₁₆ H ₃₄ | 536 | 280 | | 8·078 | 113 |

Each of the hydrocarbons of this group, with the exception of marsh gas, is isomeric with one of the group of alcohol radicles, if not identical with it; in the case of dimethyl at least the recent experiments of Schorlemmer seem to indicate that it is identical with ethyl hydride (*note*, p. 265); for example:—



Those compounds marked with an asterisk have been already prepared, and the others might be easily procured, if needed. The marsh gas series are regarded as being formed of saturated molecules (pp. 59, 60), inasmuch as the whole of the *bonds* of carbon already have their combining power neutralized by union with hydrogen. These hydrocarbons may further be looked upon as the starting-point of the alcohol series:—

| Marsh gas. | Alcohol. | Glycol. | Glycerin. |
|--------------|-------------------|---------------------|------------------|
| $C H_4$ | $C H_3 (HO)$ | | |
| $C_2 H_6$ | $C_2 H_5 (HO)$ | $C_2 H_4 (HO)_2$ | |
| $C_3 H_8$ | $C_3 H_7 (HO)$ | $C_3 H_6 (HO)_2$ | $C_3 H_5 (HO)_3$ |
| $C_4 H_{10}$ | $C_4 H_9 (HO)$ | $C_4 H_8 (HO)_2$ | $C_4 H_7 (HO)_3$ |
| $C_5 H_{12}$ | $C_5 H_{11} (HO)$ | $C_5 H_{10} (HO)_2$ | $C_5 H_9 (HO)_3$ |

the *monatomic alcohols* being compounds in which one atom of hydrogen may be theoretically regarded as displaced by one atom of hydroxyl (HO), the *diatomic alcohols* or *glycols*, having 2 atoms of the original hydrogen displaced by 2 of hydroxyl, and the *triatomic alcohols* or *glycerins* being produced by the displacement of 3 atoms of hydrogen by 3 of hydroxyl.

The hydrocarbons of this class are not absorbed by sulphuric anhydride or by oil of vitriol, and are not acted upon by chlorine or by iodine in the dark, but in diffused daylight chlorine slowly gives rise to substitution compounds, and in direct sunlight it decomposes them rapidly, often with explosion. Antimony pentachloride is without action upon them. These hydrocarbons are all neutral or saturated bodies; consequently they do not unite directly with chlorine or the other halogens; but they are capable of gradual oxidation; even the solid paraffins are attacked by chromic and by nitric acid.

(1207) 1. *Methyl Hydride*, or *Hydride of Methyl* (CH_4)^o or (CH_3, H). *Sp. gr.* 0.5596; *Rel. wt.* 8.—This compound has already been described under the name of *marsh gas* (491).

In addition to the mode of preparing it by heating the acetates with a hydrate of one of the alkalies or alkaline earths, marsh gas may be procured by the decomposition of zinc-methyl by water. It may also be obtained from chloroform ($CHCl_3$), or carbon tetrachloride (CCl_4), by reducing their alcoholic solutions by means of an amalgam of sodium or potassium.

2. *Ethyl Hydride*, or *Hydride of Ethyl* (C_2H_6)^o or (C_2H_5, H). *Sp. gr.* 1.075; *Rel. wt.* 15.—This compound is a permanent gas, destitute of smell or taste. It is insoluble in water, but alcohol takes up more than its own bulk of it. The best manner of preparing this gas consists in decomposing a mixture of equal parts of water and ethyl iodide by means of zinc, in a sealed tube, at a temperature of about 329° (165° C.), as already described when speaking of diethyl (1204). After the lapse of a couple of hours, the tube is opened under water, and the gas escapes with great violence. It may also be obtained by decomposing hydrocyanic ether with potassium. The potassium is placed in a flask, fitted with a condenser and a bent tube for carrying off the gas as it

is disengaged; the ether is allowed to fall, drop by drop, upon the potassium, whilst the gas which is disengaged is collected over water. Potassic cyanide and cyanthine (1149) remain in the flask, and ethyl hydride is obtained in the gaseous state.

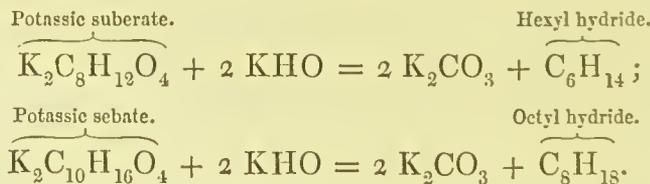
3. *Propyl- or Trityl Hydride* (C_3H_7, H), is gaseous at ordinary temperatures.

4. *Butyl- or Tetryl Hydride* (C_4H_9, H), is one of the products of the decomposition of butyl alcohol when distilled with zinc chloride. It is liquefiable at a few degrees below 32° .

5. *Amyl Hydride, or Hydride of Amyl* (C_5H_{11}, H). *Sp. gr. of liq.* 0.638; *of vap.* 2.5; *Rel. wt.* 36; *Boil. pt.* 86° ($30^\circ C.$).—This body was obtained by Frankland by acting on equal bulks of amyl iodide and water, by means of zinc in a sealed tube, at a temperature not exceeding 302° ($150^\circ C.$). Frankland considers it to be probable that it is identical with *Eupion*, which Reichenbach obtained during the rectification of the products from wood tar, and from rape oil; and he also thinks that it constitutes one of the condensable hydrocarbons of coal gas. Schorlemmer has shown that it forms one of the components of American petroleum.

Amyl hydride is a volatile, mobile, colourless liquid, with an odour resembling that of chloroform. It has a smaller density than any other known liquid; it remains unfrozen at -11.2° ($-24^\circ C.$). Its vapour burns with a brilliant white flame, without smoke.

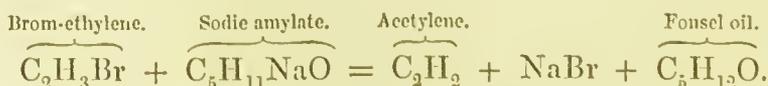
Hexyl Hydride (C_6H_{14}) may be obtained by the cautious distillation of potassic suberate with caustic potash, and *Octyl hydride* (C_8H_{18}), by similar treatment of potassic sebate:—



(c) *Hydrocarbons of the Form* C_nH_{2n-2} .

(1208) The representative of this class of hydrocarbons is acetylene, but several others—viz., *allylene* (C_3H_4), *crotonylene* (C_4H_6), *valerylene* (C_5H_8), *rutylene* ($C_{10}H_{18}$), and *benzylene* ($C_{15}H_{28}$), have lately been announced.

Acetylene (C_2H_2). *Sp. gr. calcd.* 0.898, *by expt.* 0.92; *Rel. wt.* 13.—If brom-ethylene (C_2H_3Br) be subjected to the action of sodium-fousel oil at 212° , under pressure, gradual decomposition takes place, sodic bromide and amyl alcohol are produced; and a permanent gas, which is rapidly absorbed by an ammoniacal solution of eupreous chloride is obtained:—



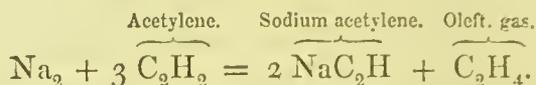
If the flocculent red precipitate which is thus occasioned in the solution of copper be washed, and treated with hydrochloric

acid, it is decomposed, and pure acetylene is obtained (Sawitsch). Acetylene appears to have been discovered by E. Davy in 1836, when decomposing with water a compound of potassium and carbon formed during the preparation of potassium; $C_2K_2 + 2H_2O = C_2H_2 + 2KHO$; he called it *klumene*. Berthelot, who first carefully investigated this interesting compound, obtained it by decomposing olefiant gas by heat. Marsh gas likewise yields it when passed through red hot tubes; $2CH_4 = C_2H_2 + 3H_2$. It may also be obtained by passing vapour of chloroform over ignited copper; $2CHCl_3 + 6Cu = C_2H_2 + 3Cu_2Cl_2$; or by heating the vapour of methyl chloride to low redness; $2CH_3Cl = C_2H_2 + 2HCl + H_2$. It is present in coal gas in small quantity, and is one of the products furnished by transmitting the vapour of alcohol, of aldehyd, or of ether through red-hot tubes. Acetylene may be readily freed from the hydrocarbons with which it is contaminated, by causing the mixed gas to pass through a solution of cupreous chloride in ammonia, which absorbs acetylene rapidly, and forms with it a flocculent dark-red insoluble substance; this cupreous compound when dry detonates powerfully on the application of heat, or on receiving a sudden blow. It is said that the occasional formation of this compound in the copper service pipes used for distributing coal gas, has in some cases caused explosions where the pipes were undergoing repair.

The cupreous compound according to Berthelot (*Ann. de Chimie*, IV. ix. 385) when washed with ammonia until free from chlorine, and then with water, furnishes a flocculent brown-red precipitate to which he assigns a composition, indicated by the formula $(C_2Cu'_2H)_2O$, *cupreo-acetyl oxide*: when dry it detonates by a blow, or by a temperature exceeding 248° ($120^\circ C.$). This body is soluble in cold hydrochloric acid, but is decomposed on boiling the liquid with evolution of acetylene. The cupreo-acetyl oxide has the power of forming a series of double salts.

A similar compound may be obtained with silver, *argent-acetyl oxide* $(C_2Ag_2H)_2O$, by transmitting any gas mixed with acetylene through an ammoniacal solution of argentic nitrate; and if an ammoniacal solution of argentic chloride be substituted, a white curdy precipitate, consisting of C_2Ag_2HCl , is deposited. If the gas be passed into a solution of neutral argentic nitrate it is absorbed, and a white deposit is formed, which when dry explodes violently when heated, but does not detonate when struck. If the gas is passed into a solution of auro-sodie hyposulphite, a yellow explosive compound is formed. When sodium

or potassium is heated gently in excess of acetylene, part of the hydrogen is displaced, and sodium or potassium acetylene (C_2HK) is formed, whilst olefiant gas is produced by the union of the disengaged hydrogen with another portion of acetylene:—



If sodium in excess be heated to dull redness in acetylene, both atoms of hydrogen are expelled, and the compound C_2Na_2 is formed. Both these sodium compounds are immediately decomposed by water, and acetylene is reproduced, whilst sodic hydrate is formed in the solution.

Berthelot found that a large number of organic compounds, such as marsh gas, olefiant gas, ether, benzol, and naphthalin, when burned with an insufficient supply of air, furnish acetylene among their products. This may be shown by simply moistening a tall narrow jar filled with the gas or vapour for combustion, with an ammoniacal solution of cupreous chloride; on setting fire to the mixture, and holding the jar in a position nearly horizontal, causing it to revolve whilst it is burning, so as to distribute the cupreous solution over the sides of the jar, a considerable deposit of the brownish red copper acetylide will be obtained upon the sides of the jar. A still better method consists in burning a jet of atmospheric air in coal gas (Maclcod, *Journ. Chem. Soc.* 1866, p. 152), and transmitting the products through an ammoniacal solution of cupreous chloride. Another remarkable mode of preparing this gas, though not of any practical value, as the quantity obtained is very small, was also discovered by Berthelot; who found that by igniting intensely in the voltaic arc, two carbon electrodes in a current of pure hydrogen, direct combination between the carbon and hydrogen occurs, and a little acetylene is formed.

Acetylene is a transparent colourless gas, of a peculiar disagreeable odour, which is distinctly perceived when coal gas is imperfectly burned in the air. Acetylene is somewhat soluble in water. It burns with a bright smoky flame. It has not yet been liquefied by cold or pressure. It can unite either with one or with two molecules of hydrobromic or of hydriodic acid, forming in the second case compounds which are isomeric with the Dutch liquids in the ethylene series, though not identical with them. It also unites with bromine, forming acetylene dibromide ($C_2H_2Br_2$). When sealed up in a tube and exposed to the heat at which glass softens for half an hour, acetylene gradu-

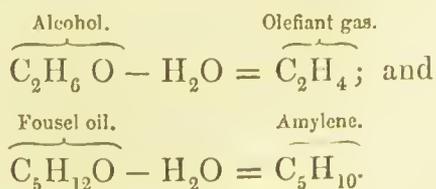
ally contracts in bulk, and becomes condensed into the isomeric hydrocarbon styrolene (C_8H_8), and on cooling, this compound is obtained in the liquid form, exhibiting a remarkable instance of condensation, and conversion from a simple to a more complex molecule by the prolonged effect of heat.

If mixed with chlorine, acetylene explodes spontaneously almost immediately, even in diffused light, a portion of carbon being separated, and a jet of the gas takes fire spontaneously if directed into a vessel filled with chlorine. When agitated with sulphuric acid, the gas is readily dissolved, forming a colligated acid, the *acetyl-sulphuric* (H, C_2H_2, SO_4), which furnishes a crystallizable salt with barium. When acetyl-sulphuric acid is diluted and distilled, it yields a liquid metameric with aldehyd, and with ethylene oxide, which Berthelot terms *acetylic*, or *vinyl alcohol* (C_2H_4O); the nature of this liquid, however, is at present but imperfectly known.

Acetylene may be reconverted into olefiant gas by acting upon its compound with cupreous chloride, by means of nascent hydrogen; this change is best effected by suspending the compound of acetylene with cupreous chloride, in a solution of ammonia, and adding zinc.

(d) *Olefines, or Olefiant Gas Series* (C_nH_{2n}).

(1209) The hydrocarbons of this series may be obtained by the decomposition of the hydrochloric ether of the particular alcohol by exposing it to an elevated temperature, either alone, or by passing its vapour over heated lime; under these circumstances the ether is resolved into hydrochloric acid and the hydrocarbon of the alcohol; for instance, C_2H_5Cl becomes $C_2H_4 + HCl$. But the hydrocarbons of this class are more usually formed by the action of sulphuric acid or of zincic chloride upon their corresponding alcohols, from which their formulæ differ by containing the elements of one molecule less of water; for instance:—



The formation of these compounds, however, does not appear to consist simply in the abstraction of water from the alcohol; for, in some cases, the substance which is obtained has a vapour-density double of that which the corresponding hydrocarbon should

possess: when, for instance, fousel oil is distilled with sulphuric acid, the hydrocarbon which is liberated is not amylene (C_5H_{10}); for it has undergone condensation, and has been converted into the polymeric paramylene ($C_{10}H_{20}$), the vapour of which has a density exactly double of that of the true amylene obtained by distilling fousel oil with zinc chloride.

The researches of Wurtz and of Hofmann have shown that the olefines are basylous dyad radicles: olefiant gas (C_2H_4) being equivalent, in combination, to two atoms of hydrogen, as will be seen when glycol (1214 *et seq.*) and its derivatives are described.

The olefines combine readily with sulphuric anhydride, and with antimony pentachloride; they are also generally freely soluble in absolute alcohol and in ether: ethylene and propylene are, moreover, slowly absorbed by oil of vitriol when agitated with it, and the solution when diluted with water and distilled, yields the corresponding alcohol. The olefines also combine directly with hydrochloric and with hydrobromic acid, and when heated with them to 212° in the gaseous form for many hours, they become converted into the corresponding hydrochloric or hydrobromic ether; and these ethers, if digested with water upon argentic oxide, are partially converted into their alcohols or into an isomeric body; *e.g.*, $2 C_2H_5I + Ag_2O + H_2O = 2 AgI + 2 C_2H_6O$. Part, however, is usually reconverted into the original hydrocarbon by the following reaction; $2 C_2H_5I + Ag_2O = 2 C_2H_4 + 2 AgI + H_2O$. Each molecule of an olefine unites directly with two atoms of chlorine, of bromine, or of iodine, forming compounds which correspond with Dutch liquid in composition, and from which a similar series of substitution products may be obtained: for example, we may form—

| | |
|-------------------------------|-----------------------|
| Ethylene Dutch liquid . . . | $(C_2H_4)''Cl_2$. |
| Propylene " " . . . | $(C_3H_6)''Cl_2$. |
| Amylene " " . . . | $(C_5H_{10})''Cl_2$. |

The following are the more important of the olefines:—

1. *Methylene* (CH_2 ?).—Dumas and Péligot believed that they obtained methylene by transmitting the gaseous methyl chloride through a red-hot porcelain tube: CH_3Cl becoming $CH_2 + HCl$; but probably the gas which they analysed was only a mixture accidentally possessing this composition, since other chemists have failed to obtain the compound by this or by any other means.

2. *Ethylene, Olefiant Gas, or Elayl* (C_2H_4 ; *Rel. wt.* 14; *Sp. gr.* 0.978) has already been described (487). It is produced, abundantly mixed with other hydrocarbons, during the dry distillation of pit coal, and of many fatty and resinous bodies. It is also present in small quantity, amongst other bodies, in the

product of the dry distillation of baric formiate ($\text{Ba } 2 \text{ CHO}_2$). Olefiant gas is the principal luminous constituent of coal gas. When required in a state of purity it is always obtained by decomposing alcohol by means of sulphuric acid in excess.

Berthelot has shown that olefiant gas and marsh gas in small quantity, diluted largely with free hydrogen, may be obtained by passing a current of sulphuretted hydrogen mixed with the vapour of carbon disulphide over finely divided copper heated to dull redness; a process which possesses some interest from the circumstance that it indicates a method, though an imperfect one, for procuring from compounds of inorganic origin, hydrocarbons, which previously had been obtained only by the decomposition of organic products.

(1210) 3. *Tritylene* or *Propylene* (C_3H_6); *Sp. gr.* 1.498; *Rel. wt.* 21.—Reynolds obtained this gas mixed with marsh gas and some other compounds, by decomposing the vapours of fousel oil by transmission through a porcelain tube heated to redness; but it is best procured by the action of phosphorus diiodide (PI_2) upon glycerin. Pure propylene is readily obtained for laboratory use by distilling 1 part of allyl iodide (1472) with 5 parts of mercury and 2 of concentrated hydrochloric acid. An ounce of allyl iodide treated thus yields more than 150 cubic inches of the gas; $\text{C}_3\text{H}_5\text{I} + \text{HCl} + 2 \text{Hg} = \text{C}_3\text{H}_6 + \text{HgI} + \text{HgCl}$. Propylene remains gaseous at -40° , but it may be liquefied under pressure. Its odour resembles that of olefiant gas. It is dissolved to some extent by essence of turpentine, ether, chloroform, and benzol, each of which absorbs from 13 to 18 times its volume of this gas.

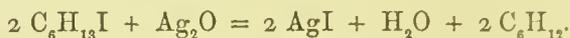
Oil of vitriol readily takes up about 200 times its volume of the gas, converting it into propyl-sulphuric acid. Hydrochloric acid also absorbs it, and forms propyl-hydrochloric ether or trityl chloride, $\text{C}_3\text{H}_7\text{Cl}$. The action of iodine and of bromine upon propylene yields compounds of considerable interest in connexion with the allylic series (1469).

(1211) 4. *Tetrylene*, *Butylene*, or *Oil Gas* [C_4H_8]; *Sp. gr.* 1.854; *Rel. wt.* 28], has been already described (495). This gas was ascertained by Faraday to be one of the products furnished by the destructive distillation of oil; and it appears also to be contained amongst the products of the distillation of caoutchouc. It was afterwards obtained by Kolbe during the voltaic decomposition of potassic valerate; and by Wurtz as one of the compounds produced by the action of zincic chloride upon butylic alcohol; and it has been procured from erythrite (1243) by decomposing it with hydriodic acid, and treatment of the distillate with argentic oxide (v. Luynes).

5. *Amylene* [C_5H_{10}], *Boil. pt.* $102^\circ.2$ (39°C.) may be procured by decomposing amyl chloride with fused caustic potash, or by distilling a concentrated solution of zincic chloride with fousel oil; or by acting upon amyl iodide in a sealed tube with an amalgam of zinc: in the latter case it is mixed with amyl hydride. Amylene is a colourless, very mobile liquid, with the odour of decaying cabbage. An attempt was made to substitute it for chloroform as an anæsthetic in surgical operations; but its use has been abandoned, as in some cases its employment has occasional fatal results.

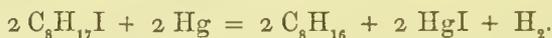
(1212) 6. *Hexylene* or *Caproylene* (C_6H_{12}); *Boil. pt.* $159^\circ.8$ (71°C.) (G. Williams).—This compound is a colourless liquid, lighter than water, of a nauseous, penetrating alliaceous odour. It is scarcely soluble in water, but

freely so in alcohol and in ether. It appears to act injuriously when respired. It is procured during the destructive distillation of several fatty acids (Fremy), and is stated by G. Williams to be one of the products obtained from the distillation of the Boghead canal: it may likewise be procured by acting upon mannite with hydriodic acid, and decomposing the β hexyl-iodide so obtained, by acting upon it with argentic oxide:—



7. *Heptylene* or *Ænanthylene* (C_7H_{14}); *Sp. gr. of liq.* 0.718; *of vap.* 3.32; *Rel. wt.* 49; *Boil. pt.* 210°.2 (99° C.).—This body was also reported by Williams to occur in the Boghead distillate; and was likewise obtained by Bouis from the distillation of ænanthol (1255) with phosphoric anhydride.

8. *Octylene* or *Caprylene* [(C_8H_{16}) , *Boil. pt.* 257° (125° C.)] was obtained as a colourless liquid, insoluble in water, by distilling the castor oil (octylic) alcohol with sulphuric acid, or with zincic chloride. The action of potassium or of mercury on chloride or iodide of octyl gives rise to the same compound:—

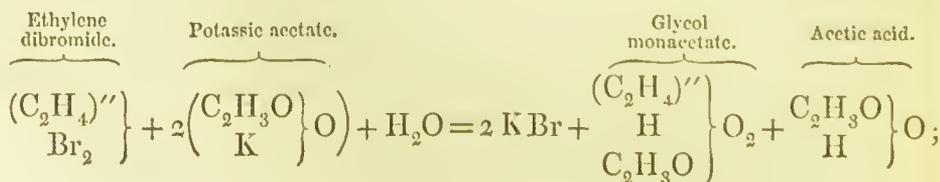


9. *Nonylene* or *Elaene* (C_9H_{18}), was obtained mixed with hexylene, by Fremy, during the distillation of several fatty acids.

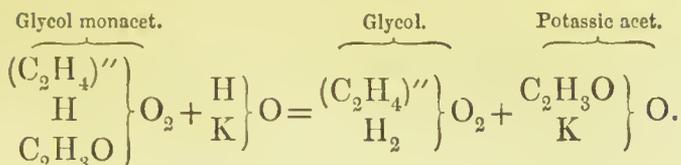
10. *Paramylene* or *Diamylene* ($C_{10}H_{20}$); *Sp. gr.* 0.777; *Boil. pt.* 329° (165° C.), is procured by the distillation of fousel oil with phosphoric anhydride in excess. Bauer has obtained two other hydrocarbons, *triamylene* [$C_{15}H_{30}$; *Sp. gr.* 0.8139; *of vap.* 7.6; *Boil. pt.* about 473° (245° C.)], and *tetramylene* [$C_{20}H_{40}$; *Sp. gr.* 0.871; *Boil. pt.* about 743° (395° C.)], by distilling fousel oil with zincic chloride and separating the products by fractionated distillation. Fousel oil, it will be seen, gives rise to at least five isomeric hydrocarbons of this series—viz., to propylene, amylene, diamylene, triamylene, and tetramylene.

(B.) DIATOMIC ALCOHOLS, OR GLYCOLS.

(1213) THE GLYCOLS, as it has already been stated, are a purely artificial class of compounds, the existence of which, as an intermediate series between the monatomic alcohols and the glycerins, was inferred by Wurtz. They are formed from ethylene and its homologous dyad hydrocarbons, by preparing the dibromide or the diiodide of the olefine, and decomposing it with potassic or argentic acetate, and obtaining the monacetate or diacetate of the glycol (1214), and on distilling these compounds with baric hydrate, or caustic potash, the corresponding glycol is liberated:—



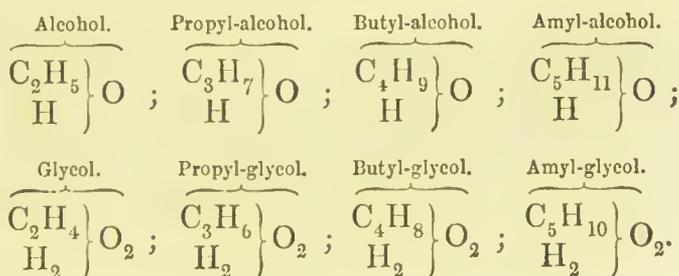
and



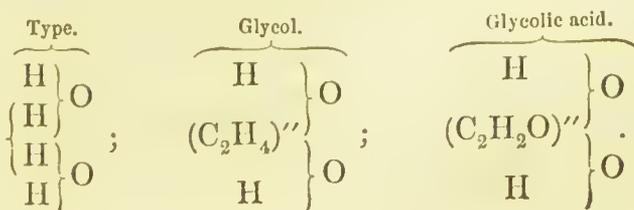
By analogous reactions the following compounds have been prepared :—

| Compound. | Formula. Mol. = $\left[\begin{array}{c} \square \\ \\ \square \end{array} \right]$ | Boiling Point. | | Specific Gravity. | | Rel. wt. H = 1. |
|---|---|----------------|-------|-------------------|---------|--------------------|
| | | ° F. | ° C. | Liquid. | Vapour. | |
| Glycol | $\left. \begin{array}{c} (\text{C}_2\text{H}_4)'' \\ \text{H}_2 \end{array} \right\} \text{O}_2$ | 386·6 | 197 | 1·125 | 2·164 | 31 |
| Trityl-glycol (Propyl-glycol) | $\left. \begin{array}{c} (\text{C}_3\text{H}_6)'' \\ \text{H}_2 \end{array} \right\} \text{O}_2$ | 370·4 | 188 | 1·051 | 2·596 | 38 |
| Tetryl-glycol (Butyl-glycol) | $\left. \begin{array}{c} (\text{C}_4\text{H}_8)'' \\ \text{H}_2 \end{array} \right\} \text{O}_2$ | 361·4 | 183 | 1·048 | 3·188 | 45 |
| Amyl-glycol | $\left. \begin{array}{c} (\text{C}_5\text{H}_{10})'' \\ \text{H}_2 \end{array} \right\} \text{O}_2$ | 350·6 | 177 | 0·987 | | 52 |
| Hexyl-glycol | $\left. \begin{array}{c} (\text{C}_6\text{H}_{12})'' \\ \text{H}_2 \end{array} \right\} \text{O}_2$ | 404·6 | 207 | 0·967 | | 59 |
| Octyl-glycol | $\left. \begin{array}{c} (\text{C}_8\text{H}_{16})'' \\ \text{H}_2 \end{array} \right\} \text{O}_2$ | about 464 | 235·2 | 0·932 | | 73 |

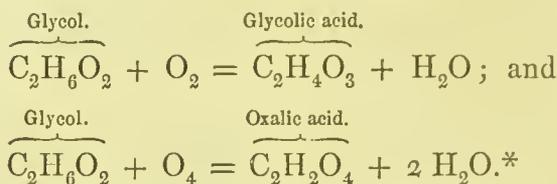
Each of these glycols corresponds to a monatomic alcohol which contains 1 atom less of oxygen :—



In the monatomic alcohols, a single typical atom of hydrogen only admits of displacement by one of an acid radicle; whereas in the diatomic alcohols, or glycols, two typical atoms of hydrogen may be displaced by a corresponding number of atoms of an acid radicle. The glycols are therefore to be regarded as formed upon the type of 2 atoms of water, the two atoms being bound into a single molecule by the displacement of two atoms of hydrogen by one molecule of the dyad hydrocarbon; as for example :—



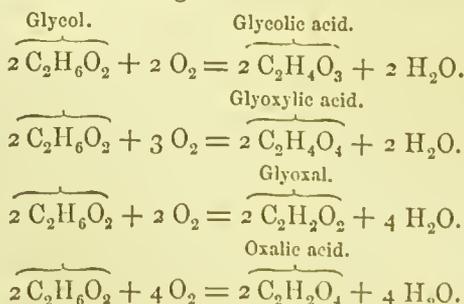
The glycols when exposed to the action of air or oxygen under the influence of platinum black, or when heated with caustic potash, speedily become oxidized, and furnish acids which belong either to the lactic or to the oxalic acid series:—



The glycols exhibit an anomaly in their boiling points; for in the first four terms, instead of rising, the boiling point becomes progressively lower. It will be unnecessary to enter minutely into a description of the glycols, as the general properties of these compounds will be sufficiently understood from the following account of ethylic glycol; for further details the reader is referred to Wurtz's papers on the subject. (*Ann. de Chimie*, III. lv. 400, IV. iii. 129.)

(1214) *Glycol or Ethylene Alcohol*, $[\text{C}_2\text{H}_6\text{O}_2 = \left. \begin{array}{c} (\text{C}_2\text{H}_4)'' \\ \text{H}_2 \end{array} \right\} \text{O}_2]$.
Boil. pt. 386°·6 (197° C.); *Sp. gr. of liq.* 1·125; *of vap.* 2·164; *Rel.*

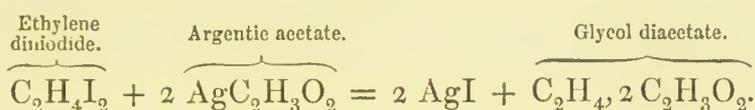
* It is indeed probable that there is a class of compounds represented by glyoxal, intermediate between these glycols and the glycolic or lactic acid series, corresponding to the aldehyds of the monatomic alcohols (Debus); and the researches of Debus have further rendered it not unlikely that between the lactic and the oxalic series of acids is a third intermediate group of acids, the representative of which is the glyoxylic (1151), so that the different stages of the oxidation of glycol would be the following:—



The relation of these bodies may further be thus represented:—

$\text{C}_2\text{H}_6\text{O}_2$ Glycol.
 $\text{C}_2\text{H}_4\text{O}_2$ Aldehyd (as yet unknown).
 $\text{C}_2\text{H}_4\text{O}_3$ Glycolic acid.
 $\text{C}_2\text{H}_4\text{O}_4$ Glyoxylic acid.
 $\text{C}_2\text{H}_2\text{O}_2$ Second aldehyd (glyoxal).
 $\text{C}_2\text{H}_2\text{O}_3$ Glyoxalic acid.
 $\text{C}_2\text{H}_2\text{O}_4$ Oxalic acid.

wt. 31.—When ethylene diiodide ($C_2H_4I_2$) is triturated with anhydrous argentic acetate, in the proportion of 10 parts or one atom of the former to 12 parts or 2 atoms of the latter, and the mixture is introduced into a flask, a brisk reaction speedily begins to take place; the temperature rises, and the mass becomes yellow, owing to the formation of argentic iodide; while carbonic anhydride and olefiant gas, the result of a secondary decomposition, are evolved in abundance. The product of this reaction is then to be submitted to distillation, and the portions which come over between 320° and 392° (160° and 200° C.), are to be collected separately, and rectified from litharge. By repeating the distillation and collecting the product in separate portions, a liquid is at length obtained which boils at 365° (185° C.), and may be distilled without undergoing decomposition. This liquid is *glycol diacetate*, and if the secondary products of the reaction be neglected, its formation may be thus represented:—



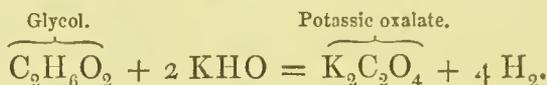
Glycol diacetate is a colourless neutral liquid, which emits a faint acetic odour when heated. It is heavier than water, in which it is but slightly soluble: alcohol dissolves it freely.

Glycol dibenzoate appears to be formed when ethylene diiodide is acted upon by anhydrous argentic benzoate; other salts of silver likewise attack ethylene diiodide with facility, so that various compound glycolic ethers may be obtained without difficulty.

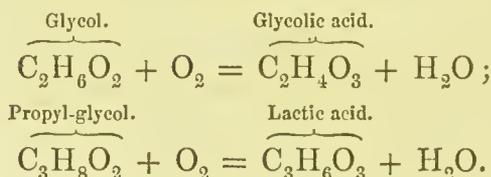
When glycol diacetate is digested upon powdered baric hydrate, or on caustic potash, an energetic action speedily commences; but the mixture must be maintained at a temperature of about 356° (180° C.) for a few hours, in order that the decomposition may be complete: if it be then submitted to distillation, glycol passes over, and may be purified by fractionated distillation. The name *glycol* is a compound of *glycerin* and *alcohol*, intended to indicate the intermediate position occupied by glycol between these two bodies.

Glycol is a colourless, slightly viscous liquid, with a sweet taste. It does not solidify even in the cold produced by a bath of carbonic anhydride and ether. It may be distilled unaltered, and yields an inflammable vapour. It is soluble in water and in alcohol, in all proportions. Ether does not dissolve it in any considerable quantity.

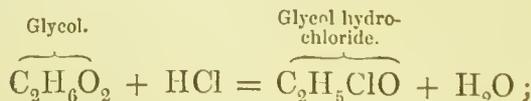
Glycol is immediately attacked by sodium, one or both of its typical atoms of hydrogen being displaced: with a single atom of sodium a white saline mass is formed ($C_2H_5NaO_2$), *monosodium glycol*; this compound when heated with more sodium in an oil bath to 374° (190° C.), fuses, and is gradually converted into a white deliquescent mass, *di-sodium glycol* (C_2H_4)'' Na_2O_2 , or glycol which contains two atoms of sodium in the place of two of hydrogen. If glycol be heated with caustic potash, it experiences oxidation, and pure hydrogen is evolved, whilst potassic oxalate is the chief product in the residue:—



Glycol is also oxidized with great energy by nitric acid, oxalic acid being formed in abundance; if the acid be allowed to mix very gradually by diffusion into glycol diluted with twice its bulk of water, the product of the oxidation is chiefly glycolic acid. If the same experiment be made with propyl-glycol, lactic acid is the result of the oxidation:—

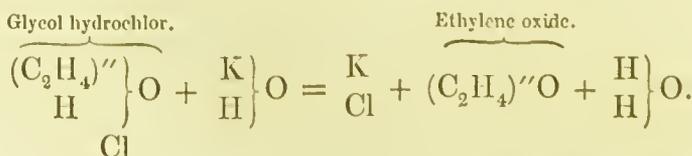


(1215) *Ethers of Glycol.*—When glycol is saturated with hydrochloric acid, and heated in a sealed tube to 212° for 24 hours, combination between the two takes place, *glycol hydrochloride* or *chlorhydrin of glycol* is formed, whilst water is separated:—



in this reaction one atom of chlorine changes place with one of hydroxyl (HO).

Glycol hydrochloride is a neutral, colourless liquid, freely soluble in water, boiling at $262^\circ.4$ (128° C.). A solution of potash instantly decomposes it, furnishing ethylene oxide:—

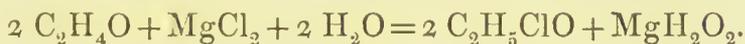


Ethylene oxide (C_2H_4)''O: *Sp. gr. of vap.* 1.422; *Rel. wt.* 22;

Boil. pt. $56^{\circ}.3$ ($13^{\circ}.5$ C.).—This is a volatile liquid, metameric with aldehyd, but it has a lower boiling point, and it does not form any crystalline compound with ammonia. It is polymeric with glycolic ether $(C_2H_4)''_2O_2$, a substance which, however, Wurtz has been unable to obtain.

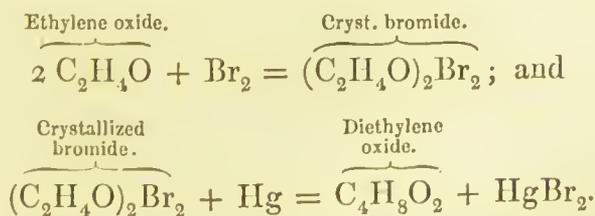
Ethylene oxide is freely soluble both in water and in alcohol. It presents several remarkable reactions. If heated in a strong closed vessel with water for some days, it recombines with water, forming glycol; and by long continuance of the action, several condensed glycols are formed, and remain in solution (1216). Ethylene oxide also unites with ammonia; if mixed at common temperatures with a strong aqueous solution, the reaction is attended with considerable elevation of temperature, and three different bases are formed, viz., C_2H_4O, H_3N ; $(C_2H_4O)_2H_3N$; and $(C_2H_4O)_3H_3N$; one molecule of each of these compounds saturates one molecule of hydrochloric acid.

Ethylene oxide also has the power of gradually decomposing aqueous solutions of some of the metallic salts, precipitating the metallic oxide as a hydrate, and forming one of the ethers of glycol; for example:—



Ethylene oxide likewise unites directly with monobasic acids such as the hydrochloric and the acetic, forming chlorhydrin of glycol, and glycol hydric-acetate; if digested with acetic anhydride it combines in like manner, but furnishes glycol diacetate and some polyethylenic ethers. It also unites with nascent hydrogen if treated with sodium amalgam, and then furnishes ordinary alcohol; $C_2H_4O + H_2 = C_2H_6O$.

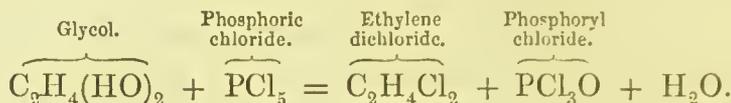
If treated with bromine, a crystalline compound is formed with ethylene oxide, which is decomposed if agitated with mercury, and then furnishes a polymeride of ethylene oxide, containing two atoms of the oxide condensed into its molecule:—



Finally by direct combination with oxygen, ethylene oxide becomes converted into glycolic acid:—

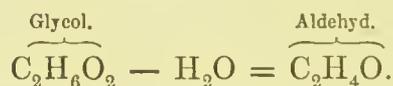


If glycol be treated with phosphoric chloride (PCl_5) a dichloride or normal ethylene chloride is produced by the substitution of two atoms of chlorine for two of hydroxyl (HO) in the molecule of glycol, this dichloride being identical with Dutch liquid:—

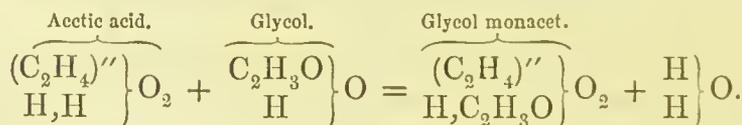


Ethylene dibromide and ethylene diiodide are the corresponding normal hydrobromic and hydriodic ethers of glycol.

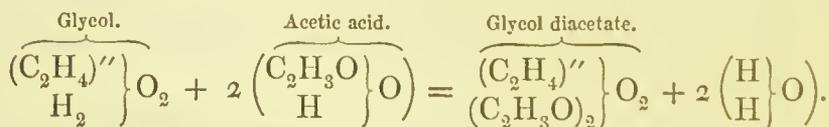
On attempting to deprive glycol of water by treatment with zinc chloride, true aldehyd was obtained, mixed with some of its polymerides:—



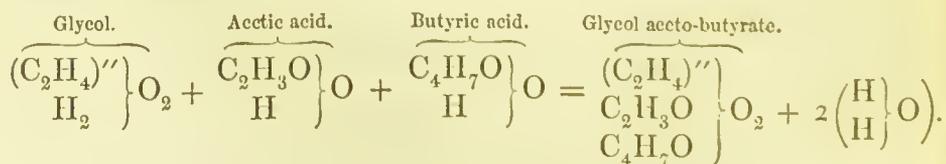
Glycol forms compound ethers, in which either one atom or two atoms of a monobasic oxion may be present, according to the proportion of typical hydrogen displaced by the acid radicle: the first is exemplified in the monacetate of glycol or glycol hydric-acetate:—



The second case is exemplified in glycol diacetate:—



Each typical atom of hydrogen in the molecule of glycol admits of being displaced by a different acid radicle, as in the aceto-buturate:—

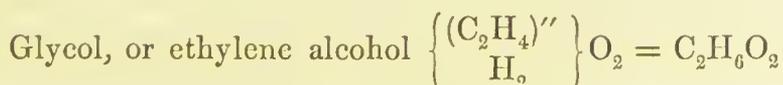


The following table represents the composition and some of the physical characters of the more important compounds of glycol:—

Ethylene Glycol and its Ethers.

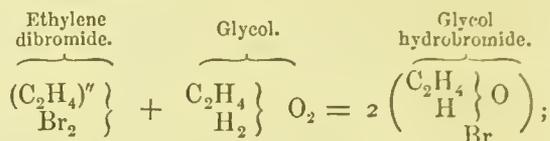
| Compound. | Formula. | Boiling Point. | | Specific Gravity. | | Rel. Wt. H=1. |
|---|--|------------------|------------------|-------------------|---------|---------------|
| | | ° F. | ° C. | Liquid. | Vapour. | |
| Glycol | $(C_2H_4)_n \left. \begin{array}{l} \\ H_2 \end{array} \right\} O_2$ | 386.6 | 197 | 1.125 | 2.164 | 31 |
| Ethylene oxide | $(C_2H_4)_n O$ | 56.3 | 13.5 | | 1.422 | 22 |
| Ethyl-glycol | $(C_2H_4)_n \left. \begin{array}{l} H \\ C_2H_5 \end{array} \right\} O_2$ | about 275 | 135 | | | |
| Diethyl-glycol | $(C_2H_4)_n \left. \begin{array}{l} C_2H_5 \\ (C_2H_5)_2 \end{array} \right\} O_2$ | 254.3 | 123.5 | 0.7993 | 4.095 | 59 |
| Glycol hydric-acetate, or mono- acetate of glycol | $(C_2H_4)_n \left. \begin{array}{l} H \\ C_2H_3O \end{array} \right\} O_2$ | 359.6 | 182 | | | |
| Glycol diacetate, or diacetate of glycol | $(C_2H_4)_n \left. \begin{array}{l} \\ (C_2H_3O)_2 \end{array} \right\} O_2$ | 368 | 186.5 | 1.128 | 4.744 | 61 |
| Glycol dibutyrate, or dibuty- rate of glycol | $(C_2H_4)_n \left. \begin{array}{l} \\ (C_4H_7O)_2 \end{array} \right\} O_2$ | 464 | 240 | 1.024 | | |
| Glycol acetobutyrate, or ace- tobutyrate of glycol | $(C_2H_4)_n \left. \begin{array}{l} C_2H_3O \\ C_4H_7O \end{array} \right\} O_2$ | 406 to 419 | 208 to 215 | | | |
| Glycol acetochloride | $(C_2H_4)_n \left. \begin{array}{l} \\ C_2H_3O \\ Cl \end{array} \right\} O$ | 293 | 145 | 1.1783 | 4.369 | 61.2 |
| Chlorhydrin of glycol | $(C_2H_4)_n \left. \begin{array}{l} \\ HCl \end{array} \right\} O$ | 262.4 | 128 | | | |
| Glycol dichloride (Dutch liquid) | $(C_2H_4)_n \left. \begin{array}{l} \\ Cl_2 \end{array} \right\}$ | 184 | 48.5 | 1.28 | 3.45 | 49.5 |
| Glycol dibromide (Ethylene dibromide) | $(C_2H_4)_n \left. \begin{array}{l} \\ Br_2 \end{array} \right\}$ | 265 | 129.5 | 2.163 | 6.845 | 94 |

(1216) *Condensed Glycols*.—Wurtz finds that if ethylene oxide (C_2H_4O) be sealed up in a tube with glycol and be heated with it for some days, a series of compounds is produced, to the members of which he assigns the following composition, starting with glycol:—

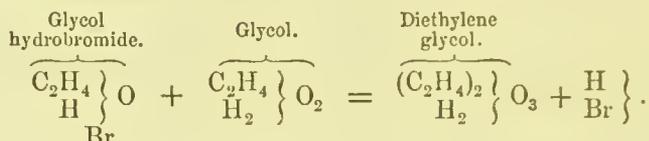


Compounds of this kind up to hexethylene glycol, $(C_2H_4)''_6 \left. \begin{array}{l} \\ H_2 \end{array} \right\} O_7 = C_{12}H_{26}O_7$ have been obtained. These bodies all resemble alcohols in their properties, and are termed *polyethylene alcohols* by Wurtz, or *condensed glycols*, glycol being formed on the diatomic type, diethylene alcohol on the triatomic type, and triethylene alcohol on the tetratomic type, and so on.

A better process of preparing these condensed glycols consists in heating ordinary glycol in a sealed tube with one of its ethers: for instance, if ethylene dibromide be heated with glycol, glycol hydrobromide is first formed,—

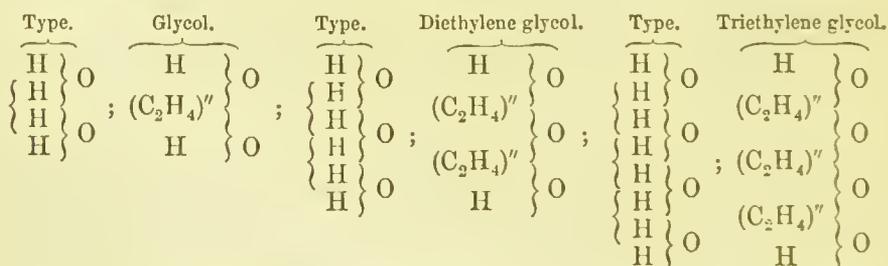


and if this be heated with excess of glycol, hydrobromic acid is liberated, and a condensed glycol is the result:—

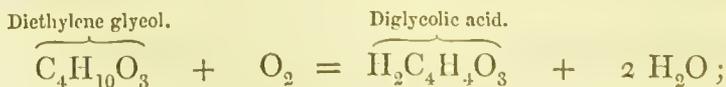


This hydrobromic acid reacting on fresh glycol forms fresh glycol hydrobromide, which reacts on the condensed glycol, producing the third term of the series, and so on in succession.

These condensed glycols are formed from ordinary glycols by the exchange of one of the typical atoms of hydrogen in each molecule of glycol for the hydrocarbon C_2H_4 , whilst a second atom of hydrogen is removed along with the typical atom in combination with an atom of oxygen:—

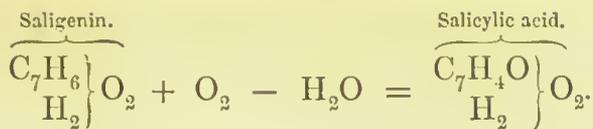


Each of these condensed glycols acts as a *diatomic* alcohol, and furnishes an oxide; diethylene oxide, $\text{C}_4\text{H}_8\text{O}_2$, being, for example, the oxide corresponding to diethylene glycol. They also form acids by oxidation with elimination of water, *e.g.*:—



and with acids they furnish two sets of ethers analogous to those of ordinary glycol.

It appears to be not improbable that there are diatomic alcohols in the isologous groups to which the benzoic and salicylic series belong; for instance, it has been suggested that saligenin (1461) may be the diatomic alcohol, which by its oxidation would furnish salicylic acid:—



This subject awaits further elucidation from experiment.

Wurtz found that just as there are secondary alcohols (1124) which are isomeric with the monatomic alcohols, so there is a class of secondary glycols isomeric with the true or primary glycols.

CHAPTER IV.

FATS AND FIXED OILS.—TRIATOMIC ALCOHOLS, AND THEIR COMPOUNDS.

§ I. NATURAL FATS AND OILS.

(1217) BEFORE proceeding to the examination of the important triatomic alcohol glycerin, it will be convenient to examine the general nature of its most abundant natural compounds. The fats and fixed oils constitute an important and well-defined natural group of organic compounds, which are obtained abundantly both from the animal and the vegetable kingdom. In their chemical relations they present a close analogy with the compound ethers, and are indeed now regarded as the compound ethers of a tribasic alcohol, glycerin, formed by the action of this alcohol upon certain monobasic acids, as will be fully shown hereafter (1240). The predominating elements in their composition are carbon and hydrogen; and as a general rule, the greater the proportion of carbon and the less that of oxygen which they contain, the higher is their melting point. The vegetable fats and oils occur in various parts of the plant, but they are most abundant in the seed. The seeds of the *cruciferae* are particularly remarkable for the large quantity of oil which they furnish; rape-seed contains from 35 to 40 per cent. of oil, and linseed furnishes more than a fifth of its weight. The fleshy fruit of the olive also yields oil in great abundance, and the same is the case with the *Elais guineensis* or palm-oil fruit. In animals, fat is particularly liable to accumulate immediately beneath the cutis, also in the omentum, and around the kidneys. The fatty bodies obtained from warm-blooded animals are generally solid at ordinary temperatures; whilst those from fish and from cold-blooded animals are liquid.

In all cases, both in the animal and in the plant, a certain quantity of some albuminoid substance occurs associated with the oily body, and this substance exerts an important chemical influence upon the fat when kept. In the extraction of the oil, simple pressure is generally sufficient to separate it from the cells of the tissues in which it is contained. If it be solid at ordinary temperatures, it may often be procured by boiling the tissue with water; it then rises to the surface and forms a layer which solidifies on cooling.

The fats and oils are lighter than water, having a specific gravity varying from about 0.91 to 0.94; they have different degrees of solidity, and do not consist of any single proximate principle in a state of purity, but are for the most part mixtures, in varying proportions, of at least four different closely allied bodies; three of which, viz., *stearin* (from *στέαρ*, suet) and *palmitin*, so called from palm oil, in which it is abundant, and *margarin* (from *μάργαρον*, a pearl, owing to its pearly lustre), are solid at ordinary temperatures; whilst the third, *olein*, is liquid. The larger the proportion of olein which is present, the softer is the fat, and the lower is its fusing point.

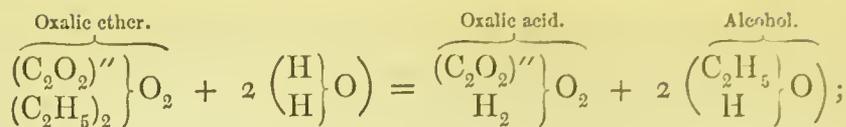
All fats are soluble in ether, and to a certain extent also in alcohol. Oil of turpentine and benzol likewise dissolve them with facility, and the different fats and oils may be mixed with each other in all proportions. They possess the property of rendering paper semitransparent, producing what is well known as a greasy stain. The fats and oils may be heated to nearly 500° (260° C.) without undergoing any important change, but they cannot be distilled without experiencing decomposition. Hence the term, *fixed oils*, is applied to these bodies in contradistinction to that of *volatile oils*, which is given to the fragrant essences obtained from the vegetable kingdom, which may be distilled without alteration, and which have no analogy to the fixed oils in chemical composition. At about 500° the fats and oils begin to give off acrid and offensive vapours, and at a little above 600° (315°.5 C.), they are rapidly decomposed with evolution of gaseous hydrocarbons, the escape of which gives to the oil the appearance of ebullition: as the result of the distillation, a mixture of solid and liquid hydrocarbons, of water, and of various fatty acids, accompanied by a peculiarly irritating substance termed acrolein (1242), is formed, and may be condensed in the receiver.

(1218) *General Nature of the Neutral Fats*.—The fatty bodies when heated with the caustic alkalies, experience a peculiar

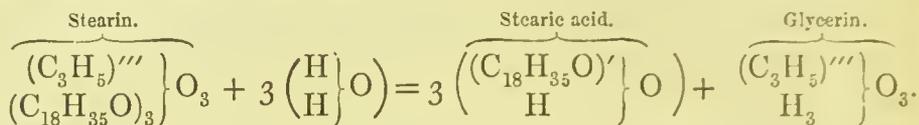
change, long known under the title of *saponification*, or conversion into soap (1233), during which process all fats yield up a viscid liquid, which, owing to its sweet taste, has been termed *glycerin* (from $\gamma\lambda\upsilon\kappa\upsilon\varsigma$, sweet). The nature of this change may be ascertained by dissolving the soap in water, and then adding some acid, such as the tartaric or the hydrochloric, which combines with the alkali, and forms a soluble compound with it. Unctuous flocculi are thus separated, and on the application of heat they melt, and form an oily layer on the surface of the fluid. This substance when cold is found to possess properties very different from those of the original fat. It is crystalline, freely soluble in alcohol, and the spirituous solution reddens litmus paper strongly. It possesses distinctly acid characters, and it is soluble at once, and without the appearance of milkiness, in hot alkaline liquids.

This unctuous matter varies in consistence and quality with the nature of the fat from which it is procured: it is for the most part a mixture of acids (derived from the olein, stearin, and palmitin already mentioned as forming the greater number of the fats), and termed respectively, *oleic*, *stearic*, and *palmitic* acids. It is found that the united weight of the glycerin and of these fatty acids, always exceeds by 3 or 4 per cent. that of the fat originally employed. In fact, olein, stearin, and palmitin are each compounds of the radicle of their respective fatty acid, with the basis of glycerin, which has been displaced by the alkali in the act of forming soap: the alkali, in displacing the radicle of the glycerin, gives up a portion of water to it, and hence increases its weight; while the radicle of the acid, on being separated from the soap, also combines with a portion of hydrogen. Simple intermixture of the glycerin with the fatty acid, therefore, does not again produce the oil or fat from which they were obtained.

The masterly analytical researches of Chevreul upon the fats, have recently received complete explanation in the parallel remarkable synthetic experiments of Berthelot, which have shown that the ordinary varieties of natural fats and oils are the tribasic ethers of the triatomic alcohol glycerin. We have already seen that compound ethers of the monatomic alcohols, by the action of water, become converted into the corresponding acid and alcohol; in a similar manner, the fats, by saponification, or by the action of water at an elevated temperature, are converted into the corresponding fatty acid, and glycerin. Oxalic ether, for instance, undergoes the following decomposition:—



and the formation of stearic acid and glycerin from stearin, may be represented by an analogous equation; thus:—



When the oils are mixed with an aqueous solution of the alkalis, saponification takes place slowly, but if the oil be dissolved in alcohol, and then mixed with the necessary quantity of an alcoholic solution of the caustic alkali, both at a boiling temperature, the saponification is instantaneous and complete.

The saponification of the fats and oils may be effected by heating them with the anhydrous bases, such as caustic lime or plumbic oxide: but a large proportion of the glycerin is always destroyed in the operation, for want of water upon which the glycol (C_3H_5) can react at the moment of its liberation from the fat; and unless the heat be carefully regulated, the fatty acid itself is liable to become decomposed.

When the oily seeds, such as almonds, walnuts, or poppy seeds, are crushed or pulverized, so as to break up the cellular tissue, and bring their several components into mixture with each other, the neutral fatty bodies which the seeds naturally contain are gradually converted into fatty acids, and glycerin is liberated. This change has been shown by Pelouze to depend upon the action of an albuminous ferment contained in the pulp, and to be independent of any absorption of oxygen.

The fats are more fusible than the acids which they furnish on saponification, but when exposed to a low temperature, they become much harder than the fatty acids. Generally they are destitute of odour and taste; the peculiar scent emitted by some of them depending upon the presence of a small proportion of some glycerin compound of one of the volatile oily acids, such as the butyric, valeric, or ricinic. It is worthy of remark, that although the fats themselves are but sparingly soluble in alcohol, their solubility is greatly increased by the presence of a free fatty acid. Ammonia appears to combine with many of the oils, but it converts them into amides, and not into true soaps (Rowney). The compounds of ammonia with almond oil and with castor oil are crystalline.

(1219) *Rancidity of Oils*.—Fats and oils are subject to a peculiar change in their properties, popularly distinguished by the term 'rancidity.' This change is attended with a slight absorption of oxygen, and it appears to be due to the decomposition of certain mucilaginous and albuminous matters contained in the oil, which during their decay react on the fat, setting free the fatty acids, and decomposing the glycerin. Perfectly pure fats and oils do not become rancid; and rancidity may be completely removed by melting or washing them, first with boiling water, and subsequently with a cold weak alkaline ley. When the vegetable oils are to be employed for purposes of illumination, it is necessary to purify them from these mucilaginous matters, which would otherwise become charred and encrust the wick, thus impairing its capillary structure, so that the oil would be prevented from burning freely. To effect this purification, the oil may be mixed with one-fiftieth of its weight of oil of vitriol, which is to be added in small portions at a time, keeping the mixture in continual agitation; dark flocculi are thus formed, which subside when the mixture is left at rest. The supernatant oil is then to be drawn off, and the adhering acid is to be removed by agitating it with one-fourth of its volume of water, mingled with a small proportion of lime. Lastly, the oil is rendered fit for use by filtration through charcoal.

(1220) *Drying and Non-drying Oils*.—Oils may be further arranged under two distinct classes, according as they possess or do not possess the property of absorbing oxygen, by which they are gradually converted into a solid mass: those which become solid in this manner, are termed *drying oils*. Some oils, such as linseed oil, in undergoing this change do not evolve any gas; but during the solidification of most others, an evolution of carbonic anhydride, attended sometimes with an escape of hydrogen, takes place.

The non-drying oils do not absorb oxygen, but are converted into elaidin, by means of mercurous nitrate or by peroxide of nitrogen, a reaction of which those of the first variety are not susceptible. The solidification of olive oil is effected by a quantity of peroxide of nitrogen, NO_2 , not exceeding $\frac{1}{100}$ of the weight of the oil (1298).

The principal drying oils are those known as linseed, walnut, hemp, poppy, and cod-liver oil. The absorption of oxygen by some of these oils, and consequent elevation of temperature, is, under favourable circumstances, so rapid as to be attended with heat sufficient to cause the mass to take fire; and several serious

conflagrations have been traced to the spontaneous ignition of cotton, wool, or tow, soaked in oil, which had been thrown aside in refuse heaps after it had been used in cleaning machinery. The siccativ or drying property of these oils may be much increased by heating them with about one-twentieth of their weight of litharge, which becomes completely dissolved by the oil. Black manganese oxide may be used for the production of a similar effect: linseed oil which has thus been treated is technically known as *boiled oil*. Chevreul, however, states that it is unnecessary to heat the oil for so long a time, or to so high a temperature as is commonly practised; he found that linseed oil if heated to 140° (60° C.) in contact with one-tenth of its weight of manganese oxide, acquires powerful siccativ properties.

The drying oils are not solidified by contact with peroxide of nitrogen, or with mercurous nitrate, and a fraudulent mixture of them with olive or almond oil may thus be detected. The oleic acid which they furnish on saponification differs from ordinary oleic acid, and it absorbs oxygen much more rapidly than the latter: in consequence of this oxidation it speedily becomes converted into a transparent solid varnish. For a careful investigation of the changes which occur during the drying of oils, the reader is referred to a paper by Chevreul (*Ann. de Chimie*, III. xlvii. 209). The most important of the oils which do not become dry by exposure to the air are olive oil, almond oil, rape oil, and colza oil, besides many animal oils.

Tomlinson (*Phil. Mag.* 1861, p. 249) has indicated a method of distinguishing different oils from each other, and in many cases of detecting the admixture of a cheaper with a more valuable oil. It consists in allowing a drop of each oil to spread over a surface of water, in a vessel 4 or 6 inches in diameter (12 or 15 centimetres). The dish must be scrupulously freed from every trace of grease (57). On observing the phenomena of colour exhibited by the film of oil as it spreads upon the water, and watching the way in which it gradually breaks up, characteristic differences may be noticed, which, with a little practice, enable the experimenter readily to distinguish the more important varieties of oil from each other.

(a) *Composition and Properties of the principal Oils and Fats.*

(1221) 1. *Olive oil* (*Sp. gr.* 0.918) is prepared in great abundance in the southern countries of Europe; it furnishes the principal oily material employed in making Marseilles and

Castile soap. The ripe olives are first subjected to pressure without the application of heat, and in this manner the finest oil, or *virgin oil*, is obtained: the residuc is afterwards heated with water, when a large quantity of an inferior mucilaginous oil rises to the surface; it is this which is chiefly employed in soap-making. The oil is always of much finer quality if extracted immediately after the fruit has been crushed, as otherwise it experiences a kind of fermentation, which injures the flavour of the product. The solid ingredient in olive oil is almost exclusively palmitin. Olive oil soon becomes rancid when kept; it becomes partially solid at a few degrees below 32° (0° C.)

2. *Almond oil* [*Sp. gr.* 0.918 at 59° (15° C.)] solidifies at about -13° (-25° C.) It is extracted from the kernel of the *Amygdalus communis*, by a process similar to that adopted for olive oil, but it is much less extensively employed than this oil.

3. *Colza oil* (*Sp. gr.* 0.913) becomes nearly solid at 22° ($-5^{\circ}.5$ C.). It is largely used for illuminating purposes, and is obtained from the seeds of the *Brassica oleifera*. It is of a yellow colour, and is nearly free from odour. Colza oil is sparingly soluble in cold alcohol, but is readily dissolved by boiling alcohol.

(1222) 4. *Linseed oil* [*Sp. gr.* 0.939 at $53^{\circ}.6$ (12° C.)] remains liquid till within a few degrees of 0° ($-17^{\circ}.8$ C.). This oil is pressed from the seeds of the *Linum usitatissimum*, which yield about one-fifth of their weight of it. It has a slight peculiar odour, and is of a yellow colour. Owing to its powerful drying properties, which are much increased after heating it with a small quantity of litharge or of black oxide of manganese, it is extensively used as a 'vehicle' for mixing with colours for painting in oil: it is also largely employed in the preparation of printer's ink, in the preparation of black enamel for leather, and in the varnishing of oiled silk. If exposed for some time to a high temperature it becomes converted into a dark tenacious mass, which when cold may be drawn out into threads; in this state, if mixed with lampblack, it constitutes printer's ink. If the tenacious residuc obtained by heating the oil be boiled for some hours with dilute nitric acid, it acquires a consistence resembling that of ordinary lead plaster, and becomes hard on exposure to the air; but it softens again by the heat of boiling water, and acquires a consistence resembling that of caoutchouc, for which it has been substituted in some instances. This *caoutchouc of oils* is soluble in oil of turpentine, in carbon disulphide, and in dilute alkaline solutions: on neutralizing these alkaline solu-

tions of the caoutchouc by means of an acid, the caoutchouc is precipitated unaltered. Other drying oils beside linseed oil yield a similar substance, though less abundantly.

The liquid acid furnished by the saponification of linseed oil differs from ordinary oleic acid; Sacc terms it *linoleic acid*. Mulder assigns to it the formula ($C_{16}H_{28}O_2$). It absorbs oxygen rapidly from the air, furnishing a colourless *oxylinoleic acid*, which does not solidify even at low temperatures. It is freely soluble in alcohol and in ether. It becomes blood red when acted on either by acids or by alkalis, or by simply heating to 212° . If exposed in thin layers to the air it increases in weight, yielding what Mulder terms *hydrated oxylinoleic acid* ($C_{16}H_{26}O_5, H_2O$), a colourless resinoid substance which at 212° loses 6.7 per cent. of water, and becomes of a blood red colour. By prolonged exposure to the air it becomes brittle, and furnishes a substance no longer soluble in ether, *linoxyn* ($C_{32}H_{54}O_{11}$). The chief interest of these changes is connected with the drying of paint, and with the deterioration of pictures, and of the varnish used to protect them, owing to the lapse of time.

(1223) 5. *Sperm oil* (*Sp. gr.* 0.868) is the liquid portion of the fat of the spermaceti whale: it becomes semisolid at about $44^\circ.6$ (7° C.). It is of a yellow colour, and has a disagreeable odour and taste, due to the presence of a small quantity of a peculiar oil, termed *phocenin* by Chevreul; this body when saponified yields glycerin, and a volatile acid, apparently identical with the valeric. The other constituents of the oil are palmitin and olein. The olein contained in sperm oil differs from that of olive oil, since, although it becomes solid under the action of peroxide of nitrogen, it possesses a drying quality. Sperm oil may be purified by agitating 100 parts of the oil with a mixture of 4 parts of chloride of lime and 12 of water; a small quantity of decoction of oak bark is afterwards added to remove traces of a gelatinous matter which it retains, and the mixture is left to settle; the clear oil is afterwards agitated with a small proportion of sulphuric acid, again clarified by subsidence, and washed to remove adhering sulphuric acid.

6. Ordinary *whale oil* (*Sp. gr.* 0.927) does not become solid above 32° (0° C.). It is of a darker yellow colour, and has a more disagreeable odour than the foregoing oil.

7. *Cod-liver oil* (*Sp. gr.* 0.928) has acquired importance from its extensive employment as a therapeutic agent. It is extracted from the liver of the *Gadus morrhua*, or common cod fish. Its colour varies from a pale, scarcely perceptible yellow, to a deep

brown, according to the mode of its extraction. It has a peculiar fishy odour and taste. In addition to the usual components of the fish oils, it appears to contain a compound of acetic acid with glycerin (acetic, 1240); it also contains a certain proportion of the constituents of the bile, and a small quantity of a phosphorized fat, besides minute quantities of iodine and bromine in a state of combination with some organic substance. Ether dissolves the oil without difficulty, but cold alcohol takes up only a small quantity of it. The iodine and bromine are not in the form of a metallic iodide or bromide; indeed, their presence cannot be detected until the oil has been saponified and the soap charred. When a drop of concentrated sulphuric acid is allowed to fall into the oil it produces a beautiful crimson colour, owing to the action of the acid upon the biliary matter present.

8. *Castor oil* (*Sp. gr.* 0.969) is of a very viscid consistence, but it does not become solid even at a temperature of 0° ($-17^{\circ}8$ C.). This oil is obtained from the seeds of the *Ricinus communis*; it forms a connecting link between the drying and non-drying oils, since it gradually becomes hard by long exposure to air. Castor oil has an acrid taste, which it is stated may be removed by agitation with magnesia. Castor oil differs from the other fixed oils in being soluble in alcohol in all proportions. The principal acid obtained by its saponification is a modification of oleic acid, termed *ricinoleic acid* ($\text{HC}_{18}\text{H}_{33}\text{O}_3$), which remains fluid at a temperature considerably below 32° . By the action of peroxide of nitrogen this acid becomes converted into a solid isomeric fat, termed *ricinelaic* or *palmic acid*. When treated with ammonia, castor oil yields a solid crystalline amide, *ricinolamide* ($\text{C}_{18}\text{H}_{35}\text{NO}_2$). The oil, when distilled, furnishes cœnanthyllic acid ($\text{HC}_7\text{H}_{13}\text{O}_2$; 1288), and a large quantity of the aldehyd of this acid ($\text{C}_7\text{H}_{14}\text{O}$; 1255), which was termed cœnanthol by Bussy. When castor oil is distilled with caustic potash it is decomposed, the principal products being potassic sebate (1306), which remains in the retort, whilst hydrogen gas is liberated, and a quantity of a volatile liquid (oetyllic or caprylic alcohol mixed with caprylic aldehyd), is distilled over (1132).

(1224) *The Solid Fats*.—The solid fats of vegetable origin which are in most frequent use are cocoa-nut oil, nutmeg-butter, and palm oil; those of animal origin are butter, suet, lard, spermaceti, and bees' wax.

Palm oil, nutmeg-butter, and cocoa-nut oil, each contains a

different solid fatty acid, the oxion of which, in combination with the hydrocarbon of glycerin (C_3H_5), constitutes the principal portion of the solid part of the oil.

1. *Cocoa-nut oil* [*Fusing pt. about* 68° (20° C.)] is obtained from the *Cocos nucifera*. It is largely consumed in the manufacture of caudles; it is also used in the preparation of some of the lower priced kinds of soap (1233). Cocoa-nut oil is a very complex fat, for it yields not fewer than six different acids on saponification. These acids, according to Georgey, are—

| | | | | |
|-----------------|--------------------|--|-----------------|--------------------|
| Caproic acid . | $HC_6H_{11}O_2$ | | Lauric acid . | $HC_{12}H_{23}O_2$ |
| Caprylic acid . | $HC_8H_{15}O_2$ | | Myristic acid . | $HC_{14}H_{27}O_2$ |
| Rutic acid . | $HC_{10}H_{19}O_2$ | | Palmitic acid . | $HC_{16}H_{31}O_2$ |

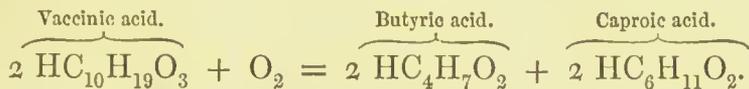
Cocoa-nut oil probably also contains olein, since it yields sebacic acid when distilled.

2. *Palm oil*, which is of a bright orange or golden yellow colour, is produced from the pulp of the ripe fruit of the *Elais guineensis*. The oil is obtained by heating the crushed fruit with boiling water. It has an agreeable odour resembling that of violets. The solid portion of palm oil consists chiefly of a peculiar fat, which has received the name of palmitin, and which, when saponified, yields palmitic acid ($HC_{16}H_{31}O_2$). Palm oil speedily becomes rancid when kept, and though when fresh it melts at about $80^\circ.6$ (27° C.), it gradually becomes less fusible, till it remains solid at a temperature of $100^\circ.4$ (38° C.). This change is due to the spontaneous decomposition of the palmitin, and the liberation of palmitic acid, under the influence of an azotised constituent of the fruit, which accompanies the oil in the process of extraction. Palm oil is readily decolorized by exposure to air at a high temperature, but it is more usual to effect this bleaching of the oil by the addition of a small quantity of sulphuric acid and potassic dichromate. This oil constitutes an important article of commerce, being chiefly imported from the western coast of Africa. It is consumed in immense quantities in the manufacture of candles and of soap.

3. *Butter* consists of a mixture of olein with several fats, amongst which palmitin is the principal solid constituent. According to Heintz, the solid portion of butter contains, in addition to palmitin, another fat, termed by him *butin*, which when saponified yields *butic acid* ($HC_{20}H_{39}O_2$). The characteristic odour and flavour of butter are owing to the presence of a small quantity of some peculiar fats, viz., butyric, caproic, and caprylic; each of these fats, when saponified, yields glycerin, and a peculiar

volatile acid, viz., butyric acid ($\text{HC}_4\text{H}_7\text{O}_2$), caproic acid ($\text{HC}_6\text{H}_{11}\text{O}_2$), and caprylic acid ($\text{HC}_8\text{H}_{15}\text{O}_2$).

In certain instances Lerch found no butyric or caproic acid in butter, but in their stead he discovered an acid, which he has termed the *vaccinic* ($\text{HC}_{10}\text{H}_{19}\text{O}_3$). This acid contains the elements of 1 atom of butyric acid and 1 of caproic acid, minus 1 of oxygen:—



A solution of boric vaccinate, when exposed to the air, absorbs oxygen, and thus becomes converted into a mixture of boric butyrate, and caproate.

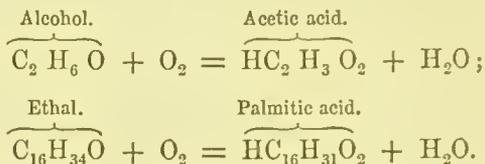
4. *Lard* is the soft fat of the pig, in which the olein predominates over the palmitin and stearin.

5. *Suet* is the fat of the ox or of the sheep: when melted down it forms tallow. Mutton suet is of a firmer consistence than that from the ox; its solid portion consists almost exclusively of stearin.

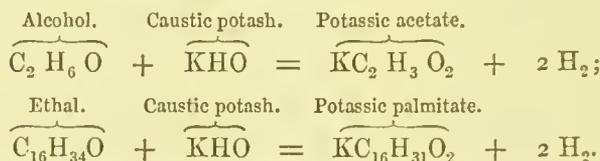
(1225) SPERMACETI [*Sp. gr.* 0.940; *Fusing pt.* about 120° ($48^\circ.9$ C.)] is the solid crystalline fat which is extracted from the brain of the spermaceti whale; it is accompanied by a fluid oil (sperm oil). Spermaceti differs from the ordinary fats in not yielding glycerin when saponified, but in furnishing in its stead a monatomic alcohol termed *ethal* ($\text{C}_{16}\text{H}_{34}\text{O}$). Pure spermaceti, or *ctin* ($\text{C}_{32}\text{H}_{64}\text{O}_2$), after melting, solidifies to a silky semitransparent crystalline fat of delicate whiteness. It is insoluble in cold alcohol of sp. gr. of 0.816, but is soluble in hot anhydrous alcohol, and is freely soluble in hot ether, from which it crystallizes on cooling. It is acted on with difficulty by an aqueous solution of potash. If subjected to distillation, it is decomposed; a liquid hydrocarbon, $\text{C}_{16}\text{H}_{32}$, called *cetene* or *cetylene*, passes over, and ultimately palmitic acid (the ethalic of Dumas, $\text{HC}_{16}\text{H}_{31}\text{O}_2$) distils over.

The same acid is formed when spermaceti is fused with half its weight of solid caustic potash at a heat of about 221° (105° C.). Under these circumstances, the mass, which is at first fluid, gradually solidifies. When this has occurred, it must be treated with water, and decomposed by hydrochloric acid: the fatty mass is boiled with lime, and then treated with alcohol; calcic palmitate remains undissolved, whilst the new fatty alcohol, ethal, is recovered by evaporation. It is purified by redissolving it in ether and evaporating.

Ethal [(C₁₆H₃₄O), *Fusing pt.* 118°.4 (48° C.)] is a white solid, and is soluble in hot alcohol, from which it crystallizes in plates as the solution cools. It may be volatilized by heat without experiencing decomposition. If distilled with phosphoric anhydride it yields *cetylene*, C₁₆H₂₂, a hydrocarbon homologous with olefiant gas. Ethal possesses the properties of a true alcohol; it stands in the same relation to palmitic acid that ethylic alcohol does to acetic acid; for example:—



When the vapour of alcohol is passed over heated caustic potash, hydrogen escapes, and potassic acetate remains behind; whilst ethal, under similar treatment, also evolves hydrogen, and produces potassic palmitate:—



With sulphuric acid ethal forms a coupled acid, the *cetylsulphuric* (HC₁₆H₃₃SO₄), which corresponds with ethylsulphuric acid. A *cetylic ether* (C₁₆H₃₃)₂O has also been obtained, spermaceti being, in fact, a compound ether formed from ethal and palmitic acid, or cetyl palmitate (C₁₆H₃₃.C₁₆H₃₁O₂), and a homologue of acetic ether (C₂H₅.C₂H₃O₂). Spermaceti, when oxidized by nitric acid, yields œnanthylic, adipic, and pimelic acids, and a large quantity of succinic acid.

(1226) BEES' WAX [*Sp. gr.* 0.96, *Fusing pt.* about 145°.4 (63° C.)] has been the subject of numerous investigations, but its true nature was first satisfactorily explained by Brodie (*Phil. Trans.*, 1848, 1849). Many vegetables produce substances in appearance greatly resembling the wax furnished by the honey-bee, but these bodies have not been thoroughly examined. Bees, even though fed upon pure sugar only, have the power of converting it into wax, which is therefore to be regarded in the light of an animal secretion. Bees' wax at ordinary temperatures is tough and solid: it has a yellow colour, a peculiar smell, and an unctuous feel. When exposed in thin slices to the air it becomes bleached, and is then somewhat less fusible. It may also be bleached by means of nitric acid; but chlorine, though it destroys the colour, cannot be employed for this purpose with advantage; for it was observed by Gay Lussac that a substitution of chlorine for a portion of hydrogen occurs under these circumstances, and when candles made from such wax are burned, irritating vapours of hydrochloric acid are evolved.

Wax consists of three different substances, which may be par-

tially separated from each other by means of alcohol. These bodies are, 1. *Myricin*, which is insoluble in boiling alcohol; 2. *Cerin*, or cerotic acid, which is dissolved by boiling alcohol, but crystallizes out on cooling; and, 3. *Cerolein*, which is retained in the cold alcoholic liquid.

Cerolein [*Fusing pt.* about $82^{\circ}\cdot4$ (28° C.)], the substance soluble in cold alcohol, is a greasy body, to which the colour, odour, and tenacity of the wax are due; it has an acid reaction; it is readily soluble in ether: but it has been only incompletely examined. It constitutes not more than 4 or 5 per cent. of the wax.

Cerotic acid [$\text{HC}_{27}\text{H}_{53}\text{O}_2$, Brodie; *Fusing pt.* $174^{\circ}\cdot2$ (79° C.)] so named from *cera*, wax, is extracted from wax by means of boiling alcohol, and is purified by recrystallization from alcohol until its melting point rises to $161^{\circ}\cdot6$ (72° C.) It is then recrystallized from ether until it fuses at $174^{\circ}\cdot2$, which is the melting point of the pure acid. The proportion of free cerotic acid contained in wax varies in different samples. In a specimen from Ceylon it was entirely wanting. In a sample of genuine bees' wax, operated on by Brodie, the cerotic acid constituted about 22 per cent. of the wax.* If due care be taken, cerotic acid may be distilled without undergoing decomposition.

The portion of the wax insoluble in alcohol, formerly called *myricin*, constitutes upwards of two-thirds of the bulk of ordinary bees' wax. It melts at $147^{\circ}\cdot2$ (64° C.). It is a mixture of two different bodies, both of which are insoluble in alcohol, but soluble in ether; a portion crystallizes from the ethereal solution in feathery scales; by repeated crystallization from ether a compound may be obtained which solidifies at $161^{\circ}\cdot6$ (72° C.). To this substance the name of *myricin* is confined by Brodie. The other more fusible body which accompanies it is less abundant, and has not been completely investigated.

Purified *myricin* when fused with caustic potash, or when boiled with an alcoholic solution of potash, is easily saponified; by this means a salt of palmitic acid is obtained, and another

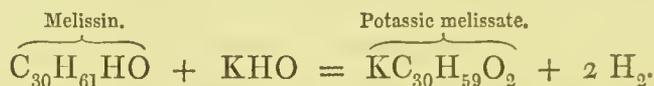
* Chinese wax ($\text{C}_{54}\text{H}_{108}\text{O}_2$), the produce of a species of insect of the coccus tribe, contains cerotyl cerotate, which fuses at 182° ($83^{\circ}\cdot3$ C.), and is homologous with spermaceti, which in its crystalline appearance it considerably resembles:—



Chinese wax, when decomposed by fusion with caustic potash, yields potassic cerotate; and at the same time *cerotin* ($\text{C}_{27}\text{H}_{55}$)H,O, the alcohol of cerotic acid (corresponding to the ethal of spermaceti) is obtained.

wax alcohol, *melissyl* alcohol, or *melissin* ($C_{30}H_{62}O$), is liberated. From this decomposition it appears that myricin is a body analogous to spermaceti and to Chinese wax; pure myricin being *melissyl palmitate* ($C_{30}H_{61}, C_{16}H_{31}O_2$), or ($C_{46}H_{92}O_2$).

Melissin fuses at 185° (85° C.). It is soluble with difficulty even in boiling alcohol. It crystallizes from a hot solution in ether in satiny crystals. Benzol is a better solvent for it than either alcohol or ether. When melissyl alcohol is distilled with heated caustic potash, it is decomposed, hydrogen is evolved, and potassic melissate is formed; the reaction being analogous to that by which potassic acetate is produced when ordinary alcohol is treated in a similar manner:—



Melissic acid ($H, C_{30}H_{59}O_2$) fuses at $192^\circ.2$ (89° C.), and may be volatilized without decomposition. It is homologous with acetic acid.

Wax, when submitted to distillation, yields several solid hydrocarbons, among which is *melene*, to which Brodie assigns the formula, $C_{30}H_{60}$; though, as it is a paraffin, it is more probably $C_{30}H_{62}$: it fuses at $143^\circ.6$ (62° C.). The principal product of the oxidation of wax by means of nitric acid is succinic acid.

From the foregoing statements it appears, therefore, that bees' wax is a mixture of cerotic acid (cerin) with melissyl palmitate (myricin), in addition to which is a portion of a third body allied to myricin, as yet but imperfectly examined; with a small quantity of a soft greasy substance, cerolein. The following well-defined substances may be enumerated as derivatives from wax:—

| | Fusing point. | | Formula. |
|---|---------------|-------------|--------------------|
| | $^\circ$ F. | $^\circ$ C. | |
| Cerotic acid (<i>cerin</i>) | 174.2 | 79 | $HC_{27}H_{53}O_2$ |
| Ceryl alcohol (<i>cerotin</i>) | 177.8 | 81 | $C_{27}H_{55}HO$ |
| Chinese wax | 182 | 83.3 | $C_{54}H_{108}O_2$ |
| Cerene (<i>paraffin</i>) | 134.6 | 57 | $C_{27}H_{56}$ |
| Melissyl alcohol (<i>melissin</i>) | 185 | 85 | $C_{30}H_{61}HO$ |
| Melissic acid | 192.2 | 89 | $HC_{30}H_{59}O_2$ |
| Palmitic acid | 143.6 | 62 | $HC_{16}H_{31}O_2$ |
| Myricin (<i>melissyl palmitate</i>) | 161.6 | 72 | $C_{46}H_{92}O_2$ |
| Melenc (<i>paraffin</i>) | 143.6 | 62 | $C_{30}H_{62}$ |

(b) Proximate Constituents of the Fats and Oils.

(1227) From the preceding general description of the oils and fats, it is evident that these bodies contain several distinct substances, which are analogous to each other in chemical composition. The most important of these neutral fats are stearin, palmitin, margarin, and olein.

STEARIN ($C_{57}H_{110}O_6$; Berthelot) is a white crystalline fat, soluble in about seven times its weight of boiling alcohol, and much more freely so in hot ether. Nearly the whole of the stearin separates from these liquids as they cool. Duffy (*Q. J. Chem. Soc.*, v. 210) finds that stearin may exist in three modifications, each of which has a different fusing point. Under ordinary circumstances, the melting point is $143^{\circ}6$ (62° C.), but this temperature varies in a remarkable manner under the influence of slight differences of the temperature to which the stearin is exposed during the act of fusion:—1. If stearin be heated to 66° C., and allowed to cool, it remains liquid till it reaches 51° C., and after solidification it may be melted at 52° C.;—2. but if stearin, which has been melted at this temperature, be again allowed to solidify, it requires a temperature of $64^{\circ}2$ C. for its liquefaction;—and 3. stearin which has been melted at 62° C., and the temperature of which has not been raised above 64° , solidifies at 61° C., but after solidification it requires a temperature of $69^{\circ}7$ C. for its liquefaction. These three modifications of stearin have different densities:—

| | | Sp. Gr. |
|----|--|---------|
| 1. | Modification α , fusible at $125^{\circ}6$ F. . 52° C. | 0.986 |
| 2. | Modification β , fusible at $147^{\circ}4$. $64^{\circ}2$ | 1.010 |
| 3. | Modification γ , fusible at $157^{\circ}5$. $69^{\circ}7$ | 1.017.* |

Similar modifications are produced by heat upon palmitin.

Stearin is the most abundant of the solid constituents of the fats and fixed oils. It is generally prepared from mutton suet, in which it is mixed with but small quantities of other fats: the suet is heated with about ten times its volume of ether; when it cools, the olein and palmitin are held in solution, while the stearin crystallizes in pearly scales. These must be pressed between

* Heintz, on repeating Duffy's experiments upon pure stearin prepared synthetically by Berthelot's process (1240) obtained only the varieties α and γ ; Duffy's β he considers to have been produced from the presence of a slight impurity in the stearin. The fusing points given by Heintz are a little higher than those of Duffy—viz., for α 131° (55° C.), and for γ $160^{\circ}7$ ($71^{\circ}5$ C.).

folds of blotting paper, redissolved in ether, and recrystallized until the melting point becomes constant.

Berthelot has succeeded in preparing stearin artificially, by heating stearic acid and glycerin together in closed vessels for several hours under pressure. He has also obtained all the other neutral fats by similar means (1240).

(1228) PALMITIN ($C_{51}H_{98}O_6$; Berthelot).—This fat is contained abundantly in palm oil, from which it has received its name. It is extracted from the oil by first pressing out the liquid portion, treating the residue with boiling alcohol to remove free palmitic acid, and then crystallizing repeatedly from ether. According to Duffy, the lowest point at which palmitin remains liquid is $113^{\circ}9$ ($45^{\circ}5$ C.); but it has three different melting points, viz., $114^{\circ}8$ (46° C.), 143° , and 145° ($62^{\circ}8$ C.), which correspond to three different modifications like those of stearin. Palmitin is also present in bees' wax, in cocoa-nut oil, and (according to Heintz) in human fat. The tree wax of Japan consists of pure palmitin (Sthamer).

(1229) MARGARIN ($C_{54}H_{104}O_6$; Berthelot) crystallizes in pearly scales, which are fusible at about $116^{\circ}6$ (47° C.) It requires about 400 times its weight of boiling alcohol for solution, and is deposited almost entirely on cooling. Margarin is stated to constitute the solid ingredient of goose grease, of human fat, and of olive oil. It may be extracted from olive oil by lowering its temperature to 32° , and then submitting it to pressure; the solid portion is again melted and cooled slowly, and a second time submitted to pressure, at a temperature of from 55° to 60° . After two or three crystallizations from boiling alcohol, the margarin is obtained nearly pure.

According to Heintz, margarin is not a simple fat; for when saponified, the acid which it yields, and which is commonly described as margarie acid, admits of separation into palmitic and stearic acids; hence what is called margarie acid appears to be a mere mixture of these acids (1293).

(1230) OLEIN ($C_{57}H_{104}O_6$; Berthelot).—Pure olein is colourless; it is not solidified by a cold of 32° (0° C.). By exposure to the air it absorbs oxygen slowly, with evolution of carbonic anhydride, and becomes resinoid in appearance. Olein when distilled gives rise, amongst other products, to the formation of sebacic acid ($H_2C_{10}H_{16}O_4$), which is a characteristic product of the destructive distillation of oleic acid. Peroxide of nitrogen converts

olein into an isomeric solid fat, which has received the name of *elaidin*. Mercurous nitrate which has been prepared without the aid of heat, retains a sufficient quantity of peroxide of nitrogen to enable it, when placed in contact with olein, to convert it into elaidin; and the mercurial salt produces a similar effect upon all oils which contain that variety of olein which is present in the non-drying oils. The drying oils contain a form of olein which does not become solid when mixed with mercurous nitrate; hence this salt has been employed in testing olive oil suspected to have been adulterated with poppy and other cheap drying oils:—the oil is agitated with $\frac{1}{12}$ of its weight of a solution of the mercurial salt; the purer the oil the more rapidly does it become solid when thus treated.

The purification of olein is attended with considerable difficulty: it may, however, be obtained either by solidifying olive oil at a temperature of 32° and pressing out the liquid portion, or by dissolving the oil in boiling alcohol, which, as it cools, deposits nearly the whole of the stearin and margarin, but retains the whole of the olein in solution: the olein may then be recovered by driving off the alcohol by heat. Olein is saponified with greater difficulty than the solid fats which accompany it, and it has been proposed to apply this circumstance to its purification. If olive oil be boiled for twenty-four hours with a solution of caustic soda of moderate strength, containing a quantity of alkali equal to about half that required for the complete saponification of the oil, the olein remains unchanged, whilst the solid fats are saponified. The mixture of soap and olein is treated with dilute alcohol, which dissolves the soap, while the olein collects as an oily layer upon the surface.

It has been already mentioned that the liquid portion of the oils has not the same composition throughout the different varieties of these substances: the olein of olive oil differs from the olein of linseed oil, or *linolein*; and both of these differ from the olein contained in castor oil.

Adipocire is the name (from *adeps*, fat, *cera*, wax) which has been given to a fatty residue often obtained from the slow decay of the bodies of men or of animals which have been interred in a soil kept constantly moist. Wetherill finds it to consist chiefly of solid fatty acids, free from cholesterin, from ammonia, and from glycerin, so that it is most probably the result of the gradual decomposition of fat originally present in the body, from which, during the decay of the muscular tissue, most of the glycerin and oleic acid have been removed.

(c) *Action of Bases upon Fatty Matters.—Soap-making.*

(1231) It is well known that however thoroughly water and oily matters may be incorporated by mixture, they do not unite to form a homogenous material ; but that after a short time the grease separates and floats upon the surface. If, however, a quantity of a solution of caustic soda be added to the mixture, and it be then agitated, a milky-looking fluid or emulsion will be formed, and the oil will remain mixed with water.

If a sufficient quantity of alkali be added, this emulsion when boiled for some hours gradually becomes clear ; and a period arrives at which a transparent rosy fluid is formed, which froths strongly on agitation, and presents the characters of a concentrated solution of soap.

If to a portion of this clear liquid a strong solution of common salt be added, a curdling is immediately produced : the liquid separates into a clear solution which retains the glycerin, whilst a granular substance rises to the surface : this substance, if drained, pressed, and dried, exhibits the properties of soap.

Ordinary soap is freely soluble in hot water, forming with it a transparent solution, which, if tolerably strong, becomes a white opaque jelly as it cools. Soap may also be dissolved by hot alcohol, which as it evaporates leaves the soap in transparent blocks. It is quite insoluble in strong brine, and in a concentrated solution of caustic potash or of soda ; hence by the addition of sodic chloride, or of caustic alkali, to a solution of soap, the soap is separated from the liquid in the solid form.

(1232) *Varieties of Soap.*—There are various kinds of soap, dependent on the nature of the fat, as well as upon that of the base used in its preparation. The base of the *hard soaps* is soda, that of the *soft soaps* is potash. The common soft soaps have always a more powerfully alkaline reaction than the hard soaps, owing to the presence of an excess of alkali, which adds to their detergent power : they also usually contain the whole of the spent leys and the glycerin of the fat, which the manufacturer has not been at the pains to separate. Such soaps as are made without separation of the leys and glycerin, are known technically as *close soaps* ; in opposition to soaps made by *open boiling*, or with separation of the leys and glycerin.

If the oil be heated with plumbic oxide, instead of with alkali, a white, solid, fusible compound, well known as *lead plaster*, is formed ; which is, in fact, a soap containing plumbic oxide as its base, instead of soda or potash. The earths if boiled with the oils

also produce soaps ; but such soaps are insoluble in water, and it is owing to the formation of these compounds that the *curdling* of soap by *hard* water is occasioned. Now, hard waters are waters which contain a certain quantity of earthy salts—usually salts of calcium or of magnesium. When ordinary soap is dissolved in these waters, double decomposition occurs : the calcium displaces the alkaline metal in the soap, whilst the alkaline metal in turn combines with the acid radicle which was previously united with the calcium ; and the insoluble calcium soap thus formed produces the curdling in question.

The soaps of the alkali metals, or commercial soaps, are the only ones which are soluble in distilled water as well as in alcohol and in ether ; but alcohol dissolves many of the compounds which the fatty acids form by their action upon the oxides of copper, iron, and manganese. Oil of turpentine and the fixed oils likewise dissolve small quantities of these soaps.

(1233) *Process of Soap-making.*—The unctuous materials used in this country in the preparation of hard soap are, tallow, which gives the hardest soap, palm oil, and kitchen grease ; rosin is also an ingredient in yellow soap ; cocoa-nut oil is largely used in admixture with other fatty substances in the cheaper kinds of soap ; but it always imparts to the product a peculiar and disagreeable odour. The coarse soft soaps are made of common fish oil and hemp-seed oil.

The manufacture of soap is carried on in large iron boilers, technically called *coppers*, in which the mixture of ley and fat is heated by means either of an open fire or of steam : the steam is either admitted into the copper by a perforated pipe, or it is made to circulate within it through a closed coil or worm. For hard soaps the leys of caustic soda are prepared in large iron vats, which are also heated by steam. Water is put into the vat and made to boil ; a mixture of soda ash and slaked lime is then added in quantity sufficient to make the ley of the sp. gr. of 1.15 ; after boiling for some time the steam is turned off, the calcic carbonate allowed to subside, and the clear ley is drawn off. Fresh water is added to the residue, and thus a weaker ley is obtained.

Mottled soap is prepared from tallow, palm oil, and kitchen stuff. For every ton of tallow or fat introduced into the boiler about 150 gallons of partly-exhausted soda ley is added from a previous charge, in successive quantities of 10 or 12 gallons at a time. When it first boils, a milky liquid is formed, which by degrees becomes more and more viscid ; stronger leys are then gradually added, and the boiling is continued until the soap ceases

to feel greasy. A quantity of common salt is next added to separate the spent leys; these contain the glycerin and some impurities derived from the grease; they are drawn off from the bottom, and are thrown away. Strong ley is then added, and the boiling continued, until the soap separates from the ley, which retains an excess of alkali. It is then *cleansed* or transferred to the soap frames to cool. These frames are rectangular in shape, and consist of cast-iron plates clamped together by bolts and nuts; in these frames a small portion of the ley contained in the hot soap gradually separates, and accumulates in the lower part of the frame; this part of the soap is pared off, and is remelted and added to the next charge. The soap remains in the frames for four or five days to cool and harden. At the end of that time it is cut up with wires into bars.

The *mottling* occurs in the moulds spontaneously, and is due to the separation from the mass of a small portion of iron soap, which gradually arranges itself in blue veins. Good soap contains about 30 per cent. of water; and 100 parts of fat or oil yield from 150 to 155 of such soap. A soda soap, before drying, contains about 6 or 7 per cent. of alkali.

Cocoa-nut oil soap requires a very large excess of salt to cause it to separate from its solution; it is therefore rarely salted out. This oil requires stronger leys than other fats for its saponification, and when once the process has commenced it is very rapid. Soap made from cocoa-nut oil will absorb fully one-third more water than ordinary soap, without any sensible loss of firmness. Hence, when mixed with curd soap, it is employed largely in the preparation of the lower priced soaps. *Marine soap* was a name given to a cocoa-nut oil soap commonly containing excess of caustic or carbonated alkali, which enabled it to be used with sea water.

Curd soap is usually obtained from tallow only, a small portion of olive oil or of lard being sometimes added. The soap while hot is put into a pan and *crutched*, or stirred forcibly, to break up the grain; it is then conveyed to the frames. When cut it should be perfectly smooth and white. *Yellow soap* is made from tallow and palm oil, and in addition to the alkali and fat, contains a considerable proportion of common rosin, which possesses acid properties and unites with the alkali: it is manufactured by a process similar to that used for mottled soap, but instead of being *cleansed*, or put into the frames immediately after boiling, it is *fitted*, or mixed in the copper with a small quantity of water, this in two or three days carries down the excess of alkali, forming the *negur*, which subsides to the bottom; while a

spongy crust, termed the *fob*, rises to the surface. The fob is skimmed off, and the semi-solid pasty mass of soap is transferred to the frames. The negur and fob are added to the next boil.

Marseilles and Castile soaps are made from olive oil and soda; they are mottled by the addition of green vitriol and sulphuretted ley to the soap while in the pasty state.

(d) *Manufacture of Fatty Acids for Candles.*

(1234) Large quantities of the fats are converted into the form of free acids, in the manufacture of what are often incorectly termed stearin candles. This branch of industry has within the last few years acquired enormous magnitude. The fatty acids are prepared for this purpose by three principle methods:—in the first of these processes the fat is saponified by means of lime; in the second the fat or oil is decomposed by sulphuric acid; and in the third process the fat is separated into glycerin and the fatty acid, under the influence of water at an elevated temperature. The acids furnished by the fats are, at ordinary temperatures, whiter and harder than the fats from which they are obtained, and they are at the same time cleaner and more combustible.

1. *Saponification by Lime.*—Until recently it was the general practice to saponify the oils or fats by means of lime, which readily effects the desired change, and has the advantage of being much cheaper than either potash or soda: this process is still extensively followed in France. The tallow is melted by injecting hot steam into the vat which contains it, and milk of lime is added; the whole being maintained at the temperature of 212° by continually injecting steam through a perforated pipe, whilst the mixture is kept constantly stirred. An insoluble calcium soap is thus formed; it is drained from the solution of glycerin, and then decomposed by the cautious addition of sulphuric acid diluted to the sp. gr. 1.160. The melted fatty acids thus rise in the form of an oil to the surface of the heated mixture; they are now decanted, and are washed, first with a fresh portion of heated dilute sulphuric acid, and afterwards with water. The fused acids are then cast into thin plates or cakes not much exceeding an inch (25 millim.) in thickness; these cakes when cold are placed between layers of cocoa-nut matting, and are piled up one above another with iron plates interposed between every four or five cakes, and the pile thus formed is subjected to intense pressure by the aid of a powerful hydraulic press. By this means the oleic acid is in great measure forced out, whilst the harder palmitic

and stearic acids remain, and are afterwards subjected to pressure at a higher temperature; a fresh portion of the more fusible fat is removed by this operation, and the residue becomes beautifully white. In order to remove any traces of oxide of iron which the fat may have absorbed from the machinery, it is again washed, first, with warm dilute sulphuric acid, and then with water; finally, it is melted and moulded into candles. The oleic acid furnishes with soda a soap sufficiently hard to be used for many purposes in the arts.

M. De Milly has ascertained that the complete saponification of fats may be effected by a proportion of lime not exceeding 4 per cent. of the weight of the fat, by exposing the mixture, in a Papin's digester, with water, to a high temperature. This temperature, according to Pelouze, need not be higher than from 311° to 329° (155° to 165° C.). If water alone be employed to effect the decomposition, a temperature of not less than 428° (220° C.), prolonged for many hours, is needed.

(1235) 2. *Acidification of the Fats by Sulphuric Acid.*—The action of sulphuric acid upon the fixed oils has been particularly examined by Fremy (*Ann. de Chimie*, II. lxx. 113). When concentrated sulphuric acid is made to act at ordinary temperatures upon an oil or fat, the fat at first combines with the acid, and the compound thus formed gradually becomes decomposed into sulpho-glycerin (1239), *sulpholeic*, *sulphopalmitic*, and *sulphostearic* acids. The last three sulpho-acids are insoluble in acidulated water, but are dissolved by pure cold water. They have an oily bitter taste. On raising the temperature of the solution, they all become decomposed, the sulphuric acid is set at liberty, and the glycerin or the fatty acids are separated. The sulpholeic acid is more permanent than the sulpho-compounds of the solid fatty acids.

If the sulphuric acid and the oil or fat be made to act upon each other at a high temperature, the fat is immediately broken up into glycerin and the fatty acids, whilst the glycerin is in its turn decomposed, at the expense of a portion of the sulphuric acid, and sulphurous and carbonic anhydrides are evolved. This reaction is employed on a large scale for the preparation of the so-called composite or stearin candles, and in England it has very nearly superseded the lime process.

The following is an outline of the method in which sulphuric acid is applied for this purpose at the works of Price's Patent Candle Company:—The fat is first melted and freed from impurities, then mixed with from one-twelfth to one-seventeenth of its weight of oil of vitriol in large copper boilers, where it is raised gradually by means of a current of highly heated steam to a temperature

of about 350° ($176^{\circ}\cdot8$ C.). This temperature is maintained for about two hours, the mass being frequently stirred briskly: during this process carbonic and sulphurous anhydrides are disengaged in large quantities, nearly all the glycerin and sulphuric acid being decomposed in the course of the operation. The liberated fatty acids are of a dark colour, and require thorough washing with water to free them from adhering sulphuric acid.

The impure fatty acids thus obtained are then subjected to distillation, which is effected by placing them in a copper vessel, into the lower part of which a current of steam at the ordinary pressure is injected; previous to its admission to the still this steam is heated to about 600° ($315^{\circ}\cdot5$ C.), by transmitting it through pipes heated nearly to redness. The distillation does not take place below 400° ($204^{\circ}\cdot5$ C.), but towards the latter part of the process the temperature frequently rises to 500° (260° C.). After the acidified fats have been distilled as far as is advantageous, the dark residuc in the retort may yet be made to yield a considerable amount of fat by submitting it to pressure; the black solid mass which still remains is used as fuel. The distilled fat is broken up into fragments, and distributed in layers of about three-fourths of an inch in thickness upon squares of cocoa-nut matting, which are piled one above another, and submitted to the action of a hydraulic press. The fat thus obtained is sufficiently firm to be made at once into candles suited to European climates, but for the Indian market it is necessary again to subject the fat to pressure, which this time is effected at a temperature of 122° (50° C.).

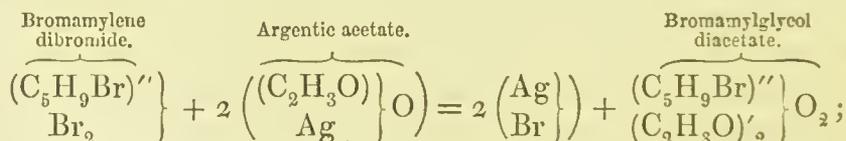
(1236) 3. *Action of Water at a high Temperature on Fats and Oils.*—Mr. Tilghmann a few years ago made the important observation, that when a mixture of fat and water is forced under strong pressure through tubes heated nearly to redness, so as to raise the temperature of the mass to 400° or 500° ($204^{\circ}\cdot5$ to 260° C.), the fat is entirely decomposed into glycerin and fatty acids; the elements of water enter into combination with those of the fat, so that by this means a result is obtained exactly the reverse of that effected by Berthelot at lower temperatures (1240), when the acid and glycerin are digested together.

Mr. Wilson by injecting superheated steam at a temperature of between 500° and 600° (260° and $315^{\circ}\cdot5$ C.) into heated fat, was able to produce a similar separation of hydrated glycerin and of the acids with which it was previously in combination, and at the same time he succeeded in effecting the distillation not only of the fat, but also of the glycerin; the latter is thus obtained in

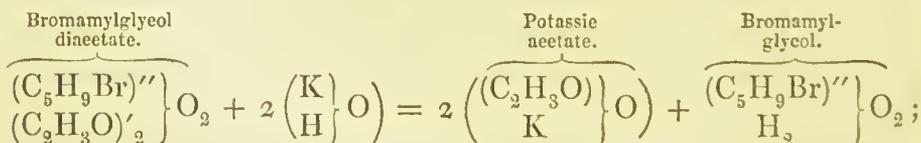
a high degree of concentration, as a beautiful, colourless, syrupy liquid, which can be prepared in almost unlimited quantity. The fatty acids are also procured by the same operation in a very pure form, so that this process, from its simplicity, and from the purity of the products which it yields, bids fair to supersede those previously employed in the preparation of the fatty acids for illuminating purposes. The operation, however, cannot be conducted so rapidly as the process of decomposition by sulphuric acid.

§ II. THE GLYCERINS—GLYCERIDES.

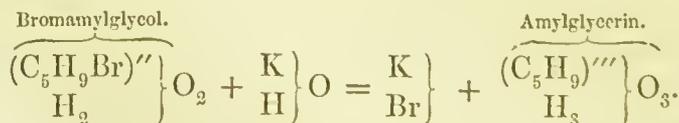
(1237) At present only two forms of glycerin are known: normal glycerin or propyl-glycerin (C_3H_5, H_3O_3), which is by much the most important, and amyl-glycerin (C_5H_9, H_3O_3), recently formed by Wurtz by the following reactions:—First, bromamylene dibromide, when heated with argentic acetate, furnishes the bromamylglycol diacetate:—



and then by heating this new diacetate with caustic potash, bromamylglycol is first produced, with potassic acetate:—



finally, an excess of caustic potash transforms bromamylglycol into amylglycerin with elimination of potassic bromide:—



(1238) GLYCERIN ($C_3H_5O_3$), *the Sweet Principle of Oils. Sp. gr.* 1.28 at 59° (15° C.).—This substance is separated from all fatty and oily bodies (with the exception of spermaceti and the different varieties of wax), during their saponification by alkalies. According to Pasteur it is also formed in small quantities during the process of alcoholic fermentation. Glycerin is a viscid, colourless liquid of a sweet taste, soluble in water and alcohol in all proportions, but sparingly soluble in ether. It dissolves most of the deliquescent salts, as well as many other substances which

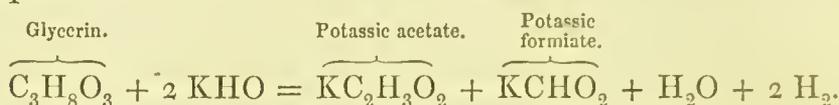
are soluble in water. Baryta, lime, and strontia are freely soluble in glycerin, and the solutions are not precipitated by carbonic anhydride. Glycerin solidifies if exposed to a very low temperature, furnishing a mass resembling loaf-sugar in appearance; it does not liquefy till heated a little above 32° . As long as any crystals remain it freezes again by a slight depression of temperature, but when once liquefied it may be cooled to -4° (-20° C.) without freezing. Glycerin is slightly volatile at 212° , but, if distilled alone, the greater part of it experiences decomposition, with disengagement of intensely pungent vapours of acrolein (C_3H_4O ; 1242), which excites a most painful irritation of the eyes. When heated sufficiently in air, glycerin burns with a luminous flame. It may, however, be distilled without alteration, in a current of superheated steam which has been raised to a temperature of between 500° and 600° (260° and $315^{\circ}5$ C.); advantage is taken of this fact in order to prepare glycerin in large quantities (1236). The usual method of obtaining glycerin on a small scale consists in saponifying olive oil by heating it with an equal weight of litharge: the plumbic oxide is mixed with water and added to the oil, with which it is boiled till the saponification is complete: fresh portions of water being added from time to time to supply the place of that which is evaporated. The glycerin is dissolved by the water, and is easily freed from the insoluble *lead plaster*, or mixed plumbic oleate and margarate which is formed. The aqueous solution retains a small quantity of plumbic oxide, which may be separated by transmitting through it a current of sulphuretted hydrogen, and filtering from the precipitated plumbic sulphide; the water may then be expelled by evaporation *in vacuo* at a temperature not exceeding 302° (150° C.). If the solution be evaporated in the open air it becomes brown. Glycerin forms a valuable preservative liquid in which small and delicate tissues may be mounted for anatomical purposes. Like sugar, it possesses strong antiseptic powers, and has been applied in curing meat. It also forms a useful application to the surface of the skin when dry and irritable.

Like the alcohols in general glycerin forms the following series of derivatives:—

1. Combinations with acids, corresponding to the compound ethers, such as the natural and artificial fats.
2. Combinations with alcohol radicles, corresponding to the mixed ethers, such as diethylin (1241).
3. A compound corresponding to the simple ethers, such as glyceric ether.

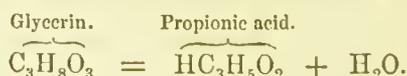
4. Hydrocarbons, such as propylene.
5. Combinations with ammonia analogous to the ethyl bases.
6. Oxidized derivatives, corresponding to the aldehyds.
7. Other oxides possessing acid properties, such as glyceric acid.

When glycerin is heated with caustic potash it is decomposed into a mixture of potassic acetate and formiate, whilst hydrogen escapes :—



By digesting glycerin for some weeks at a temperature of 100° (37°8 C.) with poor cheese in contact with chalk, it may be made to furnish alcohol, the amount of which never exceeds one-tenth of the weight of glycerin employed, the greater part of the glycerin remaining unaltered in the liquid; equal volumes of carbonic anhydride and hydrogen being disengaged during the process (Berthelot); $\text{C}_3\text{H}_8\text{O}_3 = \text{C}_2\text{H}_6\text{O} + \text{CO}_2 + \text{H}_2$.

According to Redtenbacher (*Liebig's Annal.* lvii. 174), if a dilute solution of glycerin be mixed with well washed yeast, and kept for some weeks at a temperature of from 68° to 86° (20° to 30° C.), water being added as it evaporates, it becomes slowly converted into propionic acid; very little evolution of gas occurs, but the liquid becomes mouldy and acquires an acid reaction: if the mixture be neutralized from time to time with sodic carbonate, and as soon as the further development of acid ceases, the liquid is filtered and evaporated, a yellow saline mass is obtained, possessing the smell of *sauer-kraut*; when this saline mass is distilled after the addition of sulphuric acid, propionic acid is the principal product condensed in the receiver. The connexion between the composition of propionic acid and glycerin is very simple, 1 molecule of glycerin containing the elements of 1 molecule of propionic acid with 1 of water:—

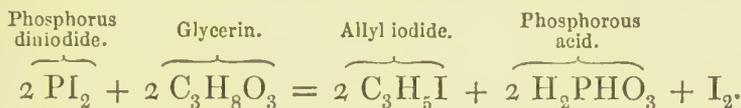


Berthelot found that glycerin, like mannite, was convertible into a true fermentible sugar under the influence of the testicular tissue (1244).

Glycerin admits of oxidation without difficulty; if distilled with diluted sulphuric acid and black manganese oxide, formic acid is amongst the products; and under the combined influence of platinum black and atmospheric air it absorbs oxygen rapidly, and yields an acid, the nature of which has not been ascertained.

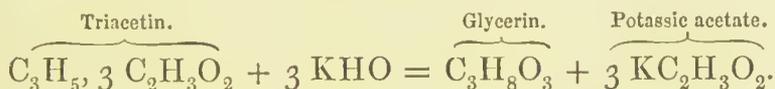
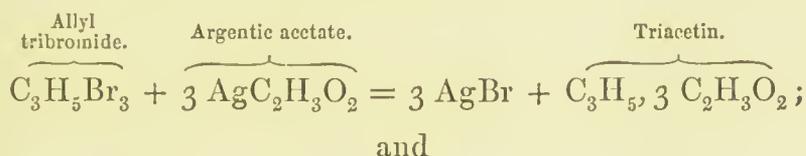
An interesting series of experiments was made by Berthelot and de Luca, upon the action of phosphorus diiodide upon glycerin (*Ann. de Chimie*, III. xliii. 257). When equal weights of crystallized phosphorus diiodide (PI_2) and of glycerin are mixed in a capacious retort, considerable heat is developed; a new compound, *allyl iodide* ($\text{C}_3\text{H}_5\text{I}$), mixed with water distils over (1472); a considerable volume of pure gaseous tritylene

(propylenc) is also evolved, whilst free iodine and phosphorous acid remain in the retort, mixed with the excess of glycerin employed. The reaction is a remarkable one, for it will be observed that the whole of the oxygen of the glycerin is removed, and unites with the phosphorus to form phosphorous acid, whilst the carbon remains in the form of allyl iodide :—

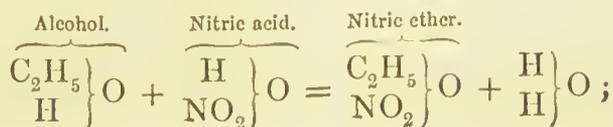


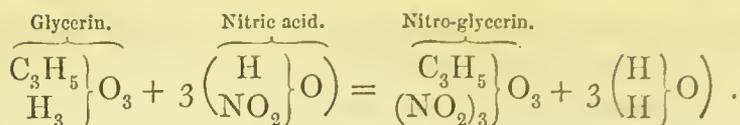
The tritylene which is disengaged is the result of a secondary action, connected probably with the formation of a peculiar iodized compound (? iodhydrin, $\text{C}_6\text{H}_{11}\text{IO}_3$) which is found in the retort in small quantity.

Glycerin may be reproduced by the decomposition of allyl tribromide by means of argentic acetate, and the subsequent treatment of the acetate so obtained with caustic potash :—



(1239) *Action of Acids upon Glycerin.*—Nitric acid attacks glycerin rapidly, and converts it into carbonic and oxalic acids. If glycerin be allowed to fall drop by drop into a mixture of equal measures of nitric acid and oil of vitriol, care being taken to prevent the temperature from rising too high, a heavy oily-looking liquid collects at the bottom of the acid. It is powerfully explosive, and detonates either by a blow or by elevation of temperature; a single drop, placed upon paper and struck upon an anvil, producing a deafening report. By exposure to a low temperature it solidifies to a crystalline mass, which appears to explode by a very slight amount of friction or pressure. This body is a substitution-compound of glycerin, in which 3 atoms of hydrogen are displaced by an equal number of atoms of nitroxyl, NO_2 ; from its composition it might be regarded as the trinitric ether of glycerin, as may be seen by comparing it with ordinary nitric ether :—





It has been termed *nitro-glycerin*, or *glonoin* [$\text{C}_3\text{H}_5(\text{NO}_2)_3\text{O}_3$]. It is soluble in alcohol and in ether, as well as in wood naphtha, from which it may be separated unaltered on dilution with water. It has a sweetish, pungent, aromatic taste, and if but a single drop be placed upon the tongue, it produces a painful aching in the back of the head, which lasts for many hours. Nitro-glycerin has been employed with effect in blasting hard rocks as a substitute for gunpowder; but it has been the cause of several disasters, attended with great loss of life and enormous destruction of property, owing to the spontaneous explosion of the tin-cases in which it was contained.

With many of the polybasic acids, glycerin, like ordinary alcohol, forms compounds analogous to ethylsulphuric acid. For example, when oil of vitriol is mixed with half its weight of glycerin, considerable evolution of heat is occasioned, and a compound acid which yields soluble salts with calcium and barium is formed; the calcium salt has a composition which may be represented by the formula ($\text{Ca}_2\text{C}_3\text{H}_7\text{SO}_6$), the *sulphoglyceric* acid saturating only half the quantity of basyl which would be required by the sulphuric acid which it contains. A compound similar to the foregoing one may be formed with glycerin and phosphoric acid; it is very soluble both in water and in alcohol, but is easily decomposed into free phosphoric acid and glycerin. Phosphoglyceric acid exists ready formed in the yolk of the egg (Gobley), and probably also in the brain.

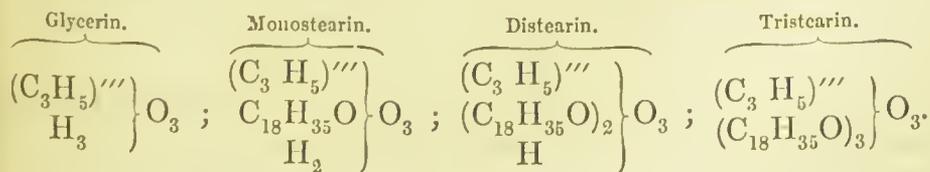
(1240) *Artificial Formation of Fats.—Glycerides.*—The most important compounds which are produced by the action of acids upon glycerin are the compound ethers of glycerin, or the *glycerides*, which are analogous in composition to the various fats and oils. Berthelot has succeeded in forming these bodies by the direct action of the fatty acids upon glycerin, and has not only reproduced several of the natural fats (*Ann. de Chimie*, III. xli. 216), but has also obtained a large class of such bodies which were not previously known. According to the researches of this chemist, stearic, palmitic, and oleic acid each forms three compounds by its union with glycerin; and the act of combination is attended by the separation of water in each case.

Berthelot finds that tristearin, tripalmitin, and triolein are identical with the stearin, palmitin, and olein of the natural fats:

they are produced by the action of 3 molecules of one of the normal fatty acids of the group $C_nH_{2n}O_2$ upon 1 molecule of glycerin, the act of combination being attended with the separation of 3 molecules of water. These combinations of glycerin with the acids may be obtained either by heating the acid and the glycerin together for several hours in closed vessels at an elevated temperature; or by mixing the glycerin and fatty acid with hydrochloric, sulphuric, phosphoric, or tartaric acid, and exposing the mixture for many hours to a temperature of 212° . A partial formation of these bodies occurs, even without the aid of the stronger acids, if the glycerin and the fatty acid be kept in contact for several months at the ordinary temperature.

All these neutral compounds of the higher fatty acids with glycerin are insoluble in water, but are soluble to some extent in boiling alcohol, and are readily soluble in ether. If treated with concentrated acids they are decomposed and acidified in the same manner as the natural fats; and they are all saponifiable,—that is, they are decomposed like the natural fats, into a fatty acid and glycerin, when boiled with an alkali. It has been found that whether monacid, diacid, or triacid in composition, these fats are all neutral in their reactions, and moreover, when decomposed, they all yield glycerin of the same composition and condition of hydration.

Glycerin indeed, as a triatomic alcohol, forms three classes of ethers, just as the tribasic phosphoric acid forms three classes of salts, the three classes of ethers being severally represented by monostearin, distearin, and tristearin; the three bodies being represented by the following formulæ, in which glycerin is supposed to contain the triad radicle $(C_3H_5)'''$, each of the three typical atoms of hydrogen in the glycerin being successively displaced by one, two, or three atoms of the radicle of stearic acid, whilst one, two, or three atoms of water are eliminated:—

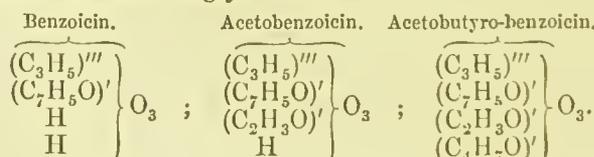


This view will explain the possibility of displacing the hydrogen by different acids, as in aceto-chlorobromhydrin, and some other complicated ethers of glycerin which will be briefly alluded to.

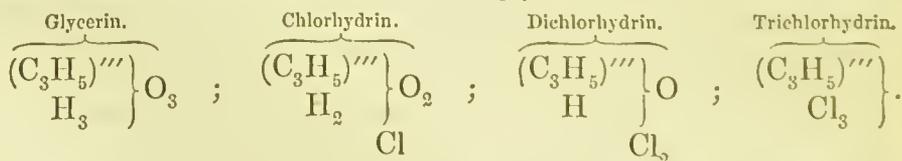
Monostearin has the aspect of bees' wax; it fuses at $141^\circ.8$ (61° C.), and solidifies at 140° (60° C.). It is prepared by heating equal weights of stearic acid and glycerin to 392° (200° C.), for a couple of days in a sealed tube: the

substance thus formed is freed from excess of stearic acid by digestion with slaked lime at a temperature of 212° for a quarter of an hour. The lime combines with the excess of stearic acid, but does not decompose the monostearin, which is afterwards separated from the lime soap by digesting the mixture in hot ether, from which the stearin crystallizes in stellate doubly refracting needles. *Distearin* may be prepared by heating to 212° , for six days, equal weights of glycerin and stearic acid; it resembles the first compound in appearance, crystallizing in oblique doubly refracting plates, which fuse at $136^{\circ}.4$ (58° C.), and become solid at 131° (55° C.). *Tristearin*, which is identical with natural stearin, may be obtained by digesting monostearin for three hours at a temperature of 518° (270° C.) with 15 or 20 times its weight of stearic acid: it is purified from the excess of stearic acid by lime and ether, as directed for monostearin. Valeric, butyric, and acetic acids have each, in like manner, been combined with glycerin in three proportions; but no compound could be obtained with formic acid. It is interesting to remark that even the compounds with acetic acid present the appearance of oily bodies, though many of the simpler glycerides, such as monobutylin ($C_7H_{14}O_4$), chlorhydrin ($C_5H_7ClO_2$), and monacetin ($C_5H_{10}O_4$), are very soluble in water. It is not unlikely that triacetin is one of the components of cod-liver oil, since acetic acid is found amongst the products of the saponification of this oil.

(1241) Glycerin has also been similarly combined with other organic acids, such as the benzoic and the camphoric; as well as with hydrochloric, hydrobromic, and hydriodic acids. In addition to the monacid and diacid derivatives of glycerin, Berthelot and De Luca (*Ann. de Chimie*, III. lii. 433) have succeeded, by methods which we proceed to exemplify, in forming compounds of glycerin, each of which contains three different acids, thus exhibiting in glycerin the existence of a property parallel to that which has been long recognized in phosphoric acid; as, for example, may be seen in the following compounds which illustrate the different classes of glycerin ethers from a monobasic acid:—



Glycerin furnishes with each hydracid three different ethers by three successive steps of etherization; the three hydrochloric ethers may be compared thus with glycerin itself:—

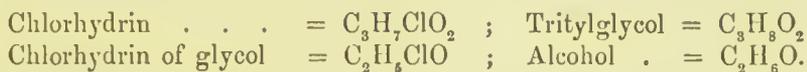


The first two stages of etherization may be effected by reacting upon glycerin with the hydracid, which removes successively the first and second atom of hydroxyl, HO, substituting an atom of chlorine or other halogen in its place; but the third atom of hydroxyl can only be removed by the action of the perchloride, or perbromide of phosphorus.

Chlorhydrin [$C_5H_7ClO_2$, *Boil. pt.* $440^{\circ}.6$ (227° C.)] is obtained by saturating glycerin with hydrochloric acid gas, and maintaining the mixture at 212° for thirty-six hours: it is then to be neutralized with potassic carbonate, and agitated

with ether; the ethereal solution when evaporated leaves chlorhydrin as a neutral oil, with a cooling ethereal odour, and a sweetish, pungent taste. It is soluble in water and in ether, and may be distilled unchanged.

The formula of chlorhydrin only differs from that of tritylglycol by the substitution of an atom of chlorine for one of hydrogen; and Lourenço, by dissolving chlorhydrin in about its own bulk of water, and treating it with an amalgam of sodium, has succeeded in obtaining tritylglycol from it. By a reaction exactly analogous, the chlorhydrin of ordinary glycol has been converted into vinic alcohol:—



Dichlorhydrin ($\text{C}_3\text{H}_6\text{Cl}_2\text{O}$). *Sp. gr.* 1.37; *Boil. pt.* $352^{\circ}.4$ (178° C.).—This is a neutral oil which has a well marked ethereal odour. It remains liquid at -30° ($-34^{\circ}.5$ C.). It burns with a white flame bordered with green.

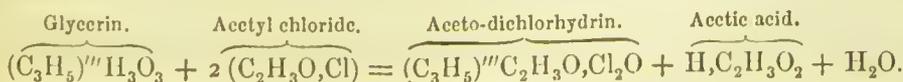
Trichlorhydrin [$\text{C}_3\text{H}_5\text{Cl}_3$, *Boil. pt.* 311° (155° C.)] may be obtained by acting upon the preceding compound with phosphoric chloride. It is a neutral liquid, insoluble in water. Besides these regularly formed ethers, two other chlorinated compounds may be obtained, viz., epichlorhydrin, and epidichlorhydrin:—

Epichlorhydrin ($\text{C}_3\text{H}_5\text{OCl}$). *Sp. gr.* between 1.2 and 1.3.—This substance is a limpid oil which boils between 248° and 260° (120° and 130° C.), emitting a vapour of an ethereal odour resembling that of hydrochloric ether. It differs from chlorhydrin by containing the elements of one atom less of water. It is prepared by heating dichlorhydrin for several hours in a sealed tube to 212° , with 12 or 15 parts of fuming hydrochloric acid; after which it is neutralized with lime and distilled. This compound is regarded by Reboul as the hydrochloric ether of a substance not known in its isolated form, which he has termed *glycide* ($\text{C}_3\text{H}_5\text{HO}_2$), and which would contain one atom of water less than glycerin.

Epidichlorhydrin [$\text{C}_3\text{H}_4\text{Cl}_2$, *Boil. pt.* 248° (120° C.)] is formed in small quantity during the preparation of trichlorhydrin, and it is procured more abundantly by acting upon trichlorhydrin with caustic potash; it assumes the form of a neutral, ethereal oil. It contains the elements of one atom of water less than dichlorhydrin and of one atom of hydrochloric acid less than trichlorhydrin: it would be the dihydrochloric ether of glycide.

All these chlorinated compounds when digested with moist argentic oxide slowly exchange their chlorine for hydroxyl, and reproduce glycerin.

Aceto-dichlorhydrin ($\text{C}_5\text{H}_8\text{Cl}_2\text{O}_2$); *Boil. pt.* 401° (205° C.).—If a quantity of pure glycerin be placed in a tubulated retort kept cool by immersion in water, and acetyl chloride be added drop by drop until it ceases to produce any action, a compound is formed attended with violent extrication of heat. The product must be distilled, washed first with water, then with a weak solution of alkali, and after allowing it to stand upon a mixture of calcic chloride and caustic potash in fragments, must be redistilled. A neutral, limpid, colourless oil with an ethereal cooling odour is obtained, whilst water and acetic acid are separated, by the reaction of hydrogen and oxygen derived from the glycerin upon acetyl chloride:—



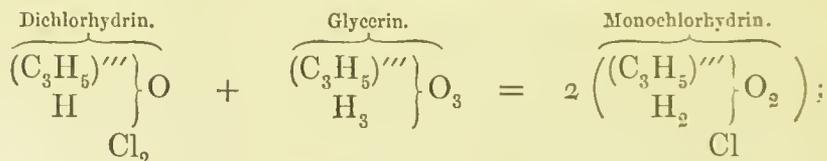
A small quantity of *aceto-chlorhydrin* [$\text{C}_5\text{H}_9\text{ClO}_3$; *Boil. pt.* 482° (250° C.)] is formed at the same time.

Aceto-chlorobromhydrin ($\text{C}_5\text{H}_8\text{ClBrO}_2$). *Boil. pt. about* $442^{\circ}.4$ (228° C.).—

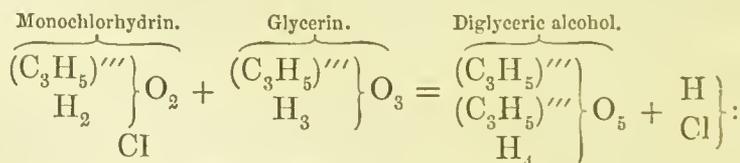
If a mixture of equivalent quantities of acetyl chloride and acetyl bromide be made to act upon glycerin in the manner just described, a compound will be formed in which, by the elimination of three atoms of water, the acetic, hydrochloric, and hydrobromic acids will have entered into combination with the glycerin, giving rise to a limpid, colourless, ethereal liquid, which is insoluble in water. Various other analogous compounds have been obtained, but they are often difficult to purify, owing to their tendency to become decomposed if distilled.

Glycerin forms with hydrobromic acid compounds analogous to those which it yields with hydrochloric acid, such as *monobromhydrin* ($C_3H_7BrO_2$), *dibromhydrin* ($C_3H_6Br_2O$), and *tribromhydrin* ($C_3H_5Br_3$).

We find further, that condensed glycerins may exist, like condensed glycols (p. 283), and that in consequence cases occur in which two, three, or n molecules of glycerin become combined into a single molecule with the elimination of one, two, or $n-1$ molecules of water. These polyglycerins are formed by digestion of a mixture of chlorhydrin and dichlorhydrin, with excess of glycerin. As for example:—

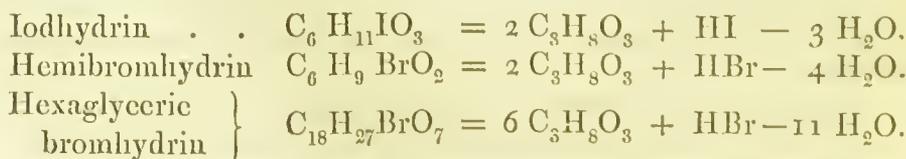


and the monochlorhydrin reacting upon glycerin produces diglyceric alcohol with elimination of hydrochloric acid:—



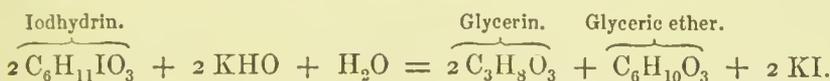
the hydrochloric acid reacting upon more glycerin produces a fresh portion of monochlorhydrin, and this, acting upon diglyceric alcohol, converts it into triglyceric alcohol ($(C_3H_5)'''_3H_5O_7$), and so on.

It is in consequence of the formation of these condensed compounds that sometimes several molecules of glycerin react upon a single molecule of an acid, whilst a variable number of molecules of water is eliminated. The following compounds, for example, have been obtained:—



Iodhydrin ($C_6H_{11}IO_3$). *Sp. gr.* 1.783.—When glycerin is saturated with hydriodic acid gas, and heated to 212° for forty hours, then treated with potash and with ether, it yields a golden yellow syrupy liquid, which dissolves one-fifth

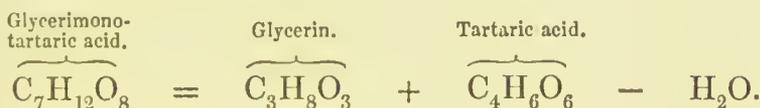
of its bulk of water, but is not itself soluble in water. In the formation of this body two molecules of glycerin become condensed into one during the reaction, as above explained. Iodhydrin has a sweet taste; it is combustible, and cannot be distilled without experiencing decomposition. When treated with an aqueous solution of potash, it is slowly decomposed; potassic iodide and normal glycerin are formed, together with a volatile compound, which is soluble in ether, and which has a composition represented by $C_6H_{10}O_3$. This substance would correspond to the ether of glycerin. This supposed *glyceric ether* contains the elements of two molecules of glycerin, minus three of water: $2 C_3H_8O_3 - 3 H_2O = C_6H_{10}O_3$; and its formation from iodhydrin might be thus represented:—



Wurtz, however, did not succeed in procuring it.

When an alcoholic solution of dibromhydrin ($C_3H_6Br_2O$) is submitted to the action of gaseous ammonia, the hydrobromate of a new base, *glyceramine*, $C_3H_9NO_2$ (Berthelot and De Luea), is produced, whilst ammonie bromide is formed.

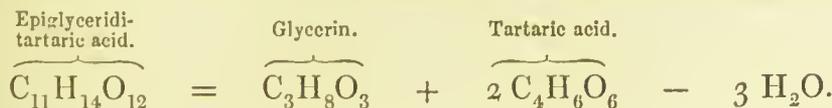
Acid glycerides may be formed by causing glycerin to combine with a dibasic acid; thus we may obtain a monobasic glyceritartaric acid:—



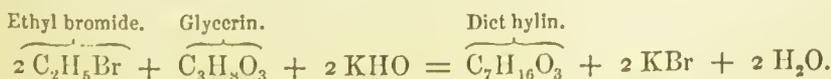
Also a dibasic acid formed by a decomposition which may be thus represented:—



in addition to which an intermediate monobasic acid is known:—



Diethylin [$C_3H_5(C_2H_5)_2HO_3$], *Sp. gr.* 0.92, *Boil. pt.* $375^{\circ}.8$ (191° C.), is a limpid oil of a pungent, ethereal odour; it does not become solid at -40° ; it is scarcely soluble in water. This singular compound is obtained by acting upon a mixture of ethyl bromide, glycerin, and caustic potash; the materials are enclosed in a sealed tube, and submitted for four days to a temperature of 212° :—



It may be regarded as the result of the reaction of 2 molecules of alcohol upon 1 of glycerin, attended with the separation of 2 molecules of water, representing a

double or mixed ether, $\left. \begin{array}{c} (C_3H_5)'''' \\ H \\ (C_2H_5)_2 \end{array} \right\} O_3$, or a glycerin containing 2 atoms of ethyl instead of 2 of hydrogen. For the further prosecution of this subject the reader

is referred to the papers of Berthelot in the *Annales de Chimie*, and to a paper on the ethers of *glycide* by Reboul, *ib.* III. lx. 5.

(1242) *Acrolein, or Acrylic Aldehyd* (C_3H_4O). *Sp. gr. of vap.* 1.897; *Rel. wt.* 28; *Boil. pt.* about 125° ($51^\circ.6$ C.).—When glycerin or any of its compounds is submitted to the ordinary process of distillation, it undergoes decomposition; and amongst the products is a substance which, from its intensely irritating effects upon the mucous membrane of the eyes and organs of respiration, has received the name of *acrolein*. A remarkable reaction by which acrolein is obtained is the decomposition of acetone bromide by heat; $C_2H_3O(CH_3)Br_2 = 2HBr + C_2HO(CH_3)$. But it is best obtained in a state of purity (Redtenbacher, *Liebig's Ann.* xlvii. 114) by distilling in a capacious retort a mixture of glycerin with phosphoric anhydride, or with hydriopotassic sulphate ($KHSO_4$); the vapours must be condensed in a properly cooled receiver, which is luted on to the retort, and provided with a tube opening into a chimney with a good draught.

The object of using phosphoric anhydride in the distillation, is to effect the dehydration of the glycerin, since glycerin contains the elements of one molecule of acrolein and two molecules of water; $C_3H_8O_3 - 2H_2O = C_3H_4O$.

The distilled liquid separates into two layers, the upper one consisting of acrolein, and the lower one of an aqueous solution of the same substance mixed with a quantity of acrylic acid. This distillate, after digestion with finely powdered litharge, with the view of neutralizing the acid, must be rectified by the heat of a water-bath: the acrolein so obtained must be submitted to a second rectification from calcic chloride, after which it is nearly free from impurity. All these operations must be carried on in vessels filled with carbonic anhydride, for the purpose of excluding atmospheric oxygen, because acrolein becomes rapidly oxidized when exposed to the air.

Acrolein is a limpid, transparent, colourless liquid, lighter than water and possessed of a high refracting power. It has a burning taste, and emits a vapour which is intolerably irritating. It burns with a clear luminous flame. Acrolein when pure is neutral to test paper, but, like ordinary aldehyd, it becomes acid rapidly by the absorption of oxygen from the air; a mixture of acrylic, acetic, and formic acids being produced. In fact acrolein contains an atom of oxygen less than acrylic acid, to which it stands in the same relation as ordinary aldehyd does to acetic acid. Acrolein is freely soluble in ether, but requires 40 parts of water for solution. It cannot long be preserved without change, even in sealed

tubes; but becomes converted into a white, flocculent, and probably isomeric substance, termed *disacryl*: this compound is insoluble in water, acids, alkalies, oils, and carbon disulphide. Sometimes the acrolein becomes transformed into a resinoid body, which melts at 212° , and forms a brittle, transparent mass on cooling; this substance, though insoluble in water, is soluble in alcohol, in ether, and in alkaline solutions.

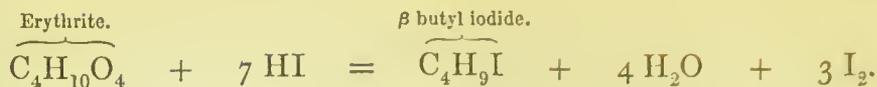
The reaction of acrolein with the alkalies, further shows its similarity to aldehyd:—when mixed with a solution of potash or of soda it is rapidly acted upon; its irritating odour disappears and is succeeded by one of cinnamon, whilst a brown resinous substance is formed. The ethereal solution of acrolein when mixed with ammonia yields a white amorphous body, destitute of odour. When mixed with argentic nitrate it gives a white curdy precipitate, which is reduced to metallic silver on boiling, though without coating the glass with the reduced metal; argentic acrylate remains in solution. Argentic oxide oxidizes acrolein rapidly, with great evolution of heat, and converts it into acrylic acid (1296); the acid is indeed easily prepared by this means from the crude liquid obtained by the destructive distillation of the fixed oils.

Hofmann and Cahours have succeeded in discovering the *allylic alcohol* (C_3H_5, HO), a compound which stands in the same relation to acrolein that ethylic alcohol does to ordinary aldehyd: many of the derivatives of this alcohol have been long known as compounds of *allyl* (C_3H_5). (1469.)

§ III. OTHER POLYATOMIC ALCOHOLS.

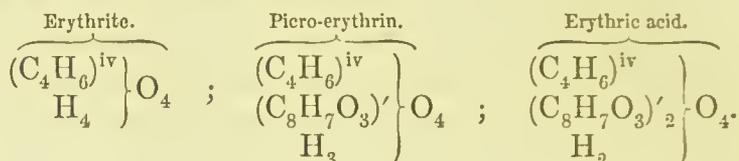
(1243) No triatomic alcohols except the glycerins have yet been definitely proved to exist; but it appears that erythrite or lichen mannite is a tetratomic alcohol; and it is probable that mannite and its isomeride dulcete are hexatomic alcohols; possibly also, pinite and quercite, as well as glucose and some other sugars, are polyatomic alcohols.

Erythrite, Erythromannite, or Pseudo-Orcin ($C_4H_{10}O_4$). *Sp. gr.* 1.59; *Fusing pt.* 248° (120° C.)—This substance appears to be a tetratomic alcohol, the fundamental hydrocarbon of which is derived from the dyad radicle (C_4H_8)'' butylene, which by loss of H_2 becomes tetrad in function. When erythrite is subjected to the action of hydriodic acid, β butyl iodide is obtained by the following reaction:—



This reaction is analogous to the corresponding one with mannite, and it definitely fixes the formula for erythrite, which may be written $\left. \begin{matrix} (\text{C}_4\text{H}_6)^{\text{iv}} \\ \text{H}_4 \end{matrix} \right\} \text{O}_4$, (v. Luynes, *Ann. de Chimie*, IV. ii. 416).

The compound known as erythric acid, and found in the colour-producing lichens, is probably the diorsellie ether of erythrite (1527); and Stenhouse's picro-erythrin is monorsellie erythric ether, as shown in these formulæ:—



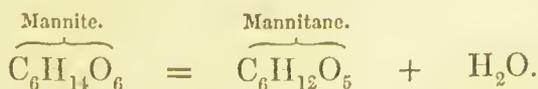
Erythrite (so named from *έρυθρος* red, in allusion to the red colour obtainable from the lichen) is usually obtained from the litmus lichen, *Roccella montagnei*; by digesting the powdered lichen with milk of lime, boiling the filtered solution for some hours, and then removing the excess of lime by carbonic anhydride. In this process the erythric acid of the lichen is separated by the lime, and subsequently decomposed by boiling into erythrite, and orein (1530) which last, after evaporation, may be removed by digestion with ether and alcohol. The erythrite crystallizes after a few days from the aqueous solution of the residue. It may be purified by recrystallization from boiling absolute alcohol. It may also be extracted from a species of fucus, the *Protococcus vulgaris* (Lamy).

Erythrite crystallizes in square prisms which are rather hard. They are very soluble in water, and have a sweet taste; the solution has no rotatory power on a polarized ray. It is also soluble in boiling absolute alcohol. When heated it fuses at 248° (120° C.), and it may be heated to 482° (250° C.) without undergoing decomposition; it is not susceptible of fermentation. By the action of fuming nitric acid it is converted into an explosive nitro-compound, $\text{C}_4\text{H}_6(\text{NO}_2)_4\text{O}_4$, resembling nitro-mannite; this is soluble in boiling alcohol, from which it may be obtained in brilliant laminae, fusible at $141^\circ.8$ (61° C.). By prolonged treatment with nitric acid erythrite yields oxalic, but no mucic acid. When fused with caustic potash, hydrogen is evolved, and oxalate and acetate of the base are formed. A solution of erythrite does not reduce the potassic-erythric tartrate, nor does it give a precipitate with ammoniacal plumbic acetate.

Erythrite, when heated with stearic or benzoic acid for some hours, in sealed tubes, to between 392° and 482° (200° and 250° C.) yields colligated acids with elimination of water. Similar compounds may be obtained with acetic and tartaric acids. No erythric ethers containing four atoms of a monacid radicle are as yet known, unless nitro-erythrite be so regarded.

(1244) MANNITE ($C_6H_{14}O_6$).—This substance constitutes the principal portion of the drug known as *manna*, the inspissated saccharine juice of the *Fraxinus ornus*, a tree which grows abundantly in Sicily and Calabria. Mannite is moreover contained in considerable quantity in celery, in onions, asparagus shoots, and in certain kinds of fungi. Stenhouse also found it largely in many species of sea-weed; *Laminaria saccharina*, when dried, containing as much as 12 or 13 per cent. of mannite. It is likewise a constituent of the juice which exudes from many varieties of apple and pear trees; and it is always formed during the viscous fermentation of sugar to which the juice of the beet-root is particularly liable. Linnemann has also found that by treating an alkaline solution of inverted cane sugar (1086) with amalgam of sodium, the sugar may be made to unite with hydrogen, and that it is thereby converted into mannite. Lævulose is the only variety of sugar susceptible of this change.

Mannite may be readily extracted from the manna of the *Fraxinus ornus* by digesting it in hot alcohol; as the solution cools the mannite crystallizes in tufts of silky quadrangular prisms. It fuses at about 320° (160° C.) without losing weight, forming a colourless liquid, which solidifies, on cooling, into a mass of radiated crystals. Mannite may be heated in a sealed tube to 482° (250° C.) without experiencing decomposition; but when raised in the open air to a temperature not exceeding 400° ($204^{\circ}\cdot4$ C.) it loses water, and a large portion is converted into a substance termed *mannitane* ($C_6H_{12}O_5$), which is a syrupy liquid with a sweetish taste: this substance is insoluble in ether, but freely soluble in water and in alcohol: if exposed to the air it deliquesces, and is slowly reconverted with assimilation of water into crystallized mannite:—



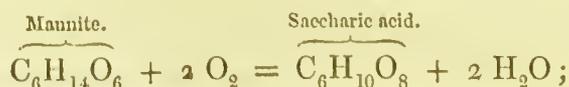
Mannite is very soluble in water: it has an agreeable sweet taste, and is easily distinguished from cane sugar by the absence of any charring effect when it is treated with sulphuric acid; in

fact, the acid combines with it and forms *disulphomannitic acid* ($\text{H}_2\text{C}_6\text{H}_{10}\text{O}_4\text{S}_2\text{O}_7$). A *trisulphomannitic acid* ($\text{H}_3\text{C}_6\text{H}_{11}\text{O}_6\text{S}_3\text{O}_9$) also has been obtained. Mannite may also be distinguished from grape sugar with facility, since it does not become brown when heated with alkaline solutions. If fused with caustic potash hydrogen is evolved, and a mixture of potassic formiate, acetate, and propionate is obtained. Mannite combines with bases, and dissolves lime freely; this solution when boiled becomes turbid, but the precipitate is redissolved as the liquid cools. When a concentrated aqueous solution of mannite is mixed with one of ammoniacal plumbic acetate, a precipitate ($\text{C}_6\text{H}_{10}\text{O}_4, 2 \text{PbO}$) is formed, which consists of mannite, in which 2 atoms of plumbic oxide have displaced 2 H_2O . Solutions of mannite do not reduce the alkaline solution of cupric tartrate when boiled with it, but when heated with a solution of argentie nitrate they precipitate the metal. They likewise reduce gold from a solution of its trichloride.

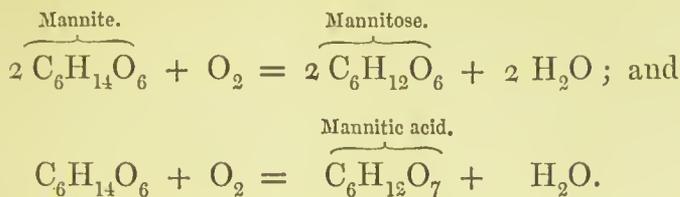
Mannite is further characteristically distinguished from true sugar by its want of rotatory power upon a ray of polarized light. Nitric acid produces saccharic and oxalic acids when heated with mannite, but no mucic acid. With a mixture of concentrated nitric and sulphuric acids, mannite yields a crystalline explosive substitution product, *hexanitromannite*, $\text{C}_6\text{H}_8(\text{NO}_2)_6\text{O}_6$. When mannite is heated with hydriodic acid the mixture furnishes the iodide of a monatomic alcohol radicle, called iodide of β hexyl (Erlenmeyer and Wanklyn); $\text{C}_6\text{H}_{14}\text{O}_6 + 11 \text{HI} = \text{C}_6\text{H}_{13}\text{I} + 5 \text{I}_2 + 6 \text{H}_2\text{O}$.

It is generally stated that mannite is insusceptible of the alcoholic fermentation, and it certainly does not ferment when its solution is mixed with yeast; but Berthelot has shown (*Ann. de Chimie*, III. l. 334) that if a solution of mannite be maintained for some weeks at a temperature of 104° (40°C .) in contact with chalk, or with some other insoluble carbonate by which any acid which may be produced is neutralized as soon as it is formed, and with a quantity of poor cheese or of pancreatic tissue, or with some analogous azotised matter capable of acting as a ferment, it is partially fermentable; a quantity of alcohol, varying from 13 to 33 per cent. of the weight of the mannite used, being obtained. Small quantities of lactic, butyric, and acetic acids are formed at the same time, and carbonic anhydride and hydrogen gases are liberated. The formation of alcohol from mannite may be represented by the equation $\text{C}_6\text{H}_{14}\text{O}_6 = 2 \text{C}_2\text{H}_6\text{O} + 2 \text{CO}_2 + \text{H}_2$; two volumes of carbonic anhydride being liberated for each volume of hydrogen. The formation of lactic acid may be represented still more simply, $\text{C}_6\text{H}_{14}\text{O}_6 = 2 \text{C}_3\text{H}_6\text{O}_3 + \text{H}_2$. The butyric and the acetic acids are secondary results of the decomposition of the lactic acid and of the oxidation of the alcohol.

By gradual oxidation, mannite yields an acid either isomeric or identical with saccharic acid, whilst water is eliminated:—

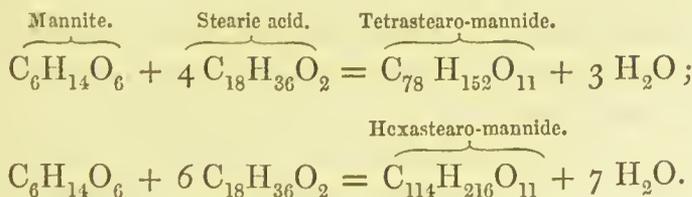


and by the action of platinum, carefully conducted, it yields mannitic acid, whilst a species of sugar, *mannitose*, is formed:—



Berthelot has also converted mannite into mannitose, which is susceptible of fermentation with yeast, by digesting it with several substances of organic origin. The organic body with which he succeeded almost uniformly in producing this effect was the tissue of the testicle, either of man or of animals, such as the cock, the horse, or the dog. In this experiment a solution of 1 part of mannite in 10 of water is digested at a temperature ranging between 50° and 68° (10° and 20° C.) in an open flask upon the animal tissue, which should amount to about $\frac{1}{20}$ of the weight of the mannite (both estimated in the dry form). No putrefaction or mouldiness occurs if the operation be successful, and in the course of a few weeks the transformation is effected. The fragments of testicular tissue, if removed to a fresh solution of mannite, continue their sugar-producing action in this fresh solution. In a few cases as much as $\frac{1}{10}$ of the mannite employed was converted into sugar. This sugar resembles glucose, but has not yet been obtained in a crystalline form.

(1245) *Mannides, or Compounds of Mannite with the Acids, analogous to Fats.*—When mannite is heated for some hours with various acids in sealed tubes under pressure, it gives rise to a series of compounds, termed *mannides*, which run exactly parallel with those obtained by treating glycerin in a similar manner (Berthelot, *Ann. de Chimie*, III. xlvii. 297). If stearic acid be thus heated with mannite it forms two compounds, viz., *tetrastearo-mannide* and *hexastearo-mannide*, which may be represented as formed thus:—



These substances can scarcely be distinguished from distearin and tristearin, which are the corresponding compounds of glycerin; they are solid crystalline fats, of about the same degree of fusibility as the stearins. They admit of being saponified in the same manner as the true fats; and when decomposed by bases they yield stearic acid, but do not produce mannite; in its place the sweet syrupy compound, mannitane ($\text{C}_6\text{H}_{12}\text{O}_5$), is obtained, containing in its molecule one atom of H_2O less than mannite. This solution so greatly resembles that of glycerin in appearance and

properties, that Berthelot thinks it is by no means improbable that some of the natural fats which are at present supposed to be compounds of glycerin, may turn out to be derivatives of mannite.

Compounds of mannite similar to those which it forms with stearic acid, have been obtained by heating it with palmitic, valeric, butyric, acetic, benzoic, and other acids. Its compound with acetic acid *aceto-mannide* ($C_{10}H_{16}O_7 = C_6H_{14}O_6 + 2 C_2H_4O_2 - 3 H_2O$) is a viscid, intensely bitter liquid, which emits, when warm, a peculiar odour like that possessed by many of the umbelliferous plants. On decomposing the butyric compound, Berthelot obtained instead of mannitane a still more dehydrated compound, which he terms *mannide*, $C_6H_{10}O_4$. This body also reproduces mannite by gradual absorption of water. With hydrochloric acid, mannite yields a white, neutral, well-crystallized body, *chlorhydromannide* ($C H_{10}Cl_2O_3$), which has a bitter aromatic taste: it is very soluble in ether, and may be volatilized without residue. The fat-like derivatives of mannite are neutral bodies.

The reactions which attend the formation of these bodies have led Berthelot to regard mannitane rather than mannite as the alcohol from which they are formed; but there are still some obscure points which require further elucidation, as the mode of formation of these substances does not admit of being represented by any general equation. Those which are produced from two atoms of a monobasic acid may be supposed to be formed by the union of 1 atom of *mannitane* and 2 atoms of the normal acid, attended with the separation of 2 atoms of water; whilst those containing 6 atoms of acid are formed from 1 of mannitane and 6 of the normal acid, with the separation of 6 atoms of water.

Mannite also furnishes compounds with the polybasic acids, such as the sulphuric, the tartaric, and the phosphoric acids; these compounds have an acid character, and are analogous to the sulphoglyceric and phosphoglyceric acids (1239).

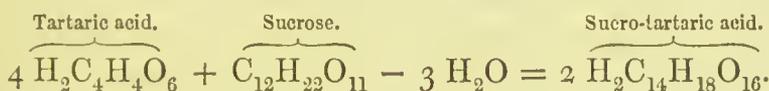
(1246) *Action of Polybasic Acids upon the Sugars.*—Berthelot has shown that most of the saccharine bodies enter into combination with various polybasic acids, forming with them colligated acids analogous in composition to tannic acid (1331). If, for example, powdered tartaric acid be intimately mixed with an equal weight of sucrose, glucose, lactose, sorbin, pinite, quercite, mannite, or erythrite, and be exposed in an open vessel for a day or two to a temperature of about 248° (120° C.), the acid enters into combination with the saccharine body more or less perfectly. In order to isolate the new body, the mass is allowed to cool, and is afterwards triturated with water and calcic carbonate. The excess of tartaric acid is thus removed in the form of calcic tartrate, which is insoluble, whilst a calcium salt with the new colligated acid remains in solution, mixed with the excess of uncombined saccharine matter. On the addition to the filtrate of twice its bulk of alcohol, the calcium salt is precipitated, and may be purified by washing with alcohol of sp. gr. 0.920. The purification is completed by redissolving the salt in water and repeating the precipitation with alcohol, once or twice more. If the salt

thus obtained be treated with an equivalent proportion of oxalic acid, the new acid is set at liberty.

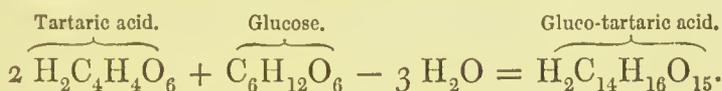
During the formation of these colligated acids the saccharine body loses the elements of water in the act of combining with the polybasic acid, whilst the basic power of the acid is diminished, as in the analogous case of the combination of sulphuric acid with the elements of alcohol (1135) in the preparation of ethyl-sulphuric acid.

The following equations will serve to elucidate the composition of some of these sacro-acids:—

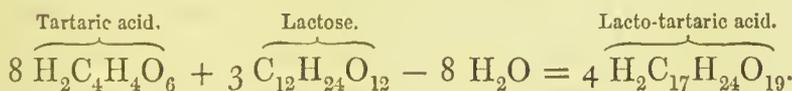
1. *Sucro-tartaric acid*, dibasic:—



2. *Gluco-tartaric acid*, dibasic:—



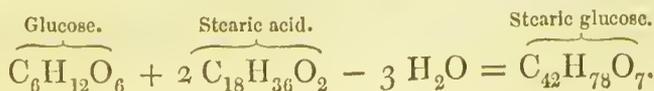
3. *Lacto-tartaric acid*, dibasic:—



A tribasic lacto-tartaric acid was obtained on one occasion. A tribasic *mannitartaric* and a tribasic *gluco-citric* acid appear likewise to exist.

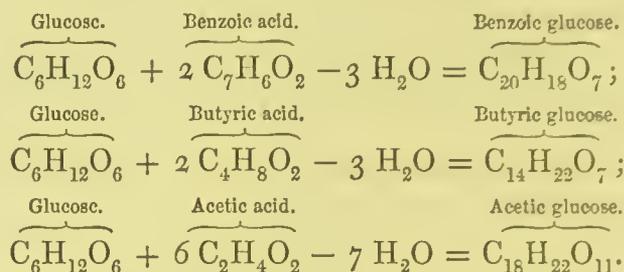
(1247) *Saccharides and Glucosides*.—In pursuing these researches Berthelot (*Ann. de Chimie*, III. lx. 93) has succeeded in forming a variety of neutral compounds by the action of acids upon glucose, and on other varieties of sugar. The formation and the splitting up of these saccharides are effected under conditions similar to those which are applicable to the neutral fats (1240); indeed the chemical and physical properties of these two groups of complex principles are very similar. The saccharides are however much more alterable and are more difficult to procure than the neutral fats, or even than the still more closely allied mannitic compounds of this nature.

A stearic glucose, for example, may be formed by heating to 248° (120° C.) for 50 or 60 hours a mixture of anhydrous grape sugar, of cane sugar, or of trehalose with stearic acid:—



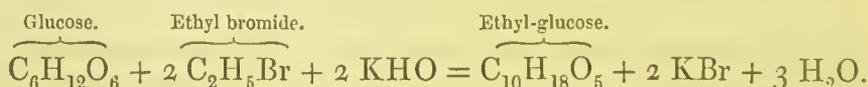
It is a colourless, waxy, fusible solid, soluble in ether, and in absolute alcohol, but insoluble in water:—

By analogous methods benzoic, butyric, and acetic glucose have been obtained as neutral oils:—



Diluted sulphuric acid decomposes these compounds when heated with them, the elements of water being assimilated, whilst the organic acid and fermentable sugar are reproduced. If heated with a mixture of alcohol and hydrochloric acid, fermentable sugar is liberated, whilst the ether of the organic acid—benzoic, butyric, or acetic ether—is produced. They all reduce the alkaline potassic-cupric tartrate.

Not only do the sugars thus unite with the acids whilst water is separated, but like the polyatomic alcohols they may also combine with the radicles of other alcohols, or with the radicles of both acids and alcohols. These compounds are analogous to the glycerides. *Ethyl-glucose*, for example, is obtained by heating to 212° for several days a mixture of cane sugar, ethyl bromide, and caustic potash. The new product is dissolved by means of ether, and remains after the ether is evaporated *in vacuo*:—



A coloured oil which is not volatilizable is thus obtained. It is of a bitter taste, and faint agreeable odour resembling that of old paper. Many substances resembling this compound occur naturally, such, for instance, as salicin, phloridzin, arbutin, and others.

It will be observed that the glucosides are formed from a quantity of glucose, which yields an atom more of water than might have been expected from the analogous reactions with glycerin; the body which corresponds to the alcohol having the composition $\text{C}_6\text{H}_{10}\text{O}_5$. It may be procured by heating glucose cautiously. Berthelot suggests for it the name of *glucosane*, to indicate its analogy with mannitane (p. 99).

Sucrose yields, by careful heating, a mixture of dextrose and levulosane (p. 94).

Further researches upon the derivatives of sugar are, however, needed to clear up several points, which are still but little understood.

CHAPTER V.

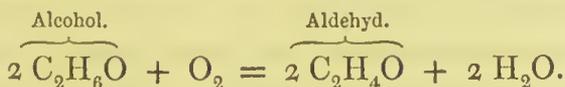
PRODUCTS OF THE OXIDATION OF THE ALCOHOLS—ACIDS.

§ I. THE ALDEHYDS AND KETONES.

(a) *The Aldehyds.*

(1248) ALLUSION has been already made on several occasions to the important series of acids which are produced by the oxidation of the monatomic alcohols; but a series of compounds may be obtained which are less highly oxidized than the acids, and are intermediate in position between the alcohols and the acids. They have received the name of aldehyds. Many of the properties of these bodies are remarkable.

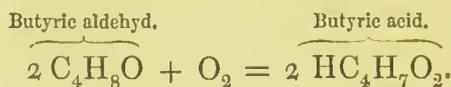
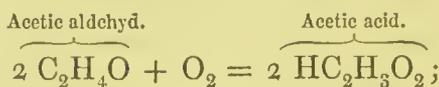
It has already been mentioned that when alcohol is burned with free access of air, the sole products are carbonic anhydride and water. If, however, the combustion be effected at a lower temperature, and with a limited supply of air, numerous other compounds are formed, and the vapours emitted have a peculiar irritating effect on the eyes and nose, due principally to the production of a remarkable body, named *aldehyd*. The alcohol, in fact, is imperfectly burned; in each molecule of alcohol 2 atoms of hydrogen are converted into water by union with oxygen from the air, and aldehyd (*alcohol dehydrogenated*) is obtained:—



Similar compounds are furnished by the imperfect combustion of the other alcohols. The glycols also yield aldehyds by oxidation; each glycol probably furnishing two aldehyds: one by the removal of 2 atoms of hydrogen, the other by the removal of 4 atoms. Glyoxal is a compound of this second class, and is the only glycol aldehyd which has been carefully examined (*note*, p. 278). The following are the principal aldehyds of the group of monatomic alcohols of the formula $(\text{C}_n\text{H}_{2n+2}\text{O})$ at present known:—

| Compounds. | Formula. $C_n H_{2n} O$. | Specific Gravity. | | Rel. wt. H = 1. | Boiling Point. | |
|----------------------|------------------------------|-------------------|----------|--------------------|----------------|------|
| | | Liquid. | Gaseous. | | ° F. | ° C. |
| Acetic aldehyd . . | $C_2 H_4 O$ | 0·79 | 1·532 | 22 | 68 | 20 |
| Propionic aldehyd . | $C_3 H_6 O$ | 0·79 | 2·169 | 29 | about 140 | 60 |
| Butyric aldehyd . . | $C_4 H_8 O$ | 0·80 | | 36 | about 158 | 70 |
| Valeric aldehyd . . | $C_5 H_{10} O$ | 0·82 | 2·93 | 43 | 204·8 | 96 |
| Caproic aldehyd (P) | $C_6 H_{12} O$ | | | 50 | | |
| Enanthylic aldehyd . | $C_7 H_{14} O$ | 0·827 | 4·178 | 57 | about 312·8 | 156 |
| Caprylic aldehyd . . | $C_8 H_{16} O$ | 0·818 | | 64 | 339·8 | 171 |
| Rutic aldehyd . . . | $C_{10} H_{20} O$ | | | 78 | | |
| Euodic aldehyd . . . | $C_{11} H_{22} O$ | 0·849 | 5·87 | 85 | 415·4 | 213 |
| Lauric aldehyd . . . | $C_{12} H_{24} O$ | | 6·182 | 92 | 449·6 | 232 |

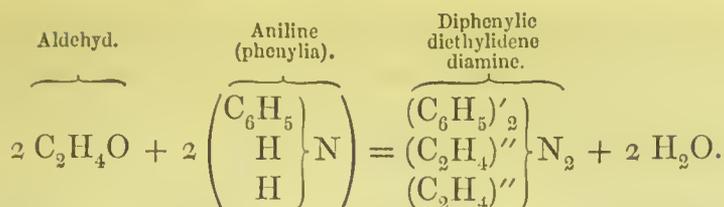
The aldehyds are characterized by their remarkable tendency to combine with oxygen, in consequence of which they absorb it by mere exposure to the air, and become acid. Each molecule of aldehyd absorbs an atom of oxygen, and is converted into the corresponding acid; for example:—



The aldehyds of the form $(C_n H_{2n} O)$ combine with ammonia and furnish with it crystalline compounds which are insoluble in ether. When mixed with a solution of potash, they form with the alkali a brown resinous mass. Many of them when heated with a solution of argentic nitrate, to which a small quantity of ammonia has been added, decompose the salt of silver, and reduce the metal in the form of a mirror-like coating upon the inner surface of the vessel in which they are heated. Another remarkable property of the aldehyds is their power of forming with hydric-potassic or hydric-sodic sulphite crystalline compounds of stable character and sparing solubility. These compounds contain the elements of one molecule of hydric-sulphite of the alkali-metal, and one of the aldehyd, with or without water of crystallization, having the general formula $(KHSO_3, C_n H_{2n} O, x H_2 O)$.

Many essential oils, such as those of bitter almonds, cinnamon, cumin, and spiræa, form similar compounds. These essences are regarded as the aldehyds of a different class of alcohols (1122).

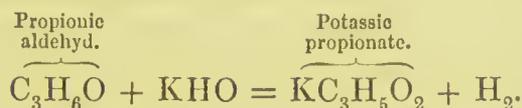
Aniline reacts upon the aldehyds with elimination of water, giving rise to diammonias isomeric with the corresponding compounds derived from the glycols:—



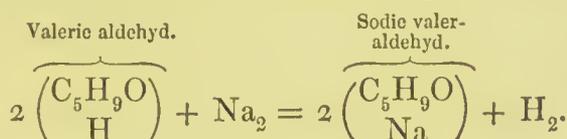
According to Schiff this reaction with aniline is as characteristic of an aldehyd as that with the hydric-sulphites of the alkali-metals.

When digested with an amalgam of sodium in the presence of water, Wurtz has shown that the aldehyds combine with nascent hydrogen, one molecule of the aldehyd uniting with two atoms of hydrogen, and being thereby reconverted into its corresponding alcohol.

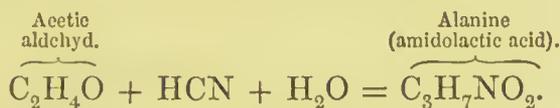
If the vapour of an aldehyd be transmitted over heated caustic potash, hydrogen is evolved, and the corresponding acid is formed; as for example:—



The aldehyds are decomposed by potassium and sodium with evolution of hydrogen, and the formation of a soluble compound with an alkaline reaction, which absorbs oxygen readily; forexample:



When hydrocyanic acid is mixed with an aldehyd, and acted upon by hydrochloric acid, a remarkable amido-acid is formed; as for example:—

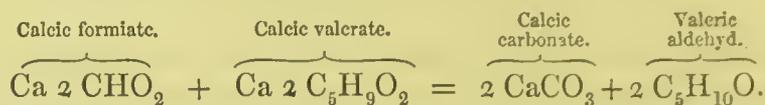


The aldehyds are polymeric with the ethers of the monobasic acid in the series to which they belong, but they yield vapours of only half the density of that of the corresponding compound ether. For example, acetic aldehyd is polymeric with acetic ether; $2 \text{ C}_2\text{H}_4\text{O} = \text{C}_4\text{H}_8\text{O}_2 = \text{C}_2\text{H}_5\text{,C}_2\text{H}_3\text{O}_2$; and valeric aldehyd is polymeric with amyl valerate: $2 \text{ C}_5\text{H}_{10}\text{O} = \text{C}_{10}\text{H}_{20}\text{O}_2 = \text{C}_5\text{H}_{11}\text{,C}_5\text{H}_9\text{O}_2$.

The aldehyds are metameric with the oxide of the glycol of the same series; for example:—



They may be prepared synthetically by a reaction first suggested by Piria; viz., by distilling a mixture of equivalent quantities of calcic formiate, with the calcic salt of the acid corresponding to the aldehyd sought; for example:—



The constitution of the aldehyds has been variously represented; they are now often conveniently regarded as compounds in some measure analogous to hydrogen itself, acetic aldehyd being represented by the formula $\left. \begin{array}{c} \text{C}_2\text{H}_3\text{O} \\ \text{H} \end{array} \right\}$, in accordance with the hydrogen type $\left. \begin{array}{c} \text{H} \\ \text{H} \end{array} \right\}$. These views will be discussed more fully when the properties of acetic aldehyd are considered.

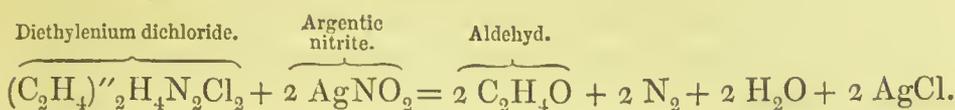
The aldehyds are unstable compounds, several of them passing into bodies which are isomeric with them, but which possess properties entirely different from the true and rapidly oxidizable aldehyds.

1. FORMIC ALDEHYD has not hitherto been satisfactorily isolated; but it is among the products obtained by the oxidation of the vapour of wood spirit in air by means of a coil of platinum wire; and *methylal*, a body homologous with acetal, is contained amongst the products of the gradual oxidation of wood spirit by means of manganese dioxide and sulphuric acid.

(1249) 2. ALDEHYD, *Acetic Aldehyd* ($\text{C}_2\text{H}_4\text{O}$). *Sp. gr. of liq. at 32°*, 0.8009; *of vap.* 1.532; *Rel. wt.* 22; *Boil. pt.* 68°, (20° C.) Kopp.—Acetic aldehyd was the earliest discovered member of the group of aldehyds, and owing to its connexion with the process of acetification it is by far the most important of them.

Preparation.—Aldehyd may be obtained by the gradual oxidation of alcohol in various ways. It is formed, for example, when the vapour of alcohol mixed with air is transmitted through a porcelain tube heated to low redness, or when alcohol is acted upon by dilute nitric or chromic acid: owing to the action of nitric acid upon the elements of alcohol, it is produced during the preparation of the fulminates of silver and mercury, and it is always present in nitrous ether: it may likewise be procured by the dry distillation of lactic acid, or of enipric lactate: dilute alcohol also furnishes it when acted on by chlorine. Another remarkable mode in which aldehyd may be obtained has been pointed out by Natanson: he finds that when diethylenium dichloride (1383) is mixed with argentic nitrite and a little sulphuric acid,

a copious evolution of nitrogen occurs, and aldehyd is formed abundantly :—



Diethylenium is itself derived from Dutch liquid by the action of ammonia upon it; whence it would appear that a close relationship exists between olefiant gas and aldehyd.

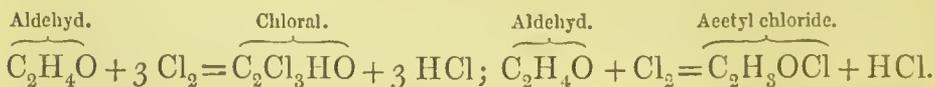
None of these reactions are employed for the preparation of aldehyd, since there are more convenient methods. One of these consists in placing 3 parts of powdered potassic dichromate ($K_2Cr_2O_7$) in a retort, and allowing a cold mixture of 4 parts of sulphuric acid diluted with 3 times its volume of water to flow into the retort, containing 2 parts of alcohol, cooled by immersion in a freezing mixture; on removing the freezing mixture distillation commences without the aid of heat; the vapours must be condensed in a proper refrigerator.

Aldehyd is however usually procured by Liebig's method of distilling in a capacious retort, a mixture of 6 parts of sulphuric acid, 4 of alcohol (sp. gr. 0.850), 4 of water, and 6 of finely powdered black manganese oxide. In this process the oxide of manganese is decomposed, manganous sulphate is formed, whilst the second atom of the oxygen of the manganese dioxide combines with the hydrogen of part of the alcohol, and aldehyd is formed and passes over. The product being very volatile must be condensed in vessels cooled with ice, and the process must be stopped when about 6 twentieths of the mixture has come over, and the distillate becomes acid. Since, however, it is in a very dilute and impure condition, it is to be rectified from an equal weight of calcic chloride, in order to free it from alcohol and water. This operation is repeated twice, or even three times. The distilled liquid still retains alcohol, besides a small quantity of acetic ether, and a liquid termed acetal (1251). For the purpose of obtaining it free from these impurities it is mingled with twice its bulk of anhydrous ether, and saturated with dry ammoniacal gas, while the liquid is artificially cooled; prismatic needles of snowy whiteness are thus formed; these crystals consist of a compound of aldehyd with ammonia (H_3N, C_2H_4O) which is insoluble in ether though very soluble in water; they may be dried in the open air; they fuse at a heat a little below 212° , and at 212° may be sublimed unchanged. If heated in the open air they take fire, and burn with flame. After a time, even when kept in closed vessels, the crystals become brown, and emit an odour like that

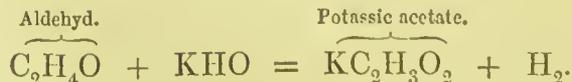
of burned feathers. To obtain pure aldehyd from them, 2 parts of the crystals dissolved in 2 of water, are distilled with 3 of oil of vitriol diluted with 4 parts of water; the product is received in vessels surrounded with ice, and is finally rectified from calcic chloride.

Properties.—Aldehyd is a volatile inflammable liquid, with a peculiar pungent irritating odour, which has a faint resemblance to that of apples. It may be mixed in all proportions with alcohol, ether, and water. It has no acid reaction upon litmus paper, but it can scarcely be exposed to the air without absorbing oxygen, and it then forms an acid compound. Aldehyd yields with ammonia the peculiar crystalline body already described, but when similarly treated with caustic potash it gives a brown resinous mass: this is one of its most characteristic reactions. Another striking one is its power of reducing the salts of silver, and of yielding, when boiled with their solutions, a mirror-like coating of silver upon the sides of the tube in which the experiment is made: the solution should be rendered feebly alkaline by the addition of a few drops of a weak solution of ammonia. In this experiment a portion of the aldehyd is converted into an acid, at the expense of the oxygen derived from a portion of the salt of silver which is thus reduced to the metallic state, and the newly formed acid enters into combination with a portion of the excess of alkali.

Chlorine acts rapidly upon aldehyd, converting it into chloral and acetyl chloride by displacing a portion of its hydrogen (1176):—



Sulphuretted hydrogen produces sulphaldehyd and removes the oxygen; $\text{C}_2\text{H}_4\text{O} + \text{H}_2\text{S} = \text{C}_2\text{H}_4\text{S} + \text{H}_2\text{O}$. Aldehyd, when transmitted over a mixture of lime and caustic potash in a heated tube, first becomes brown, and is then decomposed with disengagement of hydrogen, leaving a white mass composed of potassic acetate:—



Potassium when placed in contact with aldehyd disengages hydrogen, and forms a soluble compound ($\text{C}_2\text{H}_3\text{OK}$) which possesses an alkaline reaction, and absorbs oxygen readily. This compound contains the elements of aldehyd, in which one atom of potassium has displaced one of hydrogen.

According to Lieben (*Liebig's Annal.* cvi. 336), if aldehyd be saturated with dry hydrochloric acid, while kept cold by immersion in a freezing mixture, the liquid separates into two layers, the lower one being an aqueous solution of hydrochloric acid, and the upper one consisting of $C_4H_8Cl_2O$; [*Sp. gr. of liq.* 1.1376; *of vap.* 5.08; *Boil. pt.* 240.8 (116° C.)]. He terms this liquid *ethylidene oxychloride*. It is decomposed by hot water into aldehyd and hydrochloric acid.

If treated with phosphoric chloride, aldehyd is decomposed with elevation of temperature, and *ethylidene chloride*, a colourless liquid, boiling at 140° (60° C.) is obtained; it is isomeric, but not identical with ethylene dichloride, $C_2H_4Cl_2$.

Aldehyd, if heated with acetic anhydride to 356° (180° C.) in a sealed tube, unites with it, forming a colourless liquid ($C_2H_4O, C_4H_6O_3$) isomeric with glycol diacetate; it boils at 336°.2 (169° C.). Similar compounds may be formed with benzoic and succinic anhydrides. If aldehyd be heated with acetyl chloride, in sealed tubes, the two bodies unite, forming a liquid ($C_4H_7ClO_2$) which boils between 248° and 255°.2 (120° and 124° C.).

Aldehyd, even when preserved in sealed tubes, has been known to undergo a remarkable spontaneous conversion into two new substances, each isomeric with it; one of these is a solid crystalline body, *metaldehyd*, which may be sublimed at 248° (120° C.) before undergoing fusion; the other retains the liquid form and is termed *elaldehyd* [*boil. pt.* 201°.2 (94° C.); *freezing pt.* 35°.6 (2° C.)]; the latter may be mixed with water, alcohol, and ether in all proportions. The density of its vapour according to Fehling is 4.5157, which is three times that of aldehyd; elaldehyd appears therefore to have been formed by the condensation of the elements of three molecules of aldehyd into one. A third isomeric body termed *paraldehyd*, is a liquid which solidifies at 50° (10° C.) and boils at 257° (125° C.); it is formed when aldehyd, diluted with an equal bulk of water, is exposed with a trace of sulphuric or nitric acid to a cold of 32°; crystals of metaldehyd are deposited, and paraldehyd remains in the liquid; the sp. gr. of its vapour is 4.583, and its molecular volume coincides with that of elaldehyd, with which indeed it is by some chemists believed to be identical. A similar change of aldehyd into paraldehyd occurs when the aldehyd is digested for some hours at 212° in a sealed tube with ethyl iodide or with cyanogen (Lieben).

Aldehyd absorbs sulphurous anhydride with avidity. This appears to be a simple case of solution, as the sulphurous anhydride may be entirely displaced by a current of carbonic anhydride; but the aldehyd gradually passes into paraldehyd, which if heated gently with dilute sulphuric acid is converted into ordinary aldehyd.

If glycol be distilled with zincic chloride aldehyd is liberated, and this at the moment of its formation becomes converted into a liquid of irritating odour, termed hence *acraldehyd*; its vapour density (2.877) leads to the formula ($C_4H_8O_2$), or double that of aldehyd; it boils at 230° (110° C.).

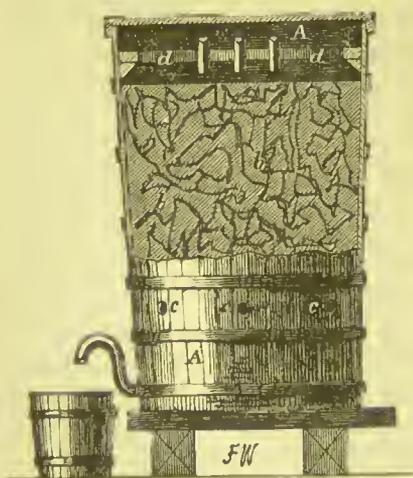
When aldehyd is digested in a sealed tube for some hours at 212° with a saturated solution of sodic formiate, or of potassic-sodic tartrate, it gradually loses the elements of water, and a new compound (C_4H_6O) is formed; $2 C_2H_4O - H_2O = C_4H_6O$ (Lieben).

The nature of aldehyd and its isomerides is at present only imperfectly understood; but it has recently attracted much attention owing to its close relation to glycol and its derivatives, as well as to the polyatomic bases of the ethylene series (1382).

(1250) *Preparation of Acetic Acid*.—The principal interest, however, with which aldehyd is invested, arises from the facility with which it absorbs oxygen, and its consequent connexion with

the process of acetic acid. When alcohol is exposed to the united influence of atmospheric air and finely divided platinum, partial oxidation occurs, and aldehyde is produced in abundance: owing to the readiness with which aldehyde absorbs oxygen, an attempt was made to carry the oxidation a step further, and thus to prepare acetic acid on a large scale by this method. The use of platinum, however, is now abandoned, but the manufacture of vinegar upon this principle is still extensively followed. In Germany, and in other countries where the legislature imposes no duty upon alcohol, dilute spirit mixed with a small quantity of infusion of malt is the ordinary material employed in the manufacture of vinegar. The mode of procedure is the following:—

FIG. 389.



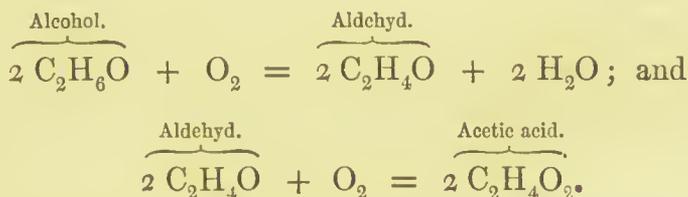
Large vats, of the form shown at A, A, fig. 389, provided with a loosely fitting lid, are filled with deal or beech shavings, *b*, first dried, and then soaked in strong vinegar; these shavings rest upon a perforated shelf which is supported just above the level of the lower apertures, *c, c*. Near the top of these vats is a shelf, *d, d*, perforated with a multitude of minute holes, through each of which passes a piece of packthread, knotted at its upper end to prevent it from falling through: this arrangement is intended to allow the spirit of

wine to be slowly and equably distributed over the shavings. Through this shelf a few glass tubes project, to allow free egress to the spent air, and at about two-thirds of the depth of the cask is a row of apertures, *c, c*, to admit air. A mixture consisting of 1 part of alcohol, sp. gr. 0.850, of 6 parts of water, and $\frac{1}{1000}$ of honey, yeast, or wort, is then allowed to trickle slowly through the shavings, whilst the temperature is raised to about 80° (26.7 C.).

Pure diluted alcohol does not absorb oxygen when exposed to the atmosphere; to induce its oxidation it requires the presence of some vegetable matter which is itself prone to absorb oxygen, and it is for this reason that honey or sweet wort is added. Liebig supposes that these bodies act much in the same way as yeast does, during its development and change, in disturbing the chemical equilibrium of the atoms of sugar and causing it to

ferment. The acetification does not proceed rapidly until the process has been in operation for some days. By degrees a peculiar kind of fungus or slimy vegetable mould is formed upon the shavings, and which is known under the name of *mother of vinegar*; this substance acts somewhat in the manner of a ferment, and accelerates the oxidation, probably owing to its own tendency to combine with oxygen. It is remarkable that the presence of a very minute quantity of any empyreumatic or tarry matter is sufficient entirely to put a stop to the transformation, so that if the shavings become scorched in drying they are entirely unfit for use. As the operation proceeds, the heat rises to about 100° or 105° (from $37^{\circ}\cdot 8$ to $40^{\circ}\cdot 5$ C.); at which point it remains stationary.

When the alcohol has been made to pass through the vat four or five times, its conversion into vinegar is usually complete. Well-burned charcoal, purified from saline matters by hydrochloric acid, and then thoroughly washed, may be substituted for the shavings with good effect. In this operation the alcohol is spread over a large surface and freely exposed to the air, aldehyd is formed, and this immediately absorbs oxygen from the atmosphere, being thus at once converted into common vinegar or acetic acid:—



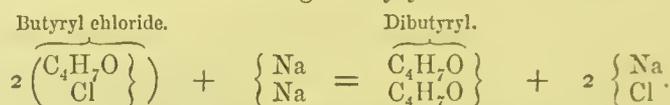
If the supply of air be insufficient, a large quantity of alcohol is wasted, owing to the formation of aldehyd, which, from its great volatility, passes off in vapour before it has become oxidized and converted into acetic acid.

Different views have been taken of the nature of aldehyd. Gerhardt considered that the radicle of acetic acid contains oxygen, representing this radicle as $\text{C}_2\text{H}_3\text{O}$, and he supposed that the other acids of the same series all contain homologous oxidized radicles; the radicle of formic acid, for instance, being CHO , that of butyric acid being $\text{C}_4\text{H}_7\text{O}$, and so on. The aldehyds were regarded by him as hydrides of these radicles with a tendency to become oxidized: both the hydrogen and the assumed radicle of the acid becoming oxidized simultaneously. These relations may be thus indicated:—

| Assumed radicle. | Aldehyd. | Derived acid. |
|---|----------------------------------|-------------------------------------|
| Formic . . . C H O | HC H O | HC H O, O |
| Acetic . . . C ₂ H ₃ O | HC ₂ H ₃ O | HC ₂ H ₃ O, O |
| Butyric . . . C ₄ H ₇ O | HC ₄ H ₇ O | HC ₄ H ₇ O, O |
| Valeric . . . C ₅ H ₉ O | HC ₅ H ₉ O | HC ₅ H ₉ O, O |

Considerable probability is given to this view by the existence of many compounds in which the atom of oxygen assumed to exist in the radicle is preserved in the compounds derived from it.

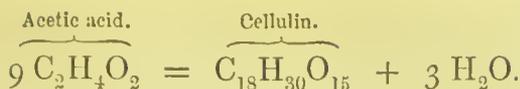
These oxidized radicles of the aldehyds and of acids, appear to be isolable compounds, so far as any radicles are truly isolable. Freund, for example (*Liebig's Annal.* cxviii. 33), by acting upon butyryl chloride with an amalgam of sodium, has succeeded in obtaining dibutyryl:—



When distilled with caustic potash, dibutyryl yields potassic butyrate and a liquid of an agreeable fruity odour, which boils between 347° and 365° (175° and 185° C.), and has the composition of butyrene (C₇H₁₄O).

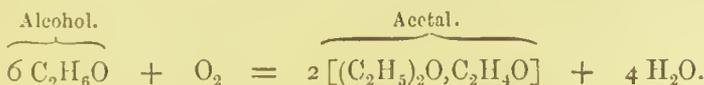
Some of the decompositions of aldehyd are, however, more easily explained by regarding it as a simple oxide of ethylene (C₂H₄)"O. In truth, its molecular arrangement is so unstable that it is not possible at present to assign its rational constitution with any degree of confidence.

The tendency of aldehyd to rapid oxidation affords an explanation of the fact that platinum black always furnishes an acid product by its reaction on alcohol. Aldehyd is first formed, but it immediately undergoes partial oxidation, by which it is converted into a mixture consisting chiefly of acetal and acetic acid. By a process somewhat similar, weak fermented, but not distilled, liquors frequently become sour when exposed to the air in warm weather,—a change which forms the basis of the usual method of preparing white wine and malt vinegars; the mucilaginous and albuminous matters present in the wort or beer absorb oxygen, and appear to induce a similar process of oxidation in the alcohol, in consequence of which acetic acid is formed. The more completely fermentation has taken place, the less likely is vinegar to be formed; since, during the fermentation, the azotised and other matters necessary to further the oxidation of the alcoholic portion are gradually destroyed. If much albuminous matter remain in solution in the vinegar after it is formed, the acid is itself liable to undergo a further change: a peculiar mould or fungus appears upon the surface of the liquid, and the acid is slowly decomposed; the cellulose or ligneous tissue of the fungus being formed at the expense of the constituents of the acetic acid:—



The formation of aldehyd appears always to precede the production of vinegar, just as the transformation of cane into grape sugar precedes the vinous fermentation; acetification, however, is not a true process of fermentation; it is rather one of gradual oxidation, and differs from fermentation in the important fact that the absorption of oxygen is necessary during the whole course of the operation: one part of alcohol requiring more than two-thirds of its weight of oxygen for acetification; and if the supply of oxygen be arrested, the further production of acid is immediately stopped.

(1251) *Acetal* [$\text{C}_6\text{H}_{14}\text{O}_2 = (\text{C}_2\text{H}_5)_2\text{O}, \text{C}_2\text{H}_4\text{O}$]: *Sp. gr. liq.* 0.821; *of vap.* 4.24; *Rel. wt.* 59; *Boil. pt.* 221° (105° C.).—This compound was discovered by Döbereiner among the products furnished by the slow oxidation of alcohol under the influence of finely divided platinum. But it may be obtained more easily and abundantly from the erude distillate procured in the preparation of aldehyd (1249). The aldehyd is got rid of by distillation, and passes over with the more volatile portion; whilst the acetal is separated from the portion which distils between 176° and 203° (80° and 95° C.), by agitating it with caustic potash to remove the aldehyd and compound ethers, and then rectifying from calcic chloride. Acetal forms a colourless liquid, of an agreeable characteristic odour, and a flavour resembling that of hazel nuts. It is soluble in about 6 parts of water, but its solubility diminishes as the temperature rises; it is soluble in all proportions in alcohol and in ether. Aqueous solutions of the alkalis, if excluded from the air, do not decompose acetal. (Stas, *Ann. de Chimie*, III. xix. 151.) Oxidizing agents transform it first into aldehyd, and then into acetic acid. Acetal may be regarded as a combination of aldehyd with ether; 3 molecules of alcohol concurring to the production of 1 molecule of acetal:—



Wurtz, however, views it as glycol in which 2 atoms of hydrogen are displaced by 2 of ethyl; and by distilling wood spirit with manganese dioxide and sulphuric acid he has obtained a corresponding compound [$\text{C}_2\text{H}_4(\text{CH}_3)_2\text{O}_2$], in which 2 atoms of methyl have taken the place of the 2 of hydrogen in glycol: this is a liquid which boils at about 185° (85° C.), of sp. gr. 0.853, with a vapour density of 3.475.

(1252) 3. *Propionic Aldehyd* ($\text{C}_3\text{H}_6\text{O}$). *Sp. gr. of liq.* 0.79; *of vap.* 2.169; *Rel. wt.* 29.—The aldehyds which still remain to be noticed are comparatively unimportant.

Propionic aldehyd was found by Guckelberger amongst the products furnished by distilling albuminous substances with a mixture of sulphuric acid and black manganese oxide. It passes over mixed with acetic and butyric aldehyds, as well as with the oil of bitter almonds (benzoic aldehyd). Propionic aldehyd is a limpid liquid of an ethereal odour; it is soluble in water, alcohol, and ether, in all proportions. It boils between 131° and 149° (55° and 65° C.), and becomes slowly acid when exposed to the air, yielding propionic acid.

(1253) 4. *Butyric Aldehyd* ($\text{C}_4\text{H}_8\text{O}$; *Sp. gr. of liq.* 0.8) is obtained during

the same process as the foregoing compound. It is a colourless liquid which is very sparingly soluble in water, but is freely dissolved both by alcohol and ether. It has an ethereal pungent odour and a burning taste, and becomes rapidly converted into butyric acid by exposure to the air. It forms with ammonia the crystalline compound characteristic of the aldehyds, and when heated with a solution of argentic nitrate gives a brilliant mirror of reduced metal. It boils between $154^{\circ}\cdot4$ and $163^{\circ}\cdot4$ (68° and 73° C.).

Butyral [*Sp. gr. of liq. at $71^{\circ}\cdot6$ (22° C.), $0\cdot821$; of vap. $2\cdot61$; Rel. wt. 36*] was the name given by Chancel to a compound isomeric with the foregoing body, obtained by the distillation of dry calcic butyrate: when exposed to the air, it absorbs oxygen, and becomes rapidly converted into butyric acid. It, however, yields no compound with ammonia, and does not reduce argentic nitrate.

(1254) 5. *Valeric Aldehyd*, or *Valeral* ($C_5H_{10}O$). *Sp. gr. of liq. $0\cdot82$; of vap. $2\cdot93$; Rel. wt. 43; Boil. pt. $204^{\circ}\cdot8$ (96° C.).*—This compound may be obtained in various ways. One of the best consists in oxidizing fousel oil by means of a mixture of sulphuric acid and potassic dichromate: 37 parts of the dichromate dissolved in warm water and placed in a retort, are to be gradually mixed with 49 parts of oil of vitriol, previously diluted with an equal bulk of water; 33 parts of fousel oil are then to be carefully added: the aldehyd distils over without the necessity for applying heat. If the distillate be mixed with a saturated solution of hydric-sodic sulphite ($NaHSO_3$), the compound of this salt with valeric aldehyd crystallizes readily, and may be purified by recrystallization from alcohol. If these crystals be mixed with a solution of potassic carbonate, and distilled, valeric aldehyd passes over, and may be dried over calcic chloride. This aldehyd is a highly mobile, limpid, colourless liquid, with a burning taste, and a pungent penetrating odour; its vapour takes fire easily. It is insoluble in water, but soluble in alcohol and in ether. By oxidation it is converted rapidly into valeric acid.

6. *Caproic Aldehyd* is scarcely known.

(1255) 7. *Ænanthylie Aldehyd*, or *Ænanthol* ($C_7H_{14}O$). *Sp. gr. of liq. $0\cdot8271$ at 63° ; of vap. $4\cdot178$; Rel. wt. 57; Boil. pt. about $312^{\circ}\cdot8$ (156° C.).*—This aldehyd is furnished by the destructive distillation of castor oil. In order to purify the crude distillate, it is agitated with baryta water, which retains the volatile acids; the oil, which rises to the surface on standing, is submitted to distillation, and is then dried by digestion on calcic chloride. Water dissolves it sparingly. It absorbs oxygen rapidly from the air, and becomes converted into ænanthylie acid.

(1256) 8. *Caprylic Aldehyd* ($C_8H_{16}O$). *Sp. gr. of liq. $0\cdot818$; Rel. wt. 64; Boil. pt. $339^{\circ}\cdot8$ (171° C.).*—This is a powerfully refracting colourless liquid, with an odour of banana, and a burning taste. It is insoluble in water, and exhibits very little tendency to become oxidized; but it forms a crystalline compound with the hydric-potassic sulphite, and it reduces argentic nitrate, producing a beautiful mirror-like deposit of the metal. It is easily obtained by the dry distillation of sodic caprylate.

9. *Pclargonic Aldehyd* has not been examined.

(1257) 10, 11, and 12, *Rutic*, *Euodic*, and *Lauric Aldehyd*.—These sub-

stances appear to be among the constituents of oil of rue. Gerhardt considered that this oil consisted mainly of rutic aldehyd, but G. Williams appears to have shown that euodic aldehyd (so named from *εὐώδης*, sweet smelling) [$C_{11}H_{22}O$; *Sp. gr. of liq.* 0·8497; *of vap.* 5·87; *Rel. wt.* 85; *Freez. pt.* $44^{\circ}6$ ($7^{\circ} C.$); *Boil. pt.* $415^{\circ}4$ ($213^{\circ} C.$)] is its most abundant component. Oil of rue has a somewhat viscid consistence; it possesses the strong disagreeable odour of the plant, and an acrid, bitterish, somewhat aromatic taste. Nitric acid acts rapidly upon oil of rue, and furnishes different products according to the degree of concentration of the acid: by the prolonged action of the concentrated acid, pelargonic acid ($HC_9H_{17}O_2$) and the lower homologues of the group of acids to which it belongs are obtained; by moderating the action of the nitric acid, rutic acid ($HC_{10}H_{19}O_2$) is procured. Essence of rue does not absorb oxygen very rapidly, nor is it easily converted when heated with caustic potash into the rutate of this base; but it combines readily with the hydric sulphites of the alkali-metals, and forms with them crystallizable compounds which correspond with those formed with the other aldehyds.

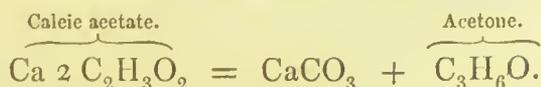
(b) *The Ketones, or Acetones.*

(1258) The ketones constitute a class of compounds closely related to the aldehyds.

When the calcium or barium salt of any of the volatile mono-basic acids (the molecules of which contain two atoms of oxygen) is submitted to dry distillation, the acid undergoes decomposition, and amongst the volatile products which come over, is a body which has been termed the *ketone* of the acid, a term referring to acetone, the representative of this group; the new body which is formed bears the same relation to the acid from which it is obtained that acetone does to acetic acid.

The general properties of this class of compounds may be illustrated by a description of acetone, which has been examined with care.

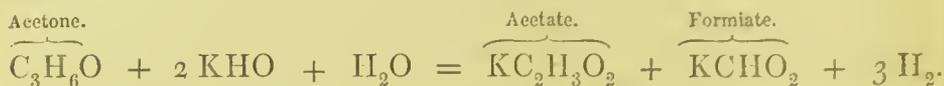
(1259) *Acetone* (C_3H_6O). *Sp. gr. of liq.* 0·792; *of vap.* 2·002; *Rel. wt.* 29; *Boil. pt.* $132^{\circ}8$ ($56^{\circ} C.$).—When calcic acetate is mixed with an excess of quicklime, and submitted to distillation, calcic carbonate is formed, whilst the residues from two molecules of acetic acid coalesce, and a volatile inflammable liquid passes over, to which the formula C_3H_6O has been assigned:—



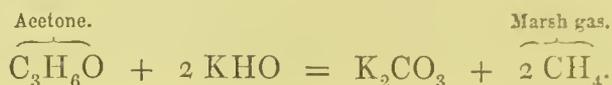
When the vapours of acetic acid are transmitted through a heated porcelain tube they are resolved into acetone, carbonic anhydride, and water; $2\ C_2H_3O_2 = CO_2 + H_2O + C_3H_6O$; but a better mode of preparing acetone than either of the foregoing ones consists in distilling crystallized plumbic acetate with half its weight of quicklime.

Acetone is a colourless liquid, with an agreeable ethereal

odour, and a pungent taste. When heated it gives off an inflammable vapour, which burns with a clear white flame. If heated with caustic potash, it yields at a moderate temperature a mixture of potassic acetate and formiate, with liberation of hydrogen :—



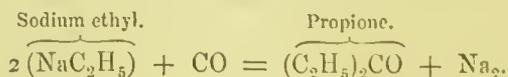
At a higher temperature potassic carbonate and marsh gas are the result :—



When acetone with water is acted upon by an amalgam of sodium, it combines with two atoms of nascent hydrogen, $\text{C}_3\text{H}_6\text{O} + \text{H}_2$ becoming $\text{C}_3\text{H}_8\text{O}$, which is Friedel's secondary alcohol, $\text{C}(\text{CH}_3)_2\text{H}_2\text{HO}$ (p. 176), isomeric with propylic alcohol. The ketones by the action of nascent hydrogen furnish secondary alcohols; whilst the aldehyds by similar treatment yield primary alcohols, and this is a characteristic difference between the two groups.

Some doubt still exists as to the true nature of the ketones. Kane at one time regarded acetone, which has been more thoroughly examined than any of the others, as a sort of alcohol ($\text{C}_6\text{H}_8\text{O}, \text{HO}$; $\text{C} = 6$ and $\text{O} = 8$), which he termed *mesitic alcohol*; it is metameric with allyl alcohol. By distilling it with sulphuric acid he obtained a compound having the composition $\text{C}_6\text{H}_8\text{O}$, which corresponds to the ether of such an alcohol, and is metameric with allyl ether. He also produced other bodies corresponding to iodide and chloride of ethyl. Acetone forms with sulphuric acid a double acid ($2 \text{HO}, \text{C}_6\text{H}_8\text{O}, \text{S}_2\text{O}_6$). But this sulpho-acid is dibasic, unlike the true vinic acids; moreover, acetone cannot be recovered from it when it is decomposed by the hydrated alkalis; whilst all the true alcohols may be reproduced from the vinic sulpho-acids when they are decomposed in this manner by the alkalis. Kane has recently published some additional experiments upon the subject (*Journ. Chem. Soc.*, 1866).

The ketones may also be obtained by the action of sodium ethyl and its homologues upon carbonic oxide (Wanklyn), as for instance :—



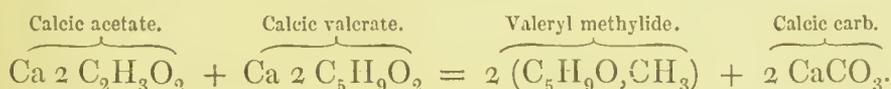
Neither does acetone, nor do the ketones in general, admit of direct oxidation like an aldehyd, and this is another well-marked difference between this group and the aldehyds, which they otherwise so much resemble.

The ketones, like the aldehyds, have the power of forming crystalline compounds with the hydric-sulphites of potassium and sodium, but they do not react upon aniline; nor do they reduce ammoniacal solutions of argentic nitrate.

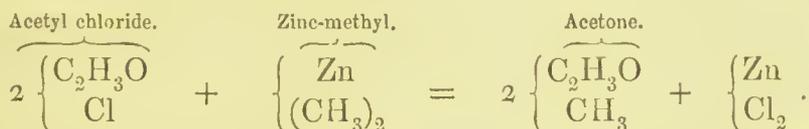
The ketones may be regarded as aldehyds, in which an atom of hydrogen is displaced by its equivalent of methyl or other alcohol radicle :—

Ethylic aldehyd = C_2H_4O , or C_2H_3O, H , acetyl hydride,
 Acetone = C_3H_6O , ,, C_2H_3O, CH_3 , acetyl methylide,
 Propione = $C_5H_{10}O$, ,, C_3H_5O, C_2H_5 , propionyl ethylide,
 Butyrone = $C_7H_{14}O$, ,, C_4H_7O, C_3H_7 , butyryl tritylide,
 Valerone = $C_9H_{18}O$, ,, C_5H_9O, C_4H_9 , valeryl tetrylide,
 and so on.

The experiments of Williamson show that a series of intermediate double or mixed ketones may be formed by distilling mixtures of equivalent quantities of the homologous salts of calcium; for example, by distilling a mixture of calcic acetate and valerate in equivalent proportions, the compound $C_6H_{12}O (=C_5H_9O, CH_3)$ is formed, boiling at 248° (120° C.).



Freund has also succeeded in obtaining acetone and propione synthetically, by decomposing acetyl chloride by means of zinc-methyl and zinc-ethyl; thus:—

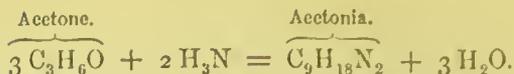


Limpricht, in pursuing this subject, found that by mixing calcic formiate in equivalent proportion with calcic acetate, with calcic valerate, with calcic œnanthylate, or with calcic caprylate, and distilling,—the corresponding aldehyds, viz., acetic, valerie, œnanthylie and caprylie aldehyds, were formed: calcic formiate when distilled, yielding hydrogen instead of methyl (CH_3), as in Williamson's experiment:—



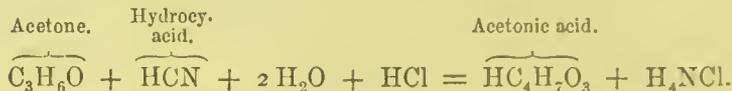
The following results obtained by Stædeler from acetone (*Ann. de Chimie*, III. xlii. 226) have tended to confirm these views. Chlorine forms with acetone various substitution-products, the most remarkable of which is one in which five atoms of hydrogen are displaced by five of chlorine: a compound, C_3HCl_5O , analogous to chloral is thus formed; it has a sp. gr. of from 1.6 to 1.7, it is not solidified by a cold of -4° (-20° C.), and it boils at about 374° (190° C.). This body has the property of combining with four atoms of water, with which it forms a soluble crystallizable substance analogous to hydrate of chloral.

Acetone when saturated with gaseous ammonia yields a liquid which reduces the salts of silver, in a manner similar to the corresponding mixture with aldehyd. If this acetonie solution of ammonia be left to itself for some time, it is spontaneously transformed into a new base, *acetonine* or *acetonie* ($C_9H_{18}N_2$); and the same change is effected more rapidly by exposing the mixture for some hours in a sealed tube to a heat of 212° . The decomposition by which it is formed is similar to that by which benzoline is produced from the oil of bitter almonds (1387):—



Acetonia is a colourless alkaline liquid, of a peculiar urinous odour and burning taste. It is readily soluble in water, alcohol, and ether. Acetonia hydrochlorate forms with platinic chloride an orange-yellow crystalline double salt [$2 (\text{C}_9\text{H}_{18}\text{N}_2, \text{HCl}), \text{PtCl}_4$]. The acid oxalate ($\text{C}_9\text{H}_{18}\text{N}_2, \text{H}_2\text{C}_2\text{O}_4, \text{H}_2\text{O}$) is soluble in alcohol, and crystallizes readily from this solution.

Acetone may also be made to furnish an acid homologous with the lactic. This compound, termed *acetic acid* ($\text{HC}_4\text{H}_7\text{O}_3$) may be obtained by heating a mixture of acetone and hydrocyanic acid with hydrochloric acid, when the following reaction occurs:—

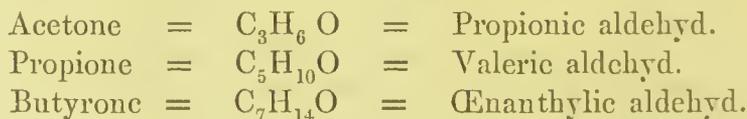


Acetic acid crystallizes in prisms; it has a sour taste, and is freely soluble in water, in alcohol and in ether. It forms crystallizable salts: *zincic acetate* ($\text{Zn } 2 \text{C}_4\text{H}_7\text{O}_3, 2 \text{H}_2\text{O}$) is very sparingly soluble. The barium salt is soluble in alcohol.

The attempt to procure a base homologous with glycocine and alanine, by the action of hydrocyanic acid upon acetone, was unsuccessful.

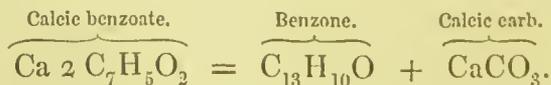
It is probable that each of the other ketones would yield compounds analogous to those which Stædeler has procured from acetone.

Each of the ketones is metameric with a corresponding term in the series of true aldehyds; for example:—



By careful oxidation, Stædeler succeeded in converting acetone into propionic acid.

The formation of ketones has also been observed in the case of several monobasic acids which do not belong to the series of the fatty acids. Benzoic acid, for example, is decomposed in the following manner, yielding *benzene* or *benzophenone*, ($\text{C}_7\text{H}_5\text{O}, \text{C}_6\text{H}_5$):—



The products of the distillation of the calcium salts of the dibasic acids, such as the suberic acid, do not fall strictly into the class of ketones. The substance termed *suberone*, for instance, consists of $\text{C}_8\text{H}_{14}\text{O}$, instead of $\text{C}_7\text{H}_{12}\text{O}$.

§ II. GENERAL REMARKS ON THE ORGANIC ACIDS.

(1260) It will be useful here, before passing to the consideration of the special series of acids produced by the oxidation of the aldehyds, to consider briefly the general properties of the

organic acids, as a class, and some of the more important groups of derivatives from them.

The organic acids constitute an extremely numerous and important class of compounds; but many of them are so intimately related to a large number of other well-defined natural groups, that it would be far from advantageous to detach each acid from the group to which it properly belongs, for the sake of describing it with other bodies to which, often, it may bear little resemblance save in the circumstance that, like them, it possesses the power of forming salts with bases. Accordingly, some of these bodies have already been described in the previous sections, where they seemed to be naturally connected with the compounds under examination; and although it will be convenient to associate together certain of the acids in the present chapter, the consideration of others will be postponed until the substances to which they are most nearly allied pass under review.

(1261) *Monobasic and Polybasic Acids.*—The organic acids may be subdivided into *monobasic*, *dibasic*, *tribasic*, or *polybasic*, according as, when treated with a hydrated base, (554) they contain one, two, three or more atoms of hydrogen, susceptible of displacement by a metal. The important group derived from the monobasic alcohols by oxidation, furnishes a good illustration of the monobasic acids; while some of the more important and widely diffused vegetable acids, such as the citric, the tartaric, and the malic, afford examples of the polybasic class, and have been traced to the polybasic alcohols.

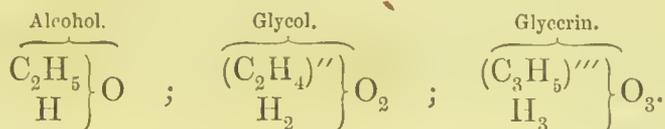
The following table may serve to illustrate the connexion of several of the most interesting groups of acids, and of their relation to the corresponding alcohol groups:—

| ALCOHOLS. | | ACIDS. | | |
|--|--|--|----------|-----------|
| | | Monobasic. | Dibasic. | Tribasic. |
| Monatomic. | $\begin{array}{c} C_n H_{2n+1} \\ H \end{array} \left. \vphantom{\begin{array}{c} C_n H_{2n+1} \\ H \end{array}} \right\} O$ | $\begin{array}{c} C_n H_{2n-1} O \\ H \end{array} \left. \vphantom{\begin{array}{c} C_n H_{2n-1} O \\ H \end{array}} \right\} O$ | | |
| $\begin{array}{c} H \\ H \end{array} \left. \vphantom{\begin{array}{c} H \\ H \end{array}} \right\} O$ | (1) Wood Spirit. $\begin{array}{c} CH_3 \\ H \end{array} \left. \vphantom{\begin{array}{c} CH_3 \\ H \end{array}} \right\} O$ Ethylic alcohol. | Formic. $\begin{array}{c} C H O \\ H \end{array} \left. \vphantom{\begin{array}{c} C H O \\ H \end{array}} \right\} O$ Acetic. $\begin{array}{c} C_2 H_3 O \\ H \end{array} \left. \vphantom{\begin{array}{c} C_2 H_3 O \\ H \end{array}} \right\} O$ | | |
| | (2) Propylic alcohol. $\begin{array}{c} C_2 H_5 \\ H \end{array} \left. \vphantom{\begin{array}{c} C_2 H_5 \\ H \end{array}} \right\} O$ | Propionic. $\begin{array}{c} C_2 H_5 O \\ H \end{array} \left. \vphantom{\begin{array}{c} C_2 H_5 O \\ H \end{array}} \right\} O$ | | |
| | (3) $\begin{array}{c} C_3 H_7 \\ H \end{array} \left. \vphantom{\begin{array}{c} C_3 H_7 \\ H \end{array}} \right\} O$ | $\begin{array}{c} C_3 H_5 O \\ H \end{array} \left. \vphantom{\begin{array}{c} C_3 H_5 O \\ H \end{array}} \right\} O$ | | |

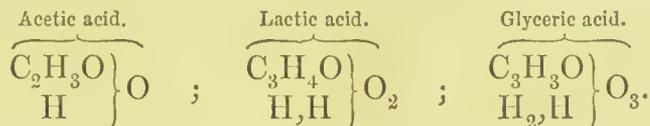
| | | ACIDS: | | | |
|-------------|-----|--|---|--|--|
| | | ALCOHOLS. | Monobasic. | Dibasic. | Tribasic. |
| Diatomic. | | $C_n H_{2n} \left. \vphantom{C_n H_{2n}} \right\} O_2$ | $C_n H_{2n-2} O \left. \vphantom{C_n H_{2n-2} O} \right\} O_2$ | $C_n H_{2n-4} O_2 \left. \vphantom{C_n H_{2n-4} O_2} \right\} O_2$ | |
| | (2) | Glycol. $C_2 H_4 \left. \vphantom{C_2 H_4} \right\} O_2$ | Glycolic. $C_2 H_2 O \left. \vphantom{C_2 H_2 O} \right\} O_2$ | Oxalic. $C_2 O_2 \left. \vphantom{C_2 O_2} \right\} O_2$ | |
| | (3) | Trityl-glycol. $C_3 H_6 \left. \vphantom{C_3 H_6} \right\} O_2$ | Lactic. $C_3 H_4 O \left. \vphantom{C_3 H_4 O} \right\} O_2$ | Malonic [?] $C_3 H_2 O_2 \left. \vphantom{C_3 H_2 O_2} \right\} O_2$ | |
| | (4) | Tetryl-glycol. $C_4 H_8 \left. \vphantom{C_4 H_8} \right\} O_2$ | Acetonic. $C_4 H_6 O \left. \vphantom{C_4 H_6 O} \right\} O_2$ | Succinic. $C_4 H_4 O_2 \left. \vphantom{C_4 H_4 O_2} \right\} O_2$ | |
| Triatomic. | | $C_n H_{2n-1} \left. \vphantom{C_n H_{2n-1}} \right\} O_3$ | $C_n H_{2n-3} O \left. \vphantom{C_n H_{2n-3} O} \right\} O_3$ | $C_n H_{2n-5} O_2 \left. \vphantom{C_n H_{2n-5} O_2} \right\} O_3$ | $C_n H_{2n-7} O_3 \left. \vphantom{C_n H_{2n-7} O_3} \right\} O_3$ |
| | (3) | Glycerin. $C_3 H_5 \left. \vphantom{C_3 H_5} \right\} O_3$ | Glyceric. $C_3 H_3 O \left. \vphantom{C_3 H_3 O} \right\} O_3$ | Tartronic [?] $C_3 H O_2 \left. \vphantom{C_3 H O_2} \right\} O_3$ | |
| | (4) | | | Malic. $C_4 H_3 O_2 \left. \vphantom{C_4 H_3 O_2} \right\} O_3$ | |
| Tetratomic. | | $C_n H_{2n-2} \left. \vphantom{C_n H_{2n-2}} \right\} O_4$ | $C_n H_{2n-4} \left. \vphantom{C_n H_{2n-4}} \right\} O_4$ | $C_n H_{2n-6} O_2 \left. \vphantom{C_n H_{2n-6} O_2} \right\} O_4$ | $C_n H_{2n-8} O_3 \left. \vphantom{C_n H_{2n-8} O_3} \right\} O_4$ |
| | (4) | Erythrite. $C_4 H_6 \left. \vphantom{C_4 H_6} \right\} O_4$ | | Tartaric. $C_4 H_2 O_2 \left. \vphantom{C_4 H_2 O_2} \right\} O_4$ | |
| | (5) | | | Glycomalic [?] $C_5 H_4 O_2 \left. \vphantom{C_5 H_4 O_2} \right\} O_4$ | |
| | (6) | | | | Citric [?] $C_6 H_4 O_3 \left. \vphantom{C_6 H_4 O_3} \right\} O_4$ |
| Hexatomic. | | $C_n H_{2n-4} \left. \vphantom{C_n H_{2n-4}} \right\} O_6$ | $C_n H_{2n-6} O \left. \vphantom{C_n H_{2n-6} O} \right\} O_6$ | $C_n H_{2n-8} O_2 \left. \vphantom{C_n H_{2n-8} O_2} \right\} O_6$ | $C_n H_{2n-10} O_3 \left. \vphantom{C_n H_{2n-10} O_3} \right\} O_6$ |
| | (6) | Mannite. $C_6 H_8 \left. \vphantom{C_6 H_8} \right\} O_6$ | | Saccharic. $C_6 H_4 O_3 \left. \vphantom{C_6 H_4 O_3} \right\} O_6$ | |

Many attempts have been made, without success, to account for the polybasic or monobasic character of the acids from their

composition. Kekulé has offered the following ingenious suggestions upon this subject. According to this chemist,—1. Bodies whether monatomic or polyatomic, which are formed upon the type of water—*i.e.* which are of the form $x \left. \begin{array}{c} \text{H} \\ \text{H} \end{array} \right\} \text{O}$, and which contain only carbon and hydrogen in the radicle that displaces the typical hydrogen in the molecule, belong to the class of *alcohols*; as for example:—

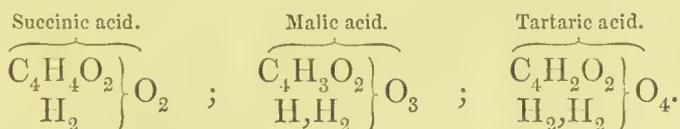


2. Those bodies which, in addition to carbon, or to carbon and hydrogen, contain oxygen in the displacing radicle, constitute acids. When the oxygen in the radicle is limited to a single atom a monobasic acid is formed;* for example:—



They allow one atom only of the typical hydrogen in the molecule to be displaced readily by a monad metal.

3. Those compounds which contain 2 atoms of oxygen in the displacing radicle, constitute dibasic acids, whether they contain 2, 3, or 4 atoms of oxygen external to the radicle; as for example:—



The basicity of the acid, therefore, upon this view, depends on the amount of oxygen in the radicle, and not upon the molecular type of the compound; for in the case of the three acids last cited the first is diatomic, the second triatomic, and the third tetratomic.

Frankland considers that the organic acids owe their acidity to the presence of *oxatyl* (HCO_2) in their molecule, the basicity of each acid depending upon the number of atoms of oxatyl which it contains, or as he phrases it, “an organic acid containing n atoms of oxatyl is n basic.”

* It is obvious that this statement is not universally true. Carbonic acid, which in combination with potassium may be represented as $\left. \begin{array}{c} \text{CO} \\ \text{K}_2 \end{array} \right\} \text{O}_2$, is manifestly dibasic, though it ought to be monobasic by the foregoing rule.

There are 5 well marked groups of monobasic organic acids, each of which corresponds to an alcohol group:—

| Acid series. | General formula. | Alcohol series. |
|-----------------|--------------------|-----------------|
| 1. The Acetic | $C_n H_{2n} O_2$ | True Alcohols. |
| 2. The Oleic | $C_n H_{2n-2} O_2$ | Allylic. |
| 3. The Lactic | $C_n H_{2n} O_3$ | Glycols. |
| 4. The Glycolic | $C_n H_{2n} O_4$ | Glycerins. |
| 5. The Benzoic | $C_n H_{2n-6} O_2$ | Aromatic. |

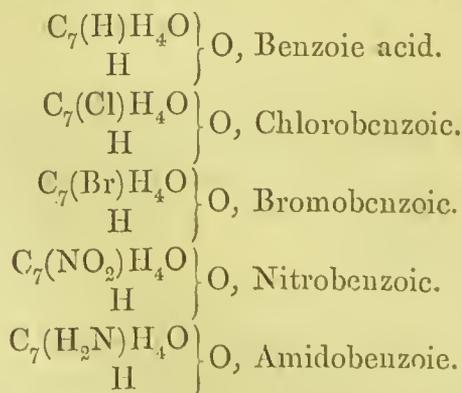
(1262) *Simple, and Compound or Colligated Acids.*—The organic acids may further be regarded as belonging to one or other of the following classes:—

a. *Hydrated oxides of organic radicles*, and acids derived from them by substitution.

b. *Compound or colligated acids.*

(a) *Hydrated Oxides of Organic Radicles.*—Examples of this class occur in cyanic acid $[H(CN)O]$, as well as in the series of volatile fatty acids (1274), the first member of which is formic acid ($HCHO_2$), and the last as yet discovered is the melissic ($HC_{30}H_{59}O_2$). The fatty acids may be viewed as hydrated oxides of a compound radicle of the form $(C_n H_{2n-1}O)$. The name given to the radicle terminates in *yl*, and is derived from the name of the acid into which it enters; the radicle of formic acid being *formyl*, CHO , that of acetic acid *acetyl*, C_2H_3O , and so on. Another group which falls under this subdivision is that represented by the general formula $[H(C_n H_{2n-9}O)O]$; this has been characterized as the group of aromatic acids, of which benzoic acid, with its radicle *benzoyl* (C_7H_5O) is the type.

If a certain number of atoms of the hydrogen in the radicle of any of these acids is displaced by chlorine, bromine, iodine, nitroxyl (NO_2), or amidogen (H_2N), in equivalent amounts, we obtain chloro-, bromo-, iodo-, nitro-, or amido-acids; for example:



In benzoic acid as many as 3 atoms of the hydrogen in the radicle

may be displaced by chlorine. The number of hydrogen atoms thus susceptible of displacement varies with the composition of the radicle. In such cases of substitution within the radicle the basicity of the acid is not altered.

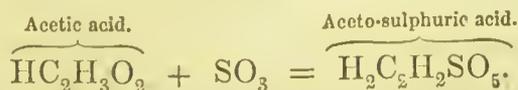
(b) *Compound Acids*.—These acids consist of an organic compound, which may be either acid or neutral in character, united with an acid either of inorganic or organic origin, the properties of which are modified. These compound acids may be subdivided into two groups, in the first of which the saturating power of the combining acid is not affected, while in the second it is more or less diminished.

1. *Compound Acids in which the Capacity of Saturation of the Components is unchanged*.—An excellent instance of this class is afforded in the case of formobenzoylic acid ($\text{HCHO}_2, \text{C}_7\text{H}_6\text{O}$). This compound consists of a combination of formic acid with the oil of bitter almonds; the new acid thus formed possesses a saturating power exactly proportioned to the quantity of formic acid which it contains. Acetonic acid ($\text{HCHO}_2, \text{C}_3\text{H}_6\text{O}$) is another example of the same kind, consisting of formic acid united with acetone as its *colligate*, or associated organic compound.

2. *Compound Acids of diminished Basic Power—Sulpho-acids*.—Numerous instances of this kind occur in the colligated sulphuric acids, such as the ethylsulphuric ($\text{HC}_2\text{H}_5\text{SO}_4$), and glycerisulphuric acid ($\text{HC}_3\text{H}_7\text{SO}_6$); in these cases the sulphuric acid and the organic group, in entering into combination, part with a certain number of atoms of water; the loss of basic power in most instances corresponding to the number of atoms of hydrogen which are displaced from the sulphuric acid when the latter is estimated in the form of the normal acid, H_2SO_4 .

The formation of the vinic acids from the alcohols (1134 *et seq.*), shows one mode in which these bodies are produced, but this series of compounds constitutes but a single subdivision of the colligated sulpho-acids, which recent researches have proved to be very numerous.

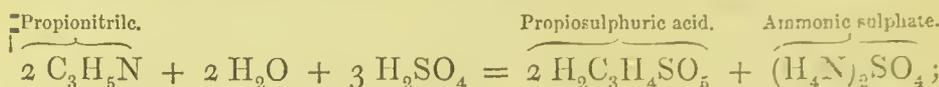
(1.) When sulphuric anhydride is brought into contact with one of the normal monobasic organic acids, whilst the mixture is kept cool artificially, each molecule (SO_3) of the anhydride generally combines with one molecule of the organic acid, and a dibasic acid is the result. For example:—



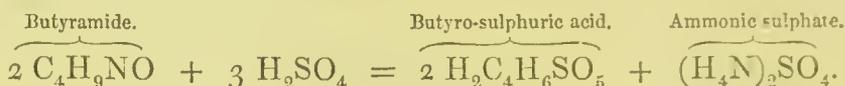
The following acids belong to this class:—

| | |
|-------------------------------|-----------------|
| Aceto-sulphuric acid | $H_2C_2H_2SO_5$ |
| Propio-sulphuric acid | $H_2C_3H_4SO_5$ |
| Butyro-sulphuric acid | $H_2C_4H_6SO_5$ |
| Benzo-sulphuric acid | $H_2C_7H_4SO_5$ |

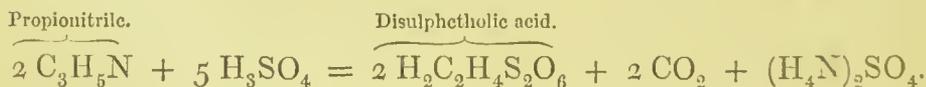
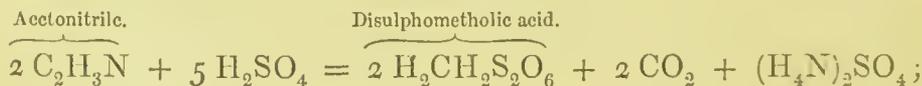
The same compounds may be formed by heating the amides or nitriles of the series with fuming sulphuric acid. Thus, propionitrile yields propiosulphuric acid :—



and butyramide by similar treatment furnishes butyrosulphuric acid :—



(2.) But if the mixture be heated, in addition to these sulpho-acids, a second series of acids is formed, termed by Hofmann and Buekton (*Phil. Trans.*, 1856) *disulpho-acids*. The reaction is attended with the evolution of carbonic anhydride; and a compound is produced which belongs to the series immediately below that of the nitrile acted upon; for example :—



These acids are all dibasic. In this manner they obtained the first four terms of the following series; and by treating aniline in a similar manner they also obtained a disulpho-acid from it. The first compound upon this list is identical with Liebig's *methionic acid*; the disulphonaphthalic acid was discovered previously by Berzelius :—

| | |
|-----------------------------|--|
| Disulphometholic acid . . . | $H_2C H_2S_2O_6$, or $C H_4 2 SO_3$ |
| Disulphetholic acid . . . | $H_2C_2H_4S_2O_6$, or $C_2H_6 2 SO_3$ |
| Disulphotritolic acid . . . | $H_2C_3H_6S_2O_6$, or $C_3H_8 2 SO_3$ |
| Disulphobenzolic acid . . . | $H_2C_6H_4S_2O_6$, or $C_6H_6 2 SO_3$ |
| Disulphonaphthalic acid . | $H_2C_{10}H_6S_2O_6$, or $C_{10}H_8 2 SO_3$ |
| Disulphanilie acid . . . | $H_2C_6H_5NS_2O_6$, or $C_6H_7N 2 SO_3$ |

Irrespective of any theoretical view of the molecular composition of the first three of these bodies, it is clear that they contain the elements of 1 molecule of a hydrocarbon corresponding to

marsh gas, with 2 of sulphuric anhydride (SO_3); as is represented in the second series of formulæ contained in the table.

(3.) There can be no doubt of the possibility of forming a monobasic series of sulpho-acids corresponding to these, in which the hydrocarbon has been acted upon by 1 instead of by 2 molecules of sulphuric anhydride. These compounds would have the following composition; but at the present only two of them—viz., sulphobenzolic and sulphanic acid, have actually been obtained:—

| | |
|---------------------------|---|
| Sulphometholic acid . . . | $\text{HC H}_3\text{SO}_3$, or $\text{C H}_4\text{SO}_3$ |
| Sulphetholic acid . . . | $\text{HC}_2\text{H}_5\text{SO}_3$, or $\text{C}_2\text{H}_6\text{SO}_3$ |
| Sulphotritolic acid . . . | $\text{HC}_3\text{H}_7\text{SO}_3$, or $\text{C}_3\text{H}_8\text{SO}_3$ |
| Sulphobenzolic acid . . . | $\text{HC}_6\text{H}_5\text{SO}_3$, or $\text{C}_6\text{H}_6\text{SO}_3$ |
| Sulphanilic acid . . . | $\text{HC}_6\text{H}_6\text{NSO}_3$, or $\text{C}_6\text{H}_7\text{NSO}_3$. |

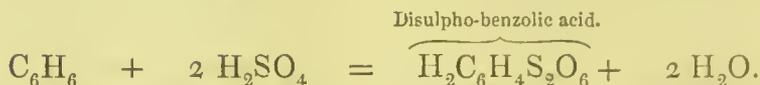
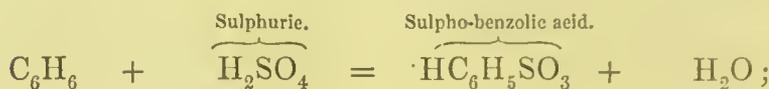
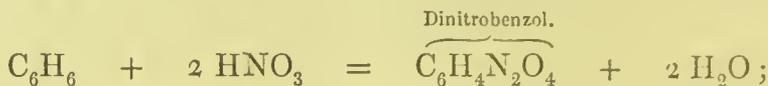
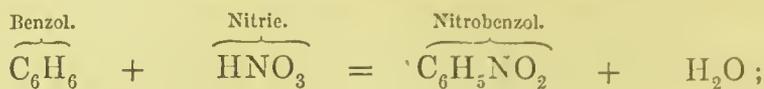
(4.) Certain of these sulpho-acids may be obtained by the direct action of sulphuric anhydride upon the hydrocarbons:— For example, when olefiant gas is subjected to the action of the anhydride, it forms the compound which Magnus termed *sulphate of carbyle* (1137); this body, when treated with water, forms ethionic or *disulphethylic* acid. This body is one of the terms of a new series of disulpho-acids, which might probably be formed by submitting the hydrocarbons homologous with olefiant gas, to similar treatment.

(5.) The ordinary vinic acids (1134) constitute the series of sulpho-acids produced by the reaction of 1 molecule (SO_3) of sulphuric anhydride upon the alcohol, whilst ethionic acid is one of the corresponding disulpho-acids produced by the action of 2 molecules of sulphuric anhydride upon each molecule of the alcohol. Thus it appears that each alcohol may be made to furnish at least 4 different sulpho-acids, two of which are monobasic and two dibasic. They are typified by the following acids of the ethylic series:—

| | |
|------------------------------------|--|
| Sulphetholic acid | $\text{H C}_2\text{H}_5\text{S O}_3$ |
| Disulphetholic acid | $\text{H}_2\text{C}_2\text{H}_4\text{S}_2\text{O}_6$ |
| Sulphethylic acid | $\text{H C}_2\text{H}_5\text{S O}_4$ |
| Ethionic (disulphethylic) acid . . | $\text{H}_2\text{C}_2\text{H}_4\text{S}_2\text{O}_7$ |

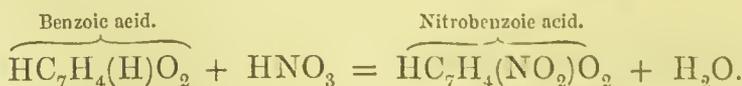
Hofmann and Buckton conclude, as the general result of their investigation of the sulpho-acids (*Proceed. Roy. Soc.* viii. 165)— That all organic molecules, particularly in the nascent state, appear to be capable of assimilating the elements either of 1 or of 2 molecules of sulphuric anhydride. The formation of the two groups of acids which are thus produced, presents a great analogy with the production of the nitro-substitutes generated under the

influence of nitric acid. All these compounds are generated with the elimination of water.* In the action of nitric acid and sulphuric acid upon benzol, for instance, we have:—



The action of nitric acid upon organic bodies is by no means limited to the production of nitro-compounds corresponding to nitro-benzol and dinitro-benzol; frequently additional substitutes are formed, with elimination of 3, 4, and in a few isolated cases, even of 5 atoms of water. Hitherto, however, no substances have been observed except mannite, in which the assimilation of sulphuric acid has gone further than in the disulpho-acids.

Nitro-acids.—When nitric acid unites with an organic acid, the compound which is formed is generally one which is the result of a simple process of substitution. The change is accompanied by the separation of water: no apparent decomposition occurs in these cases, but the saturating power of the new acid is not increased by the nitrogen and oxygen which have entered into its composition. The nitric acid in reality has been partially deoxidized; an atom of hydrogen has been removed from the organic acid, and its place has been supplied by an atom of nitroxyl (NO_2). For example, when benzoic acid is acted upon by nitric acid, the change which occurs may be represented as follows:—



Many of the nitro-acids obtained in this manner are yellow, and yield salts which have a yellow colour; these salts generally fuse, and often detonate, when they are exposed to heat; and when heated with sulphuric acid and manganese dioxide, they emit

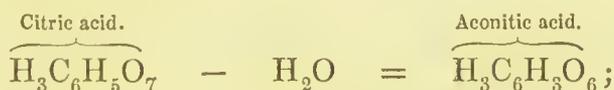
* This refers, however, to the case in which it is supposed that the reaction takes place between oil of vitriol or *normal* sulphuric acid and the organic compound, and not when the *anhydride* is used; as the equations which follow sufficiently show.

red nitrous fumes. A few of the best known of these compounds are enumerated below:—

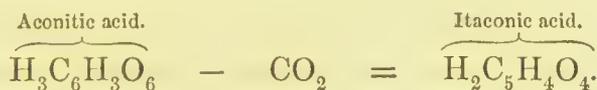
| | |
|---------------------------------------|--|
| Dinitrophenic acid | $\text{HC}_6\text{H}_3(\text{NO}_2)_2\text{O}$ |
| Trinitrophenic (earbazotic) | $\text{HC}_6\text{H}_2(\text{NO}_2)_3\text{O}$ |
| Nitrobenzoic | $\text{HC}_7\text{H}_4(\text{NO}_2)\text{O}_2$ |
| Dinitrobenzoic | $\text{HC}_7\text{H}_3(\text{NO}_2)_2\text{O}_2$ |
| Nitrocinamic | $\text{HC}_9\text{H}_6(\text{NO}_2)\text{O}_2$ |
| Nitrosalicilic | $\text{HC}_7\text{H}_4(\text{NO}_2)\text{O}_3$ |
| Nitranisic | $\text{HC}_8\text{H}_6(\text{NO}_2)\text{O}_3$ |

(1263) *Action of Heat upon the Organic Acids.*—A large number of the normal monobasic vegetable acids, which contain 2 or 3 atoms of oxygen, may be volatilized without decomposition; but the greater number of the more complicated polybasic organic acids are decomposed by the application of heat. Many of them give rise to acids of simpler composition, which are formed by the abstraction of the elements of water; or by the removal of the elements of carbonic anhydride; or by the loss of both water and carbonic anhydride. Several of these new acids are volatile; others undergo complete decomposition if subjected to a higher temperature than that at which they were formed.

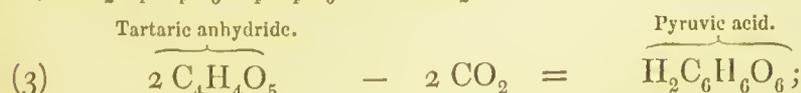
For example, citric acid, by losing the elements of water, furnishes aconitic acid:—



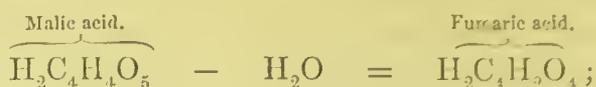
and at a higher temperature aconitic acid loses carbonic anhydride:—



The action of a gradually increasing temperature upon tartaric acid is remarkable. This acid undergoes two different stages of dehydration, and then loses carbonic anhydride in the manner shown in the subjoined equations:—

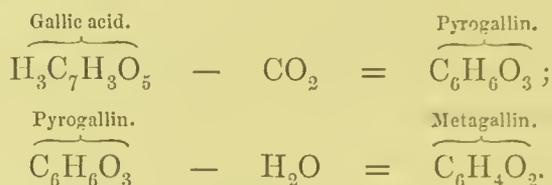


Again, malic acid, by the loss of water, yields fumaric (paramalæic) acid:—

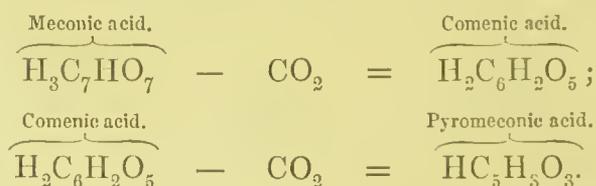


and fumaric acid by sublimation is converted into its isomeride, malæic acid.

In like manner, gallic acid by the loss of 1 atom of carbonic anhydride yields pyrogallin; and pyrogallin in its turn, by the loss of 1 atom of water, furnishes metagallin (1334):—



Results closely analogous are afforded by the decomposition of meconic acid: a solution of which, at a temperature not exceeding that of boiling water, is converted into comenic acid by the loss of 1 atom of carbonic anhydride; and comenic acid itself if subjected to distillation loses an atom of carbonic anhydride, and furnishes another distinct volatile acid, the pyromeconic:—

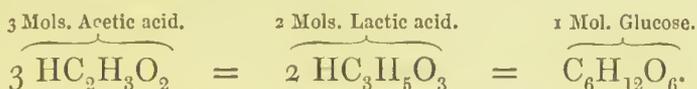


(1264) *Effects of Chlorine and other Halogens upon the Acids.*—Chlorine generally acts upon the monobasic acids simply by displacing hydrogen, thus producing a body of the same chemical type as the original acid, and containing the same number of elements similarly arranged. In the radicle of acetic acid, for instance, the 3 atoms of hydrogen may be displaced by 3 of chlorine: and trichloroacetic acid, which is analogous to the original acetic acid, is produced; $\text{HC}_2\text{H}_3\text{O}_2 + 3\text{Cl}_2 = \text{HC}_2\text{Cl}_3\text{O}_2 + 3\text{HCl}$. By a substitution of a somewhat similar kind, benzoic acid ($\text{HC}_7\text{H}_5\text{O}_2$) yields ehlorobenzoic acid, ($\text{HC}_7\text{H}_4\text{ClO}_2$). In other instances, especially in the more complex acids, the original group of elements is broken up into two or more groups of simple constitution. For example, citric acid ($\text{H}_3\text{C}_6\text{H}_5\text{O}_7$), when treated with chlorine, yields a neutral chlorinated body ($\text{C}_5\text{Cl}_{12}\text{O}_3$), besides other products.

The action of bromine and of iodine is analogous to that of

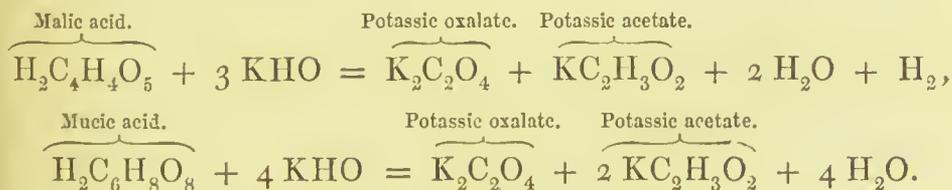
chlorine, but with differences depending chiefly upon the feebler character of their attractions. Nitroxyl may also be substituted for a part of the hydrogen, atom for atom; and in this case the acid character of the nitric acid whence the nitroxyl was derived entirely disappears.

It is remarkable that several of the organic acids have a composition identical with that of anhydrous glucose, if the ultimate analysis only be considered; thus furnishing additional evidence that chemical character depends quite as much upon the mode of arrangement among the elements as upon the nature of those elements themselves:—

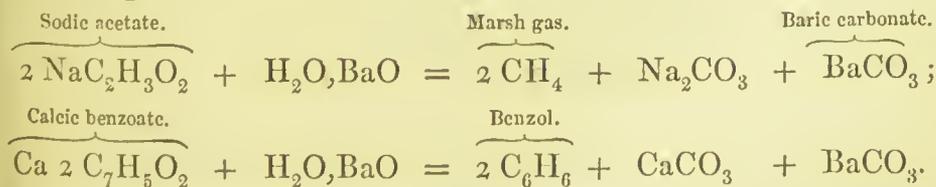


Many of the acids contain oxygen and hydrogen in exactly the proportions required to form water: such, for example, as the lactic, the acetic, the quinic, the pyrotartaric, and some others.

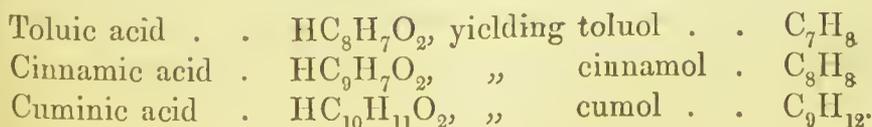
(1265) *Combined Action of Heat and Bases on the Acids.*—Many of the organic acids when fused with caustic potash are decomposed by it into salts of acetic and oxalic acid, with separation of water, and sometimes with evolution of hydrogen; for example:—



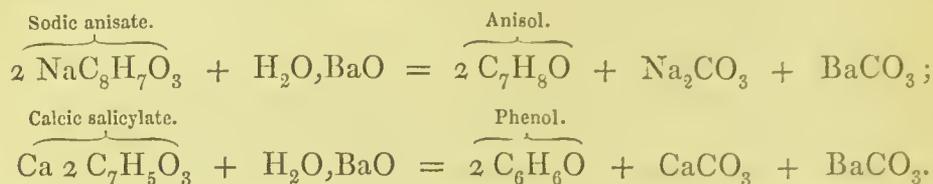
When the salts of any of the monobasic acids, which in their state of normal hydrates contain 2 atoms of oxygen, are distilled with boric hydrate, they undergo a peculiar decomposition: boric carbonate is formed, and a hydrocarbon, the hydride of the alcohol radicle of the next inferior term of the series, is given off; for example:—



In this manner the salts of the following acids may be decomposed:—



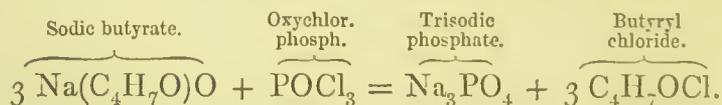
When the salts of acids, which in the state of normal hydrates contain 3 atoms of oxygen, are similarly treated, oxidized compounds are obtained, and a carbonate of the metal remains in the retort, as in the former case:—



Reference has already been made to the ketones, which are produced when the calcium or barium salt of any of the volatile acids, the normal hydrates of which contain 2 atoms of oxygen, are submitted to dry distillation (1258).

a. Oxychlorides of the Acids, or Chlorides of the Acid Radicles.

(1266) *Chlorides of the Radicles of the Monobasic Acids.*—The acids of the lower members of the series $\text{HC}_n\text{H}_{2n-1}\text{O}_2$, can readily be made to furnish volatile compounds in which one atom of hydroxyl (HO), as contained in the normal acid, has its place supplied by chlorine. With acetic acid $[(\text{C}_2\text{H}_3\text{O})\text{HO}]$ *acetyl chloride* may be obtained, consisting of $\text{C}_2\text{H}_3\text{OCl}$. In preparing these compounds Gerhardt (*Ann. de Chimie*, III. xxxvii. 290) heats together a mixture of 1 molecule of the oxychloride of phosphorus (phosphoryl chloride, POCl_3 ; 460), with 3 molecules of the anhydrous potassium or sodium salt of the acid. For instance:—



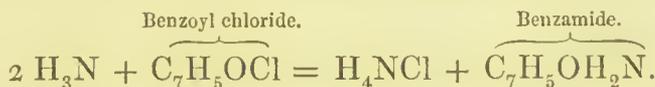
In some cases it is more advantageous to mix phosphorous chloride (PCl_3) with the normal acid, in the proportion of 2 molecules of the acid to 1 of the trichloride. In the case in which acetic acid is employed, the reaction is as follows:—



and on distilling the mixture, the new compound passes over, whilst phosphorous acid remains in the retort. By these methods the following oxychlorides amongst others have been prepared:—

| Oxychlorides. | Formula. Mol. Vol. = <input type="text"/> | Boiling Point. | | Specific Gravity. | | Rel. wt. H=1. |
|-----------------------|--|----------------|------|-------------------|---------|------------------|
| | | ° F. | ° C. | Liquid. | Vapour. | |
| Acetyl chloride . . . | C ₂ H ₃ OCl | 131 | 55 | 1·125 | 2·87 | 39·2 |
| Propionyl „ . . . | C ₃ H ₅ OCl | 176 | 80 | | | |
| Butyryl „ . . . | C ₄ H ₇ OCl | 203 | 95 | | | |
| Valeryl „ . . . | C ₅ H ₉ OCl | 239 | 115 | 1·005 | | |
| Pelargonyl „ . . . | C ₉ H ₁₇ OCl | 448 | 220 | | | |

One molecule of each of these bodies yields two volumes of vapour. The vapour of these compounds is extremely irritating to the lungs, and their manipulation consequently demands great care, otherwise the health of the operator would be seriously endangered. Water immediately decomposes these oxychlorides into the normal acid and free hydrochloric acid. The action of a few drops of water upon acetyl chloride is so violent as to amount to an explosion; C₂H₃OCl + H₂O becoming HC₂H₃O₂ + HCl. When they are mixed with an alcohol, they furnish hydrochloric acid, and a compound ether of the acid to which they correspond; valeryl chloride, C₅H₉OCl + (C₂H₅)HO, becoming valeric ether (C₂H₅)C₅H₉O₂ + HCl. With ammonia they react violently, producing an amide, and ammoniac chloride:—



Oxychlorides corresponding to the foregoing compounds may also be obtained with the aromatic acids, such as the benzoic, toluic, cinnamic, and cuminic acids:—

| Oxychlorides. | Formula. Mol. Vol. = <input type="text"/> | Boiling Point. | | Specific Gravity. | |
|--------------------------|---|----------------|------|-------------------|---------|
| | | ° F. | ° C. | Liqu. d. | Vapour. |
| Benzoyl chloride | C ₇ H ₅ O Cl | 384·8 | 196 | 1·25 | 4·987 |
| Toluy „ | C ₈ H ₇ O Cl | 419 | 215 | 1·175 | |
| Cinnamyl „ | C ₉ H ₇ O Cl | 501·8 | 261 | 1·207 | |
| Cuminy „ | C ₁₀ H ₁₁ O Cl | 494·6 | 257 | 1·070 | |
| Anisyl „ | C ₈ H ₇ O ₂ Cl | 503·6 | 262 | 1·261 | |

(Cahours, *Ann. de Chimie*, III. xxiii. 337.)

These oxychlorides, though unimportant in themselves, have in the hands of Gerhardt led to the discovery of a general method of procuring the anhydrides of the acids from which they are derived (1268).

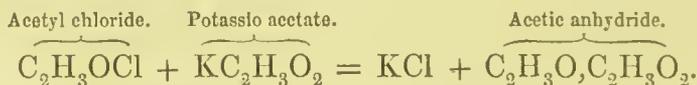
If oxybromide of phosphorus (phosphoryl bromide, POBr₃) be used instead of oxychloride for decomposing the salt of the

organic acid, oxybromides of corresponding composition may be procured.

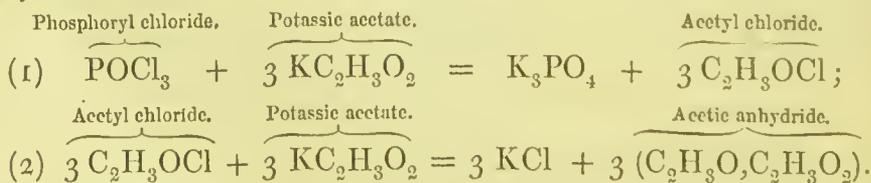
(1267) *Oxychlorides of the dibasic acids*, such as succinyl chloride ($C_4H_4O_2Cl_2$), and citraconyl chloride ($C_5H_4O_2Cl_2$), may also be procured; but it is best in these cases to act upon the anhydrides of these acids with phosphoric chloride (PCl_5): they are obtained in a state of purity with difficulty, since they are generally decomposed at a temperature below their point of volatilization.

b. The Anhydrides, or Anhydrous Acids.

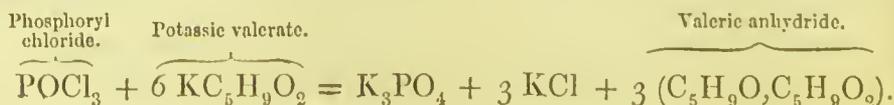
(1268) The oxychlorides of the monobasic acids may be employed to furnish the anhydrides of their respective acids, by causing one molecule of the oxychloride to decompose one molecule of the dry potassium or sodium salt of the acid to which it corresponds. For instance, in the preparation of acetic anhydride, an equivalent of acetyl chloride is treated with an equivalent of anhydrous potassic acetate, when the following reaction occurs:—



It is not necessary to isolate the oxychloride in order to procure the anhydride of the acid, for if one molecule of phosphoryl chloride be made to act upon six molecules of the anhydrous salt, instead of upon three, as would be required in the preparation of the oxychloride of the organic acid, a compound reaction occurs. The oxychloride of the acid is first formed, and this body in the moment of its formation reacts upon the excess of the salt employed, and the anhydride is at once liberated. For example, in the preparation of acetic anhydride, these two stages may be thus indicated:—



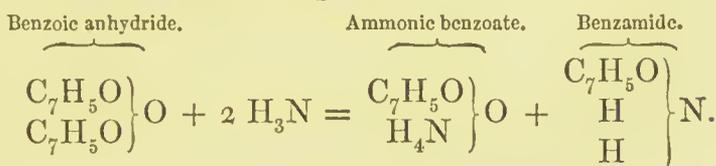
Or the whole may be comprehended in a single equation such as the following, which represents the preparation of valeric anhydride:—



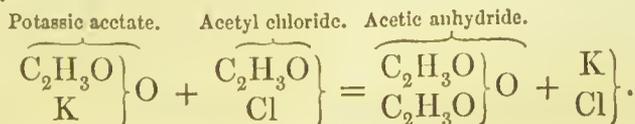
Gerhardt and Chiozza have thus obtained, amongst others, the anhydrides of the following acids:—

| Anhydrides. | Formula. Mol. Vol. = <input type="text"/> | Boiling Point. | | Specific Gravity. | | Rel. wt. H=1. |
|--------------------|--|----------------|-------|-------------------|---------|------------------|
| | | ° F. | ° C. | Liquid. | Vapour. | |
| Acetic | (C ₂ H ₃ O, C ₂ H ₃ O ₂) | 279·5 | 137·5 | 1·073 | 3·47 | 51 |
| Butyric | (C ₄ H ₇ O, C ₄ H ₇ O ₂) | 374 | 190 | 0·978 | 5·38 | 79 |
| Valeric | (C ₅ H ₉ O, C ₅ H ₉ O ₂) | 419 | 215 | 0·934 | 6·23 | 93 |
| Caproic | (C ₆ H ₁₁ O, C ₆ H ₁₁ O ₂) | | | | | |
| Enanthylic | (C ₇ H ₁₃ O, C ₇ H ₁₃ O ₂) | | | 0·92 | | |
| Caprylic | (C ₈ H ₁₅ O, C ₈ H ₁₅ O ₂) | 536 | 280 | | | |
| Pelargonic | (C ₉ H ₁₇ O, C ₉ H ₁₇ O ₂) | | | | | |

These anhydrides assume the form of neutral oily bodies, which are insoluble in water, but which by contact with this liquid slowly combine with it and are gradually converted into the corresponding normal acids. They are susceptible of volatilization without undergoing decomposition. They possess, in many cases, an odour distinct from that of the acids to which they give rise. In entering into combination with ammonia, they form one molecule of the amide (1341) and one of the normal ammonium salt of the acid; as for example:—



But the mode in which these compounds are formed is of greater interest to chemical theory than the mere fact of their existence. They are formed, it will be observed, not by the abstraction of water from the normal acids, nor by the removal of a metallic oxide from one of the salts of the acid, but by a true process of substitution, so that the anhydrides of these monobasic acids cannot be accurately represented by any formula which would indicate that they consist of a salt deprived of its base, or of a hydrate deprived of its water. For example, normal acetic acid, in its most concentrated form, is represented as (HC₂H₃O₂), and potassic acetate as (KC₂H₃O₂); but acetic anhydride is not simply, C₄H₃O₃ (C=6; O=8); it is truly (C₂H₃O, C₂H₃O₂) since it is formed by substituting an atom of acetyl (C₂H₃O) in the place of an atom of hydrogen or of potassium:—

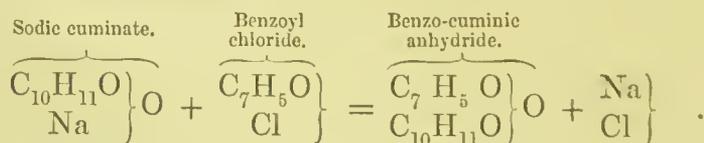


The normal (1278) specific gravity of the vapour of acetic acid at 482° (250° C.) is 2.080; that is to say, one molecule ($C_2H_4O_2$) yields two volumes of vapour: whilst the vapour-density of the anhydride is 3.47,—consequently its molecule (supposing it to yield two volumes of vapour) must be represented by the empirical formula $C_4H_6O_3$. But the following proof of the correctness of the theory of this duplicate composition of the anhydrides, will, perhaps, by many be esteemed still more convincing.

(1269) *Double or Mixed Anhydrides*.—The anhydrides already enumerated are not the only ones which Gerhardt succeeded in obtaining. Benzoic, cinnamic, and cuminic oxychlorides may be procured by processes analogous to those already described for the preparation of the acetic and other oxychlorides; and the corresponding anhydrides were obtained by employing these oxychlorides to decompose the anhydrous salts of benzoic, cinnamic, and cuminic acids:—

| | Oxychlorides. | Anhydrides. |
|------------------------|-------------------|------------------------------------|
| Benzoic | C_7H_5OCl | $(C_7H_5O, C_7H_5O_2)$ |
| Cinnamic | C_9H_7OCl | $(C_9H_7O, C_9H_7O_2)$ |
| Cuminic | $C_{10}H_{11}OCl$ | $(C_{10}H_{11}O, C_{10}H_{11}O_2)$ |
| Nitrobenzoic | $C_7H_4(NO_2)OCl$ | $[C_7H_4(NO_2)O, C_7H_4(NO_2)O_2]$ |
| Salicylic | $C_7H_5O_2Cl$ | $(C_7H_5O_2, C_7H_5O_3)$ |

Gerhardt, however, did not stop here; he employed the oxychlorides already described, to decompose the salts of *other* acids. Thus benzoyl chloride was made to decompose dry sodic cuminate, and in this manner a *benzo-cuminic* anhydride was obtained by the following reaction:—

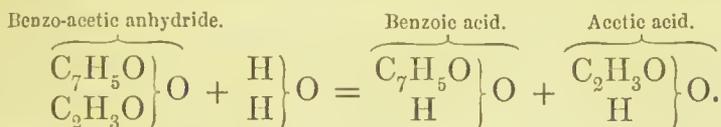


By decomposing sodic cinnamate by benzoyl chloride, *benzo-cinnamic* anhydride was obtained: and by similar methods the various compounds enumerated in the following list were procured:

| | |
|---|----------------------------|
| Benzo-cuminic anhydride | $C_7H_5O, C_{10}H_{11}O_2$ |
| Benzo-cinnamic anhydride | $C_7H_5O, C_9H_7O_2$ |
| Benzo-benzoic anhydride | $C_7H_5O, C_7H_5O_2$ |
| Benzo-acetic anhydride | $C_7H_5O, C_2H_3O_2$ |
| Cinnamo-acetic anhydride | $C_9H_7O, C_2H_3O_2$ |
| Benzo-nitro-benzoic anhydride | $C_7H_5O, C_7H_4(NO_2)O_2$ |
| Benzo-salicylic anhydride | $C_7H_5O, C_7H_5O_3$ |
| Aceto-salicylic anhydride | $C_2H_3O, C_7H_5O_3$ |
| Benzo-valeric anhydride | $C_7H_5O, C_5H_9O_2$ |

These compounds are liquid at ordinary temperatures, and

assume the form of neutral oils, which are heavier than water ; if left in contact with water they are gradually converted into a mixture of the two normal acids from which they are derived ; benzo-acetic anhydride, for instance, combines with one molecule of water, and forms a mixture of normal benzoic and acetic acids :—

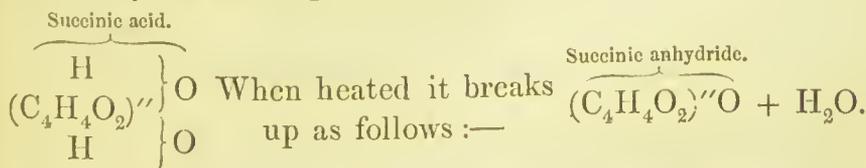


If it be attempted to submit these double anhydrides to distillation, they become decomposed, and are generally resolved into their component anhydrides. It is obvious that the foregoing list might be increased almost indefinitely, were there any inducement to add to the number of these compounds ; intrinsically they are unimportant, but the interesting point which is indicated by their discovery, is the fact that the anhydrides of the monobasic acids are really complex bodies, resulting from the combination of two substances of similar composition : the true benzoic anhydride, or benzo-benzoic compound, which stands third upon the foregoing list, being perfectly analogous, not only in its mode of formation, but also in its properties, to the other bodies with which it is associated ; it is, however, more stable than they are, and can be distilled without experiencing decomposition.

(1270) *Anhydrides of the Dibasic Acids.*—With the dibasic acids the case is different. The anhydrides of these compounds can often be obtained from the corresponding normal acids, by the simple application of heat to these bodies, or by distilling them with dehydrating agents, such as phosphoric anhydride. In this manner, for instance, chemists have been enabled to procure the following anhydrides of dibasic acids :—

| | | | | |
|----------------------|----------------------------------|--|---------------------|--|
| Succinic anhydride . | $\text{C}_4\text{H}_4\text{O}_3$ | | Citraconic | $\text{C}_5\text{H}_4\text{O}_3$ |
| Malæic | $\text{C}_4\text{H}_2\text{O}_3$ | | Phthalic | $\text{C}_8\text{H}_4\text{O}_3$ |
| Tartaric | $\text{C}_4\text{H}_4\text{O}_5$ | | Camphoric | $\text{C}_{10}\text{H}_{11}\text{O}_3$ |
| Pyrotartaric | $\text{C}_5\text{H}_6\text{O}_3$ | | | |

These being residues of dibasic acids are already *double* anhydrides. They are residues from a compound formed upon the type of at least two molecules of water. Succinic acid, for example, may be thus represented :—

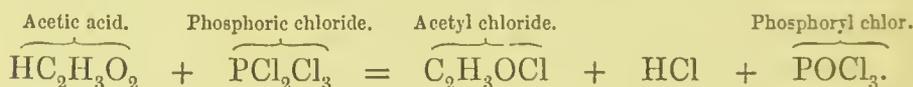


And a similar explanation may be applied in other cases.

It is worthy of remark that the dibasic acids form vinic or ethylic acids, such as ethylsulphuric, ethyloxalic, and ethyl-tartaric: they likewise furnish the amidated acids, such as the sulphamic, oxamic, and tartramic acids. Monobasic acids do not form vinic acids nor amidated acids in the strict sense of the term.

If instead of causing an oxychloride of a monobasic acid to act upon one of the salts of another monobasic acid (as when benzoyl chloride is made to act upon dry potassic acetate), the oxychloride be made to act upon the corresponding salt of a dibasic acid, a double anhydride is not formed, but a mixture of two separate anhydrides is the result. If, for instance, benzoyl chloride be made to act upon dry sodic succinate, a mixture of succinic and benzoic anhydrides is obtained.

Phosphoric chloride never yields the anhydride of a monobasic acid by acting upon the normal acid; but the corresponding oxychloride is formed at once, whilst phosphoryl chloride and hydrochloric acid are liberated. For example:—



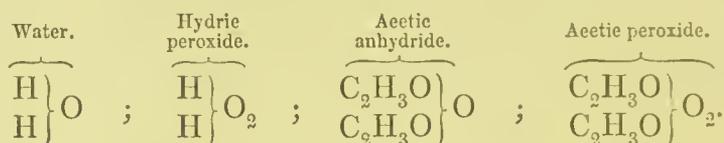
(1271) *Organic Peroxides.*—The foregoing theory of the organic acids, which represents them as formed upon the model of water, has received further confirmation from Brodie's discovery of a class of organic peroxides corresponding to hydric peroxide (H_2O_2 ; *Phil. Trans.*, 1863, 410).

These peroxides may be obtained by decomposing the organic anhydrides or oxychlorides by means of pure barium dioxide (BaO_2). The barium dioxide must be procured by dissolving the ordinary dioxide in hydrochloric acid, then precipitating by baryta water and drying the precipitate *in vacuo* over sulphuric acid. One or two illustrations of these compounds may be admitted here.

Benzoyl Peroxide $[(\text{C}_7\text{H}_5\text{O})_2\text{O}_2]$ is procured by mixing equivalent quantities of benzoic oxychloride and barium dioxide in water. A solid is obtained, which is freely soluble in ether, from which it is deposited in large brilliant crystals. When heated to a little beyond 212° it is decomposed with a slight explosion and with escape of carbonic anhydride. If boiled with a solution of potash, oxygen is evolved, and potassic benzoate formed.

Acetyl Peroxide $[(\text{C}_2\text{H}_3\text{O})_2\text{O}_2]$ may be procured in like manner by decomposing acetic anhydride with an equivalent quantity of

barium dioxide in anhydrous ether. The mixture must be effected slowly, as the reaction is attended with evolution of much heat. The ethereal solution is filtered from the baric acetate and evaporated at a low temperature, and the residual fluid washed three or four times with water. The viscid liquid thus obtained is acetyl peroxide. It has a burning taste like that of cayenne pepper: if mixed with an aqueous solution of sulphate of indigo, it immediately discharges the colour. It converts protoxide into dioxide of manganese, and the yellow into the red prussiate of potash. Baryta water decomposes it, forming baric acetate and dioxide; a single drop placed in a watch-glass and heated, explodes with a loud report, shattering the glass to pieces. The analogy of water and the peroxide of hydrogen to the organic anhydride and the organic peroxide may be thus exhibited:—



(1272) The table on the preceding page will assist in explaining the relations of the principal classes of the derivatives of the monobasic acids.

§ III. THE FATTY ACIDS.

(1273) THE fats and fixed oils when saponified yield a number of acids, which belong to two different homologous series, both of which are regarded as monobasic. Stearic and palmitic acids

| Acids of the form $\text{C}_n\text{H}_{2n}\text{O}_2$, or $\text{HC}_n\text{H}_{2n-1}\text{O}_2$. | Acids of the form $\text{C}_n\text{H}_{2n-2}\text{O}_2$, or $\text{HC}_n\text{H}_{2n-3}\text{O}_2$. | Acids of the form $\text{C}_n\text{H}_{2n-2}\text{O}_4$, or $\text{H}_2\text{C}_n\text{H}_{2n-4}\text{O}_4$. |
|---|---|--|
| Formic . . . $\text{C}_1\text{H}_2\text{O}_2$ | | |
| Acetic . . . $\text{C}_2\text{H}_4\text{O}_2$ | | Oxalic . . . $\text{C}_2\text{H}_2\text{O}_4$ |
| Propionic . . . $\text{C}_3\text{H}_6\text{O}_2$ | Acrylic . . . $\text{C}_3\text{H}_4\text{O}_2$ | Malonic . . . $\text{C}_3\text{H}_4\text{O}_4$ |
| Butyric . . . $\text{C}_4\text{H}_8\text{O}_2$ | Crotonic . . . $\text{C}_4\text{H}_6\text{O}_2$ | Succinic . . . $\text{C}_4\text{H}_6\text{O}_4$ |
| Valeric . . . $\text{C}_5\text{H}_{10}\text{O}_2$ | Angelic . . . $\text{C}_5\text{H}_8\text{O}_2$ | Lipic . . . $\text{C}_5\text{H}_8\text{O}_4$ |
| Caproic . . . $\text{C}_6\text{H}_{12}\text{O}_2$ | | Adipic . . . $\text{C}_6\text{H}_{10}\text{O}_4$ |
| Enanthylic . . . $\text{C}_7\text{H}_{14}\text{O}_2$ | Damaluric . . . $\text{C}_7\text{H}_{12}\text{O}_2$ | Pimelic . . . $\text{C}_7\text{H}_{12}\text{O}_4$ |
| Caprylic . . . $\text{C}_8\text{H}_{16}\text{O}_2$ | | Suberic . . . $\text{C}_8\text{H}_{14}\text{O}_4$ |
| Pelargonic . . . $\text{C}_9\text{H}_{18}\text{O}_2$ | | Anchoic . . . $\text{C}_9\text{H}_{16}\text{O}_4$ |
| Rutic . . . $\text{C}_{10}\text{H}_{20}\text{O}_2$ | | Sebacic . . . $\text{C}_{10}\text{H}_{18}\text{O}_4$ |
| Lauric . . . $\text{C}_{12}\text{H}_{24}\text{O}_2$ | | |
| Myristic . . . $\text{C}_{14}\text{H}_{28}\text{O}_2$ | Moringic . . . $\text{C}_{15}\text{H}_{28}\text{O}_2$ | |
| Palmitic . . . $\text{C}_{16}\text{H}_{32}\text{O}_2$ | Physetoleic . . . $\text{C}_{16}\text{H}_{30}\text{O}_2$ | |
| Stearic . . . $\text{C}_{18}\text{H}_{36}\text{O}_2$ | Oleic . . . $\text{C}_{18}\text{H}_{34}\text{O}_2$ | |
| Arachidic . . . $\text{C}_{20}\text{H}_{40}\text{O}_2$ | Doeglic . . . $\text{C}_{19}\text{H}_{36}\text{O}_2$ | |
| Cerotic . . . $\text{C}_{27}\text{H}_{54}\text{O}_2$ | | |
| Melissic . . . $\text{C}_{30}\text{H}_{60}\text{O}_2$ | Erucic . . . $\text{C}_{22}\text{H}_{42}\text{O}_2$ | |

may be taken as the types of one series, in which the general formula of the normal acids is $C_nH_{2n}O_2$. The general formula of the other series is $C_nH_{2n-2}O_2$; this series is represented by oleic acid, but only a few terms of it are known. By the oxidation of the members of these two groups a third series of acids may be obtained, to which suberic and succinic acids belong. The acids of this third group are dibasic: their normal hydrates have the general formula $C_nH_{2n-2}O_4$. In the preceding table the corresponding acids in each of these three groups are enumerated.

(a) *Acids belonging to the Acetic or Stearic Series* ($HC_nH_{2n-1}O_2$).

(1274) THE acids which are comprised in this series are monobasic; they constitute one of the most numerous and most carefully examined groups of homologous compounds; all the terms of which, commencing with the formic and proceeding as far as the rutic, are well known. It has been remarked, that in the terms which contain more carbon than the rutic, the number of atoms of carbon in all the acids which have been satisfactorily examined, is divisible by 2; although many chemists admit the existence of acids corresponding in composition to all the hydrocarbons from CH_2 , increasing step by step by successive increment of CH_2 , up to $(C_{20}H_{40})$. The fusing point of Brodie's cerotic acid ($C_{27}H_{54}O_2$) is, however, so much lower than that which might have been expected from an acid so high in the series, that Heintz has suggested that this exceptional case may possibly arise from the acid being a mixture of two others; since he finds it to be a general rule, that a mixture of any two of the solid acids of this series has a fusing point considerably below that of either of its components (1293). As the number for n increases, the boiling point rises, and at the same time the acid property decreases excepting in particular cases; the lower terms in the series generally displace those above them from their combinations with bases; for example, formic or acetic acid will displace the valeric.

The acids belonging to this group may all be distilled, either partially or completely, without undergoing decomposition. Many of them exhibit a remarkable variation in the volume of vapour which they furnish at different temperatures; for instance, the formic, the acetic, the butyric, and the valeric acids, at low temperatures, furnish a much smaller volume of vapour than they do at more elevated temperatures:—

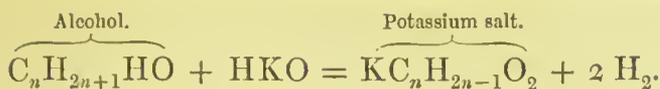
| | °F. | °C. | Vapour Density. | |
|-----------------------------|-------|------|-----------------|----------------|
| | | | Observed. | Calcd 2 vol's. |
| { Formic acid at | 51 | 10.5 | 3.23 | |
| { Ditto | 415.4 | 213 | 1.61 | 1.589 |
| { Acetic acid at | 69.8 | 21 | 3.95 | |
| { Ditto | 320 | 160 | 2.48 | |
| { Ditto | 482 | 250 | 2.08 | 2.073 |
| { Butyric acid at | 350.6 | 177 | 3.68 | |
| { Ditto | 501.8 | 261 | 3.07 | 3.041 |

At the higher temperatures, and at all points above them (until the acid undergoes decomposition), each molecule of the compound yields 2 volumes of vapour; but at low temperatures the vapour volume does not correspond exactly to any specific multiple of the volume of hydrogen.

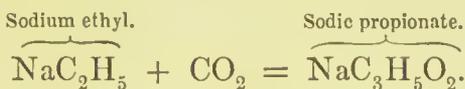
All of the acids of this group when melted, with the exception of the formic and the acetic, exhibit the properties of an oil which is imperfectly soluble in water; though some of the lower members of the series are soluble in water to a considerable extent: they are all abundantly soluble both in alcohol and ether.

These acids are regarded as monobasic, though several of them form both neutral and acid salts with the alkalies; an acid formiate, an acid acetate, and an acid stearate of potassium, for example, may be readily obtained. Many of them yield with plumbic oxide, not only the usual normal salt, but also basic salts, which contain 3 equivalents of plumbic oxide for each equivalent of acid. Some of these basic salts are freely soluble in water.

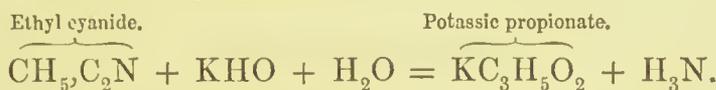
Formation.—1. The remarkable relation which these acids bear to the alcohols has already been pointed out; the acid containing an atom of oxygen more than the alcohol, and two atoms of hydrogen less, whilst the number of atoms of carbon in the two compounds is the same (p. 37). For every alcohol there is a corresponding acid, which may be obtained from the alcohol by a regulated process of oxidation, the aldehyd being formed as an intermediate step in the process if it be carefully regulated: this oxidation may sometimes be effected directly—as in the conversion of wine alcohol into vinegar—by the operation of finely divided platinum; but more usually it is necessary to resort to indirect means, such as heating the alcohol with caustic potash; in the latter case hydrogen is eliminated, whilst oxygen enters into the compound, the general form of the equation being:—



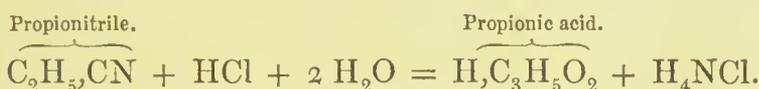
2. The fatty acids may be reproduced by causing carbonic anhydride to act upon the metallic compound of one of the alcohol radicles, such as sodium or potassium-ethyl; for instance:—



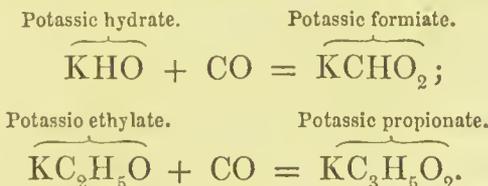
3. We have already referred (1149) to the reproduction of the salts of the fatty acids from their nitriles, or the hydrocyanic ethers of the alcohols, when these compounds are heated with one of the hydrated alkalis, whilst ammonia is liberated, as indicated by the following equation:—



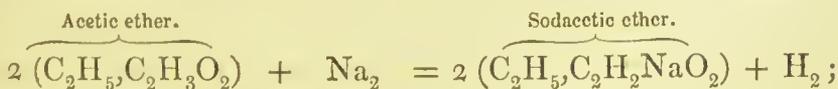
4. The acids of this group may also be obtained by the action of the acids upon the nitriles; as for instance:—



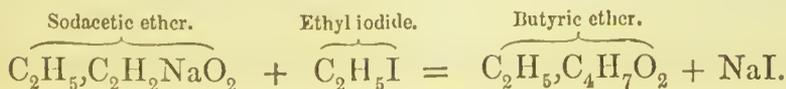
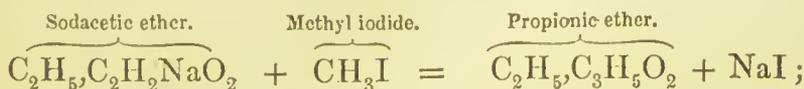
5. It is also possible to ascend synthetically, from one series to another, by introducing carbonic oxide into the potassic hydrate, ethylate, or other corresponding alcohol compound; for example:—



6. The ascent of the series of fatty acids may also be effected by displacing a part of the hydrogen in acetic ether with sodium, and then acting upon the compound by the successive iodides of the alcohol radicles, when the corresponding ethers of the successive terms of the acids are obtained (Frankland and Duppa), *e.g.*:—

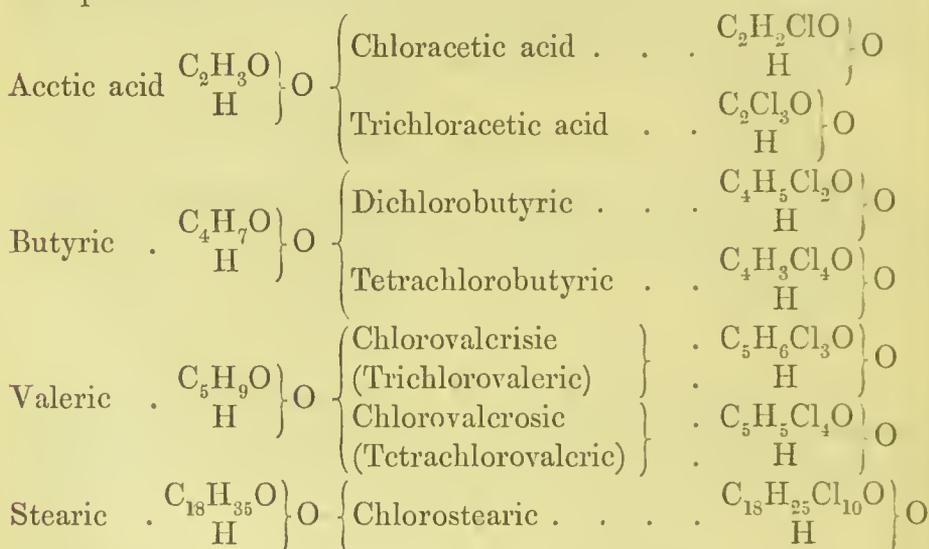


and



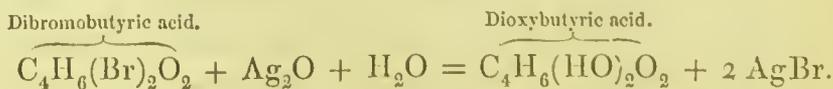
The ethers may then be decomposed into the potassium salts of the acid, by treatment with a solution of caustic potash in alcohol.

The action of gaseous chlorine upon the acids of this group gives rise to the formation of chlorinated acids, in which a certain number of atoms of the hydrogen in the radicle is displaced by an equal number of atoms of chlorine; but the basicity or saturating power of the acid is not altered. In some acids this substitution takes place at ordinary temperatures; in others, heat is necessary, and in some the direct rays of the sun are required to bring about the reaction. In many cases more than one chlorinated acid may be formed from the original acid; for example:—



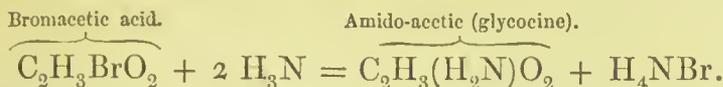
In many cases corresponding compounds with bromine may be obtained, such as bromacetic ($\text{H}_2\text{C}_2\text{H}_2\text{BrO}_2$) and dibromacetic ($\text{H}_2\text{C}_2\text{HBr}_2\text{O}_2$) acids. The iodized substitution-products cannot be obtained unless the brominated bodies are first formed; on heating these with potassic iodide, double decomposition occurs, and an iodized acid is obtained.

When a brominated or a chlorinated acid is boiled with argentic oxide and water, the acid sometimes breaks up completely, as occurs with trichloroacetic acid; but usually an exchange of each atom of chlorine or bromine for one of hydroxyl (HO) takes place. Bromacetic ($\text{C}_2\text{H}_3\text{BrO}_2$) may thus be converted into glycolic acid ($\text{C}_2\text{H}_4\text{O}_3$), and dibromobutyric ($\text{C}_4\text{H}_6\text{Br}_2\text{O}_2$) into dioxybutyric acid ($\text{C}_4\text{H}_8\text{O}_4$): as for example:—



If the mono-brominated acids be treated with an alcoholic

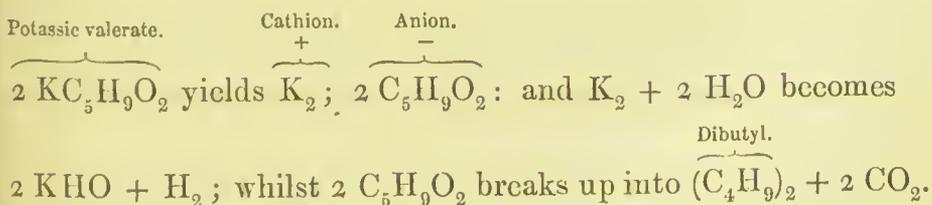
solution of ammonia, an amido-acid is the result (Perkin), whilst ammoniac bromide is separated; for instance:—



Several of these acids also furnish nitro-acids, when treated with fuming nitric acid; such, for example, as the following:—

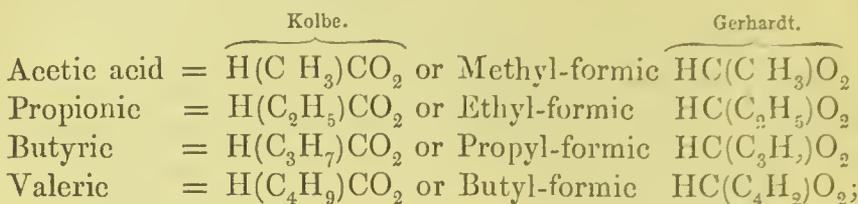


An interesting observation was made by Kolbe regarding the mode in which the salts of these acids are decomposed by the voltaic battery. The first stage of the electrolysis consists in the separation of the salt into two portions; the metal going to the negative plate, whilst the radicle of the acid travels towards the positive electrode. Here the second stage of the process commences; as the constituents of the acid radicle react upon each other in a definite manner. When, for example, a strong solution of potassic valerate is submitted to the action of a voltaic current from 4 cells of Bunsen's or of Grove's battery, the temperature of the solution being prevented from rising much beyond 32°, the potassium of the salt is evolved as usual at the negative electrode; and by here decomposing water it immediately forms potassic hydrate, and liberates an equivalent of hydrogen; but instead of pure valeric acid being liberated at the positive plate, carbonic anhydride and a quantity of an ethereal oil, with a portion of undecomposed valeric acid, are set free. This ethereal oil consists chiefly of tetryl or dibutyl (C₄H₉)₂, the radicle of the fourth alcohol. No oxygen escapes; the valeric acid having undergone oxidation in the manner indicated by the following symbols:—

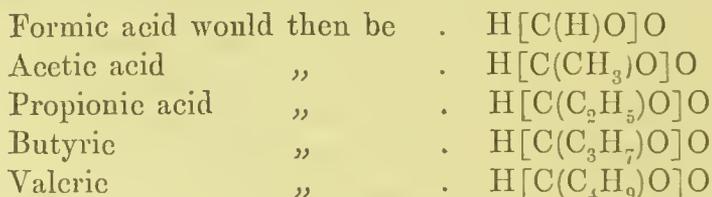


Other salts of the same class of acids present analogous phenomena; the acetates yield dimethyl; the butyrates, trityl (dipropyl); and, generally, it is found that on decomposing the salts of the stearic group by the voltaic current, they yield at the positive electrode, carbonic anhydride and the radicle of the alcohol immediately below them in the series. Hence, Kolbe was

led to regard the acids of this group as coupled oxalic acids; each acid containing the radicle of the particular alcohol which is separated during its electrolysis; for instance:—



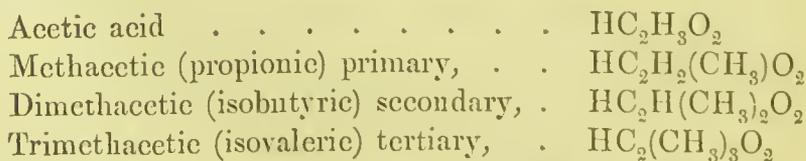
and so on. Gerhardt preferred to regard them as derivatives of formic acid, in which the hydrogen of the formic acid is displaced by the radicles of the alcohols, and this view accords equally well with the results of electrolysis. Such a supposition, however, does not indicate any theory as to the molecular constitution of formic acid; it merely states that in whatever way formic acid be constituted, the higher acids of the group are probably similar in their atomic arrangement: formic acid might therefore possibly be an oxide of a radicle which itself contains oxygen:—



All of these acids, containing more than 3 atoms of carbon, admit of isomeric modifications.

Subsequent researches, particularly those of Frankland and Duppa, have shown that it is possible to substitute several of the atoms of hydrogen by methyl or some other alcohol radicle. Acids produced by the substitution of one atom of the alcohol radicle are called *primary* acids; those in which 2 atoms of the alcohol radicle have been introduced are termed *secondary* acids; those in which 3 atoms have been introduced *tertiary* acids.

In acetic acid, for instance, three successive substitution acids are known:—



It is also found that the salts of these acids, when treated with an excess of a hydrated base such as sodic or calcic hydrate, lose an atom of carbon and furnish a hydrocarbon in the series

immediately below; in this way sodie acetate yields marsh gas and a carbonate:—



Some difficulty is experienced in obtaining the soluble salts of the higher fatty acids in a state of purity, since few of them crystallize readily from their aqueous solutions. The barium salts, when soluble, however, generally admit of being procured in well-defined forms. The solubility of the barium salts decreases as the number of atoms of carbon in the acid increases.

The sodium salts of this group of acids are all soluble in hot water, and are therefore easily prepared by boiling the fatty acid with a slight excess of the alkali. This excess of alkali may be removed from the sodium salts of the higher terms of the series, by taking advantage of their insolubility in a concentrated solution of sodie ehloride; for as soon as the solution of the soap is poured into strong brine, the sodium soap is separated in the form of a curdled granular mass, which can be easily collected on a linen filter and pressed, whilst the excess of soda remains in solution with the sodie ehloride. The coagulated soap is then to be re-dissolved in water, and salted out once or twice more: finally, the sodium salt may be purified from the sodie ehloride by re-crystallization from aleohol.

The foregoing process cannot be adopted with the potassium salts, since the potassium soaps are decomposed when mixed with sodie ehloride, a sodium soap being formed whilst potassie ehloride remains in solution. Potassie ehloride cannot be substituted for sodie ehloride in salting out, since the soaps are not insoluble in a solution of potassie ehloride. The method to be used in the preparation of the pure potassium salts consists, therefore, in boiling the acid with an excess of potassie carbonate, evaporating the solution to dryness, and then separating the potassium salt from the excess of carbonate by dissolving the soap in aleohol: on evaporation of the aleoholie solution, the potassium salt of the oily acid may generally be obtained in crystals.

The insoluble soaps may be procured by double decomposition: a pure and rather dilute solution of the potassium or of the sodium salt must be mixed with a dilute solution of a salt of the metal, such as euprie sulphate, plumbie acetate, or argentie nitrate; according as a compound of copper, of lead, or of silver, is desired.

The following table indieates the composition of the acids of the acetie series, and the melting point of each acid, with the source whence it is usually obtained:—

| Acid. | Formula. Mol. Vol. = □□ | Melting Point. | | Boiling Point. | | Whence obtained. |
|-------------|---|----------------|---------------|----------------|-------|---|
| | | ° F. | ° C. | ° F. | ° C. | |
| Formic . . | HC H O ₂ | 21·2 | - 6 | 221·5 | 105·3 | Red ants; distillation of oxalic acid; and oxidation of amylaceous and other organic bodies. Distillation of wood; oxidation of alcohol, &c. Fermentation of glycerin, &c. Butter; fermentation of lactic acid. Valerian root; oxidation of fousel oil. Butter. Castor oil by distillation, &c. Butter; cocoa-nut oil. Leaves of the geranium. Butter; oil of rue by oxidation. Cocoa-nut oil; berries of the bay tree. Nutmeg butter; cocoa-nut oil, &c. Palm oil; butter; bees' wax, &c. Most solid animal fats. Butter; oil of ground nut. Bees' wax. Bees' wax. |
| Acetic . . | HC ₂ H ₃ O ₂ | 62·6 | 17 | 242·6 | 117 | |
| Propionic . | HC ₃ H ₅ O ₂ | | | 284 | 140 | |
| Butyric . . | HC ₄ H ₇ O ₂ | below - 4 | below - 20 | 314·6 | 157 | |
| Valeric . . | HC ₅ H ₉ O ₂ | below - 4 | below - 20 | 347 | 175 | |
| Caproic . . | HC ₆ H ₁₁ O ₂ | | | 392 | 200 | |
| Çnanthylic | HC ₇ H ₁₃ O ₂ | below - 4 | below - 20 | 298·4 | 148? | |
| Caprylic . | HC ₈ H ₁₅ O ₂ | 59 | 15 | 456·8 | 236 | |
| Pelargonic | HC ₉ H ₁₇ O ₂ | | | 500 | 260 | |
| Rutic . . | HC ₁₀ H ₁₉ O ₂ | 86 | 30 | | | |
| Lauric . . | HC ₁₂ H ₂₃ O ₂ | 109·4 | 43 | | | |
| Myristic . | HC ₁₄ H ₂₇ O ₂ | 129·2 | 54 | | | |
| Palmitic . | HC ₁₆ H ₃₁ O ₂ | 143·6 | 62 | | | |
| Stearic . . | HC ₁₈ H ₃₅ O ₂ | 159 | 70·5 | | | |
| Arachidic . | HC ₂₀ H ₃₉ O ₂ | 167 | 75 | | | |
| Cerotic . . | HC ₂₇ H ₅₃ O ₂ | 174·2 | 79 | | | |
| Melissic . | HC ₃₀ H ₅₉ O ₂ | 192·2 | 89 | | | |

(1275) FORMIC ACID $\text{HCHO}_2 = 46$. *Sp. gr. of liq.* 1·2227 at 32°; *of vap.* 2·125; *Rel. wt.* 23; *Fusing pt.* 21°·2 (-6° C.); *Boil. pt.* 221°·5 (105°·3 C.).—This acid derives its name from the circumstance of its having been first obtained from the *Formica rufa*, or red ant. This insect, when irritated, ejects a concentrated acid liquid, which produces a stinging sensation when applied to the skin: the same acid is excreted by several other insects. It is also found in a free state in the leaves of the stinging-nettle (*Urtica urens*). Formic acid, however, derives its importance from the variety of chemical reactions by which it is produced. It is a frequent product of the oxidation of organic bodies; those which belong to the amylaceous group yield it by various processes of oxidation, such as by heating them with caustic potash, or with chromic acid, or with a mixture of sul-

phuric acid and black manganese oxide. When grape sugar is triturated with lead dioxide (PbO_2), water is eliminated, and a mixture of plumbic carbonate and formiate is produced. Gelatin and the albuminoid bodies also yield it, mixed with a variety of other products, when they are submitted to the oxidizing influence of chromic acid or of a mixture of sulphuric and black manganese oxide.

Preparation.—The preparation of formic acid may be effected in the laboratory in several ways.

1. Berthelot has established the important fact of the synthesis of potassic formiate by acting upon moist caustic potash by means of carbonic oxide: the gas becomes slowly absorbed when exposed in contact with the moistened alkali to a temperature of 212° ; $\text{KHO} + \text{CO}$ becoming KCHO_2 . This remarkable reaction occupies too much time to allow it to be made use of as an available source of the acid.

2. Oxalic acid, when mixed with an equal bulk of sand, and distilled, may also be employed as a source of formic acid, whilst carbonic anhydride is expelled:—



In the ordinary mode of conducting this operation a large quantity of the formic acid is itself decomposed, owing to the high temperature required to effect the distillation; water and carbonic oxide being the result of its decomposition:—

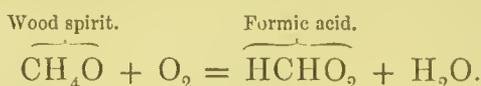


Berthelot has, however, succeeded in rendering the operation perfectly manageable; and his process has been modified by Lorin in the following manner:—

2lb. of syrupy glycerin are placed in a retort into which 2 lb. of crystallized commercial oxalic acid have been introduced: a receiver is then adapted to the retort, and the temperature is gradually raised. Decomposition begins at about 167° ($75^\circ \text{C}.$), and brisk effervescence ensues when the heat rises to about 194° ($90^\circ \text{C}.$) owing to the escape of pure carbonic anhydride, whilst diluted formic acid condenses in the receiver. As soon as the evolution of carbonic anhydride ceases, a fresh quantity of crystallized oxalic acid is added, and a more concentrated formic acid distils. The glycerin which remains in the retort may be employed as before to decompose a fresh portion of oxalic acid, and the same series of operations may be repeated with the same quantity of glycerin for an indefinite number of times. Crystal-

lized oxalic acid may thus be made to furnish two-thirds of its weight of an acid containing 50 per cent. of the normal acid. This is the best and most productive process at present known for its preparation. The principal precaution required is not to allow the temperature to rise too high: if it reach 356° or 392° (180° to 200° C.) the formic acid itself is decomposed, and an evolution of pure carbonic oxide takes place. This reaction may be taken advantage of in order to obtain pure carbonic oxide by means of oxalic acid. The glycerin acts in some manner unknown in favouring the decomposition of oxalic acid at a lower temperature than would occur if heat alone were employed to effect the metamorphosis: no chemical action, so far as is yet ascertained, takes place between the glycerin and any of the compounds concerned in the reaction (*Ann. de Chimie*, III. xlv. 484). A solution of mannite acts upon oxalic acid at 212° , in a manner similar to one of glycerin.

3. Formic acid may also be obtained by the oxidation of methylic alcohol under the influence of finely divided platinum;—



The oxidation, however, is very liable to proceed too far, water and carbonic anhydride being formed in large quantity by the oxidation of the newly-formed acid:—



4. Potassic formiate may also be obtained by heating hydrocyanic acid with an excess of an alcoholic solution of potash ($\text{HCN} + \text{KHO} + \text{H}_2\text{O} = \text{KCHO}_2 + \text{H}_3\text{N}$); the nitrogen being liberated in the form of ammonia.

5. The method which has generally been resorted to for the preparation of formic acid, is one discovered by Döbereiner, and modified by Liebig. This consists in mixing in a very capacious retort 1 part of starch,* 4 parts of black manganese oxide, and 4 of water; 4 parts of sulphuric acid are then added by degrees, when the mixture froths up to 8 or 10 times its bulk, from the abundant extrication of carbonic anhydride. When this has ceased, distillation is proceeded with, and an impure dilute formic acid distils over. It is neutralized by plumbic carbonate, and the plumbic formiate is purified by crystallization. When this salt

* Various other vegetable substances, such as sugar, chaff, bran, sawdust, tartaric acid, &c., may be substituted for starch in this operation with more or less effect.

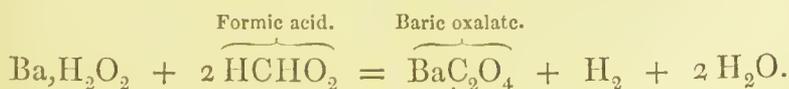
is distilled with one equivalent of sulphuric acid, the pure normal formic acid passes over.

Properties.—Normal formic acid (HCHO_2) is a fuming liquid of an irritating odour. It is extremely corrosive, and occasions vesications and painful sores if dropped upon the skin. At 21° it crystallizes in brilliant scales, and boils at $221^\circ.5$, yielding an inflammable vapour which burns with a blue flame. Formic acid yields a definite hydrate, $2\text{HCHO}_2, \text{H}_2\text{O}$.

Gerhardt was unsuccessful in his attempts to procure formic anhydride.

Formiates.—Formic acid is considered to be monobasic, but acid formiates of potassium and sodium may be obtained. All the formiates are soluble. *Sodic formiate* ($\text{NaCHO}_2, \text{H}_2\text{O}$) assumes the form of rhombic prisms, which are slightly deliquescent. *Baric formiate* (Ba_2CHO_2) crystallizes readily in brilliant anhydrous prisms. *Plumbic formiate* requires about 40 parts of cold water for solution; but it is freely soluble in hot water, from which it crystallizes in long prismatic anhydrous needles of sp. gr. 4.56. If a current of sulphuretted hydrogen be passed over this salt, while it is gently heated in a long tube, plumbic sulphide is formed, and the pure normal acid is liberated, and may be collected in a suitable receiver. A soluble *basic plumbic formiate* ($\text{Pb}_2\text{CHO}_2, 2\text{PbO}$) may also be obtained. *Cupric formiate* ($\text{Cu}_2\text{CHO}_2, 4\text{H}_2\text{O}$) crystallizes in large blue rhomboidal prisms; it forms double salts with the formiates of barium and strontium. When the dry cupric formiate is submitted to distillation it yields a very concentrated formic acid.

Formic acid is easily reconverted into oxalic acid. If a mixture of sodic formiate and baric hydrate be heated, hydrogen is evolved, and an oxalate of one of the metals is formed; for two molecules of formic acid contain the elements of one molecule of oxalic acid and two atoms of hydrogen:—



By a stronger heat the oxalic acid is decomposed, and carbonic anhydride is formed. Chlorine converts formic acid entirely into hydrochloric and carbonic acids, no chlorinated or brominated formic acids being known. Nitric acid and other oxidizing agents convert it into carbonic acid and water. Formic acid is a powerful reducing agent, the free acid at a boiling temperature reducing the salts of silver, of mercury, of gold, and of platinum, whilst pure carbonic acid is evolved. Its reducing action upon

the compounds of platinum may sometimes serve as an indication of the presence of formic acid in solution. The formiates are decomposed by strong sulphuric acid in excess, pure carbonic oxide and water being the sole products; $\text{HCHO}_2 = \text{CO} + \text{H}_2\text{O}$.

(1276) 2. ACETIC ACID ($\text{HC}_2\text{H}_3\text{O}_2 = 60$). *Sp. gr. of liq.* 1.063; *of vap. at 460°*, 2.08; *Rel. wt.* 30; *Fusing pt.* 62°·6 (18° C.); *Boil. pt.* 242°·6 (117° C.)—This acid, which derives its name from *acetum*, vinegar, was one of the earliest known of the organic acids, and it is one of the most important. In a dilute form, mixed with various impurities of vegetable origin, it constitutes ordinary vinegar, which rarely contains more than 6 per cent. of the normal acid, $\text{HC}_2\text{H}_3\text{O}_2$.

Preparation.—Acetic acid appears to exist in the juices of certain plants, such for instance as the sap of the oak, but for commercial and domestic use it is always formed artificially.

1. A large quantity of acetic acid is furnished during the destructive distillation of wood in iron retorts by means of a heat gradually raised to low redness. The wood is usually placed in these retorts in loose iron cases, by which means the charge can be rapidly introduced without loss, while the retort is still hot, and the charcoal can be withdrawn when the distillation is complete. The harder kinds of wood, particularly the oak, beech, birch, and ash, are those which yield it most abundantly, the quantity of acid varying from $1\frac{1}{2}$ to $3\frac{1}{2}$ per cent: the crude acid thus obtained is called in the arts, *pyroligneous acid*, in allusion to the mode of its formation from $\pi\tilde{\nu}\rho$, fire, and *lignum*, wood. During the operation a large quantity of tarry matter comes over, accompanied also by volatile and inflammable bodies, among which wood-spirit, methyl acetate, and acetone predominate. These bodies are condensed in suitable receivers, whilst in addition to carbonic anhydride a considerable quantity of combustible gases, composed chiefly of hydrogen and carbonic oxide, are directed into the furnaces, where they serve as fuel, and aid in heating the retorts. In about twenty-four hours, or as soon as the gases cease to escape, the loose iron cylinders containing the wood are withdrawn, and immediately closed with an air-tight cover, so as to allow the charcoal to cool excluded from the atmosphere (1536). The crude acid liquid which has been collected in the condenser is decanted from the tar, and, when submitted to distillation, furnishes *wood naphtha*, which constitutes the more volatile portions: afterwards the acetic acid is collected; the latter, however, is always accompanied by tarry

matters. In order to get rid of these, the liquid is neutralized by the addition of milk of lime, or of sodie carbonate; a quantity of tar rises to the surface of the liquid on standing; this is skimmed off, and the solution of crude acid thus obtained is evaporated, and the dry residue, if the sodium salt be used, cautiously roasted at a temperature of about 500° (260° C.) to expel the tarry matters. It is afterwards redissolved in water, decanted from the carbonaceous particles, which are allowed to subside; then re-crystallized, and submitted to distillation with sulphuric or with hydrochloric acid, the sulphuric being preferable when sodie acetate is employed, whilst hydrochloric acid answers best when calcic acetate is used. The greater part of the acetic acid consumed in the arts in this country is obtained by this method. The 'black acetate of lime' obtained by saturating the crude pyroligneous acid after the neutralized solution has been boiled with a small quantity of plumbic sulphate in order to remove colouring matter, is also extensively employed in preparing *red liquor*, a rough aluminic acetate used by the calico-printer for fixing the red dye of madder upon cloth.

Mollerat, taking advantage of the insolubility of sodic sulphate in acetic acid, obtains an acid nearly pure at once, by allowing sulphuric acid to flow into a deep vessel containing a concentrated solution of the sodic acetate in the proportion of 34 lb. or 36 lb. of oil of vitriol for every 100 lb. of sodic acetate. The sulphuric acid is caused to flow quietly under the solution of the salt without mixing with it, in order that the heat developed by the reaction shall be very moderate; the materials are then slowly mixed, and after standing for a few hours the decomposition is complete; the contents of the vessels gradually separate into two layers, the upper one containing the concentrated acetic acid, and the lower one consisting of sodic sulphate. The acetic acid is drawn off with a syphon, and is afterwards rendered pure by distillation. The last traces of empyreumatic matter may be got rid of by rectification from a small quantity of potassic dichromate.

2. In countries where alcohol is cheap, and particularly in Germany, dilute acetic acid is prepared on a large scale by the oxidation of alcohol in the manner already described (1250), the diluted spirit being made to trickle slowly over a large surface of wood shavings contained in vats of suitable construction.

(1277) 3. *Vinegar*.—The vinegar which is most esteemed for culinary purposes is that prepared from wine, from the acescent varieties of which it is extensively manufactured in France. The wine is introduced into large casks capable of containing about 100 gallons each; they are arranged in rows in a shed, the temperature of which is kept at from 77° to 86° (25° to 30° C.). The upper part of these casks is partially open to allow the access of

air. A certain quantity of good vinegar at a boiling temperature is then placed in each cask, and every eight days a few gallons of fresh wine are added until the casks are nearly two-thirds full. In about a fortnight from this time, the acidification is complete: a few gallons of the vinegar are then drawn off from each cask, and the vessels are again filled up to the same extent with a fresh quantity of the wine to be acidified. It is found that the acidification takes place much less rapidly in new casks than in those which have been used for this purpose for some time. In the old casks a quantity of a gelatinous conferva becomes developed, and this substance, which has received the name of *mother of vinegar*, favours the absorption of oxygen by the alcohol, in a manner which is supposed to be somewhat analogous to that in which platinum black acts under similar circumstances (968).

The following method of preparing vinegar, contrived by Boerhaave, is still practised extensively:—Two large vats are each provided with a false bottom supported at a height of about a foot above the floor of the vessel. Each vat is filled with vine cuttings, and *rapes*, or the footstalks and skins of grapes; the vats are then charged with wine, one of them being completely filled and the other only half filled. In this state the two vessels are left for twenty-four hours at a temperature of 75° ($23^{\circ}.9$ C.). At the expiration of this time the vat which had been left only half full is filled up from the full one, and thus every twenty-four hours a portion of the wine is transferred alternately from one vat to the other. The acidification goes on most rapidly in the vat which is only half full, and in this a sensible elevation of temperature may be perceived after the first three or four days, but it should not be allowed to rise beyond 80° ($26^{\circ}.7$ C.). The process requires from a fortnight to three weeks for its completion, according to the temperature of the atmosphere at the time. The vinegar is finally drawn off into settling casks, and when clear is fit for use.

4. Infusion of malt, weak solutions of sugar, and even mixtures of starch with yeast, furnish very good vinegar. Malt vinegar is the principal variety of vinegar employed for domestic purposes in England. According to Ure, a good vinegar for domestic use may be prepared by adding to each gallon of a syrup composed of $1\frac{1}{2}$ lb. of sugar and 1 gallon of water, a quarter of a pint of yeast. If kept for three days at a temperature between 77° and 86° (25° and 30° C.) it will be sufficiently acidified to allow of being drawn off into the ripening cask, where 1 ounce of bruised raisins and 1 ounce of crude tartar are to be

added to each gallon of liquor. When the sweet taste has quite disappeared, it should be drawn off into bottles and corked down tightly; it is stated that such vinegar will contain 5 per cent. of normal acetic acid. In all cases where vinegar is formed by the oxidation of alcohol, it is necessary to favour the absorption of oxygen and the process of acetification, by the presence of yeast, or of some albuminous matter such as is naturally contained in solution in the juices of plants or in vegetable infusions made at ordinary temperatures. A pure dilute solution of alcohol is not susceptible of acidification by exposure to the air.

Vinegar prepared by the foregoing methods from fermented or fermentable liquors contains a large quantity of foreign matters, from nearly all of which it may be freed by simple distillation: the acid liquid which comes over constitutes what is known in pharmacy as *distilled* vinegar. The strength of any vinegar is best ascertained by determining the quantity of anhydrous sodic carbonate which a given weight of it will neutralize: 100 parts of sodic carbonate corresponding to 96.2 parts by weight of acetic anhydride. Care must be taken to ascertain the absence of sulphuric or of any other acid except the acetic, when operating in this way. Commercial vinegar is allowed by law to contain $\frac{1}{1000}$ of its weight of sulphuric acid, the presence of which prevents the vinegar from becoming mouldy.

Normal acetic acid is best procured in a pure form by distilling 82 parts, or 1 molecule, of fused sodic acetate, with 98 parts or 1 molecule, of oil of vitriol, at a gentle heat, and rectifying the product from a small quantity of potassic dichromate. Dried plumbic acetate may be substituted for the sodium salt, but rather more than 1 equivalent of the salt must be taken for each equivalent of oil of vitriol, and the mixture must be digested for 24 hours before distilling. Either cupric acetate, or the acid potassic acetate, when submitted to distillation without any addition, also furnishes the concentrated acid with facility; but when prepared in this manner it is liable to be contaminated with acetone.

Harnitzky has formed acetic acid synthetically by causing carbonyl chloride, (COCl_2), mixed with marsh gas, to pass into a retort heated to 248° (120°C.); hydrochloric acid is evolved, and acetyl chloride is produced, and this, on the addition of water, yields acetic and hydrochloric acids: $\text{CH}_4 + \text{COCl}_2 = \text{C}_2\text{H}_3\text{OCl} + \text{HCl}$; and $\text{C}_2\text{H}_3\text{OCl} + \text{H}_2\text{O} = \text{C}_2\text{H}_4\text{O}_2 + \text{HCl}$. Caproic acid has also been formed by an analogous action of the carbonyl chloride upon amylenic hydride (C_5H_{12}).

(1278) *Properties of Acetic Acid.*—Normal acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$) is liquid at temperatures above 62.6° (17°C.), at which point it crystallizes in radiating tufts of plates; hence in this its

state of greatest concentration, it is frequently known as *glacial* acetic acid. It may be mingled in all proportions with water, and its density increases on dilution, until nearly one-third of its weight of water has been added, when it contains a definite hydrate ($\text{HC}_2\text{H}_3\text{O}_2, \text{H}_2\text{O}$), with a density of 1.079. If it be further diluted, the density diminishes according to the ordinary law. In consequence of this anomaly, normal acetic acid, and the same acid diluted with an equal weight of water, possess each the sp. gr. 1.063. The concentrated acid has a sharp aromatic taste, and a peculiar pungent odour; it blisters the skin if applied to it for a sufficient length of time. It boils at $242^{\circ}6$ (117° C.) and may be distilled unchanged. The vapour of this acid is inflammable, producing by its combustion, water and carbonic anhydride. The vapour of acetic acid exhibits an anomalous dilatation when exposed to a gradually rising temperature:—

| °F. | °C. | Density. | °F. | °C. | Density. |
|---------|-----|----------|----------|-----|----------|
| At 69.8 | 21 | 3.95 | At 392 | 200 | 2.22 |
| At 257 | 125 | 3.2 | At 446 | 230 | 2.09 |
| At 320 | 160 | 2.48 | At 460.4 | 238 | 2.08 |

and beyond this it undergoes no further alteration until the acid is itself decomposed. At 446° and upwards, 1 molecule of the acid follows the usual law of yielding 2 volumes of vapour (Bincau).

(1279) *Acetic Anhydride* ($\text{C}_4\text{H}_6\text{O}_3$). *Sp. gr. of liq. at* $69^{\circ}8$, (21°C.) 1.073; *of vap.* 3.47; *Rel. wt.* 51; *Boil. pt.* $279^{\circ}5$ ($137^{\circ}5$ C.).—This compound was obtained by Gerhardt by several methods; but the easiest consists in distilling 3 parts of phosphoryl chloride (POCl_3) with $6\frac{1}{2}$ of anhydrous sodic acetate, returning the liquid which passes over, upon the residue, and redistilling, until the odour of the chloride has disappeared; finally the liquid is rectified. It is a colourless, very mobile liquid of high refracting power; with a very pungent smell resembling that of acetic acid, combined with that of the hawthorn blossom. It emits a vapour which is extremely irritating to the eyes. Acetic anhydride does not mix immediately with water, but sinks through it in oily drops, which become slowly dissolved, evolving heat, and forming the ordinary hydrated acid. This anhydride gradually absorbs moisture from the air, and becomes converted into normal acetic acid. Potassium acts rapidly upon it, an inflammable gas being given off, and the compound being by degrees converted into a crystalline mass of the anhydro-potassic acetate ($2 \text{KC}_2\text{H}_3\text{O}_2, \text{C}_4\text{H}_6\text{O}_3$), or diacetate. The

same compound is also formed by dissolving dried potassic acetate in the anhydride.

(1280) *Acetates*.—Acetic acid is monobasic. Many of its salts are largely used in the arts. *Potassic acetate* ($\text{KC}_2\text{H}_3\text{O}_2=98$) which is employed medicinally as a diuretic, is an anhydrous, foliated, very deliquescent, fusible salt, abundantly soluble in alcohol. It combines with a second molecule of acetic acid when dissolved in the concentrated acid, and forms a crystallizable hydric-potassic acetate ($\text{KH} 2 \text{C}_2\text{H}_3\text{O}_2$), which when subjected to distillation is decomposed into pure normal acetic acid and normal potassic acetate. *Sodic acetate* ($\text{NaC}_2\text{H}_3\text{O}_2, 3 \text{H}_2\text{O}=82+54$; *sp. gr.* 1.40) crystallizes in oblique rhombic prisms; it fuses readily. This salt is prepared in large quantities during the purification of wood-vinegar, the crude acid being neutralized sometimes directly by means of sodic carbonate, or soda ash; but in many manufactories, after the crude acid has been neutralized by chalk and thus converted into calcic acetate, the liquid is mixed with sodic sulphate in the proportion of 2 atoms of the sulphate to 1 of the acetate; $2 \text{Na}_2\text{SO}_4 + \text{Ca} 2 \text{C}_2\text{H}_3\text{O}_2 = \text{CaNa}_3 2 \text{SO}_4 + 2 \text{NaC}_2\text{H}_3\text{O}_2$. A soluble sodic acetate is thus obtained by double decomposition, whilst a heavy crystalline sodic-calcic sulphate is formed, which can be more easily freed from the mother liquor than the pasty mass which the simple calcic sulphate would produce. *Ammonic acetate* is a very soluble salt, which is frequently used medicinally as a diaphoretic. *Baric acetate* crystallizes below 59° (15°C.) in oblique rhombic prisms ($\text{Ba} 2 \text{C}_2\text{H}_3\text{O}_2, 3 \text{H}_2\text{O}$); at higher temperatures its crystals assume the form of flattened prisms of *sp. gr.* 2.19, and retain only 1 H_2O ; it is more soluble in cold than in hot water, and is slightly soluble in alcohol; it is occasionally used as a precipitant for sulphuric acid; when distilled it furnishes acetone. *Calcic acetate* ($\text{Ca} 2 \text{C}_2\text{H}_3\text{O}_2=158$) crystallizes in silky, anhydrous needles, which are very soluble in water; if heated to 248° (120°C.) it becomes strongly phosphorescent by gentle friction.

Acetates of Aluminum.—These compounds are extensively manufactured for the use of the dyer and calico-printer. The common *red mordant* is prepared by precipitating 100 parts of alum in solution by means of 120 of crystallized plumbic acetate: the potassic sulphate of the alum remains undecomposed in the solution. Sometimes aluminic sulphate is used instead of alum. Crude calcic acetate is also extensively substituted for plumbic acetate in this operation; calcic sulphate is precipitated, and aluminic acetate remains in solution. When this liquor is

used as a mordant it is thickened with gum, and applied by means of blocks to the cloth. The aluminic acetates have been carefully studied by Crum (*Q. J. Chem. Soc.*, vi. 216), who has proved the existence of two insoluble aluminic diacetates ($\text{Al}_2\text{O}_3, 4\text{C}_2\text{H}_4\text{O}_2, 3\text{H}_2\text{O}$), and ($\text{Al}_2\text{O}_3, 4\text{C}_2\text{H}_4\text{O}_2$), besides a soluble diacetate ($\text{Al}_2\text{O}_3, 4\text{C}_2\text{H}_4\text{O}_2, 2\text{H}_2\text{O}$). The easiest method of preparing the commercial aluminic acetate consists in decomposing a solution of aluminic trisulphate with one of plumbic acetate: but although 3 equivalents of sulphuric acid are thus removed, and 3 equivalents of acetic acid liberated, no solid aluminic triacetate can be obtained from this liquid. Indeed Crum is of opinion that, even when in solution, the salt which is thus formed is a diacetate, mixed with an equivalent of free acetic acid, since the liquid has a powerful odour of acetic acid; $\text{Al}_2\text{O}_3, 3\text{SO}_3 + 3(\text{Pb}_2\text{C}_2\text{H}_3\text{O}_2) + 3\text{H}_2\text{O} = 3\text{PbSO}_4 + \text{Al}_2\text{O}_3, 4\text{C}_2\text{H}_4\text{O}_2 + 2\text{HC}_2\text{H}_3\text{O}_2$.

If a concentrated solution, containing from 4 to 5 per cent. of alumina, prepared in the manner just directed, in such atomic proportions as to contain aluminic triacetate, be purified from traces of lead by sulphuretted hydrogen, and from those of sulphuric acid by baric acetate, a liquid is obtained which, when kept at between 59° and $69^\circ\cdot 8$ (15° and 21° C.) for a few days, gradually deposits a white coating upon the sides of the vessel: this deposit, when allowed to become dry spontaneously, forms white hard plates resembling porcelain in appearance. This is a hydrated aluminic diacetate ($\text{Al}_2\text{O}_3, 4\text{C}_2\text{H}_4\text{O}_2, 3\text{H}_2\text{O}$), which is insoluble in water, but soluble in nitric acid. If the original solution of aluminic triacetate be boiled, a heavy white powder is rapidly deposited, and the solution retains scarcely a trace of alumina: Crum found this precipitate to be a different aluminic diacetate ($\text{Al}_2\text{O}_3, 4\text{C}_2\text{H}_4\text{O}_2$). When dilute solutions of the aluminic acetate are employed, no precipitate is occasioned unless a considerable excess of free acetic acid be added. When the solution of the triacetate is evaporated rapidly by spreading it in very thin films over a sheet of glass, the heat not being allowed to rise above 100° ($37^\circ\cdot 8$ C.), and the oily drops as they run together being constantly spread out with a thin platinum knife, a dry substance may be obtained in transparent scales ($\text{Al}_2\text{O}_3, 4\text{C}_2\text{H}_4\text{O}_2, 2\text{H}_2\text{O}$), which may be redissolved easily and completely in water.

From this compound, the remarkable soluble aluminic hydrate, previously alluded to (662), may be prepared in the following manner:—If a dilute solution of this soluble aluminic diacetate, containing $\frac{1}{200}$ of its weight of alumina, be placed in a closed vessel and immersed in water maintained at the boiling point, for about ten days, the solution gradually loses its astringent taste, and acquires a strong odour of acetic acid. If this liquid be now diluted with rather more than an equal bulk of water, and be boiled briskly in a shallow dish, the layer of liquid not being more than a quarter of an inch in depth, and water being supplied in proportion as it evaporates, the acetic acid may in about an hour and a half be driven off so as to be no longer sensible to litmus paper. The liquid remains limpid and transparent, but is quite tasteless. When 1 grain of sulphuric acid in 1000 grains of water is mixed with 8000 grains of such a solution (a quantity which contains 20 grains of alumina), the whole is converted into a solid, transparent jelly: by pressure in a bag, the volume of this jelly may be reduced to one-sixtieth of its original bulk, the solid coagulum retaining nearly the whole of the sulphuric acid, which amounts to about 1 equivalent of the acid to 15 of

alumina. Two molecules of the tribasic citric acid produce as powerful an effect in coagulating the solution as 3 molecules of sulphuric acid, and 1 of tartaric acid as much as 1 of sulphuric acid, but of hydrochloric or of nitric acid not less than 600 molecules are required to produce an effect of coagulation equal to that occasioned by 1 of sulphuric acid. One grain of potash dissolved in 1000 of water coagulates 9000 grains of the solution; and soda, ammonia, and lime have an equally powerful effect. An excess of potash, as well as of sulphuric or hydrochloric acid, dissolves the coagulum, converting the alumina into its ordinary modification. Solutions of the sulphates coagulate the solution as readily as free sulphuric acid.

Alumina, in this soluble condition, has lost its power of acting as a mordant.

When the precipitated aluminic diacetate is kept for an hour or two in 200 parts of boiling water with constant agitation, it becomes gradually dissolved, and may then, by digestion, be converted into free acetic acid and the soluble hydrate of alumina. The soluble hydrate of alumina, when evaporated at 212° , retains 2 atoms of water ($\text{Al}_2\text{O}_3, 2 \text{H}_2\text{O}$).

Several other acetates are also used as mordants in calico-printing; for example, those of *manganese*, *zinc* ($\text{Zn}, 2 \text{C}_2\text{H}_3\text{O}_2, 3 \text{H}_2\text{O}$), and *iron*. Acetic acid dissolves iron readily with evolution of hydrogen; the crude iron acetate, prepared by dissolving iron hoops in raw wood vinegar, is employed for preserving wood by Boucherie's process (1110). *Ferrous acetate* crystallizes in silky needles, which absorb oxygen rapidly. *Ferric acetate* is of a deep red colour.

Acetates of Lead.—Acetic acid forms several compounds with plumbic oxide—viz., the

| | | | |
|---------------------------|-------|---------------------------------------|--|
| Normal acetate . . . | Pb | 2 $\text{C}_2\text{H}_3\text{O}_2$, | 3 H_2O |
| Sesquibasic acetate . . . | 2 (Pb | 2 $\text{C}_2\text{H}_3\text{O}_2$), | PbO, H_2O |
| Tribasic acetate . . . | Pb | 2 $\text{C}_2\text{H}_3\text{O}_2$, | 2 PbO, H_2O (dried at 60°) |
| Hexabasic acetate . . . | Pb | 2 $\text{C}_2\text{H}_3\text{O}_2$, | 5 PbO, 3 H_2O . |

The normal acetate and the tribasic acetate are important salts.

Normal plumbic acetate ($\text{Pb} 2 \text{C}_2\text{H}_3\text{O}_2, 3 \text{H}_2\text{O} = 325 + 54$) may be procured by dissolving litharge in excess of acetic acid: by evaporating the solution, the salt may be obtained crystallized in right rhombic prisms, which are sometimes opaque, but generally transparent. Its more usual form, however, is that of a mass of confused minute white crystals, much resembling loaf-sugar; it also has a sweetish metallic taste, and from this circumstance it derives its common name of *sygar of lead*: when exposed to the air it is efflorescent. It is soluble in less than twice its weight of water, and is also freely soluble in alcohol. When heated it first becomes anhydrous, and then fuses to a clear liquid. If the heat be raised further, acetone, $\text{C}_3\text{H}_6\text{O}$, is formed, carbonic anhydride escapes, and the mass becomes solid. In this state it consists of *sesquibasic plumbic acetate* ($2 [\text{Pb} 2 \text{C}_2\text{H}_3\text{O}_2], \text{PbO}, \text{H}_2\text{O}$); this salt

is readily soluble both in alcohol and in water: it has a distinctly alkaline reaction, and crystallizes in pearly scales; the same salt may also be formed by adding the normal acetate in the proportion of 57 parts, or 3 molecules, to $38\frac{1}{2}$, or 1 molecule, of a concentrated boiling solution of the tribasic plumbic acetate.

Tribasic plumbic acetate ($\text{Pb } 2 \text{ C}_2\text{H}_3\text{O}_2, 2 \text{ PbO}, \text{H}_2\text{O}$), formerly known as *Goulard's Extract*, is prepared by digesting 7 parts of finely powdered litharge with 6 parts of normal plumbic acetate dissolved in 30 parts of water: it has a strongly alkaline reaction. The solution of the oxide is effected much more rapidly if a silver basin be used than if one of glass or porcelain be employed. The salt crystallizes in opaque needles. Payen obtained it in well-formed crystals, by adding a solution of ammonia to a hot solution of 1 part of the normal acetate in 3 parts of water. Tribasic plumbic acetate is insoluble in alcohol. Paper dipped in its aqueous solution and dried, burns like tinder when kindled. Solutions both of this and of the preceding salt are decomposed by carbonic acid; normal plumbic acetate is left in the liquid; and hydrated plumbic oxycarbonate is precipitated in silky, white, insoluble crystals. This fact forms the basis of the methods for preparing white lead (907).

Acetates of Copper.—Four of these compounds may be obtained, viz.—

| | | |
|----------------------------------|-----------|--|
| Normal cupric acetate (verditer) | | $\text{Cu } 2 \text{ C}_2\text{H}_3\text{O}_2, \text{H}_2\text{O}$ |
| Sesquibasic acetate | | $2 (\text{Cu } 2 \text{ C}_2\text{H}_3\text{O}_2), \text{CuO}, 6 \text{ H}_2\text{O}$ |
| Dibasic acetate (verdigris) | | $\text{Cu } 2 \text{ C}_2\text{H}_3\text{O}_2, \text{CuO}, 6 \text{ H}_2\text{O}$ |
| Tribasic acetate | | $2 (\text{Cu } 2 \text{ C}_2\text{H}_3\text{O}_2), 4 \text{ CuO}, 3 \text{ H}_2\text{O}$. |

Normal cupric acetate ($\text{Cu } 2 \text{ C}_2\text{H}_3\text{O}_2, \text{H}_2\text{O} = 181.5 + 18$) is sold in commerce under the name of *verditer*. It is prepared by mixing a solution of 1 equivalent of cupric sulphate with one of plumbic acetate, also in solution, and evaporating the clear liquid decanted from the plumbic sulphate; it yields oblique rhombic prisms of a fine green colour. By exposure to the air, a portion of the acid escapes, and the crystals become covered with an efflorescence composed of dibasic cupric acetate. If the normal acetate be crystallized from an acid solution below $39^{\circ}.2$ (4°C.) a blue salt is obtained with $5 \text{ H}_2\text{O}$.

Dibasic cupric acetate, or *verdigris* ($\text{Cu } 2 \text{ C}_2\text{H}_3\text{O}_2, \text{CuO}, 6 \text{ H}_2\text{O}$) is prepared for commercial purposes by piling up sheets of copper, interposing between the successive sheets a layer of the fermenting husk of raisins: after a lapse of some weeks the plates of copper become covered with a crust of the salt: this is detached,

made into a thick paste with vinegar, and pressed into moulds. The mass thus obtained is of a bluish-green colour; it is tough, and is reduced to powder with difficulty. In this mode of preparing the salt, the alcohol contained in the grape skins becomes slowly oxidized and converted into acetic acid; the metal also absorbs oxygen gradually from the air; and the oxide thus formed combines with the acetic acid.

Verdigris, when treated with water, is decomposed into an insoluble tribasic cupric acetate, and a soluble *sesquibasic acetate* $2(\text{Cu}_2\text{C}_2\text{H}_3\text{O}_2), \text{CuO}, 6\text{H}_2\text{O}$: the latter salt may be obtained in crystals on evaporating the solution.

The *tribasic acetate* ($2[\text{Cu}_2\text{C}_2\text{H}_3\text{O}_2], 4\text{CuO}, 3\text{H}_2\text{O}$) is the most stable of the acetates of copper; it assumes the form either of bluish grey needles, or of a green crystalline powder: when heated to 212° it becomes anhydrous.

The normal cupric acetate unites with cupric arsenite forming *Schweinfurt green*, $\text{Cu}_2\text{C}_2\text{H}_3\text{O}_2, 3(\text{Cu}_2\text{AsO}_2)$. It may be obtained by mingling boiling solutions of equal weights of arsenious anhydride and cupric acetate, and adding to the mixture an equal bulk of cold water: if it be allowed to stand for some days a beautiful crystalline green pigment is produced.

Mercurous Acetate ($\text{HgC}_2\text{H}_3\text{O}_2$) is the least soluble of the acetates; it is dissolved readily by boiling water, but it is partially decomposed by ebullition of the solution, and converted into a mixture of metallic mercury and a sparingly soluble basic acetate. This mercurous acetate crystallizes in silvery scales, which are quickly blackened by exposure to light.

Argentiac Acetate ($\text{AgC}_2\text{H}_3\text{O}_2 = 167$) is occasionally employed as a reagent; it is sparingly soluble in cold water, but is readily dissolved by hot water, which on cooling deposits it in thin, flexible, anhydrous, silky needles. It is readily obtained by mixing a concentrated solution of argentic nitrate with a solution of potassic or sodic acetate.

Tests for Acetic Acid.—The acetates are distinguished by the pungent odour of acetic acid which they emit when heated with sulphuric acid. When heated with lime they furnish acetone (1259), which has a peculiar and characteristic odour. If distilled with caustic potash they yield marsh gas; and upon this reaction the best method of obtaining this gas is founded (491).

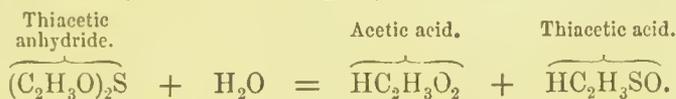
Cold solutions of the acetates give with mercurous nitrate a precipitate of the mercurous acetate. Another property of the acid, though less characteristic, is the formation with plumbic oxide of a soluble basic salt, with an alkaline reaction.

Some of the acetates, such as those of barium and strontium, form double salts with the nitrates of these bases when equivalent quantities of the two salts are dissolved in water and allowed to

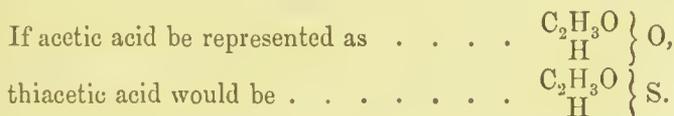
of 4 volumes of crystallizable acetic acid with 1 volume of bromine, and distilling the product; hydrobromic acid escapes in abundance, and on raising the temperature, the unaltered acetic acid passes over. When the boiling point reaches 406°, pure bromacetic acid is obtained; it crystallizes in rhombohedra, which are very deliquescent, and contaminated with dibromacetic acid. (Perkin and Duppa, *Q. J. Chem. Soc.*, xi. 22.)

(1282) *Sulphacetic* or *Acetosulphuric Acid* ($H_2C_2H_2SO_5 = C_2H_4O_2SO_3$).—Acetic acid combines with sulphuric anhydride and forms a dibasic acid, which may be obtained crystallized in deliquescent needles: it forms crystallizable salts. The solution of this acid is not decomposed by ebullition: it gives no precipitate with salts of lead or of calcium, but with barium it forms a crystalline compound of sparing solubility. Argentic acetosulphate crystallizes readily in long flattened prisms.

(1283) *Thiacetic Acid* ($C_2H_4SO = HC_2H_3OS$). *Boil. pt. about 200°* (93°·3 C.).—When normal acetic acid is acted upon by phosphorous sulphide (P_2S_3), or the phosphoric sulphide (P_2S_5), a colourless liquid is obtained which has a mingled odour of acetic acid and sulphuretted hydrogen, with an acid reaction and a sour taste: it is soluble in water in all proportions. Thiacetic acid is monobasic; when heated upon granulated zinc, the metal is dissolved with evolution of hydrogen; when added to a strong solution of a soluble salt of lead, a sparingly soluble lead salt is precipitated, which readily undergoes decomposition, even when dry; whilst plumbic sulphide is separated. *Thiacetic anhydride* [$(C_2H_3O)_2S$; *Boil. pt. 249°·8* (121° C.)] is obtained by distilling phosphoric sulphide with acetic anhydride. It is a colourless oily liquid, which emits an odour similar to that of thiacetic acid. It is heavier than water, which gradually decomposes it into a mixture of hydrated acetic and thiacetic acids. (Kekulé, *Proceed. Roy. Soc.*, vol. vii. p. 37.)



This compound is only one of a series which may be obtained by similar means from other acids homologous with the acetic: in this way *thioformic acid* (HCHSO) has been obtained. Thiacetic acid may be regarded as ordinary acetic acid in which the oxygen external to the radicle has been displaced by its equivalent of sulphur:—

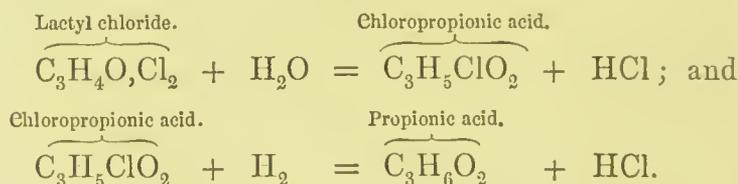


(1284) 3. *Propionic** or *Metacetic Acid*, $HC_3H_5O_2 = 74$. *Boil. pt. 284°* (140° C.).—This acid is formed in a variety of ways; for example. 1. It is one of the products of the oxidation of oleic acid. 2. It is also obtained by the action of hydrochloric acid or of potash upon hydrocyanic ether: in the latter case, ammonia is liberated and potassic propionate is formed:—



* From $\pi\rho\tilde{\omega}\tau\omicron\varsigma$ first, $\pi\acute{\iota}\omega\nu$ fat, because the first or simplest in the series of the true fatty acids.

a concentrated alcoholic solution of potash is to be heated in a tubulated retort, and ethyl cyanide added drop by drop; the distillate is to be returned into the retort until the odour of ethyl cyanide has disappeared: the residue of potassic propionate when distilled with syrupy phosphoric acid, yields pure propionic acid. 3. The action of methyl iodide on sodacetic ether yields propionic ether (1274). 4. Propionic acid may also be obtained as Wanklyn has shown, by acting upon sodium-ethyl by means of carbonic anhydride (1184), when sodic propionate is the result. 5. Another interesting reaction which furnishes propionic acid is that which establishes the connexion between lactic and propionic acids;* when lactyl chloride is decomposed by water it furnishes chloropropionic acid, and if treated with finely granulated zinc the chloropropionic acid is reduced to propionic acid (Ulrich):—



If the liquid be decanted from the zinc as soon as the odour of the chlorinated compound has disappeared, and be distilled, propionic acid, with traces of hydrochloric acid, comes over freely. A more convenient means of obtaining propionic acid consists in distilling 3.5 parts of lactic acid with 4 of phosphorus diiodide. Iodine and water are liberated, and propionic acid is formed, while phosphorous acid remains in the retort.

6. Strecker has likewise observed the formation of this acid during the fermentation of a mixture of calcic lactate and mannite, which had been set aside with the view of procuring butyric acid. Crude calcic tartrate in warm weather frequently undergoes a species of fermentation, and furnishes propionic acid. 7. The acid is also produced during the fermentation of glycerin (1238). 8. Metacetone ($\text{C}_6\text{H}_{10}\text{O}$; 1079) when oxidized with a mixture of potassic dichromate and sulphuric acid, also yields the acid, which derived its name of metacetic acid from this circumstance. Propionic acid, when prepared from the last three sources, is liable to be contaminated with acetic and other acids homologous with it. The acetic acid may be removed by saturating the distilled liquid with sodic carbonate, and evaporating to the crystallizing point; the sodic acetate crystallizes out, whilst the propionate remains in the mother liquor, from which propionic acid may be procured by distillation with sulphuric acid.

Normal propionic acid ($\text{HC}_3\text{H}_5\text{O}_2$) crystallizes in plates which melt on the application of a gentle heat, and may be distilled unaltered: it has a powerfully acid taste, and a pungent odour

* Lactic acid, $\text{C}_3\text{H}_6\text{O}_3$, contains 1 atom more of oxygen than the propionic, $\text{C}_3\text{H}_6\text{O}_2$. Kolbe calls it *oxypropionic acid*.

which is intermediate between that of butyric and of acrylic acids. Propionic acid is largely soluble in water, but, when this liquid is saturated with it, the excess of the acid floats like an oil upon the surface.

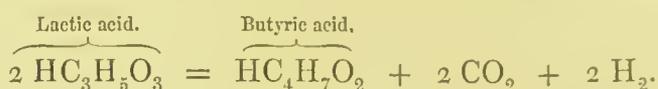
Most of the propionates are soluble and crystallizable. The propionates of *potassium* and *sodium* are deliquescent. *Calcic propionate* ($\text{Ca } 2 \text{ C}_3\text{H}_5\text{O}_2, \text{H}_2\text{O}$) crystallizes in long beautiful prisms. *Baric propionate* crystallizes in anhydrous prisms, which when thrown into water are dissolved with a gyratory motion: by spontaneous evaporation it may also be obtained in large prisms containing H_2O . *Cupric propionate* ($\text{Cu } 2 \text{ C}_3\text{H}_5\text{O}_2, \text{H}_2\text{O}$) crystallizes in oblique prisms, which are readily soluble in alcohol, but very slightly so in water. *Argentie propionate* is anhydrous, and less soluble than the acetate; it crystallizes in tufts of short needles, and blackens by exposure to light; but the acetate and the propionate of silver cannot be separated by crystallization, for they unite and form a double salt, which is deposited from a hot solution in brilliant dendritic needles.

A nitro-propionic acid [$\text{HC}_3\text{H}_4(\text{NO}_2)\text{O}_2$] may be obtained as a heavy yellow, sparingly soluble oil, by treating butyrene, $\text{C}_7\text{H}_{14}\text{O}$, with nitric acid. Its salts detonate feebly when heated.

(1285) 4. BUTYRIC ACID ($\text{HC}_4\text{H}_7\text{O}_2=88$). *Sp. gr. of liq. at* 32° , 0.9886; *of vap.* 3.07; *Rel. wt.* 44; *Boil. pt.* $314^\circ.6$, (157°C .) Kopp.—This acid is a liquid which, at 59° , has the sp. gr. 0.963; it remains fluid at -4° (20°C .), and volatilizes at ordinary temperatures with a strong smell of rancid butter; it may be distilled unchanged. Butyric acid has a sharp acid taste, and a corrosive action upon the skin; it is readily soluble in water, alcohol, and ether: the addition of a solution of hydrochloric acid or of calcic chloride to its aqueous solution causes the butyric acid to separate and rise to the surface.

Preparation.—1. Butyric acid exists ready formed in certain fruits, and it is one of the products of oxidation of azotised matters, such as fibrin or casein, when treated with black oxide of manganese and sulphuric acid. 2. It is also obtained amongst the results of the action of nitric upon oleic acid. 3. All substances which furnish lactic acid may be made to yield the butyric; and it is frequently developed during the fermentation or decay of many mucilaginous and amylaceous roots, such as the potato and the mallow. 4. Butyric acid may be obtained at pleasure in large quantities, by the following method of fermenting sugar discovered by Pelouze and Gélis (*Ann. de Chimie*, III. x. 434). A solution of 4 lb. of sugar in a quantity of water sufficient to form a liquid of sp. gr. 1.070, is mixed with a quantity of poor cheese which in its dry state would contain casein to the extent of one-eighth of the weight of the sugar used, and 2 lb. of chalk; the whole is then exposed for some weeks to a temperature ranging between 77° and 95° (25° and 35°C .). The liquid

speedily becomes ropy, lactic acid is formed abundantly, and is immediately neutralized by the lime, the mixture becoming semi-solid owing to the formation of crystals of calcic lactate; this salt in turn undergoes decomposition, and when this second reaction commences, a mixture of carbonic anhydride and hydrogen escapes from the fermenting mass, whilst calcic butyrate is formed in abundance. This reaction is explained by the following equation:



Pasteur believes this conversion of lactic into butyric acid to be effected by the agency of a special ferment consisting of infusorial animaleculæ in the form of small cylindrical bodies, varying in length from $\frac{1}{120000}$ to $\frac{1}{12000}$ of an inch; they sometimes are connected together in chains of four or more.

The acid is easily obtained in a state of purity by distilling 3 parts of calcic butyrate thus produced with 12 parts of water and 1 of concentrated hydrochloric acid: about 3 parts of liquid should be distilled over. If the distillate be digested upon an excess of calcic chloride, the solution which is formed separates into two layers, the upper one of which contains the butyric acid: it must be decanted into a retort and distilled: the first portions which pass over are aqueous, but when the temperature rises to $327^{\circ}2$ (164° C.), (Gélin and Pelouze), the acid passes over in the concentrated form ($\text{HC}_4\text{H}_7\text{O}_2$.) 5. It was originally procured from butter by saponifying that portion of it which remains liquid at 60° , adding hydrochloric or tartaric acid, and distilling; the distillate, consisting of a mixture of caproic, caprylic, and ricinic with butyric acid, is treated with baryta, and the barium salts separated by crystallization in the mode directed under the head caproic acid (1287). 6. It may also be obtained as butyric ether when sodacetic ether is decomposed by ethyl iodide.

Butyric Anhydride ($\text{C}_8\text{H}_{14}\text{O}_3$). *Sp. gr. of liq. at* $53^{\circ}6$ (12° C.), 0.978 ; *of vap.* 5.38 ; *Rel. wt.* 79 ; *Boil. pt.* 374° (190° C.).—This body may be obtained by distilling a mixture of 5 parts of benzoyl chloride, and 8 of dry sodic butyrate; it forms a colourless, very mobile liquid, with an odour which resembles that of the pine-apple. When exposed to the air it absorbs moisture, and acquires the repulsive odour of the hydrated acid.

Butyrates.—Butyric acid is monobasic. Its salts when dry are without odour; but when moist they have the smell of rancid butter. Most of them are very freely soluble; when reduced to powder, and thrown upon water, they are dissolved with a rapid

gyratory motion. *Baric butyrate* crystallizes, by spontaneous evaporation, in long prisms, with $4\text{H}_2\text{O}$; when formed by the cooling of a hot solution, it retains only $2\text{H}_2\text{O}$.* *Zincic butyrate* crystallizes in anhydrous, very soluble, pearly tables, which when heated to 212° fuse and then lose part of their acid, after which a portion of the salt undergoes sublimation in the anhydrous form. *Cupric butyrate* ($\text{Cu}_2\text{C}_4\text{H}_7\text{O}_2, 2\text{H}_2\text{O}$) is bluish green and sparingly soluble. With *lead*, butyric acid forms two anhydrous salts, one of which is normal ($\text{Pb}_2\text{C}_4\text{H}_7\text{O}_2$), while the other is basic ($\text{Pb}_2\text{C}_4\text{H}_7\text{O}_2, 2\text{PbO}$). Both *argentic* and *mercurous* butyrate are sparingly soluble; they crystallize in brilliant plates. But the most characteristic salt of butyric acid is *calcic butyrate*; it forms fusible colourless needles, which are rendered anhydrous by a temperature of 284° (140°C .): this salt is much less soluble in boiling water than it is at ordinary temperatures, and when its aqueous solution is boiled, a large proportion of the salt is precipitated, and is redissolved as the liquor cools. Butyric acid is remarkable for the facility with which it effects the etherification of alcohol. If a mixture of 2 parts of concentrated butyric acid, 2 of alcohol, and 1 part of oil of vitriol be agitated together, butyric ether is formed and rises to the surface on standing (1157). Many of the butyrates when submitted to dry distillation yield *butyrone* ($\text{C}_7\text{H}_{14}\text{O}$); it is a colourless liquid insoluble in water: *Sp. gr. of liq.* 0.83; *of vap.* 3.99; *Boil. pt.* $291^\circ.2$ (144°C .)

Chlorine acts readily upon butyric acid in the sunlight, and forms two substitution acids which are analogous to butyric acid, and which yield corresponding monobasic salts; these acids are the *dichlorobutyric* ($\text{HC}_4\text{H}_5\text{Cl}_2\text{O}_2$), and *tetrachlorobutyric* acids ($\text{HC}_4\text{H}_3\text{Cl}_4\text{O}_2$). Nitric acid converts the butyric into *nitrobutyric* acid ($\text{HC}_4\text{H}_5\text{NO}_2\text{O}_2$).

Isobutyric Acid [$\text{HC}_2\text{H}(\text{CH}_3)_2\text{O}_2$; *Sp. gr. of liq. at* 32° , 0.9598; *Boil. pt.* $309^\circ.2$ (154°C .)] may be obtained by decomposing iso-propyl cyanide [$\text{CH}(\text{CH}_3)_2\text{CN}$] with caustic potash. It has a less offensive smell than true butyric acid, and its calcium salt crystallizes from a hot aqueous solution on cooling. It is regarded as a secondary acid.

(1286) 5. VALERIC OR VALERIANIC ACID, $\text{HC}_5\text{H}_9\text{O}_2 = 102$. *Sp. gr. of liq.* 0.937; *of vap.* 3.66; *Rel. wt.* 51; *Boil. pt.* 347° (175°C .).— This compound is identical with the *phocenic* acid obtained by Chevreul from some of the fish oils. It occurs also (associated with a peculiar essential oil) in the root of the *Valeriana officinalis*; it

* On one occasion I obtained it crystallized in anhydrous square tables, presenting the appearance of the square base of the octahedron. They were, however, in reality macled crystals formed by the junction of two nearly rectangular rhombic tables. In other cases the salt forms fibrous crystals which are also anhydrous.

is likewise present in the berries of the guelder-rose (*Viburnum opulus*). If valerian root be distilled with water acidulated with dilute sulphuric acid, valeric acid passes over into the receiver: its quantity may be increased by digesting the root with a mixture of dilute sulphuric acid and potassic dichromate, since the valerian root contains a compound (valerol, $C_6H_{10}O$), which by oxidation becomes converted into valeric acid. Valeric acid is also a frequent product of the oxidation of oleic acid and of other fatty acids; it is likewise often present in decaying cheese, but it is most readily obtained by the action of oxidizing agents on amylic alcohol. If the vapours of fousel oil be sent through a tube filled with a mixture of lime and caustic soda and heated to 400° ($204^\circ.5$ C.), sodic valerate is produced, and hydrogen, mixed with carburetted hydrogen, is evolved. When cold, the mass must be plunged at once into water, to prevent it from taking fire by access of air; and the solution must be distilled with dilute sulphuric acid; valeric acid then passes over into the receiver. A still easier method of preparing it consists in distilling fousel oil with a mixture of dilute sulphuric acid and potassic dichromate; valeric acid, mixed with amyl valerate ($C_5H_{11}, C_5H_9O_2$) passes over, and the latter may be decomposed by caustic potash into potassic valerate and fousel oil. Potassic valerate when distilled with sulphuric acid furnishes pure valeric acid.

Valeric acid is a limpid colourless oil, which remains liquid at 0° F. It has a powerful odour allied to that of valerian root, and a burning taste. It may be distilled without change. It is sparingly soluble in water, but is soluble in alcohol and in ether in all proportions: it is also freely soluble in strong acetic acid. Valeric acid resembles the acetic in its property of forming a definite hydrate ($HC_5H_9O_2, H_2O$), which is obtained when the acid is liberated by a stronger acid from an aqueous solution of its salts.

Valeric Anhydride [$(C_5H_9O)_2$]; *Sp. gr. of liq.* 0.934; *of vap.* 6.23; *Rel. wt.* 93; *Boil. pt.* 419° (215° C.) is a colourless, mobile liquid, with an agreeable odour of apples; the alkalies in the presence of water convert it rapidly into a normal salt of the acid. This compound is easily obtained by allowing 1 part of phosphoryl chloride ($POCl_3$) to fall drop by drop upon 6 parts of dry potassic valerate; washing the product with a weak solution of sodic carbonate, and then dissolving out the anhydride with ether: the ethereal solution is agitated with fused calcic chloride in order to remove water; and on expelling the ether by heat, the anhydride is left in a state of purity.

The valerates when dry are destitute of odour, they have a sweetish taste, and are easily recognized by the peculiar smell of valeric acid which they emit when heated with dilute sulphuric acid. These salts, with the exception of argentic and mercurous

valerate, are soluble in water, and many of them are soluble in alcohol. Those of the alkalies are deliquescent, and crystallize with difficulty; they fuse readily on the application of a moderate heat. *Baric* valerate ($\text{Ba } 2 \text{ C}_5\text{H}_9\text{O}_2, 2 \text{ H}_2\text{O}$) crystallizes in prisms, which are brittle. *Zincic* valerate crystallizes in anhydrous plates; this salt, as well as some others of the valerates, has been used medicinally.

An ether of a tertiary isomeric valeric acid, the *trimethacetic* ($\text{HC}_2(\text{CH}_3)_3\text{O}_2$), may be obtained by decomposing trisodacetic ether with methyl iodide: $\text{C}_2\text{H}_5, \text{C}_2\text{Na}_3\text{O}_2 + 3 \text{CH}_3\text{I} = \text{C}_2\text{H}_5, \text{C}_2(\text{CH}_3)_3\text{O}_2 + 3 \text{NaI}$.

Chlorine acts upon valeric acid by displacing a portion of its hydrogen; by this means two new substitution compounds may be formed. Both of these bodies retain the monobasic character of valeric acid. They were termed by Dumas, *chlorovaleric* ($\text{HC}_5\text{H}_6\text{Cl}_3\text{O}_2$) and *chlorovalerosic* ($\text{HC}_5\text{H}_5\text{Cl}_4\text{O}_2$) acids; both of them form stable, well-defined salts.

When valeric acid is boiled for several days with concentrated nitric acid it becomes decomposed, and a great part is converted into *nitrovaleric acid* [$\text{HC}_5\text{H}_8(\text{NO}_2)\text{O}_2$], which is volatile without decomposition; it crystallizes in beautiful rhomboidal tables, and forms definite salts.

(1287) 6. *Caproic Acid* ($\text{HC}_6\text{H}_{11}\text{O}_2 = 116$). *Sp. gr. of vap.* 4.26; *Rel. wt.* 58; *Boil. pt.* about 392° (200°C).—This acid derives its name from *capra*, a goat, the smell of which animal it slightly resembles; it is liquid at ordinary temperatures: it has a characteristic odour of acid sweat, and has a pungent and sweetish taste; the concentrated acid bleaches those parts of the tongue which it touches. It may be distilled unchanged. Water dissolves it to a small extent. Caproic acid is obtained in small quantity by the saponification of butter, or of cocoa-nut oil, and it is amongst the volatile products of the oxidation of oleic by nitric acid. It may be obtained from butter by pressing out the portion which remains liquid at 59° (15°C), then saponifying this oil, and distilling the soap with sulphuric acid; rucic, caprylic, caproic, and butyric acids are thus obtained in the liquid which passes over. The distillate is to be neutralized with baryta, which forms a soluble caproate, whilst the caprylate and rutate are nearly insoluble. The caproate and butyrate are separated by crystallization, the caproate assuming the form of delicate, brilliant, anhydrous needles, if the solution be evaporated above 86° (30°C), whilst if left to spontaneous evaporation it forms hexagonal plates which effloresce in the atmosphere. Anhydrous baric caproate, if distilled with phosphoric chloride, yields *caproic anhydride* ($\text{C}_{12}\text{H}_{22}\text{O}_3$) in the form of a colourless neutral oil, lighter than water, by which it is rapidly converted into the normal acid.

Argentio caproate is sparingly soluble, but most of the other salts of the acid are readily dissolved by water.

An *isocaproic acid*, corresponding to isobutyric, has also been obtained by decomposing amylene hydrocyanate by means of potash; $\text{C}_6\text{H}_{10}\text{HCN} + \text{KHO} + \text{H}_2\text{O} = \text{KC}_6\text{H}_{11}\text{O}_2 + \text{H}_3\text{N}$.

(1288) 7. *Cenanthylic Acid* ($\text{HC}_7\text{H}_{13}\text{O}_2 = 130$). *Boil. pt.* $298^\circ.4$ (148°C).—This acid, originally supposed to be allied to cenanthic acid, is obtained as one of the products of the oxidation of oleic acid by means of nitric acid. It is also produced during the destructive distillation of castor oil; but it is most readily obtained by heating one part of castor oil in a retort with two parts of concentrated nitric acid diluted with twice its volume of water. A brisk reaction

occurs; the mixture must be maintained at a boiling temperature for a few hours, and the products which distil over must be mixed with water, when an oily stratum of cœnanthyllic acid will rise to the surface; it must be again distilled with water, and the normal acid may be obtained by distilling the liquid from the glacial phosphoric acid. Cœnanthyllic acid may be exposed to a cold of 0° F. without becoming solid; it boils and may be distilled at 298° , but it undergoes partial decomposition during the operation. One of its most characteristic salts is cupric cœnanthylate, which crystallizes in beautiful green needles; these are soluble in alcohol, but nearly insoluble in water.

Cœnanthyllic anhydride ($C_{14}H_{26}O_3$), *sp. gr.* 0.92, may be obtained as an oily liquid by distilling potassic cœnanthylate with phosphoryl chloride.

(1289) 8. *Caprylic Acid* [$(HC_8H_{15}O_2 = 144)$; *Sp. gr. of vap.* 5.31; *Rel. wt.* 72; *Fusing pt.* 59° (15° C.); *Boil. pt.* $456^{\circ}.8$ (236° C.)] was one of the volatile acids obtained by Chevreul during the saponification of butter; it is found likewise in cocoa-nut oil, as well as amongst the products of the oxidation of oleic acid by nitric acid. Caprylic acid becomes solid at about 54° ($12^{\circ}.3$ C.); it melts at 58° or 59° ; it may be distilled unaltered; it is but sparingly soluble in water, even at a temperature of 212° . It is best prepared by decomposing baric caprylate with sulphuric acid. Baric caprylate is insoluble in alcohol and in ether, but is dissolved by twice its weight of boiling water; it crystallizes from its aqueous solution in anhydrous colourless plates, which are deposited in rounded nodular masses. Caprylic acid is usually accompanied by rutilic acid, but since the caprylate is more soluble than the rutate of barium, the acids may be separated by converting them into barium salts and then crystallizing them.

Caprylic Anhydride ($C_{16}H_{30}O_3$) is a limpid oil of a disagreeable odour, which burns with a luminous flame: it becomes solid in the cold produced by a mixture of ice and salt.

(1290) 9. *Pelargonic Acid* ($HC_9H_{17}O_2$). *Boil. pt.* 500° (260° C.).—This acid was originally extracted from the leaves of the pelargonium, or geranium, by distilling them with water, purifying the essential oil which floats on the surface by neutralizing it with baric hydrate, and heating the mixture to drive off a volatile oily body which comes over with the acid. The baric pelargonate is afterwards decomposed by an acid. Pelargonic acid may also be prepared by heating oil of rue with an equal measure of nitric acid which has been diluted with its own bulk of water; and it is also produced by the oxidation of oleic acid by the same reagent. Pelargonic acid is a colourless oil which is nearly insoluble in water, but soluble in alcohol and ether: it has a faint unpleasant smell, and may be distilled unchanged.

Pelargonic Anhydride ($C_{18}H_{34}O_3$) is a colourless oil which solidifies at 32° , and has a disagreeable odour of rancid butter: it is obtained by acting upon baric pelargonate with phosphoryl chloride ($POCl_3$).

(1291) 10. *Rutic or Capric Acid* [$(HC_{10}H_{19}O_2)$; *Fusing pt.* 86° (30° C.)] is a volatile fatty acid which possesses many interesting relations to other bodies. It was discovered by Chevreul amongst the products of the saponification of butter; but it is also furnished by the oxidation of oleic acid by nitric acid. Gerhardt procured it readily, mixed with pelargonic acid, by acting upon oil of rue with fuming nitric acid; one of the constituents of oil of rue* ($C_{10}H_{20}O$) having, according to Gerhardt, the composition of the aldehyd of rutilic acid.

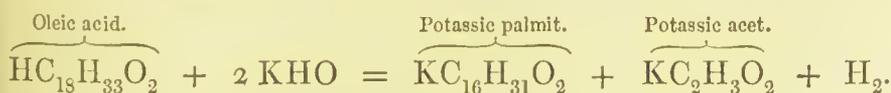
* According to Greville Williams, oil of rue consists chiefly of *croodic aldehyd* ($C_{11}H_{22}O$), mixed with a small quantity of lauric aldehyd ($C_{12}H_{24}O$), besides a hydrocarbon isomeric with oil of turpentine and with borneol.

Rutic acid is also contained in small quantity in the fatty acids of the cocoa-nut oil. Rutic acid crystallizes in colourless needles; it has a slight odour of the goat. This acid is sparingly soluble in boiling water, but it separates completely, in glistening plates, as the liquid cools; its taste is sour and burning. It is soluble in alcohol in all proportions: when distilled it is liable to undergo partial decomposition. Rutic acid is generally purified by converting it into a barium salt, which crystallizes in brilliant plates: it is soluble to a considerable extent in boiling water, but requires 200 parts of cold water for solution.

12. *Lauric Acid* [$\text{HC}_{12}\text{H}_{23}\text{O}_2$; *Fusing pt.* $110^{\circ}.3$ ($43^{\circ}.5$ C.); Heintz] was first extracted from the soft green fat of the bay berries (*Laurus nobilis*), but it has since been found in cocoa-nut oil (Georgey), as well as in the pichurim nut and in cacao butter.

14. *Myristic Acid* [$(\text{HC}_{14}\text{H}_{27}\text{O}_2)$; *Fusing pt.* $129^{\circ}.2$ (54° C.); Heintz] is comparatively unimportant; it is furnished by the solid fat of the nutmeg (*Myristica moschata*), and is one of the acids of cocoa-nut oil. According to Mulder it also forms a constituent of linseed oil, poppy oil, and nut oil, linseed oil containing about 10 per cent. of myristin.

(1292) 16. PALMITIC ACID [$(\text{HC}_{16}\text{H}_{31}\text{O}_2=256)$; *Fusing pt.* $143^{\circ}.6$ (62° C.)].—This acid is obtained most readily from palm oil, the solid portion of which consists chiefly of the glycerin compound of palmitic acid, and which, when long kept, often contains the free acid in large quantity, amounting in some instances to one-third of its weight. Under these circumstances the oil contains a considerable quantity of uncombined glycerin. Palmitic acid may also be procured by the saponification of spermaceti: according to Heintz, it is likewise present in human fat, in the solid constituent of olive oil, and generally in substances which have been described as yielding margarin. It is moreover one of the products of the decomposition of oleic acid when this body is fused with twice its weight of caustic potash:—



Palmitic acid, after repeated crystallization from alcohol, appears as a tasteless white fat, which may be obtained in tufts of delicate needles. It may, with care, be distilled without undergoing decomposition. Palmitic *anhydride*, $(\text{C}_{16}\text{H}_{31}\text{O})_2\text{O}$, was obtained by Malerba as a white solid, fusible at 129° ($53^{\circ}.8$ C.).

The neutral palmitates of the alkali-metals are readily soluble in hot water, and form solutions which gelatinize on cooling. They are sparingly soluble in cold alcohol, but freely so in boiling alcohol: this solution deposits the salts in crystals on cooling. The aqueous solutions of the normal palmitates, when largely diluted with water, are decomposed in a manner similar to those of the stearates, into an insoluble acid salt, whilst a portion of the alkali remains in solution.

(1293) 17. MARGARIC ACID ($\text{HC}_{17}\text{H}_{33}\text{O}_2$).—In order to prepare this substance, Marseilles, or olive-oil soap, is to be dissolved in boiling water, and mixed with a solution of calcic chloride; a precipitate of mingled calcic oleate and margarate is thus obtained, which after being dried is pulverized and digested in cold ether, so long as anything is dissolved: the calcic oleate is thus brought into solution, whilst the margarate is left behind. The margarate is then decomposed by boiling it with hydrochloric acid, and the fatty acid which separates is thoroughly washed, and recrystallized from alcohol. As thus obtained it melts at 140° (60°C.). Heintz, however, states that the acid so obtained may be separated into stearic and palmitic acid, by repeatedly crystallizing it from alcohol; the melting point may thus be raised till it reaches 159° ($70^\circ\cdot5 \text{C.}$), the fusing point of stearic acid. A better plan consists in adding to a boiling solution of the acid in alcohol a boiling solution of plumbic acetate, or of baric acetate, containing a quantity of the barium, or lead salt, amounting to two-sevenths of the weight of the fatty acid. As the liquid cools, a precipitate is obtained, which is to be collected upon a filter. This portion contains the whole of the stearic acid, whilst most of the palmitic acid remains in solution; the filtered liquid is now to be precipitated by an excess of the barium or lead salt. This latter precipitate contains the palmitic acid; it may be decomposed by hydrochloric acid, and recrystallized from alcohol till its melting point remains fixed at $143^\circ\cdot6$ (62°C.). If necessary, it may be again submitted to a partial precipitation with plumbic or with baric acetate.

Although the melting point of stearic acid is 159° , and that of palmitic acid is $143^\circ\cdot6$, Heintz finds that a mixture of the two acids melts at a lower temperature than either of them separately; and if 9 or 10 parts of palmitic acid be fused with 1 part of stearic acid, a mass is obtained which solidifies at 140° , the fusing point of the so-called margaric acid.

Becker, however, considers that he has obtained margaric acid artificially by decomposing ethyl cyanide by means of caustic potash; $\text{C}_{16}\text{H}_{33}\text{CN} + \text{KHO} + \text{H}_2\text{O} = \text{KC}_{17}\text{H}_{33}\text{O}_2 + \text{H}_3\text{N}$. The fusing point of this acid was as low as $127^\circ\cdot4$ (53°C.).

(1294) 18. STEARIC ACID ($\text{HC}_{18}\text{H}_{35}\text{O}_2 = 284$); *Fusing pt.* 159° ($70^\circ\cdot5 \text{C.}$)—This important fatty acid is liberated during the saponification of all the fats which contain stearin. It is found chiefly in the animal fats, but occasionally also in the vegetable fats, as in that of the *Bassia latifolia* (Hardwich).

Stearic acid may be obtained by saponifying mutton suet, and

decomposing the hot solution of the soap with hydrochloric, or still better, with tartaric acid. The oily acids are next to be submitted to pressure between hot plates, by which means a large portion of the oleic acid is separated: the solid residue is then to be recrystallized from alcohol, three or four times, and afterwards from ether, until the fusing point becomes constant at 159° . The ethereal solution, if allowed to cool very slowly, deposits the acid in beautiful colourless, transparent, rhombic plates. When fused it presents the appearance of a colourless oil, destitute of taste or odour; and, on solidifying, it concretes into a white crystalline mass, which is insoluble in water, but freely soluble in hot alcohol. This solution reddens litmus.

Stearates.—Stearic acid forms both normal and acid salts. The stearates of the alkali-metals are soluble in a small quantity of water, and in alcohol: a mixture of alcohol and ether, of sp. gr. 0.750, also dissolves them, and deposits them in crystals on cooling. When an aqueous solution of normal potassic or sodic stearate is largely diluted with water, the liquid becomes turbid, and a copious separation of silky crystalline plates of an acid stearate of the base is occasioned. Chevreul, who has carefully examined this decomposition, finds that it is not an isolated case, but that generally, when a salt is formed by the action of a base soluble in water upon an acid which is insoluble, the normal salt so obtained is decomposed by water, with the precipitation of an insoluble acid salt, while a portion of the base remains in solution.

Sodic stearate is the basis of ordinary hard soap. The soluble stearates are separated from their solution in water by the addition of a large excess of soda or of potash. Sodic chloride also causes their immediate coagulation; and some other salts have a similar effect; advantage is taken of this fact to separate soap from glycerin and other impurities in the operation of soap-making.

The other stearates are insoluble; those of barium and calcium are crystalline, and insoluble in alcohol. Magnesium stearate is fusible, and may be dissolved by boiling alcohol. Plumbic stearate is easily formed by adding a solution of plumbic acetate to one of sodic stearate: it is a heavy amorphous precipitate, fusible at about $260^{\circ}.6$ (127° C.), sparingly soluble in alcohol and in ether, but readily soluble in oil of turpentine. Plumbic stearate is one of the constituents of the ordinary lead plaster.

Stearic acid, when submitted for some weeks to a current of chlorine, at a temperature of 212° , loses a portion of its hydrogen, and becomes converted into

a yellowish, transparent, chlorinated compound, of a resinous aspect, in which Hardwich found that 10 atoms of hydrogen had been displaced by 10 of chlorine, forming *chlorostearic acid* ($\text{HC}_{18}\text{H}_{25}\text{Cl}_{10}\text{O}_2$).

When stearic acid is boiled for some days with nitric acid, it is gradually converted into succinic and suberic acids (1301, 1304).

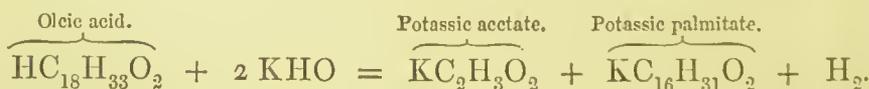
Arachidic or *Butic Acid* [$(\text{HC}_{20}\text{H}_{39}\text{O}_2)$, *Fusing pt.* 167° (75° C.)] does not appear to have been obtained from butter in a state of perfect purity; but a crystallizable fatty acid having the composition assigned to it has been extracted from the oil obtained from the seeds of the *Arachis hypogaea*, the ground-nut oil of Western Africa.

Melissic and *cerotic* acids have been already described (1226).

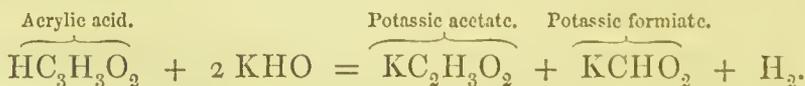
(b) *Acids of the Oleic Series*, $\text{H}(\text{C}_n\text{H}_{2n-3})\text{O}_2$.

(1295) The acids which belong to this group have been less perfectly studied than those of the foregoing one. Oleic acid is the most important member of this series. Owing to the facility with which these acids absorb oxygen, and the difficulty of purifying them from the results of this oxidation on account of their indisposition to crystallize, the investigation of these compounds is attended with considerable difficulty. Many of them occur as glycerin compounds in the fixed oils. The higher terms of this series are decomposed when they are heated with a view to effect their distillation.

The acids of this group are characterized by their tendency, when heated gently with caustic potash, to break up into acetic acid and a second acid of the stearic series, whilst hydrogen is liberated. Oleic acid in this manner yields potassic acetate and palmitate:—



Acrylic acid when similarly treated yields an acetate and formiate of the basyl:—



The acids of this group possess the remarkable property of being converted by nitrogen peroxide (NO_2) into metamerie acids, which require a much higher temperature for their fusion than the oily acids from which they were obtained. These solid acids may be distilled unchanged. When these less fusible metamerie acids are heated with caustic potash, they also undergo decomposition into acetic acid, and another acid of the stearic series; hydrogen being evolved, exactly as in the case of their more fusible metameres.

The following table contains the names of the acids of both isomeric series which are at present known.

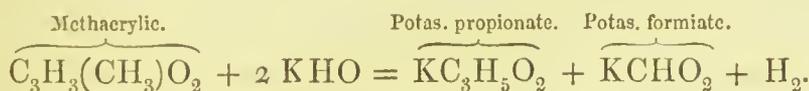
Acids of the Oleic Series ($\text{HC}_n\text{H}_{2n-3}\text{O}_2$), or ($\text{C}_n\text{H}_{2n-2}\text{O}_2$).

| Liquid Acids. | | | Metamerie solid Acids. | | | | |
|---------------|--|---------------|------------------------|--------------------|--|---------------|------|
| | | Fusing Point. | | | | Fusing Point. | |
| | | ° F. | ° C. | | | ° F. | ° C. |
| Acrylic . . | $\text{C}_3\text{H}_4\text{O}_2$ | | | β Crotonic . | $\text{C}_4\text{H}_6\text{O}_2$ | 159 | 70.5 |
| Crotonic . . | $\text{C}_4\text{H}_6\text{O}_2$ | 20 | -6.7 | Angelica . . | $\text{C}_5\text{H}_8\text{O}_2$ | 113 | 45 |
| Moringic . . | $\text{C}_{15}\text{H}_{25}\text{O}_2$ | 32 | 0 | Hypogaëic . . | $\text{C}_{16}\text{H}_{30}\text{O}_2$ | 95 | 35 |
| Physetoleic . | $\text{C}_{16}\text{H}_{30}\text{O}_2$ | | | Elaidic . . | $\text{C}_{15}\text{H}_{34}\text{O}_2$ | 113 | 45 |
| Oleic . . . | $\text{C}_{18}\text{H}_{34}\text{O}_2$ | 57.2 | 14 | | | | |
| Doeglic . . | $\text{C}_{19}\text{H}_{36}\text{O}_2$ | 62.6 | 17 | | | | |
| Erucic . . | $\text{C}_{22}\text{H}_{42}\text{O}_2$ | 93.2 | 34 | | | | |

Frankland and Duppa have prepared a number of secondary acids, metameric with the natural ones, of which the following may be mentioned:—

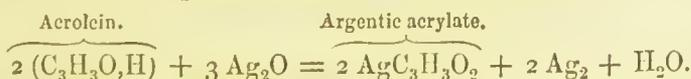
| Secondary acids. | Metamerie with |
|--|---|
| Methacrylic $\text{C}_3\text{H}_3(\text{CH}_3)\text{O}_2$ | Crotonic . . . $\text{C}_4\text{H}_6\text{O}_2$ |
| Methylcrotonic $\text{C}_4\text{H}_5(\text{CH}_3)\text{O}_2$ | Angelica . . . $\text{C}_5\text{H}_8\text{O}_2$ |
| Ethylcrotonic $\text{C}_4\text{H}_5(\text{C}_2\text{H}_5)\text{O}_2$ | Pyroterebic . . $\text{C}_6\text{H}_{10}\text{O}_2$ |

These secondary acids, when fused with caustic potash, give rise to two acids of the acetic series with separation of hydrogen; as for instance:



(1296) It will not be necessary to dwell long upon any acid of this group except the oleic.

Acrylic acid ($\text{HC}_3\text{H}_3\text{O}_2$) is obtained by the oxidation of acrolein (1242). This is best effected by digesting acrolein on argentic oxide in excess; the pungent smell of acrolein disappears, and argentic acrylate is obtained in solution, whilst metallic silver is deposited and water is eliminated:—



If the argentic acrylate be placed in a bulb tube and kept cool by immersion in ice, it may be decomposed by transmitting over it a very slow current of sulphuretted hydrogen: argentic sulphide is formed, whilst pure acrylic acid is liberated; the latter may be distilled by a gentle heat. Acrylic acid has an agreeable acid odour and a burning taste. It requires a temperature below 32° to freeze it. Its boiling point is above 212° , and it may be distilled unchanged. All its salts are soluble: the salt of silver is one of the most characteristic compounds of this acid; it crystallizes in anhydrous silky looking needles, which much resemble argentic acetate in appearance; it is sparingly soluble in cold

water: boiling water decomposes it, and partially reduces the silver. Argentic acrylate may readily be formed from the crude products of the distillation of oils; the distillate is rectified, and those portions which come over between 100° and 140° are collected separately; they are rectified anew from calcic chloride, and are then digested on an excess of argentic oxide, returning the portions which distil, until the pungent odour of acrolein has disappeared; water is next added, and the liquid is distilled to carry off the volatile oils; after which the boiling liquid is filtered, and set aside in a dark place to crystallize. *Sodic acrylate*, $2(\text{NaC}_3\text{H}_3\text{O}_2)$, $5\text{H}_2\text{O}$, crystallizes in efflorescent prisms which are very soluble. *Baric acrylate* does not crystallize.

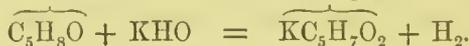
With nascent hydrogen acrylic acid unites and becomes converted into propionic acid; $\text{C}_3\text{H}_4\text{O}_2 + \text{H}_2 = \text{C}_3\text{H}_6\text{O}_2$. Bromine unites directly with acrylic acid, and converts it into the dibromopropionic, $\text{C}_3\text{H}_4\text{Br}_2\text{O}_2$.

Crotonic acid ($\text{HC}_4\text{H}_5\text{O}_2$) is the oleic acid of croton oil; it is rather soluble in water. When decomposed by caustic potash, it furnishes hydrogen and 2 molecules of potassic acetate; $\text{C}_4\text{H}_6\text{O}_2 + 2\text{KHO} = 2\text{KC}_2\text{H}_3\text{O}_2 + \text{H}_2$.

Angelica acid [$(\text{HC}_5\text{H}_7\text{O}_2)$; *Fusing pt.* 113° (45°C.); *Boil. pt.* 374° (190°C.)] is met with in the root of various kinds of *Angelica*; it is also produced by the action of caustic potash, aided by a gentle heat, upon the oxidized principle in the essence of camomile:—

Ess. camomile.

Potassic angelate.



Angelica acid forms large, striated, colourless, fusible prisms, which may be distilled without undergoing decomposition. It is sparingly soluble in cold water, but freely so in boiling water. When heated with caustic potash, it is decomposed with escape of hydrogen into potassic acetate and propionate, in accordance with the general mode of decomposition of the acids belonging to the oleic series. From its high fusing point, and from the possibility of distilling it without decomposition, it is, however, obvious that it does not belong to the true oleic series, but probably to the elaidic group.

Moringic acid [$\text{HC}_{15}\text{H}_{27}\text{O}_2$, *Fusing pt.* 32° (0°C.)] is the liquid acid extracted from the oil of ben (*Moringa aptera*). Oil of ben, from its indisposition to become rancid, has been used as the basis of Macassar oil.

Physetoleic acid ($\text{HC}_{16}\text{H}_{29}\text{O}_2$) was obtained from the oil of the ordinary sperm whale (*Physeter macrocephalus*). According to Gössmann the oil of the ground-nut contains an acid, the *hypogaëic*, of the same composition as the physetoleic, but fusing at about 95° (35°C.).

Doeglic acid [$(\text{HC}_{19}\text{H}_{35}\text{O}_2)$; *Fusing pt.* $62^{\circ}\cdot6$ (17°C.)] was extracted by Scharling from the oil of the *Balæna rostrata* (in Danish *Dögling*) a species of sperm whale. The composition of this oil is remarkable, since it does not furnish glycerin when saponified, but a compound $\text{C}_{12}\text{H}_{26}\text{O}$, which corresponds in composition to lauric alcohol. The oil when distilled gives no acrolein, showing the absence of glycerin.

Erucic acid [$(\text{HC}_{22}\text{H}_{41}\text{O}_2)$; *Fusing pt.* $93^{\circ}\cdot2$ (34°C.)] so called from *cruca*, one of the names given to white mustard, is extracted from the oil of the white and the black mustard seed, and from colza oil.

(1297) OLEIC ACID ($\text{HC}_{18}\text{H}_{33}\text{O}_2 = 282$). *Fusing pt.* $57^{\circ}\cdot2$, (14°C.).—The isolation of this acid in a state of purity is a matter of some difficulty, owing to its tendency to combine with oxygen. Oleic acid is obtained in a crude form as a secondary product in the manufacture of stearin candles. In order to obtain the pure

acid, Varrentrapp recommends that almond oil be saponified with potash or with soda, and that the soap be decomposed with hydrochloric acid. The mixed fatty acids are then to be digested with half their weight of finely powdered plumbic oxide. On digesting the mixed salts of lead with twice their volume of ether for 24 hours, the oleate is dissolved and separated from the other salts. The ethereal solution is then to be mixed with dilute hydrochloric acid, which decomposes the oleate; the oily acid is dissolved by the ether and rises to the surface. The ether is to be expelled by heat, and the acid is again to be converted into soap by the addition of an alkali; after which it is to be separated from its aqueous solution by the addition of sodic chloride, pressed, redissolved in water which has been boiled for some time to expel the air, and finally decomposed by tartaric acid in vessels filled with carbonic anhydride. The acid thus obtained always has a brown colour, owing to the action of the atmospheric oxygen upon it. Gottlieb purified it by adding to the acid thus obtained a large excess of ammonia, and then precipitating it by means of baric chloride: the baric oleate so procured is dried and boiled with alcohol. During this operation the salt melts and forms a viscous liquid, but a portion of it is dissolved, and is deposited in crystalline plates as the liquid cools; these are again crystallized from alcohol, and on decomposing them with tartaric acid pure oleic acid is obtained. The alcohol in the preceding operation retains the impurities which render the ordinary baric oleate so fusible: pure baric oleate is not fusible at 212° .

Pure oleic acid, at temperatures above 57° forms a colourless, limpid oil, without taste or smell; it does not redden litmus even when dissolved in alcohol: at $39^{\circ}.2$ (4° C.), it concretes into a hard crystalline mass, composed of fine needles. When solid it undergoes no change in the air, but when liquid it absorbs oxygen rapidly, acquiring a brown colour, a rancid odour, and an acid reaction upon litmus, its point of solidification gradually becoming lowered until it falls below 0° ($-17^{\circ}.8$ C.). Oleic acid cannot be distilled without undergoing decomposition: a large quantity of liquid and of gaseous hydrocarbons are given off in the distillation, besides several acids of the series $C_nH_{2n}O_2$; but the most characteristic product is sebacic acid (1306), the quantity of which, however, appears to diminish in proportion as the oleic acid has become more oxidized.

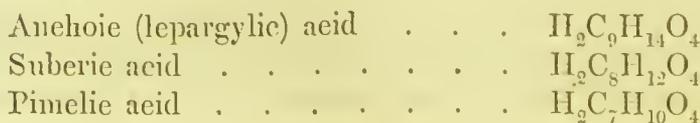
Oleic acid forms two classes of salts, normal and acid. The normal salts of the alkalis are the only soluble ones. They form soaps, and by the evaporation of their aqueous solution

they may be obtained in the condition of an amorphous mass. Potassic oleate forms a soft soap, which is the chief ingredient in Naples soap. Sodie oleate is a hard soap, and enters largely into the composition of Marseilles soap. The acid oleates of the alkalies are liquid and insoluble. The oleates of the heavier metals, such as those of copper and lead, are soluble in cold anhydrous alcohol, and in ether; they are thus separable from the stearates and palmitates, which are insoluble in these liquids.

(1298) *Action of Nitrogen Peroxide and of Nitric Acid on Oleic Acid.*—Oleic acid, by exposure to nitrogen peroxide (NO_2) becomes converted into a solid fatty acid, isomeric with oleic acid, which has been called *elaidic acid*, from $\epsilon\lambda\alpha\iota\omega\nu$, oil. In effecting this change an excess of the peroxide must be avoided, and the mass must be kept cool. The cause of this remarkable change is unknown. A small quantity of ammonia is formed during the reaction, as well as a portion of a neutral oily body. The quantity of peroxide required is very small, not exceeding $\frac{1}{200}$ of the weight of the oleic acid.

Elaidic acid fuses at about 113° (45° C.). It is very soluble in alcohol, from which it is deposited in beautiful pearly scales: it is less soluble in ether. Elaidic acid may be distilled in great part without alteration; but when fused with caustic potash it yields potassic palmitate and acetate, like oleic acid.

When oleic acid is subjected in a capacious retort to the action of a large excess of nitric acid of sp. gr. 1.42 diluted with an equal bulk of water, it gradually disappears, producing a copious evolution of nitrous fumes, attended with a violent reaction. The results of the decomposition are very complicated, but the products obtained by this method of oxidizing oleic acid present considerable interest, since they contain, according to Redtenbacher, all the terms of the homologous series of the volatile acids ($\text{C}_n\text{H}_{2n}\text{O}_2$) from the acetic to the stearic acid inclusive, these acids being found in the distillate; whilst five or six fixed acids are left in the retort, and these form contiguous terms of a group of homologous dibasic acids of the formula $\text{H}_2\text{C}_n\text{H}_{2n-4}\text{O}_4$. The quantity of the volatile acids is greater when the nitric acid used is very concentrated; if it be more dilute, that of the fixed acids is increased. The fixed acids which remain in the retort, are the following:—





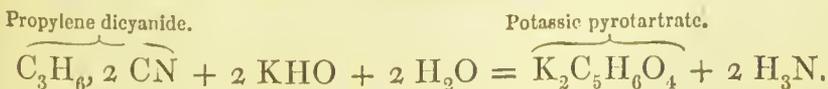
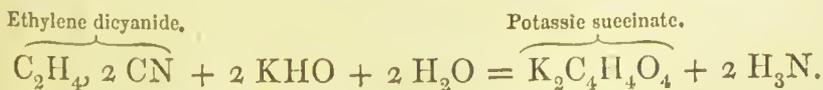
It is interesting to remark that another acid of this group, viz., the sebacic ($H_2C_{10}H_{16}O_4$), is a characteristic product of the distillation of oleic acid. Some of the acids of this dibasic series will now be described.

(c) *Dibasic Acids of the Oxalic Series*, $H_2C_nH_{2n-4}O_4$,
 or $C_nH_{2n-2}O_4$.

(1299) All the acids belonging to this series possess a considerable volatility, and may be partially sublimed without undergoing decomposition: they are soluble to a large extent in boiling water as well as in alcohol: they are likewise soluble in ether, and may be obtained in crystals without difficulty: some of them, like oxalic acid, crystallize with $2 H_2O$. Oxalic acid forms the lowest term in this group, and sebacic the highest which is at present known. The following table contains the names of the acids which have been ascertained to belong to this series:—

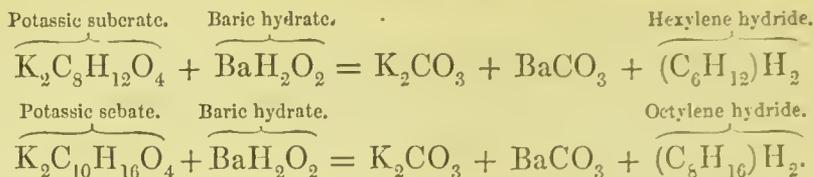
| Acid. | Formula. | Fusing Point. | | Appearance. |
|------------------|----------------------|-----------------------------|------|---------------------------------|
| | | ° F. | ° C. | |
| Oxalic . . | $H_2C_2O_4$ | { Sublimes before fusing. } | | 4-sided prisms, with $2 H_2O$. |
| Malonic . . | $H_2C_3H_2O_4$ | 284°0 | 140 | Rhombohedral crystals. |
| Succinic . . | $H_2C_4H_4O_4$ | 356°0 | 180 | Four-sided prisms. |
| Pyrotartaric . . | $H_2C_5H_6O_4$ | 233°6 | 112 | Rhombic prisms, very soluble. |
| Adipic . . | $H_2C_6H_8O_4$ | 266°0 | 130 | Radiated tufts. |
| Pimelic . . | $H_2C_7H_{10}O_4$ | 237°2 | 114 | Hard granular crystals. |
| Suberic . . | $H_2C_8H_{12}O_4$ | 257°0 | 125 | White crystalline powder. |
| Anchoic . . | $H_2C_9H_{14}O_4$ | 239°0 | 115 | |
| Sebacic . . | $H_2C_{10}H_{16}O_4$ | 260°6 | 127 | Thin pearly plates. |

Maxwell Simpson has shown that by treating the dicyanides of the olefines with caustic potash, ammonia is evolved, and a salt of one of the acids of this group obtained; for example:—

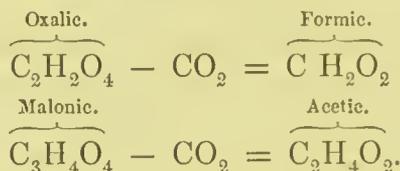


Some of these acids, when treated with boric hydrate in excess, yield a hydride of an olefine, with the loss of two atoms

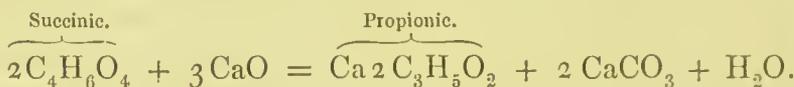
of carbonic anhydride, by a reaction analogous to that which furnishes marsh gas from the acetates; as for example:—



If a single atom of carbonic anhydride only be removed, an acid of the acetic series is obtained. Mere heat effects this with oxalic and malonic acid, which become respectively,

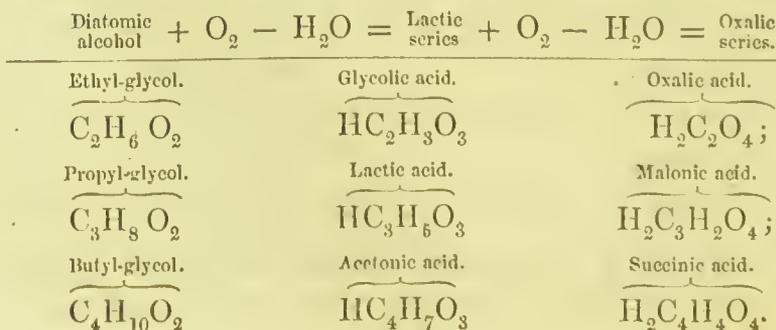


In the case of the succinic acid the presence of lime is necessary to effect the decomposition:—



Oxalic acid furnishes neither oxychloride nor anhydride, but the other acids yield both. The anhydrides of this group may often be obtained by simple dehydration of the normal acids by heat.

The acids of this group stand in the same relation to the diatomic alcohols that those of the acetic group do to the monatomic alcohols, glycol being converted by gradual oxidation into oxalic acid, as ordinary alcohol is into acetic acid. The lactic acid series appears to constitute an intermediate group of acids, the formation of which occurs during the process of oxidation of the glycols or diatomic alcohols. For example, glycol, by the absorption of 2 atoms of oxygen and the elimination of 1 atom of water, furnishes glycolic acid; and this acid, by the further absorption of 2 of oxygen and the elimination of 1 of water, furnishes oxalic acid. By a similar action of oxygen and separation of water we should expect to obtain the following compounds:—



The glycolic series of acids upon this view must be regarded as monobasic, though diatomic (1261).*

Oxalic acid ($\text{H}_2\text{C}_2\text{O}_4, 2\text{H}_2\text{O}$) has been already described, Part II., p. 278. It will therefore be sufficient here to recapitulate the different modes in which the oxalates may be procured, viz. :—

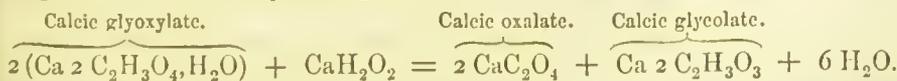
1. By the action of carbonic anhydride upon sodium or potassium (Kolbe and Dreehsel), as by passing the dried gas over a heated mixture of sodium and sand, or by heating potassium amalgam in the gas ; $2\text{CO}_2 + \text{K}_2 = \text{K}_2\text{C}_2\text{O}_4$.

2. By heating potassic formiate with excess of potassic hydrate, when hydrogen is evolved ; 2KHCO_2 becoming $\text{K}_2\text{C}_2\text{O}_4 + \text{H}_2$.

3. By the gradual decomposition of cyanogen in water, when ammoniac oxalate is formed, mixed with other products ; $(\text{CN})_2 + 4\text{H}_2\text{O}$ yielding $(\text{H}_4\text{N})_2\text{C}_2\text{O}_4$.

It is, however, always prepared by one of the two following methods :—4. By oxidizing sugar or some member of the

* An interesting acid, the *glyoxylic*, discovered by Debus (*Phil. Mag.*, Nov. 1856), is probably the type of a group connecting the glycolic with the oxalic series. It is procured by the gradual decomposition of nitrous ether by means of water. The acid liquid obtained thus is evaporated in quantities not exceeding an ounce at a time over the water-bath, till of the consistence of syrup, when a mixture of glycolic, oxalic, and glyoxylic acid with the aldehyd of glycol (glyoxal) remains. It is neutralized with calcic carbonate, and the liquid is mixed with an equal bulk of alcohol : the calcium salts are thus precipitated, and glyoxal ($\text{C}_2\text{H}_2\text{O}_2$) is retained in solution. The precipitate is pressed and treated with boiling water, which on cooling deposits small, hard prisms of calcic glyoxylate ($\text{Ca}_2\text{C}_2\text{H}_3\text{O}_4, \text{H}_2\text{O}$), while a double calcic glycolate and glyoxylate remains in the mother liquor. Glyoxylic acid ($\text{C}_2\text{H}_4\text{O}_4$) may be obtained from calcic glyoxylate by the cautious addition of oxalic acid, and by evaporation may be procured in the form of a deliquescent syrupy liquid, which may be volatilized almost without residue by heat, with the emission of white fumes. A characteristic reaction of glyoxylic acid is the formation with calcium of two salts, one of which is soluble and crystallizes in hard prisms, whilst the second, which is procured by the addition of lime water to the solution of the first, is nearly insoluble ; but the latter salt speedily undergoes spontaneous decomposition, and a mixture of water and of calcic oxalate and glycolate is the result. The same change takes place still more rapidly if the lime water is in slight excess and the liquid is boiled ; the decomposition is shown by the equation :—

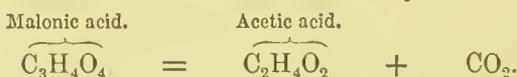


The soluble glyoxylates give a white crystalline precipitate with plumbic acetate, soluble in acetic acid ; but no precipitate with either argentic nitrate, baric nitrate, or cupric chloride. It is probable that glyoxylic acid furnishes the type of a class of similar substances, the general formula of which is $\text{C}_n\text{H}_{2n}\text{O}_4$.

Debus considers glyoxylic acid as $\text{C}_2\text{H}_2\text{O}_8$; but all its salts contain the elements of 1 atom more of water, as given above, with the exception of its so-called ammonia salt ; and this exception is probably due to its being really an amide, and not a true ammonium salt.

amylaceous group with nitric acid; or 5. By decomposing ligneous fibre by heating it with a mixture of potassic and sodic hydrates.

(1300) *Malonic Acid* ($H_2C_3H_2O_4 = 104$).—This acid, according to Desaignes (*Liebig's Annal.*, cvii. 251) may be obtained by the oxidation of malic acid. To a cold, dilute solution of malic acid, small quantities of solid potassic dichromate are to be gradually added until a quantity of the salt about equal in weight to the malic acid has been used. The liquid is diluted, and the reduced chromic oxide separated by the addition of an excess of milk of lime. To the greenish filtrate a solution of plumbic acetate is added, and the mixed precipitate of plumbic malonate and chromate is treated with nitric acid in quantity just sufficient to decompose the salt of the organic acid. The filtrate is mixed with about three-fourths of the quantity of ammonia necessary to neutralize it, and the plumbic malonate which is thrown down is washed, suspended in water, and decomposed by a current of sulphuretted hydrogen gas. On evaporating the filtrate, crystals of malonic acid are formed in a greenish syrupy liquid which contains malic acid and a little chromic oxide. The crystals are drained and recrystallized. The acid forms large rhombohedral crystals which split readily into laminae. It is freely soluble in water and in alcohol, has a sour taste, at 284° (140° C.) it melts, and at 302° (150° C.) it is partly sublimed unaltered, and partly converted into a mixture of carbonic anhydride and acetic acid:—



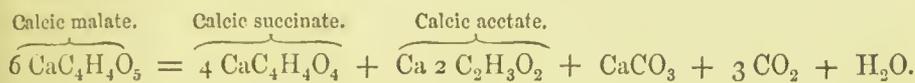
Malonates.—The malonates of the alkali-metals are soluble, their solutions give white precipitates with the solutions of the salts of calcium, barium, lead, mercury, and silver, but none with the salts of iron. The mercurous salts give with a soluble malonate a white precipitate which blackens if the liquid be boiled. The malonates of potassium and ammonium are deliquescent, but crystallizable; the barium salt forms sparingly soluble silky tufts; the calcium salt furnishes small transparent needles; the silver salt falls as a crystalline powder.

The malonic resembles oxalic acid more than it does the succinic.

(1301) *Succinic Acid* ($H_2C_4H_4O_4 = 118$). *Sp. gr.* 1.552.—This acid, as its name implies, was originally obtained from amber (*succinum*), in which it exists ready formed. When amber is submitted to destructive distillation, a quantity of succinic acid passes over amongst other substances.

Preparation.—1. Succinic acid occurs ready formed in the leaves of the wormwood and in the resins of many of the pine tribe. It has been found also in the fluid of hydrocele, and of some hydatids in the animal body. It is, however, easily obtained artificially, by acting upon stearic or palmitic acid with nitric acid. 2. Maxwell Simpson has obtained potassic succinate by heating ethylene dicyanide with caustic potash, ammonia being evolved (1299). 3. Further, it may be procured by fermentation, from asparagin, and from malic acid (Desaignes), calcic malate yielding nearly one-third of its weight of succinate. In order to procure a succinate from a malate, 3 lb. of crude calcic malate may be diffused through a gallon of warm water, and four

ounces of decayed cheese added to the mixture, which is to be kept at a temperature of 100° ($37^{\circ}\cdot 8$ C.) for about a week. Carbonic anhydride is disengaged, whilst a mixture of crystallized calcic carbonate and succinate is deposited, and calcic acetate remains in solution (1314):—



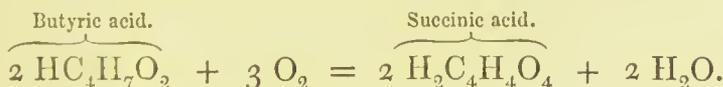
The deposited calcic succinate is to be collected upon a linen filter and washed with cold water, after which it may be decomposed by hydrochloric acid, and the succinic acid purified by crystallization.

The decomposition, however, is not always so simple as is represented in the foregoing equation. The formation of calcic lactate has often been observed to accompany the transformation of malic into succinic acid, and it frequently happens, particularly if the temperature be at all high, that a quantity of hydrogen is disengaged during the fermentation: when this occurs it indicates the formation of butyric acid, which is also accompanied by a small quantity of an essential oil with an agreeable odour of apples. Malic acid contains the elements of 1 atom of carbonic anhydride less than lactic acid:—



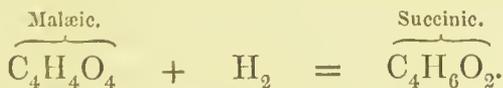
and the presence of lactic acid readily accounts for the formation of butyric acid (1310).

4. An interesting relation also exists between butyric and succinic acids; butyric acid when treated with nitric acid being convertible by oxidation into the succinic:—



5. It may also be procured by reducing tartaric with hydriodic acid; $\text{C}_4\text{H}_6\text{O}_6 + 4 \text{HI} = \text{C}_4\text{H}_6\text{O}_4 + 2 \text{H}_2\text{O} + 2 \text{I}_2$.

6. The isomeric acids, fumaric and malæic, may also be converted into succinic by the action of nascent hydrogen:—



When heated gently with slaked lime, succinic acid loses an atom of carbonic anhydride, and a propionate of the basyl is formed (Koch):—



Much of the acid is completely decomposed owing to the effect of the heat employed, which destroys propionic acid at a point but little higher than that required to decompose the succinic.

When a solution of succinic acid is electrolysed it yields ethylene, carbonic anhydride, and water:—



Succinic acid crystallizes in large, regular, rhombic tables, which require 5 parts of cold and 2 of boiling water for solution. Alcohol dissolves it freely, but it is only sparingly soluble in ether. Succinic acid melts at a temperature of from 347° to 356° (175° to 180° C.), but if suddenly heated to 455° (235° C.) it melts, boils, and sublimes completely. During the sublimation the acid loses a portion of its water, and if distilled with phosphoric anhydride, succinic anhydride ($\text{C}_4\text{H}_4\text{O}_3$) may be obtained without difficulty. This anhydride is soluble in alcohol and in water; its aqueous solution rapidly becomes converted into the normal acid.

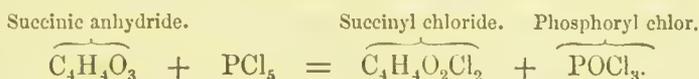
Succinic acid is a very stable compound. It may be boiled for many hours with strong nitric acid without undergoing decomposition, and its aqueous solution is not affected by chlorine, or by a mixture of potassic chlorate and hydrochloric acid. Succinic acid forms two classes of salts, normal and acid, but with potassium it yields three salts:—a normal deliquescent salt ($\text{K}_2\text{C}_4\text{H}_4\text{O}_4, 2\text{H}_2\text{O}$); an acid salt ($\text{KHC}_4\text{H}_4\text{O}_4, 2\text{H}_2\text{O}$; Döpping) which crystallizes in transparent efflorescent six-sided prisms, soluble in alcohol; and a remarkable superacid salt ($\text{KH}_3, 2\text{C}_4\text{H}_4\text{O}_4, \text{H}_2\text{O}$), corresponding to the so-called potassic quadroxalate; 2 atoms of this salt may be deprived of 3 atoms of water by raising its temperature to 212° (Fehling). *Sodic succinate* ($\text{Na}_2\text{C}_4\text{H}_4\text{O}_4, 6\text{H}_2\text{O}$) crystallizes in transparent rhomboidal prisms. *Ammonic succinate* [$(\text{H}_4\text{N})_2\text{C}_4\text{H}_4\text{O}_4$] is sometimes employed to separate iron in perfectly neutral solutions from salts of nickel, cobalt, and manganese. *Magnesian-potassic succinate* may be obtained in double six-sided pyramids ($\text{MgK}_2, 2\text{C}_4\text{H}_4\text{O}_4, 5\text{H}_2\text{O}$), by allowing the two salts mixed in equivalent proportions to crystallize together. Succinic acid forms several nearly insoluble compounds with plumbic oxide; the normal salt ($\text{PbC}_4\text{H}_4\text{O}_4$, *sp. gr.* 3.8) is white and crystalline; another compound ($2\text{PbC}_4\text{H}_4\text{O}_4, \text{PbO}$) is fusible in warm water; and if either of the foregoing precipitates be digested with ammonia, a compound may be obtained with a still larger proportion of base.

The succinates are characterized by the bulky brown precipitate of ferric succinate, which they yield in neutral solutions of ferric salts.

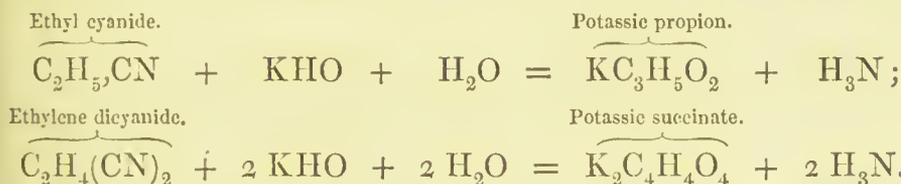
Succinic acid combines readily with sulphuric anhydride, and

forms a deliquescent crystallizable compound acid, termed *succino-sulphuric acid* ($\text{H}_3\text{C}_4\text{H}_3\text{O}_4\text{SO}_3$), which requires 3 atoms of a monad for its saturation.

(1302) *Succinyl Chloride*, or *Succinic Oxychloride* ($\text{C}_4\text{H}_4\text{O}_2\text{Cl}_2$). *Sp. gr. of liq.* 1.39; *Boil. pt.* about 374° (190°C).—When succinic anhydride is distilled with an equivalent quantity of phosphoric chloride, phosphoryl chloride passes over at first, and at a more elevated temperature succinyl chloride is obtained. This compound forms a colourless oil of high refracting power: when boiled it emits a dense suffocating vapour, which in a very dilute form has an odour of wet straw. A damp atmosphere converts it slowly into crystallized succinic acid. It derives its principal interest from its affording an illustration of the characters and mode of preparation of an oxychloride of a dibasic acid:—



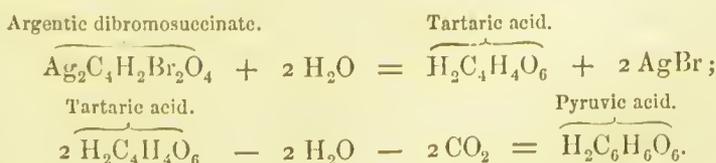
Succinic acid stands in the same relation to glycol that propionic acid does to alcohol; and just as ethyl cyanide by the action of caustic potash is converted into ammonia and potassic propionate, so, according to Maxwell Simpson, may ethylene dicyanide be converted into ammonia and potassic succinate:—



(1303) *Relation of Succinic to Tartaric and Malic Acid.*—

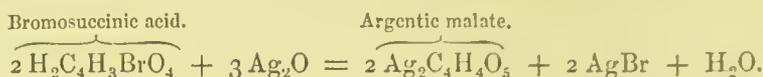
One of the most interesting points in the history of succinic acid is its convertibility into tartaric acid; the acid so formed was found by Pasteur to exert no rotatory action on polarized light. This transformation was effected by Perkin and Duppa, who first procured dibromosuccinic acid, from which they obtained tartaric acid by substitution.

Dibromosuccinic Acid ($\text{H}_2\text{C}_4\text{H}_2\text{Br}_2\text{O}_4$) may be prepared by heating succinic acid for some hours to 302° (150°C) with its own weight of water and about 3 times its weight of bromine: hydrobromic acid is formed in abundance, and the new acid is gradually deposited in crystals which may be purified by recrystallization from boiling water. If this acid be combined with sodium, and decomposed by argentic nitrate, argentic dibromosuccinate is obtained, which is readily decomposed by boiling; argentic bromide is separated, and tartaric acid is formed in the liquid, which also contains a quantity of pyruvic acid, owing to the partial decomposition of the tartaric acid, whilst carbonic anhydride escapes. The reactions may be thus represented:—

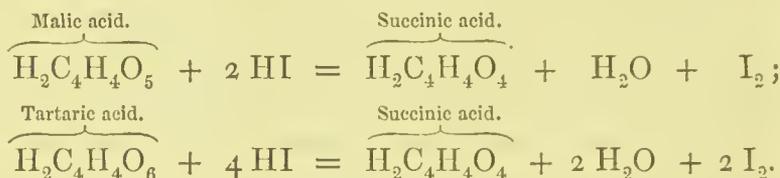


Bromosuccinic Acid ($\text{H}_2\text{C}_4\text{H}_3\text{BrO}_4$) was obtained by Kekulé by digesting

succinic acid in a sealed tube for some hours at a temperature of 356° (180° C.), with bromine and a considerable proportion of water. It is freely soluble in water, and crystallizes with greater difficulty than dibromosuccinic acid. When an aqueous solution of this acid is boiled with argentic oxide, argentic bromide is formed, and a malate is obtained, while water is separated:—



The reconversion of tartaric and malic into succinic acid may also be effected by heating them with hydriodic acid in a sealed tube for some hours: iodine is liberated and succinic acid crystallizes on evaporating the solution:—



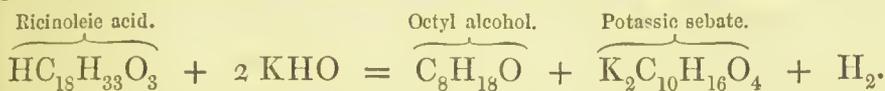
The three next terms of the series, viz., the *pyrotartaric* (with which *lipic* acid is isomeric), *adipic*, and *pimelic* acids, are unimportant: they are formed along with suberic acid during the oxidation of oleic by nitric acid. These acids may be crystallized without difficulty.

(1304) *Suberic Acid* ($\text{H}_2\text{C}_8\text{H}_{12}\text{O}_4$).—This compound was originally observed among the products of the oxidation of cork by nitric acid, and hence it derives its name (from *suber*, cork). Cork, however, yields it in but very small quantity, and even that quantity is probably owing to the presence of a small proportion of waxy matter. The acid is a somewhat frequent product of the oxidation of the fats, and particularly of the acids of the stearic series. It is easily obtained by boiling stearic acid with nitric acid for some days; upon concentrating the liquid it deposits crystals of suberic acid, mixed with a large quantity of succinic acid. The latter acid is easily removed by washing with cold water, and the sparingly soluble suberic acid is purified by crystallization from boiling water. It forms a white crystalline powder, destitute of odour, but having a slightly acid taste, and feebly reddening litmus paper. It requires about 100 times its weight of cold water for solution, but only twice its weight of boiling water. It is also soluble in alcohol and in ether. When heated it fuses at about 257° (125° C.), and creeps up the side of the vessel in which it is heated, undergoing a sort of spurious sublimation at a high temperature. The suberates of the metals of the alkalies and of the earths are soluble and crystallizable; they yield with salts of lead, silver, and zinc, white sparingly soluble precipitates.

(1305) *Anchoic*, or *Lepargylic Acid* ($\text{H}_2\text{C}_9\text{H}_{14}\text{O}_4$) was found by Buckton among the products of the oxidation of Chinese wax, and by Wirz among those of cocoa-nut oil by a similar process. It crystallizes in white warty masses, fuses at about 239° (115° C.), and is freely soluble in boiling water. Its vapours have a peculiarly irritating effect upon the organs of respiration: hence its name, from $\alpha\gamma\chi\omega$, to choke.

(1306) *Sebacic Acid* ($\text{H}_2\text{C}_{10}\text{H}_{16}\text{O}_4$).—This acid, the name of which is derived from *Sebum*, tallow, is easily obtained by the distillation of oleic acid: most of the fixed oils also yield it by distillation, owing to the decomposition of the olein which they contain; the acid is accompanied in this operation by various

hydrocarbons, and by other volatile acids. It may likewise be readily obtained in large quantity from the fixed residue of the distillation of castor oil with caustic potash; ricinoleic acid yielding octyl (capryl) alcohol, sebacic acid, and free hydrogen:—

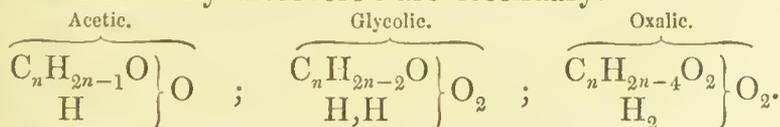


The potassic sebate is dissolved in boiling water and decomposed by the addition of hydrochloric acid; sebacic acid crystallizes in needles as the liquid cools. This acid is easily recognized by its ready solubility in boiling water, from which it crystallizes in pearly scales, as it is nearly insoluble at ordinary temperatures. It fuses at 260.6 (127° C.), and may be sublimed without decomposition, becoming condensed in needles which resemble those of benzoic acid. Its vapours have a greasy odour, and produce a very irritating effect upon the lungs. Sebacic acid is very soluble in alcohol and in ether. By oxidation with nitric acid it yields a mixture of lipic and succinic acids, mistaken by Schlieper for pyrotartaric acid.

Sebacic acid forms both normal and acid salts. The seabates of the metals of the alkalies and of the earths are soluble, but the other seabates are nearly insoluble.

(d) *Acids of the Glycolic Series* ($\text{C}_n\text{H}_{2n}\text{O}_3$).

(1307) Intermediate between the acetic and the oxalic series of acids is one which may be described as the glycolic series, which has been the subject of numerous researches, the most recent and comprehensive of which is that of Frankland and Duppa.* There are two sets of isomeric acids of this series, of which the first may be regarded as the primary acids, while the second more recently discovered are secondary.

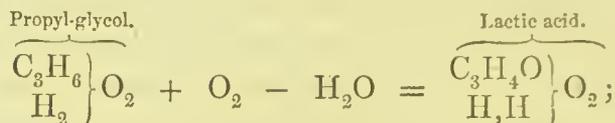


The following primary acids of the series are known:—

- | | |
|-------------------------------------|-------------------------------------|
| 1. Glycolic acid | $\text{C}_2\text{H}_4\text{O}_3$ |
| 2. Lactic acid | $\text{C}_3\text{H}_6\text{O}_3$ |
| 3. Butylactic (acetonic?) | $\text{C}_4\text{H}_8\text{O}_3$ |
| 4. Valerolactic | $\text{C}_5\text{H}_{10}\text{O}_3$ |
| 5. Leucic acid | $\text{C}_6\text{H}_{12}\text{O}_3$ |

* See particularly Kolbe, *Liebig's Annal.* cxiii. 223; Wurtz, *Ann. de Chimie*, III. lix. 161; Wislicenus, *Liebig's Ann.* cxxv. 41; cxxvi. 225; Frankland and Duppa, *Phil. Trans.* 1866.

These acids stand in a relation to the diatomic alcohols or glycols, similar to that which those of the acetic series bear to the monatomic alcohols (1299); and Wurtz has shown that the glycolic, lactic, and butylactic acids may be obtained by the gradual oxidation of their corresponding glycols. They appear to be acids formed upon the diatomic type, but to require only a single atom of a monad like potassium for their saturation. For example, lactic acid may be regarded as formed from propyl-glycol:—



but only one atom of the hydrogen of the acid is basylous, or admits of displacement by basyls under ordinary circumstances, so as to furnish a neutral salt; normal sodic lactate, for instance, being $\left. \begin{array}{c} \text{C}_3\text{H}_4\text{O} \\ \text{H, Na} \end{array} \right\} \text{O}_2$. These acids have been regarded as bodies which are intermediate in properties between true acids and alcohols, and if the second typical atom of hydrogen be expelled by sodium, a body as powerfully alkaline is obtained as sodium alcohol itself. The second typical atom of hydrogen has therefore been spoken of as *alcoholic* hydrogen, to indicate this difference in susceptibility to displacement by basyls. This distinction between the *atomicity* and the *basicity* of an acid, was first insisted on decidedly by Kekulé, and the difference is supposed by him to depend upon the fact that in these monobasic diatomic acids, there is only 1 atom of oxygen in the radicle of the acid; whereas in dibasic acids the radicle contains 2 atoms of oxygen. This view appears to explain many anomalies in the acids of this group, and accounts for the general deportment of these acids as monobasic, whilst in a few exceptional cases, where the second atom of hydrogen admits of displacement by a metal or an organic radicle like ethyl, the acids exhibit their true diatomic character (p. 345).

(1308) *Glycolic Acid* ($\text{HC}_2\text{H}_3\text{O}_3 = 76$).—This is a syrupy uncrystallizable liquid which is furnished by the gradual oxidation of glycol by nitric acid;* also by the reduction of glycocine by the action of nitrous anhydride (1615); and it is found in the mother-liquor obtained during the preparation of mercuric fulmi-

* A corresponding monobasic acid, the *diglycolic*, isomeric with malic acid, is obtained by the oxidation of diethylene alcohol; $(\text{C}_2\text{H}_4)_2\text{H}_2\text{O}_3 + 2 \text{O}_2 = \text{HC}_4\text{H}_2\text{O}_5 + 2 \text{H}_2\text{O}$; triethylene alcohol $(\text{C}_2\text{H}_4)_3\text{H}_2\text{O}_4$ yields *diglycolylethylene* acid, $\text{HC}_6\text{H}_4\text{O}_6$.

uate. It has also been procured by heating potassic mono-chloroacetate for some time to between 230° and 248° (110° and 120° C.), potassic chloride and *glycolic anhydride*, formerly called *glycolide* ($C_2H_2O_2$), being produced, in accordance with the equation $KC_2H_2ClO_2 = KCl + C_2H_2O_2$: on boiling the residue with water, each molecule assimilates 1 of water and becomes converted into glycolic acid. Glycolic acid greatly resembles the lactic acid, the zinc glycolate crystallizing in crusts, but it is distinguished from lactic acid by yielding a precipitate with solutions of normal plumbic acetate.

(1309) Little is known of the *butylactic* acid ($HC_4H_7O_3$), which is metameric, if not identical, with the acetic. Another isomeric acid, the *oxybutyric*, may be obtained by acting upon bromobutyric acid with argentic oxide in the presence of water: $2 C_4BrH_7O_2 + Ag_2O + H_2O = 2 C_4H_8O_3 + 2 AgBr$.

(1310) LACTIC ACID ($HC_3H_5O_3 = 90$).—The circumstances most favourable to the production of this important acid have already been mentioned (1119).

Preparation.—1. It is the acid which is formed when milk is allowed to become sour, and hence its name, from *lac*, milk.

2. But it is best obtained by dissolving 8 parts of cane sugar in about 50 parts of water; to this solution 1 part of casein, or of poor cheese, and 3 parts of chalk must be added: if this mixture be set aside for two or three weeks, and maintained at a temperature of 80° ($26^{\circ}.7$ C.) it gradually becomes filled with a mass of crystals of calcic lactate. These crystals must be purified by re-crystallization, and treated with about one-third of their weight, or their exact chemical equivalent, of sulphuric acid; the residue must then be digested in alcohol, which leaves the calcic sulphate and dissolves the lactic acid: pure lactic acid remains on evaporating the solution. Zincic oxide may be substituted for chalk in this operation, and from the zincic lactate so obtained, the zinc may be separated as sulphide by a current of sulphuretted hydrogen.

Pasteur considers that a specific ferment is concerned in the production of the lactic fermentation. During the fermentation of the mixture of sugar and casein with chalk, a layer of particles of a grey substance is observed upon the surface of the sediment. This substance may be obtained free from admixture by digesting washed yeast in 15 or 20 times its weight of boiling water, dissolving 1 part of sugar in 20 of the filtered liquid, adding chalk, and then a very small quantity of the grey deposit above mentioned, taken from a portion of liquid in the active stage of lactic fermentation. The acid fermentation rapidly sets in, the chalk disappears, and the grey sediment is gradually deposited in con-

siderable quantity: a solution of any nitrogenous substance may in this case be substituted for the infusion of beer yeast. The ferment thus obtained, when examined by the microscope, is seen to consist of little globules, or very short articulations, either isolated or in threads, constituting irregular floeculent particles, much smaller than those of beer yeast, and exhibiting a rapid gyratory motion. When washed with a large quantity of pure water and then diffused through a solution of pure sugar, acidification commences immediately, and proceeds gradually until arrested by the excess of free acid. The formation of lactic acid is always accompanied by the development of small quantities of butyric acid, alcohol, mannite, and a viscous substance—the proportions of these bodies varying greatly in different experiments. When the liquid is kept neutral by the addition of chalk, scarcely any mannite or gum is formed.

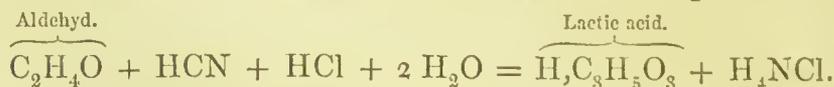
3. Lactic acid is also formed in a variety of other processes. Wurtz obtained it by the gradual oxidation of propyl-glycol (1213).

4. It may also be obtained from propionic acid, by converting this into chloropropionic, and decomposing this with caustic potash:—



5. By treating pyruvic acid ($\text{C}_6\text{H}_8\text{O}_6$) with an amalgam of sodium, 4 atoms of hydrogen unite with one of the acid, and two atoms of lactic acid are produced.

6. Wislicenus also found that by treating aldehyd with concentrated hydrocyanic acid in the presence of excess of hydrochloric acid, and leaving the mixture to itself for several days, sal ammoniac is formed, and ordinary lactic acid is produced:—



Aldehyd admits of being reconverted into ordinary lactic acid, as will be explained when speaking of alanine (1616). The relation of aldehyd to lactic acid is readily traced:—



When lactic acid is submitted to electrolysis, aldehyd and carbonic anhydride are formed at the positive electrode; and the same compounds are produced by other oxidizing processes, such as treatment of the acid with a mixture of sulphuric acid and black manganese oxide.

7. Lactic acid is a frequent product of the acidification of vegetable substances; for instance, it is formed in *sauer-kraut*, in

malt vinegar, and in the acid fermentation which takes place during the manufacture of wheat starch. It is likewise found ready formed in plants, in a few instances, and it exists in the form of calcic lactate in *nux vomica*.

8. Lactic acid is largely produced in the animal body: besides forming (in the modification of sarkolactic acid) an unfailing constituent of the fluids of the muscular tissue, it is one of the acids contained in the gastric juice; and in cases of diabetes it has been found, by Lehmann, in the saliva. It has also been met with in the urine, but it is not one of the normal constituents of this excretion: it has likewise been frequently found in the sweat.

In its pure state lactic acid forms a transparent, inodorous, uncrystallizable, syrupy liquid of sp. gr. 1.215: it has a sharp, acid taste, and is soluble in alcohol and in ether; if heated gradually in vessels from which air is excluded it may be distilled, though partial decomposition is apt to occur unless the heat be carefully regulated. When exposed to a long-continued heat of about 266° (130° C.) 2 molecules of the acid gradually lose 1 of water, and become converted into *dilactic acid*, formerly regarded as lactic anhydride ($C_6H_{10}O_5$), which is a yellowish, fusible, bitter substance, nearly insoluble in water, but soluble in alcohol and in ether: by long contact with cold water it is converted into ordinary lactic acid: the same change takes place more quickly if it be boiled with water.

If lactic acid be heated to about 500° (260° C.) decomposition ensues; water, carbonic oxide and aldehyd are formed; while a volatile acid, the citraconic, and lactic anhydride ($C_3H_4O_2$) formerly termed *lactide* distil over.

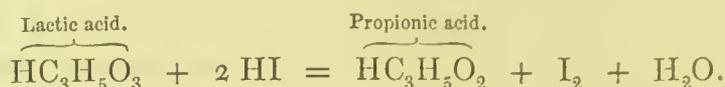
Pelouze obtained during the distillation of lactic acid, a volatile liquid to which he gave the name of *lactone* ($C_5H_8O_2$): it has a pungent odour, and boils at about 197°.6 (92° C.).

Lactic anhydride is dissolved freely by boiling absolute alcohol, and crystallizes from it on cooling, in brilliant rhombic prisms; at 224°.6 (107° C.) it fuses, and at a higher temperature it may be sublimed unchanged. Water dissolves it slowly but completely, but it cannot be crystallized from this solution, since it passes at once into normal lactic acid by assuming an atom of water. Lactic anhydride readily absorbs ammonia, and is converted into lactamide: $C_3H_4O_2 + H_3N = (H_2N)C_3H_5O_2$; this body is isomeric with sarkosine and with alanine, but is distinct from both.

When anhydrous calcic lactate is distilled with twice its weight of phosphoric chloride, it yields a colourless body, which Wurtz termed *chlorlactyl* ($C_3H_4OCl_2$), the oxychloride of lactic acid; this substance is decomposed by water, and yields hydrochloric and chloropropionic acids ($C_3H_4OCl_2 + H_2O = C_2H_5ClO_2 + HCl$); from the chloropropionic, propionic acid is easily obtained (1284).

Lautemann has also succeeded in converting lactic acid into

propionic, by saturating lactic acid with gaseous hydriodic acid, keeping the mixture cool, then sealing it in a tube, and heating it to 284° (140° C.) for some time. Iodine is liberated and propionic acid is formed:—



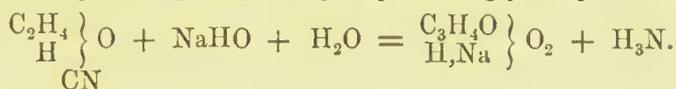
This reduction is effected still more easily by distilling 3.5 parts of lactic acid with 4 of phosphorus diiodide, when propionic acid passes over, coloured with a little free iodine.

Lactates.—The lactic was regarded by Gerhardt as a dibasic acid, and he accordingly doubled its formula, representing it as $\text{C}_6\text{H}_{12}\text{O}_6$; but later researches indicate that the older and simpler formula given above is to be preferred. The lactates are soluble in water, but insoluble in ether, and nearly so in cold alcohol: those of the alkalis do not crystallize. Normal and acid lactates may be formed with calcium and with barium. *Hydric boric lactate* ($\text{BaH}_2 \cdot 4\text{C}_3\text{H}_5\text{O}_3$) may be crystallized: the normal lactate is very soluble in water, and does not crystallize. *Hydric calcic lactate* ($\text{CaH}_2 \cdot 4\text{C}_3\text{H}_5\text{O}_3, \text{H}_2\text{O}$) crystallizes in radiated needles. *Normal calcic lactate* crystallizes in tufts of prisms, with $5\text{H}_2\text{O}$. The *zincic lactate* ($\text{Zn} \cdot 2\text{C}_3\text{H}_5\text{O}_3, 3\text{H}_2\text{O}$) is one of the most characteristic salts of this acid; it crystallizes in crusts, consisting of four-sided prisms, which require about 60 parts of cold and 6 of boiling water for solution. *Cupric lactate* ($\text{Cu} \cdot 2\text{C}_3\text{H}_5\text{O}_3, 2\text{H}_2\text{O}$) is only incompletely precipitated by caustic potash, an excess of which gives with it a deep blue solution; but the whole of the copper is separated as oxide on the addition of an excess of calcic hydrate. A *basic cupric lactate* ($\text{Cu} \cdot 2\text{C}_3\text{H}_5\text{O}_3, \text{CuO}$) may also be obtained. Several other basic lactates may be formed, analogous in composition to basic cupric lactate.

The variety of lactic acid which is obtained from the juice of flesh, yields salts which crystallize with a proportion of water differing from that contained in the salts furnished by the ordinary acid. The *sarkolactic* acid from muscular tissue may be distinguished as the variety α ; its salts crystallize with smaller proportions of water of crystallization than those of the ordinary form of the acid, which may be distinguished as the variety β . For example, it gives a salt of zinc, which contains only $2\text{H}_2\text{O}$, and crystallizes in slender needles; it begins to undergo decomposition below 302° (150° C.), whilst the salt of the ordinary acid may be heated to 392° (200° C.) without experiencing any decomposition. The normal calcic salt of the variety α also

crystallizes with $4\text{H}_2\text{O}$, and is less soluble than that of variety β , which crystallizes with $5\text{H}_2\text{O}$. Similar differences are observed in the copper salts; but the copper salt α is much the more soluble of the two.

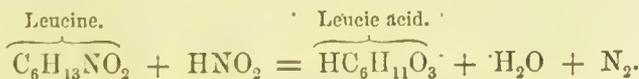
Strecker finds that the sarkolactic acid, when separated from its zinc salt by sulphuretted hydrogen and heated to between 266° and 284° (130° and 140° C.), is gradually converted into lactic anhydride, and this when redissolved in water possesses the properties of the ordinary variety β . Wislicenus obtained sodic sarkolactate by decomposing the cyanhydrin of glycol by caustic soda;



Lactic acid coagulates albumin; when present in small quantity it does not curdle milk in the cold, but does so if gently heated. The lactates, when heated with sulphuric acid, give off pure carbonic oxide, and deposit a solid brown matter resembling ulmic acid. By nitric acid the lactic is converted into oxalic acid.

The tests for lactic acid are not very definite. The best mode of identifying it (whether it be free or in combination), consists in evaporating the liquid suspected to contain it, to the consistence of a syrup over a water-bath, treating the residue with alcohol, and adding a small quantity of a solution of oxalic acid: the basyls are thus separated in the form of oxalates, but the lactic acid and the excess of oxalic acid remain dissolved. The acid liquid is carefully neutralized by baryta water, which causes a precipitate of baric oxalate, whilst the lactate of this metal remains dissolved. Baric lactate may be decomposed by adding a solution of calcic sulphate; baric sulphate is thus separated, and the calcic lactate may be crystallized from the alcoholic solution, and the form of the crystals ascertained by the microscope.

(1311) *Leucic Acid* ($\text{HC}_6\text{H}_{11}\text{O}_3 = 132$).—It was first obtained as a product of the decomposition of leucine by nitrous acid (1617):—



Leucic acid crystallizes in colourless needles, which are soluble in water, alcohol, and ether; heated to 167° (75° C.) it fuses, and sublimes unchanged at a little beyond 212° ; by a stronger heat it gives off water, and furnishes a crystallizable anhydride.

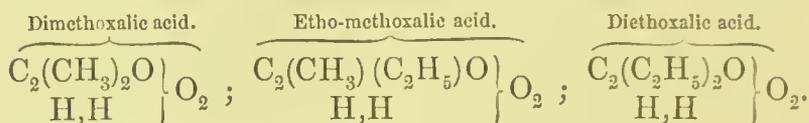
An acid isomeric with the leucic, *diethoxalic acid*, was obtained by Frankland and Duppa (*Phil. Trans.* 1866) from oxalic ether. By displacing one of the atoms of oxygen in the ether by two atoms of ethyl, diethoxalic ether was procured, and from this ether the metallic salts of the acid were obtained by treating the ether with potash or baryta. Diethoxalic ether was procured readily by heating a mixture of zinc amalgam, ethyl iodide, and oxalic ether, in equiva-

lent proportions; the resinoid mass thus obtained yields the ether if mixed with water and submitted to distillation.

The relation of oxalic ether to diethoxalic ether may be illustrated by the following formulæ:—



If methyl iodide, or a mixture of methyl and ethyl iodide in equivalent proportions be substituted for ethyl iodide, other terms of the same series of acids may be procured: three acids of this series may be thus represented:—



Frankland and Duppa have obtained other acids formed upon the same plan, and containing 7, 9 and 12 atoms of carbon.

§ IV. CERTAIN POLYBASIC VEGETABLE ACIDS.

(1312) SEVERAL polybasic acids, some of which, such as the malic, tartaric, and citric, are very extensively diffused through the vegetable kingdom, may conveniently be considered in juxtaposition with the fatty acids; as a very close connexion has recently been shown to exist between malic and tartaric acid and the succinic, a member of the oxalic acid group.

The acids which will now be described are the following:—

| | |
|--------------------------------------|--|
| 1. Malic acid | $\text{H}_2\text{C}_4\text{H}_4\text{O}_5$ |
| 2. Tartaric acid. | $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ |
| 3. Citric acid | $\text{H}_3\text{C}_6\text{H}_5\text{O}_7, \text{H}_2\text{O}$ |
| 4. Meconic acid | $\text{H}_3\text{C}_7\text{HO}_7, 3 \text{H}_2\text{O}$ |
| 5. Gallotannic acid. | $\text{H}_2\text{C}_{27}\text{H}_{20}\text{O}_{17}$ |
| 6. Gallic acid | $\text{H}_3\text{C}_7\text{H}_3\text{O}_5, \text{H}_2\text{O}$ |
| 7. Quinic acid | $\text{HC}_7\text{H}_{11}\text{O}_6$ |
| 8 and 9. Sorbic and Parasorbic acids | $\text{HC}_6\text{H}_7\text{O}_2$ |

1. Malic Acid, and its Derivatives.

(1313) MALIC ACID ($\text{H}_2\text{C}_4\text{H}_4\text{O}_5 = 134$).—This acid is extensively diffused through the vegetable kingdom; it occurs abundantly in most acidulous fruits, particularly in unripe apples, whence its name, from *malum*, an apple; it is also found in gooseberries and currants, in which it is accompanied by citric acid. The

footstalks of the garden rhubarb likewise contain it in considerable quantity, mixed with oxalic and phosphoric acids, and they furnish a convenient source of malic acid; but it is usually extracted from the unripe berries of the mountain ash. The dried leaves of the tobacco plant are also rich in acid calcic malate.

In order to obtain the acid, the expressed juice either of the mountain-ash berries or of the leafstalks of the rhubarb is nearly neutralized with milk of lime, and a certain quantity of calcic chloride is added in order to decompose the potassic malate which always accompanies the free acid. A precipitate is thus formed, which contains calcic citrate, phosphate, and tartrate. The liquid must be left with a feebly acid reaction, in order to avoid the subsequent precipitation of the colouring matter. The clear solution is then to be filtered, and the filtrate boiled for several hours: neutral calcic malate is thus gradually separated in the form of an insoluble powder. After this precipitate has been washed with cold water it is to be added in small portions at a time, so long as it continues to be dissolved, to hot dilute nitric acid (containing one part of acid to ten of water). The liquid thus obtained is to be filtered, and set aside to crystallize: well-defined crystals of acid calcic malate are then deposited. The acid malate obtained in this way may be purified by treating it with animal charcoal and recrystallizing it from water. Its solution may afterwards be converted into plumbic malate by the addition of plumbic acetate, and the plumbic malate when decomposed with sulphuric acid, yields free malic acid, from which the last traces of lead may be removed by means of sulphuretted hydrogen.

Properties.—The aqueous solution of malic acid, when evaporated to the consistence of syrup and left in a warm place, gradually deposits radiated masses composed of brilliant four or six-sided prisms. They are deliquescent in a moist air, and are soluble in alcohol; when heated they undergo fusion below 212° . Malic acid has a very sour taste; its solution, unless quite pure, becomes mouldy and viscid when kept.

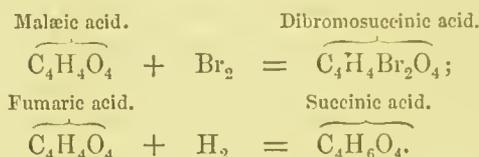
Malic acid, when heated to 356° (180° C.), is decomposed; water is expelled, and two metameric acids, the *malæic* and the *fumaric*, are formed, and at the same time malæic anhydride is obtained:—



Malæic acid, when maintained in a state of fusion at 302° (150° C.), is converted into a crystalline mass of fumaric acid. If distilled by a temperature

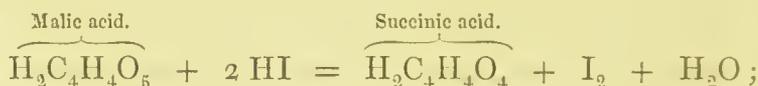
suddenly elevated to 464° (240° C.) malæic anhydride is formed. Sulphuric acid, when heated gently with malic acid, decomposes it, liberating carbonic and acetic acids; at a higher temperature it yields carbonic oxide. Nitric acid converts it first into fumaric and then into oxalic acid. If gradually oxidized by means of potassic chromate in the cold, malonic acid (1300) is formed. If heated with dilute sulphuric acid and black manganese oxide, aldehyd is among the products (Liebig). When heated with hydrochloric acid, malic acid is gradually converted into fumaric acid.

Kekulé (*Liebig's Annal.*, Suppl., 1861, 131) has shown that both fumaric acid and its metameride, malæic acid, combine directly with bromine, and furnish crystals of dibromosuccinic acid: and further, if fumaric acid be dissolved in water, and digested with an amalgam of sodium, the nascent hydrogen combines with the acid and converts it into succinic acid:—



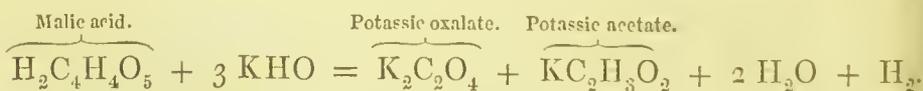
From the dibromosuccinic, tartaric acid (inactive) was obtained.

Malic acid may also be reduced to succinic acid by heating it in sealed tubes with hydriodic acid; whilst iodine is liberated (Schmitt):—



and succinic acid may be reconverted into optically inactive malic acid, by first preparing bromosuccinic acid and decomposing it with argentic oxide (1303; Kekulé).

When malic acid is fused with caustic potash at a temperature of 302° (150° C.) hydrogen is disengaged, and potassic oxalate and acetate are formed:—



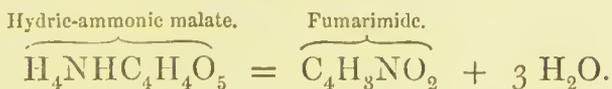
When a dilute solution of malic acid is gradually oxidized in the cold by the cautious addition of potassic dichromate, malonic acid ($\text{H}_2\text{C}_3\text{H}_2\text{O}_4$, the acid intermediate between the succinic and the oxalic) is amongst the products (1300).

(1314) *Malates* —The malic is a dibasic acid, and has a strong tendency to form acid salts. It is, however, probably formed upon the plan of three atoms of water, and is consequently tri-atomic, though only two atoms of hydrogen admit of displacement by metals under ordinary circumstances, *e.g.*:—



The hydric-ammonic malate and hydric-calcic malate are readily obtained in large regular crystals; but its most characteristic salt is *plumbic malate* ($\text{PbC}_4\text{H}_4\text{O}_5, 3\text{H}_2\text{O} = 339 + 54$), which when first precipitated is amorphous, but if left in the liquid, becomes converted into radiated tufts of silky needles. It is fusible into a pasty mass at a temperature below that of boiling water. Malic acid, like the tartaric, prevents the precipitation of iron from its solution by the alkalis. Malic acid gives no precipitate with lime-water, either when cold or hot; but by evaporation of the liquid, a crystallized calcic malate is produced, which is dissolved by boiling water. These characters distinguish the malic from oxalic, tartaric, racemic, and citric acids. Most of the malates are soluble in water, but not in alcohol. Many of the malates, such as those of calcium and barium, when heated to 392° (200°C.), lose 2 molecules of water, and become converted into fumarates, from which fumaric acid (identical with the acid of the *Fumaria officinalis*) may be obtained in characteristic broad, slender, sparingly soluble, striated prisms.

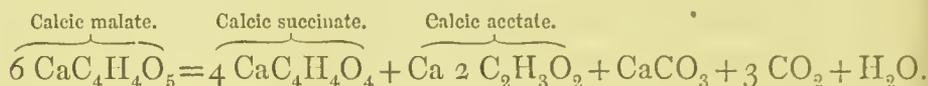
Hydric-ammonic malate, or *Bimalate of ammonium* ($\text{H}_4\text{NH C}_4\text{H}_4\text{O}_5$) is readily obtained by dividing a solution of malic acid into two equal portions, exactly neutralizing one with ammonia, and then adding to it the other portion of the acid; on evaporation, brilliant right rhombic prisms are formed (75). It is remarkable that the optically active hydric-ammonic malate (1315) forms a crystallizable double salt with ammonic dextrotartrate, but it forms no such compound with the lævotartrate. Hydric-ammonic malate, when submitted to distillation, is converted into a brick-coloured powder, termed *fumarimide*:—



Hydric calcic Malate, or *Bimalate of Lime* ($\text{CaH}_2, 2\text{C}_4\text{H}_4\text{O}_5, 8\text{H}_2\text{O} = 306 + 144$).—This salt is obtained in beautiful transparent rhombic prisms, by dissolving normal calcic malate in hot dilute nitric acid, and allowing the solution to cool. It is sparingly soluble in cold water.

Normal calcic malate exists in two modifications: one of these ($\text{CaC}_4\text{H}_4\text{O}_5, 2\text{H}_2\text{O} = 172 + 36$) is readily soluble. It is obtained by neutralizing malic acid or hydric-calcic malate with milk of lime; the solution may be evaporated at ordinary temperatures, and deposits large brilliant crystalline plates. If the solution of this salt be boiled for some hours it gradually deposits a sparingly soluble, granular, crystalline powder, which when analysed is

found to contain H_2O , but has in other respects the same composition as the soluble malate. The soluble form of calcic malate may also be obtained with $2\frac{1}{2}\text{H}_2\text{O}$ and with $3\text{H}_2\text{O}$. If calcic malate be placed beneath a layer of water, in a vessel loosely covered, it gradually undergoes decomposition: carbonic acid is disengaged, and a mixture of calcic lactate, acetate, and succinate (1301) is formed. This change is accelerated by the addition of a small quantity of yeast, or of decaying cheese, to the mixture:—



If the fermentation be conducted at a higher temperature, hydrogen gas is evolved, and calcic butyrate is the principal product.

It will be observed that the formula of malic acid differs from that of the succinic by containing one atom more, and from that of the tartaric by containing one atom less of oxygen.

Baric malate ($\text{BaC}_4\text{H}_4\text{O}_5, 2\text{H}_2\text{O}$) crystallizes in plates which are readily soluble in water; when boiled, the solution deposits heavy granular crystals of the anhydrous salt.

Zincic malate ($\text{ZnC}_4\text{H}_4\text{O}_5, 3\text{H}_2\text{O}$) is sparingly soluble in cold water, but is taken up by ten times its weight of boiling water; short, rectangular, brilliant, very hard prisms are deposited as it cools. A hydrie-zincic malate ($\text{ZnH}_2\text{C}_4\text{H}_4\text{O}_5, 4\text{H}_2\text{O}$) may also be obtained in octahedral crystals.

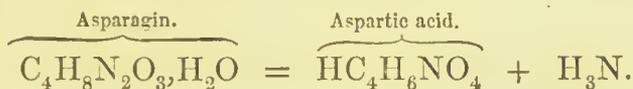
Besides the normal plumbic malate, a *basic malate* ($\text{PbC}_4\text{H}_4\text{O}_5, \text{PbO}$), may be obtained by precipitating a soluble malate by basic plumbic acetate; it is not fusible in boiling water.

Argentinc malate forms a white, anhydrous, insoluble powder.

(1315) *Metameric Modifications of Malic Acid.*—Malic acid has been ascertained by Pasteur to exist in two modifications, which may be distinguished by the letters α and β ; the ordinary variety, α , which exerts a left-handed rotatory action upon a ray of polarized light, is the ordinary form of the acid; some of its salts exert a rotation to the left, others to the right. The variety β is destitute of any such rotatory power, and hence is termed *inactive malic acid*. The latter modification of the acid presents scarcely any perceptible chemical difference from the acid α , but it crystallizes rather more readily from its aqueous solution, since it is somewhat less soluble and is not deliquescent: it also requires a temperature of $271^\circ.4$ (133°C.) for its fusion: when heated a few degrees beyond this point it is decomposed, and furnishes the same compounds as the ordinary form of the acid. Inactive malic acid is furnished by decomposing bromosuccinic acid with argentic oxide: it is also procured by the action of nitrous anhydride upon inactive aspartic acid (1317); during this reaction nitrogen escapes in abundance, and if the acid liquid be supersaturated with ammonia when the disengagement of gas has ceased, the addition of a solution of plumbic acetate causes the separation of a precipitate of inactive plumbic malate; and from this malate sulphuretted hydrogen liberates the inactive acid, β .

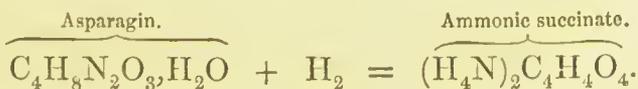
(1316) *Amides of Malic Acid—Asparagin.*—Malic acid, like the dibasic acids in general, forms two amides; one of these possesses the properties of an acid, and has been termed *malamic acid* ($\text{HH}_2\text{N}, \text{C}_4\text{H}_4\text{O}_4$); it is isomeric with aspartic acid, but not identical with it.

Asparagin ($\text{C}_4\text{H}_8\text{N}_2\text{O}_3, \text{H}_2\text{O}$).—This crystalline body is extracted from the young shoots of the asparagus and of the climbing vetch, from the roots of the marshmallow, and from several other plants. It may generally be procured in crystals by simply evaporating the expressed juice of one of these plants. The brown crystals thus obtained may be purified by treatment with animal charcoal and re-crystallization. Asparagin, when pure, forms beautiful octahedra, or rhombic prisms, which are soluble in about 60 parts of cold water, and are freely dissolved by boiling water, by dilute acids and alkalies, and by proof spirit. It has a mawkish and cooling taste. When dissolved in water, or in alkaline solutions, it exerts a left-handed rotation upon a ray of polarized light; but if dissolved in acids it produces a right-handed rotation of the ray. Asparagin is chiefly remarkable for the facility with which it is decomposed into aspartic acid and ammonia, when its aqueous solution is heated with alkalies or with acids:—

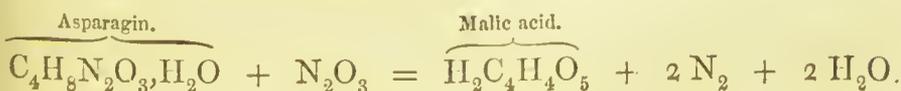


When an aqueous solution of asparagin is heated under pressure it is wholly converted into ammoniac aspartate; and the same effect takes place slowly when the solution is exposed to a temperature of 212° for a few days. At a moderate heat, asparagin loses its water of crystallization, and in its anhydrous form is isomeric with malamide; it is, in fact, the amide of aspartic acid.

Piria found that if the expressed juice of the vetch were allowed to putrefy, the asparagin which it contained was gradually converted into ammoniac succinate, by the assimilation of 2 atoms of hydrogen:—



When asparagin is treated with nitric acid which has been saturated with nitrous anhydride, it is converted into malic acid, whilst nitrogen is disengaged:—



This reaction is similar to that which occurs when the amides are thus treated, and hence Piria was led to regard asparagin as identical with malamide; but on decomposing malic ether by means of ammonia, a substance is obtained which is isomeric with asparagin, though not identical with it. Asparagin forms combinations with several of the acids in definite proportions; for instance, the nitrate, the oxalate, the dextrotartrate, and the hydrochlorate of asparagin may be obtained in crystals without difficulty. The lævotartrate of asparagin forms an uncrystallizable syrup. Asparagin also combines with bases, and even displaces acetic acid from plumbic acetate.

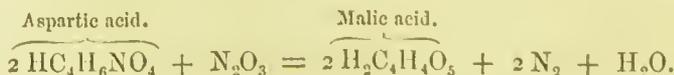
(1317) *Aspartic Acid* ($\text{HC}_4\text{H}_6\text{NO}_4$).—If ammoniac aspartate be boiled with baryta water till the ammonia is entirely expelled, baric aspartate is formed; and from this salt the barium may be precipitated by the cautious addition of sulphuric acid: on evaporating the solution thus obtained, aspartic acid crystallizes in thin rectangular tables which have a silky lustre. It is soluble both in acids and alkalis; when dissolved in the alkalis it produces left-handed rotation of the plane of polarization, but if dissolved in acids the rotation is to the right.

Aspartic acid may be represented as malic acid in which an atom of hydroxyl, HO, has been displaced by an atom of amidogen, the hydroxyl being formed at the expense of the atom of alcoholic hydrogen of malic acid; whilst malamic acid and malamide are normal amides, or corresponding bodies, in which one of the basic atoms of hydrogen has been displaced, aspartic acid bearing a relation to malic acid analogous to that existing between glycocine and acetic acid (Kekulé):—



Pasteur has discovered the existence of a second modification of aspartic acid which is without action upon polarized light. This *inactive* acid is obtained by heating hydric-ammonic malate to about 356° (180° C.), and boiling the residue (fumarimide, $\text{C}_4\text{H}_3\text{NO}_2$) for some hours with hydrochloric acid. It thus assimilates the elements of $2\text{H}_2\text{O}$; and the solution, when evaporated, yields crystals of hydrochlorate of aspartic acid ($\text{C}_4\text{H}_7\text{NO}_4, \text{HCl}$). These crystals must be dissolved in hot water, and the solution divided into two equal portions; one of these is to be exactly neutralized by the addition of ammonia, and then added to the second portion; as the liquid cools, crystals of inactive aspartic acid are deposited in abundance. It is somewhat more soluble than the active variety, but in other respects resembles it in chemical properties.

Most of the aspartates are readily soluble in water. The acid appears in a few cases to form subsalts. Aspartic acid, when dissolved in nitric acid and saturated with nitrous anhydride, yields malic acid, whilst nitrogen is disengaged; and if the inactive variety be employed, the malic acid which is obtained is likewise of the inactive form (1315):—



2. Tartaric Acid, and its Derivatives.

(1318) *Isomeric Forms of Tartaric Acid.*—The remarkable researches of Pasteur (*Ann. de Chimie*, III. xxiv. 442, and xxviii. 56) upon the optical and chemical properties of tartaric acid, have opened a new and important method of investigating the molecular composition of organic bodies. He has proved the existence of two varieties of tartaric acid, which may be distinguished by the peculiarities of their crystals. The crystals of each variety of tartaric acid are always unsymmetrical; but the deficit in symmetry displayed by the crystals of one variety is exactly the reverse of that manifested by those of the other variety. Each of these forms of tartaric acid exerts a powerful effect of rotation upon a ray of polarized light; but the effect produced by equal quantities of the two varieties of the acid, though equal in amount, is opposite in direction. One of the modifications exhibits a crystalline form, which is termed *dextro-hemihedral*; its solution produces right-handed rotation of a ray of polarized light; this variety is known as *dextrotartaric*, or *dextroracemic acid*: it is the usual form of the acid. The other modification is *levohemihedral*, and produces a left-handed rotation of a polarized ray exactly equal in amount to the right-handed rotation of the ordinary variety: this modification constitutes *levotartaric* or *levoracemic acid*. The two acids are so related in crystalline form, that if the salt of the acid which is dextro-hemihedral be held before a mirror, the reflection of the crystal will exactly represent the form of the corresponding crystal of the levohemihedral acid. Both these modifications are exactly similar in chemical properties, so long as they are combined with bodies which exert no action upon polarized light; but this identity in chemical properties disappears when they are united with bodies endowed with rotatory power upon polarized light: for example, dextrotartaric acid forms with asparagin a crystalline compound, whilst the levotartaric acid forms with this body a gummy mass.

When concentrated solutions of equal parts of dextrotartaric and levotartaric acids are mixed together, the temperature rises considerably: and on cooling, crystals of a different acid are formed. This new acid is identical with the *paratartaric* or *racemic acid*: it has no longer the power of causing the rotation of a ray of polarized light, and it presents differences in its chemical reactions (1322) from those of both of its components.

Yet, if the acid thus obtained be divided into two equal parts,

one half being neutralized with soda, then mixed with the other half of the acid and neutralized with ammonia, the solution on evaporation will yield crystals, each of which has a powerful rotatory action on polarized light; but the crystalline mass will be found to consist of a mixture of the right-handed and of the left-handed ammonio-sodic tartrate, in equal proportions. The crystals of the two salts are recognized by their opposite hemihedral form, and may be separated by hand. If all the right-handed crystals be dissolved separately in water, and decomposed by adding a solution of plumbic nitrate, a precipitate consisting of plumbic dextrotartrate will be deposited. From this precipitate the dextrotartaric acid may be separated by means of sulphuric acid, and may be obtained in crystals on evaporation: if the lævohemihedral crystals be treated in a similar manner, lævotartaric acid may also be procured.

It was by treating the natural ammonio-sodic racemate in this manner, and picking out each crystal separately, that Pasteur was enabled to prove the existence of the two modifications of tartaric acid, and to show that racemic acid consists of a mixture of two acids which exert opposite effects of rotation on polarized light.

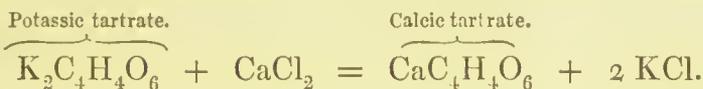
Very few of the salts of racemic acid thus spontaneously separate into two different hemihedral varieties of crystalline form; the einchonine racemate (1393) is easily separable into its component crystals, and quinine racemate also exhibits a similar property. These salts may therefore be employed for the purpose of isolating the two modifications of tartaric acid when they occur in combination: at a certain stage of concentration of the einchonine racemate the first crop of crystals consists chiefly of the lævotartrate. When quinine racemate is employed, the crystals which are first deposited consist mainly of the dextrotartrate.

(1319) ORDINARY TARTARIC ACID, or *Dextroracemic Acid* ($H_2C_4H_4O_6 = 150$).—The principal supply of this acid is obtained from the grape; but it is also present in the tamarind, and in the unripe berries of the mountain ash; it is likewise frequently met with in small quantity in other plants. Liebig also found it in the acid mother-liquor left in preparing mucic acid from sugar of milk and from gum. Mannite and dulcitate, according to Carlet, yield a portion of racemic acid when oxidized by nitric acid. Grape juice contains dextrotartaric acid in the form of acid tartrate, or, as it is sometimes called, bitartrate of potash (hydriepotassic tartrate), constituting the crust or *tartar* which is deposited in the vessel in which the wine is kept.

Preparation.—In order to prepare the acid, crude tartar is dissolved in boiling water, and chalk is added so long as effervescence occurs, 4 parts of tartar requiring about 1 part of chalk; an insoluble calcic tartrate is thus precipitated, and normal potassic tartrate remains dissolved. Tartaric acid being dibasic the change which occurs may be thus represented:—Two molecules of hydric-potassic tartrate (bitartrate) react upon one molecule of calcic carbonate, and form one of normal calcic tartrate, and one of dibasic normal potassic tartrate; thus:—

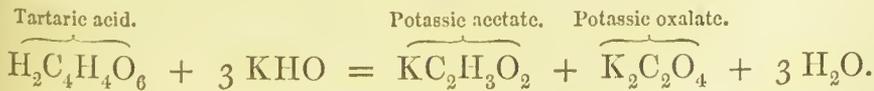


The potassic tartrate in solution may be decomposed by the addition of an equivalent quantity of calcic chloride, and the whole of the tartaric acid may thus be separated as calcic tartrate:—



The mixed product of the two operations is well washed, and digested with oil of vitriol diluted with 6 or 8 times its weight of water; for every 5 parts of tartar 3 parts of concentrated sulphuric acid are required; the solution is allowed to digest at a gentle heat, calcic sulphate is formed, and tartaric acid set free. When cool, the liquid is filtered, evaporated in leaden vessels to the consistence of syrup, and allowed to crystallize; the formation of crystals is favoured by the presence of an excess of sulphuric acid.

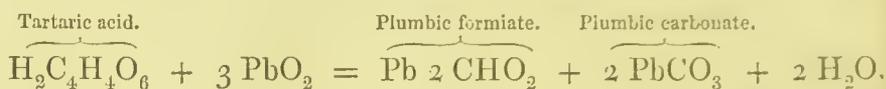
Properties.—The acid thus obtained assumes the form of oblique rhombic prisms; when pure they are colourless, transparent, and permanent in the air. Tartaric acid is very soluble in water, in alcohol, and in wood spirit; it has a sharp agreeable acid taste. If heated with the caustic alkalies, water is expelled, and oxalate and acetate of the basyl are formed:—



Its aqueous solution becomes mouldy when long kept, and is slowly converted into acetic acid.

The crystals of tartaric acid, when gently heated, become as strongly electrical as those of tourmaline. Its solutions, particularly when hot, exert a powerful right-handed rotation upon a ray of polarized light. Powdered tartaric acid furnishes with a large excess of nitric acid (sp. gr. 1.5) a nitro-acid [$\text{C}_4\text{H}_4(\text{NO}_2)_2\text{O}_6$],

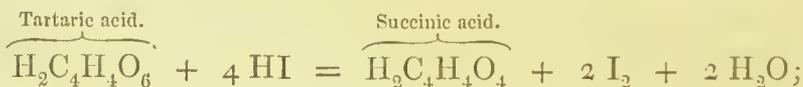
soluble in absolute alcohol, from which it may be obtained in crystals by spontaneous evaporation, but it is very unstable. When tartaric is boiled with nitric acid, oxalic acid is formed, together with an acid, the *tartronic* ($\text{H}_2\text{C}_3\text{H}_2\text{O}_5$), homologous with the malic. Tartaric acid exhibits considerable tendency to combine with oxygen. If it be boiled with lead dioxide it undergoes decomposition, water and plumbic carbonate being produced, while plumbic formiate remains in the solution:—



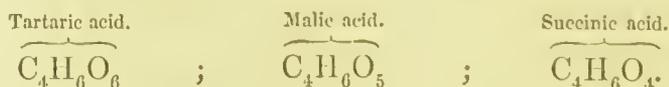
The salts of silver, of gold, and of platinum, are also reduced when boiled with tartaric acid.

Tartaric acid is extensively used by the calico-printer and dyer for the removal of certain mordants from particular portions of the cloth. It is also used in the preparation of effervescing draughts with the hydric-carbonates (bicarbonates) of the alkali metals.

An interesting relation exists between tartaric and succinic acids, in consequence of which tartaric may be reduced to succinic acid by saturating its concentrated aqueous solution with hydriodic acid, sealing it up in a strong glass tube and heating it, for six or eight hours, to a temperature not exceeding 248° (120°C). (Selmitt, *Liebig's Annal.*, cxiv. 109):—



and succinic acid may, in turn, be reconverted into the inactive variety of tartaric acid, by changing it first into dibromosuccinic acid, and then decomposing this compound with argentic oxide (Perkin and Duppa; 1303). Dessaignes, by treating tartaric acid with a mixture of phosphorus and iodine, also produced succinic acid, and at the same time obtained malic acid in the mother-liquor, the tartaric acid losing first 1 atom of oxygen, thus furnishing malic acid, and this acid in turn losing another atom of oxygen, thus yielding the succinic:—



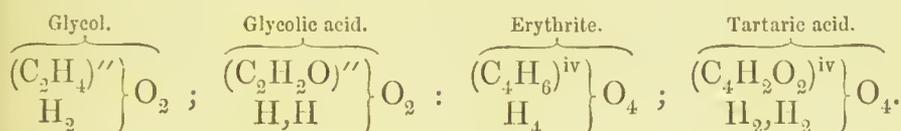
(1320) *Tartrates*.—The tartaric is a dibasic acid, but it is probably formed on the tetratomic type, the atomicity and basicity being different, as in the case of the glycolic group, which would account for the anomalous effect of heat in expelling an atom of

water from certain of the anhydrous tartrates, as will be mentioned immediately; $H_2C_4H_4O_6$ being probably of the type $\left. \begin{matrix} H_4 \\ H_4 \end{matrix} \right\} O_4$,

or $\left. \begin{matrix} C_4H_2O_2 \\ H_2H_2 \end{matrix} \right\} O_4$, the normal tartrates, such as potassic tartrate,

being $\left. \begin{matrix} C_4H_2O_2 \\ H_2K_2 \end{matrix} \right\} O_4$. Tartaric acid would then bear to erythrite

(1243) the same relation that glycolic acid bears to glycol, in which two atoms of hydrogen in the radicle are displaced by one atom of oxygen; in erythrite the exchange would be H_4 for O_2 : this exchange has not, however, as yet been actually effected:—



Tartaric acid has a strong tendency to form double salts, three varieties of which may be distinguished;—

1. Salts formed from protoxides only; such as—

| | |
|------------------------------------|-----------------------|
| Rochelle salt | $KNaC_4H_4O_6, 4H_2O$ |
| Cream of tartar | $KHC_4H_4O_6$ |
| Potassic cupric tartrate | $K_2Cu_2C_4H_4O_6$. |

2. Salts formed from both protoxides and sesquioxides, but in which the sesquioxide is combined with the same proportion of acid as the protoxide; such as—

| | |
|-------------------------------------|-------------------------------|
| Potassic ferric tartrate | $K, FeO, C_4H_4O_6$ |
| Potassic chromic tartrate | $2(K, CrO, C_4H_4O_6), 7H_2O$ |
| Potassic uranic tartrate | $K, UO, C_4H_4O_6, H_2O$. |

3. Salts analogous to tartar emetic:—

| | |
|---|----------------------------------|
| Tartar emetic, or potassic antimonious tartrate | } . $2(K, SbO, C_4H_4O_6), H_2O$ |
| Argentio-antimonious tartrate | |
| Argentio-antimonious tartrate | $Ag, SbO, C_4H_4O_6$ |
| Neutral antimonious tartrate | $(SbO)_2, C_4H_4O_6, H_2O$ |
| Potassic boro-tartrate | $K, BO, C_4H_4O_6$ |
| Potassic arsenio-tartrate | $2(K, AsO, C_4H_4O_6), 5H_2O$. |

The salts of this third class, with the exception of the compound with arsenious acid, are remarkable for the property which they possess, when apparently anhydrous, of losing an additional atom of water, so as to present a composition which may be regarded as exhibiting a certain resemblance to that of tartaric anhydride (Gerhardt): SbO (or its equivalent representative, BO)

being able to occupy the position of 1 atom of hydrogen in the compound, for example ;—

At ordinary temperatures,

| | | |
|-------------------------------------|-------------|------------------------------|
| Tartaric acid | consists of | $C_4H_6O_6$ |
| Neutral antimonious tartrate . . . | „ | $C_4H_4(SbO)_2O_6, H_2O$ |
| Tartar emetic | „ | $2[C_4H_4K(SbO)_2O_6], H_2O$ |
| Tartrate of silver and antimony . . | „ | $C_4H_4Ag(SbO)_2O_6$ |
| Potassic boro-tartrate | „ | $C_4H_4K(BO)_6$ |

But when heated they become, respectively,

| | |
|--|----------------------|
| Tartaric anhydride | $C_4H_4O_5$ |
| Neutral tartrate of antimony at 374° (190° C.) | $C_4H_2(SbO)_2O_5$ |
| Tartar emetic dried at 392° (200° C.) . . . | $C_4H_2K(SbO)_2O_5$ |
| Tartrate of silver and antimony at 320° (160° C.) | $C_4H_2Ag(SbO)_2O_5$ |
| Potassic boro-tartrate at 506° (263° C.) . . . | $C_4H_2K(BO)_5$ |

Potassic tartrate ($K_2C_4H_4O_6=226$) crystallizes readily; it is somewhat deliquescent and very soluble. The *hydric-potassic tartrate*, or *bitartrate of potash*, ($KHC_4H_4O_6=188$) is the ordinary source of the compounds of tartaric acid: it constitutes the crude tartar or *argol* of commerce, and is gradually deposited from all wines, forming a crust upon the inside of casks in which the wine is stored. This salt is very sparingly soluble in cold water, of which it requires about 180 parts for solution; boiling water dissolves about one-sixth of its weight of it, and deposits the salt in oblique rhombic prisms, which when pure are of snowy whiteness, forming common *cream of tartar*. It produces a gritty sensation under the teeth, and has a sour taste. When heated to redness in covered vessels, the acid is decomposed, and a charred mass remains, consisting of potassic carbonate and unconsumed carbon; this product is often used in the laboratory under the name of *black flux*. If the salt be calcined with twice its weight of nitre, *white flux* is obtained; in this operation the carbon of the organic acid is completely burned, and potassic carbonate is left.

Sodic-potassic tartrate ($KNaC_4H_4O_6, 4 H_2O=210+72$).—The atom of basylous hydrogen in cream of tartar may be displaced from it by sodium, and then a double salt, often called *Rochelle salt*, is produced: it forms large beautiful crystals which have the appearance of six-sided prisms, one-half of which only is developed.

Hydric-sodic tartrate ($NaHC_4H_4O_6, H_2O$) is a soluble salt, and is sometimes employed to separate potash from soda in concentrated solutions. The tartrates of *calcium* ($CaC_4H_4O_6, 4 H_2O$), *barium*, and *magnesium*, are sparingly soluble. *Iron* forms with potassium and with ammonium double ferric tartrates which are

used in medicine: the potassium salt when dried at 212° is anhydrous: ammonio-ferric tartrate has the formula $(\text{H}_4\text{N}, \text{FeO}, \text{C}_4\text{H}_4\text{O}_6, 2 \text{H}_2\text{O})$.

Potassic Borotartrate; Soluble Tartar ($\text{K}, \text{BO}, \text{C}_4\text{H}_4\text{O}_6$; at 212°).—When 1 part of boracic acid, 2 parts of cream of tartar, and 24 of water are heated together, a solution is formed, which on evaporation to dryness and treatment with alcohol (in order to remove the excess of boracic acid) furnishes the foregoing compound, in the form of a white non-crystalline powder, which is insoluble in alcohol, but very soluble in water; but it becomes anhydrous at 212° , and if heated to 563° (295° C.) it loses another atom of water, like tartar emetic under similar circumstances. This salt has been employed medicinally as a purgative.

Tartrates of Antimony.—Several tartrates of antimony may be formed. These salts are remarkable for the property which they possess, when apparently anhydrous, of losing an atom of water when heated, so as to present a composition corresponding to that of tartaric anhydride. The most important of these compounds is known as *tartarized antimony* or *tartar emetic* [$2(\text{K}, \text{SbO}, \text{C}_4\text{H}_4\text{O}_6), \text{H}_2\text{O}$], which has long been extensively used in medicine. Tartar emetic may be prepared in various ways: one of the best is the following:—3 parts of antimonious oxide, obtained by boiling to dryness sulphuric acid upon metallic antimony, and washing the residue with sodic carbonate, are mingled with 4 parts of cream of tartar, and made into thin paste with water. This mixture is allowed to digest for some hours, and is then boiled with 6 or 8 parts of water. The solution thus formed is filtered while hot, and allowed to crystallize: as the liquid cools the salt is deposited in the form of square prisms, the primary form of which is an octahedron, with a rhombic base. Tartar emetic is soluble in about 15 parts of cold water; its solution reddens litmus slightly. This salt is somewhat efflorescent; when dried at 212° it becomes anhydrous, and when heated to 392° (200° C.) it loses another atom of water, and then has a composition of $\text{KSbO}, \text{C}_4\text{H}_2\text{O}_5$; if this body be redissolved in water it furnishes ordinary tartar emetic. A solution of tartarized antimony acts as a violent emetic and cathartic poison. Sulphuretted hydrogen throws down the orange-coloured antimonious sulphide (Sb_2S_3) from it, and the alkalis and their carbonates occasion a precipitate of antimonious oxide (Sb_2O_3).

The place of the potassium in ordinary tartar emetic may be supplied by sodium, ammonium, silver, or lead; the lead and silver salts thus formed lose an atom of water at a high temperature in the same manner as the potassium salt.

A compound similar to tartar emetic may be formed with arsenious acid ($\text{KAsO}, \text{C}_4\text{H}_4\text{O}_6$).

The mother-liquors from which tartar emetic has been prepared, often

deposit a compound which may be crystallized with difficulty in oblique rhombic prisms, $(2 [KSbO, 11_2 C_4 H_4 O_6], 5 H_2 O; Knapp)$: it is a combination of tartar emetic with an additional atom of tartaric acid. Knapp also obtained a compound of tartar emetic with cream of tartar $[KSbO, C_4 H_4 O_6, 3 KHC_4 H_4 O_6]$, by boiling 5 parts of tartar emetic with 8 of cream of tartar, and a small quantity of water; it is deposited in sparingly soluble pearly scales. If antimonious oxide be dissolved in tartaric acid, the addition of alcohol in excess occasions the separation of a granular white precipitate, which, according to Berzelius, has a composition represented by the formula $[(SbO)_2 C_4 H_4 O_6, H_2 O]$. According to Péligot an acid tartrate $[2 (H_3 SbO, 2 C_4 H_4 O_6), 5 H_2 O]$ may be obtained in large crystals from a solution of antimonious oxide in excess of tartaric acid.

The presence of tartaric acid in solution is detected, if the liquid be moderately concentrated, by the addition of potassic acetate; a few drops of free acetic acid must also be added if the solution be neutral; under these circumstances the sparingly soluble hydric-potassic tartrate falls, the quantity of which is much increased by briskly stirring the mixture. With salts of silver a sparingly soluble argentic tartrate is formed: this precipitate when placed on platinum foil becomes charred, swells up on the application of heat, and leaves a residue of pure silver. A solution of calcic sulphate is not precipitated by a solution of tartaric acid. Lime-water in excess occasions a precipitate which disappears on the addition of sal-ammoniac; the precipitate is also soluble in cold solution of potash, but on boiling the liquid it reappears. Calcic chloride and plumbic acetate give white precipitates in neutral solutions of the tartrates.

The presence of tartaric acid in a solution which contains salts of iron or of copper prevents the precipitation of the oxides of these metals on the addition of an alkali. This property is sometimes taken advantage of in the operations of analysis.

The tartrates when heated strongly become blackened and are decomposed, emitting an odour of burnt sugar.

(1321) *Action of Heat on Tartaric Acid.*—The action of heat upon tartaric acid is remarkable. If heated to about $338^\circ (170^\circ C.)$ it fuses, and without losing weight is changed into a metameric acid, the *metatartaric*. Metatartaric acid forms a deliquescent uncrystallizable mass: it is dibasic, but its salts are more soluble than the ordinary tartrates, into which they are transformed by boiling their solutions.

If tartaric acid be heated to $374^\circ (190^\circ C.)$ it fuses; two atoms of the acid lose one atom of water, and thus become converted into a new acid, termed by Fremy the *tartralic*. Kekulé suggests that this is *ditartaric* acid: $\left. \begin{array}{l} (C_4 H_2 O_2)_2 \\ H_4 H_2 \end{array} \right\} O_7$; and that the second compound which is obtained by keeping the acid longer in fusion when half its basic water is expelled, is the anhydride of this acid. Fremy terms it *tartrellic acid*. This Kekulé regards as identical with Gerhardt's *isotartaric acid*, and he considers that chemist to be in error in stating that no water is expelled during its formation.

If the temperature of the fused tartaric acid be cautiously maintained for

some time at 374° (190° C.), all its basic water is driven off, and *tartaric anhydride* remains in the form of a white porous mass; in order to remove any unchanged tartaric acid, it may be washed first with cold water, and then with alcohol, after which it should be dried *in vacuo*. It is insoluble in water, alcohol, and ether, but if allowed to remain long moist it gradually becomes soluble, and is converted into crystallized tartaric acid.

By heating crystallized tartaric acid to about 392° (200° C.) in a retort, an acid liquor distils, which contains acetic acid, and a new acid, termed *pyruvic* or *pyroracemic* acid ($\text{H}_2\text{C}_5\text{H}_6\text{O}_5$). It forms an insoluble salt with lead, and a sparingly soluble one with silver. Pyruvic acid is characterized by the production of a red solution when mixed with a solution of a ferrous salt. If its salts be prepared in the cold, they are crystallizable; but if the acid be saturated with bases at a higher temperature, the salts are gummy and do not crystallize. Pyruvic acid when heated with hydriodic acid or with sodium amalgam, combines with hydrogen, and is converted into lactic acid, or by prolonging the action, into propionic:—



During the distillation of tartaric acid, a quantity of a second new acid is also formed; it crystallizes in oblique rhombic prisms, and has received the name of *pyrotartaric acid* ($\text{H}_2\text{C}_5\text{H}_6\text{O}_4$); it contains the elements of 1 atom of carbonic anhydride less than the pyruvic. Acetic acid, formic acid, aldehyd, and carbonic acid also accompany pyrotartaric acid during the distillation. Pyrotartaric acid is dibasic, it forms both normal and acid salts; the latter crystallize with facility.

(1322) *Racemic, or Paratartaric Acid* ($\text{H}_2\text{C}_4\text{H}_4\text{O}_6, \text{H}_2\text{O}$).—

Some varieties of the grape present a singular modification of tartaric acid, which is metameric with the ordinary acid, and equal amounts of the two acids saturate equal quantities of the same base. This acid, as has been already stated (1318), is plainly a compound of dextrotartaric and lævotartaric acids: it is without action upon polarized light. Racemic acid is formed in small quantity during the oxidation of mannite, dulcete, mucic acid, and sorbin, by nitric acid. Another remarkable mode of its formation has been pointed out by Löwig, who found that desoxalic acid ($\text{C}_5\text{H}_6\text{O}_8$; 1324), when heated with water, breaks up into racemic and carbonic acids; $\text{C}_5\text{H}_6\text{O}_8 = \text{C}_4\text{H}_6\text{O}_6 + \text{CO}_2$.

Racemic acid (so named from *racemus*, a bunch of grapes) generally accompanies tartaric acid in greater or less quantity. It is obtained from calcic racemate by a process precisely similar to that used for procuring tartaric acid from calcic tartrate. Racemic acid crystallizes more readily than the tartaric, in efflorescent, oblique rhombic prisms, which contain 1 atom of water of crystallization; this water is expelled by a temperature of 212° . Racemic acid is less soluble in alcohol than tartaric acid; it slowly precipitates solutions of calcic sulphate as well as those of calcic chloride; calcic racemate is soluble in hydrochloric acid, and is precipitated unchanged on adding ammonia. These re-

actions distinguish racemic easily from tartaric acid. When heated, racemic acid loses water, and its anhydride may ultimately be obtained: the products of its distillation are the same as those of tartaric acid. With antimony it forms a salt which corresponds to tartar emetic, but it crystallizes in radiated tufts of needles, not in octahedra. The ordinary salts of racemic acid occur in symmetrical crystals, and, with the exception of the ammonic-sodic racemate, and of the racemate of cinchonine and that of quinicine, they are not hemihedral. According to Pasteur (*Comptes Rendus*, xlv. 615), if a solution of ammonic racemate be mixed with about 1-2000th of its weight of any albuminous substance, and be placed whilst hot in a flask with a long neck, which is filled with the liquid to the bottom of the neck, and if when it has cooled to about 80° a small quantity of a solution of a tartrate in active fermentation be added, fermentation will then be set up, and the liquid will acquire a power of rotation to the left: the levotartaric acid resists fermentation, whilst the dextro-tartaric acid disappears. If a solution of ordinary ammonic tartrate be substituted for the racemate, the tartaric acid will disappear entirely.

(1323) *Conversion of Tartaric into Racemic Acid.*—Pasteur has succeeded in converting both the varieties of tartaric into racemic acid: for this purpose either the dextrotartrate or the levotartrate of cinchonia is exposed to a gradually rising temperature; the salt first becomes converted into cinchonine tartrate: if the heat be continued, the cinchonine loses water, it becomes coloured, and is transformed into cinchonidine. At the same time the tartaric acid also becomes modified, and after it has been exposed to a temperature of 338° (170° C.) for five or six hours, a portion of it is changed into racemic acid. The black resinoid mass into which the salt has been converted, is treated with boiling water, and the liquid thus obtained is mixed with an excess of calcic chloride, by which the whole of the racemic acid is precipitated in the form of calcic racemate, from which the acid may readily be extracted. During the process of converting the cinchonia tartrate into the racemate, another modification of tartaric acid is formed; it has been termed by Pasteur *inactive tartaric acid*, in allusion to its want of action upon polarized light. It crystallizes beautifully, and forms crystallizable salts. This inactive acid is the *meso-tartaric acid* of Dessaignes; it is distinguished from racemic acid by the circumstance that it does not admit of being resolved into dextro-tartaric and levotartaric acids.

The following are the modifications of tartaric acid which are at present known:—

| | | |
|--|-----------|----------------------|
| 1. Tartaric anhydride (insoluble) | . . . | $C_4H_4O_5$ |
| 2. Dextrotartaric acid | | $H_2C_4H_4O_6$ |
| 3. Lævotartaric acid | | $H_2C_4H_4O_6$ |
| 4. Racemic (paratartaric) acid | | $H_2C_4H_4O_6, H_2O$ |
| 5. Inactive tartaric (mesotartaric) acid | | $H_2C_4H_4O_6$ |
| 6. Metatartaric acid | | $H_2C_4H_4O_6$ |

(1324) A remarkable series of acids has been obtained by Löwig from oxalic ether, by treating it with an amalgam of sodium; he states that no fewer than five different acids may be thus procured which present a close analogy in composition and properties with malic, tartaric, and citric acids; two of these, viz., the glycomalic and desoxalic acid have been examined.

Glycomalic acid ($C_5H_8O_6$) is obtained by pouring ordinary alcohol upon an amalgam of sodium containing three per cent. of sodium, and gradually adding oxalic ether. Sodid oxalate and glycomalate are formed, and are separated by the addition of a small quantity of water, which dissolves the glycomalate and leaves the oxalate. The glycomalic acid is soluble in water and in alcohol; it has not been obtained in crystals, and generally its salts do not crystallize. The barium salt, however, furnishes good crystals.

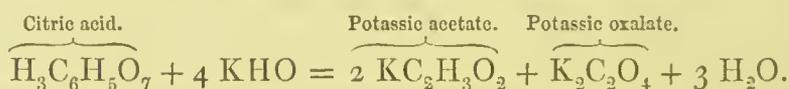
Desoxalic acid ($H_3C_5H_3O_3$) is obtained by pouring oxalic ether upon the sodium amalgam, immersing the vessel in cold water, if necessary, to moderate the action. After the reaction has ceased, the product is agitated with ether and water. The watery solution contains a fermentable sugar, besides sodid oxalate and the sodium salt of an acid not hitherto examined. The ethereal solution contains desoxalic ether, which on evaporation in the water-bath may be obtained in crystals [$(C_2H_5)_3C_5H_3O_3$]. By digestion with solution of potash, potassic desoxalate ($K_3C_5H_3O_3$) may be obtained. The acid itself may be obtained in deliquescent crystals, and is remarkable from the way in which it is decomposed when heated, racemic acid and carbonic anhydride being the products; $C_5H_6O_8 = C_4H_6O_6 + CO_2$. The same products are obtained by long boiling of the aqueous solution of desoxalic acid, and still more rapidly if sulphuric or hydrochloric acid be added. (*Journ. f. prakt. Chem.*, 1861, 676.) A further study of these remarkable acids cannot fail to give results of high interest.

3. Citric Acid and its Derivatives.

(1325) CITRIC ACID ($H_3C_6H_5O_7, H_2O = 192 + 18$; Liebig) is a powerful tribasic vegetable acid, found principally in the *Citrus medica*, or lime, and in other fruits of the *Aurantiaceæ*. Citric acid is also of frequent occurrence, associated with malic acid, in other acidulous fruits, such as gooseberries, raspberries, strawberries, cherries, and tamarinds. It is found also frequently in the *Solanaceæ*, and one of the yams contains a considerable quantity of it. This acid is extracted by neutralizing the juice of the lime or of the lemon with chalk, and decomposing the insoluble calcic citrate thus obtained with sulphuric acid, by a process similar to that directed for the preparation of tartaric acid.

Citric acid is very soluble in water; the solution has an agreeable acid taste: it is likewise soluble in alcohol, but not in ether. If the cold saturated aqueous solution be allowed to evaporate spontaneously, it crystallizes in colourless, transparent, rhombic prisms, which constitute the commercial citric acid. When heated to 212° these crystals melt, and lose 1 atom of water; the remaining compound consists of a tribasic acid ($\text{H}_3\text{C}_6\text{H}_5\text{O}_7$). If a solution of the acid, instead of being allowed to evaporate spontaneously, be crystallized at 212° , crystals are formed which contain $(2\text{C}_6\text{H}_8\text{O}_7, \text{H}_2\text{O})$.* These crystals do not lose their water of crystallization until they are heated to 266° .

A diluted aqueous solution of citric acid gradually becomes mouldy, and undergoes decomposition, acetic acid being formed. Citric acid dissolves zinc and iron with evolution of hydrogen. When heated to about 104° (40° C.), with concentrated sulphuric acid, citric acid evolves pure carbonic oxide; but if the temperature be raised, acetone and carbonic anhydride are given off. Concentrated nitric acid converts citric acid into a mixture of acetic, oxalic, and carbonic acids. When heated with caustic potash, it is converted into potassic oxalate and acetate:—



Citric acid is extensively consumed by calico-printers for discharging the mordant from the cloth in patterns; it is likewise employed in dyeing silk with safflower, and for heightening the tint of cochineal: it is also used medicinally. Lemon juice is largely employed as an antiseorbutic.

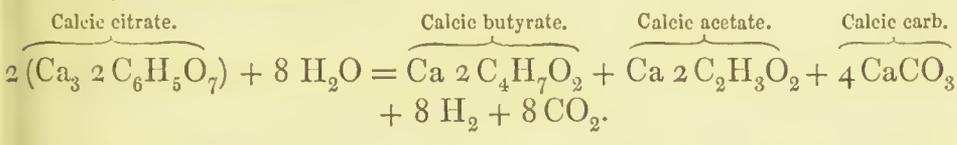
(1326) *Citrates*.—Citric acid, being tribasic, forms three series of salts, which correspond to the varieties of the tribasic phosphates; for instance, three citrates of sodium may be obtained, having the following composition (Heldt):—

| | |
|----------------------------------|--|
| Trisodic citrate | $2(\text{Na}_3\text{C}_6\text{H}_5\text{O}_7), 11 \text{ H}_2\text{O}$ |
| Hydric disodic citrate | $\text{Na}_2\text{HC}_6\text{H}_5\text{O}_7, \text{H}_2\text{O}$ |
| Sodic dihydric citrate | $\text{NaH}_2\text{C}_6\text{H}_5\text{O}_7, \text{H}_2\text{O}$ |

Calcic Citrate ($\text{Ca}_32\text{C}_6\text{H}_5\text{O}_7, 4 \text{ H}_2\text{O}$) is the most important of the citrates, since it is largely employed in the preparation of the acid; it also serves as a test by which citric acid may be recognized:—when the free acid is added to cold lime-water in quantity not sufficient to destroy its alkaline reaction, no precipi-

* These Berzelius regarded as constituting true citric acid ($\text{HO}, \text{C}_4\text{H}_2\text{O}_4$, or rather, $3 \text{ HO}, \text{C}_{12}\text{H}_6\text{O}_{12}$). ($\text{C} = 6, \text{O} = 8$.)

tate is produced; but on boiling the solution, calcie citrate is deposited. This salt is soluble without effervescence, in dilute acetic, hydrochloric, or nitric acid. The addition of an excess of ammonia in the cold does not re-precipitate it from these solutions; but upon heating the ammoniacal liquid the citrate is thrown down, and it is redissolved on cooling, if the quantity be not too considerable: these phenomena depend upon the circumstance that calcie citrate is less soluble in boiling than in cold water. Crude calcie citrate, obtained by saturating lemon-juice with chalk, cannot be preserved in a moist state without undergoing decomposition: it ferments, disengages a mixture of hydrogen and carbonic anhydride, and a mixture of calcie acetate and butyrate is formed:—



This change is accelerated by the addition of a small quantity of yeast to the mixture.

The citrates of the alkali-metals are all soluble in water; so also are many of the citrates of the heavier metals; the citrates of the earths with 3 atoms of the earthy metal are insoluble; but they become dissolved by adding an excess of citric acid, and thus form salts, which contain 1 atom or 2 atoms of the metallic basyl. *Hydric calcie citrate* (CaHC₆H₅O₇,H₂O), forms brilliant foliated crystals.

When argentic citrate is heated to 212° in a current of hydrogen gas, it becomes partially reduced, and a brown powder is formed, which, according to Wöhler, is argentous citrate. Water extracts citric acid from it, and dissolves it in small proportion, producing a red solution. This solution, when boiled, deposits reduced silver.*

* The citrates of the normal type, when heated, present a remarkable peculiarity, which led Berzelius to propose the formula (HO,C₄H₂O₄), or rather (3HO,C₁₂H₆O₁₂), as the true representative of citric acid. Assuming, for example, that the formula for potassic citrate is (3KO,C₁₂H₆O₁₂,HO), this salt, by a heat of 212°, loses 2HO, and is converted into (3KO,C₁₂H₆O₁₁), which is Liebig's formula for anhydrous potassic citrate. This residue appears not to be a simple potassic citrate, though on redissolving it in water the original citrate is reproduced; but it presents the characters of a mixture of potassic citrate and aconitate; for if the salt be treated with absolute alcohol, and decomposed by dry hydrochloric acid, so as to exclude the access of water, potassic chloride is formed, and the citric acid which is set free is found to be mixed with aconitic acid, which may be separated from the citric acid without difficulty. The same phenomenon is exhibited by argentic citrate: if this salt be precipitated at a

Ferric citrate is prepared by dissolving hydrated ferric oxide in a hot solution of citric acid. It has a sweetish taste, and forms a deep brown liquid, from which it is precipitated by the addition of alcohol. When its solution is evaporated in shallow vessels, it forms brilliant scales of a resinous aspect; and in this form it is used in medicine. The presence of citric acid prevents the precipitation of ferric oxide from its solutions on adding ammonia in excess.

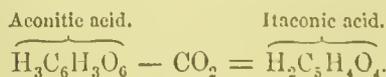
Tribasic plumbic citrate (dried at 250° ; $Pb_3 2 C_6 H_6 O_7$).—This salt is prepared by precipitating a hot alcoholic solution of trisodic citrate by an alcoholic solution of plumbic acetate; it forms a granular sparingly soluble powder. If this salt be digested with ammonia, it yields a heavy crystalline powder ($Pb_3 2 C_6 H_6 O_7, PbO, H_2O$); and if the tribasic citrate be digested with basic plumbic acetate, a salt with a still larger proportion of base ($Pb_3 2 C_6 H_6 O_7, 3 PbO, H_2O$) is formed.

Tribasic cupric citrate is soluble: a green crystalline, sparingly soluble *basic citrate* ($Cu_3 2 C_6 H_5 O_7, CuO 3 H_2O$; Heldt) is formed by boiling a solution of cupric acetate with citric acid.

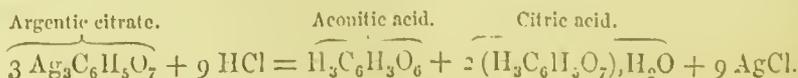
Citric acid is oxidized with great facility, manganic oxide, and lead dioxide decompose it, even without the aid of heat, carbonic anhydride being evolved.

(1327) *Action of Heat upon Citric Acid*.—If citric acid be exposed to a high temperature it undergoes decomposition. When mixed with pumice-stone, and heated to 311° (155° C.), pure carbonic anhydride is expelled; if heated alone to a temperature of about 347° (175° C.), water, acetone, and a mixture of carbonic anhydride and carbonic oxide are disengaged, and a brownish residue is obtained, which is in great part soluble in ether. This residue consists of a peculiar acid, the *aconitic* ($H_3 C_6 H_3 O_6$), which exists also in the different varieties of monkshood (*Aconitum*) and mare-stail (*Equisetum*). Aconitic acid is isomeric with fumaric and malæic acids, and it contains the elements of 1 atom of water less than citric acid. Indeed aconitic acid derives its principal interest from its close connexion with citric acid, and from the light which its composition throws upon some apparent anomalies in relation to the separation of water from the crystallized acid and its salts (*note*, p. 435). The aconitates of the alkali-metals give no immediate precipitate in solutions of the salts of barium, calcium, magnesium, or zinc, but they produce white precipitates in solutions of lead and of silver.

If citric acid be heated beyond the point at which aconitic acid is formed, the aconitic acid is itself decomposed, carbonic anhydride escapes, and the principal product consists of a volatile, oily-looking acid liquid, which contains a mixture of two isomeric acids, one of which, the *itaconic*, crystallizes with facility: and the other, termed *citraconic*, *pyrocitric*, or *citribic acid*, is much more soluble; both have the formula ($H_2 C_5 H_4 O_4$). One molecule of aconitic acid contains the elements of 1 molecule of itaconic or citraconic acid, and 1 of carbonic anhydride:—



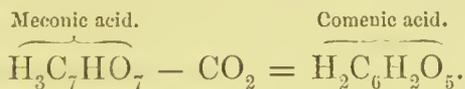
temperature below 50° (10° C.), it has a composition represented by the formula $2 (Ag_3 C_6 H_5 O_7), H_2O$, but at all higher temperatures 2 atoms of the salt contain an atom less of water ($Ag_3 C_6 H_5 O_7$). Now, if this latter salt be treated like the potassium salt, with dry hydrochloric acid in absolute alcohol, 3 atoms of the compound yield by decomposition 9 atoms of argentic chloride, 2 atoms of citric and 1 atom of aconitic acid:—



A considerable quantity of citraconic anhydride passes over with the normal acids during the distillation. Citraconic acid is also obtained during the distillation of lactic acid. When citraconic is treated with nitric acid, it is partially decomposed, and converted into oxalic acid, whilst a nitro-acid, probably $[\text{H}_2\text{C}_5\text{H}_3(\text{NO}_2)_4]$ is produced, and at the same time a new acid, isomeric with the citraconic, is formed, termed *mesaconic acid*. The latter may be obtained in minute crystals, which are sparingly soluble in water.

4. *Meconic Acid and its Derivatives.*

(132δ) MECONIC ACID ($\text{H}_3\text{C}_7\text{HO}_7, 3\text{H}_2\text{O}$).—This acid (which derives its name from *μῆκων*, a poppy) is contained in the milky juice of the *Papaveraceæ*. It is extracted from a concentrated aqueous infusion of opium by nearly neutralizing it with milk of lime and adding a solution of calcic chloride; the calcic meconate is nearly insoluble and is thus precipitated. In order to isolate the acid, one part of calcic meconate is mixed with 10 parts of water at 190° ($87^\circ.7$ C.), and decomposed by the addition of hydrochloric acid in considerable excess; the meconic acid crystallizes from the solution in scales, which, however, are strongly coloured. They must be digested with purified animal charcoal and re-crystallized, but they cannot be obtained colourless without considerable difficulty. Meconic acid is sparingly soluble in cold water, but is readily dissolved by it when hot; it is also soluble in alcohol and in ether. Its solutions have an acid, astringent taste. When its crystals are heated to 212° , 3 atoms of water are expelled. The aqueous solution of meconic acid is decomposed by ebullition, and carbonic anhydride gradually escapes. This change is effected more rapidly if some mineral acid, such as the sulphuric or hydrochloric, be added to the liquid. Similar results are obtained if the crystallized acid be heated to 248° (120° C.). In all these cases a new acid, the comenic, is obtained:—



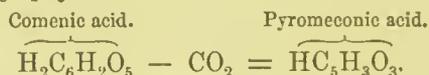
Meconates.—Meconic acid is tribasic, the formula of its normal salts being $\text{M}'_3\text{C}_7\text{HO}_7$. The meconates of the alkali-metals are soluble. The normal meconates of calcium, barium, lead, copper, and silver are nearly insoluble in water, but are soluble in acetic acid. Argentic meconate when heated is decomposed with explosion.

It is sometimes important for medico-legal purposes to be able to ascertain the presence of meconic acid in cases where opium is suspected to have been administered as a poison. With this view the following process may be adopted:—The solution is to be mixed with plumbic acetate, an impure plumbic meconate

is thus precipitated if meconic acid be present; the precipitate after it has been washed is decomposed by sulphuretted hydrogen, and the meconic acid thus set at liberty is concentrated by evaporation at a temperature not exceeding 158° (70° C.); a very dilute solution of ferric chloride is then added to the concentrated liquid. If meconic acid be present it strikes a deep blood-red colour, which may be distinguished from that due to potassic sulphocyanide by the effect of the addition of a few drops of sulphuric acid with a fragment of zinc; if the colour be due to the sulphocyanide the red tint will disappear, and sulphuretted hydrogen will be extricated; but if the compound contain meconic acid the colour will not be affected: a solution of auric chloride or of corrosive sublimate also discharges the colour of the ferric sulphocyanide, but is without effect upon the meconate.

(1329) *Comenic Acid* ($\text{H}_2\text{C}_6\text{H}_2\text{O}_5$), is dibasic. It is sparingly soluble in water, and crystallizes in hard, warty nodules. Nitric acid decomposes it rapidly into oxalic, carbonic, and hydrocyanic acids. This acid, like the preceding one, gives a blood-red solution with ferric salts, and a white precipitate with plumbic acetate, but it gives no precipitate with salts of barium.

If either the meconic or the comenic acid be distilled, a new monobasic acid, *pyromeconic acid* ($\text{HC}_5\text{H}_3\text{O}_3$) is sublimed:—



This acid is isomeric with the pyromucic, but is distinguished from it by yielding with the ferric salts a solution of a blood-red colour, and by giving no precipitate with a solution of basic plumbic acetate.

5. *Different Varieties of Tannic Acid.*

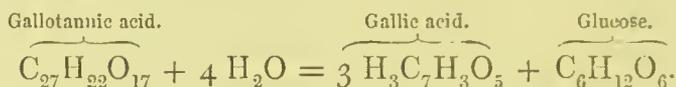
(1330) THE term *tannin* was formerly applied to the various forms of the astringent principle which were employed in the process of tanning hides. Most of these substances are now known to possess an acid reaction; but it has been ascertained that there are several distinct compounds which resemble each other in properties, though they possess a different chemical composition. These astringent principles are very extensively diffused throughout the vegetable kingdom. The bark and leaves of most forest trees, such as the oak, the elm, the willow, the horse-chestnut, and the pine, and of many fruit trees, such as the pear and plum, contain tannin in notable quantity. The wood and bark of many shrubs, such as the sumach and the whortleberry, and the roots of the tormentilla and bistort, are also powerfully astringent, owing to the presence of one of the forms of tannin. Coffee and tea, as well as Paraguay tea, likewise contain a modification of this astringent principle. All these bodies, except coffee, precipi-

tate the ferric salts of a bluish-black colour, or if a free acid be present, the solution assumes a dark-green colour. Many vegetables contain an astringent principle which precipitates the salts of iron of a dark-green instead of a blue colour: catechu and kino offer good instances of this variety of tannin. Some few astringent plants yield an infusion which precipitates ferric salts of a grey colour; among these plants are *matricaria*, rhatany (*Krameria triandra*), and the common nettle (*Urtica urens*). Tannic acid in all its forms absorbs oxygen rapidly when moist.

The most important of these acids, and the one which has been most accurately studied, is the tannic acid of the gall nut, or *gallotannic acid*; that of the oak or *quercitannic acid* is also a distinct species (Stenhouse), as well as that of the fustic (*Morus tinctoria*): *moritannic acid*, as the latter variety is termed, is a yellow crystalline solid, which, according to the experiments of Wagner, may be represented by the formula ($C_{18}H_{16}O_{10}$). *Quinotannic acid*, or the tannin of the cinchona, according to Hlasiwetz, is represented by the formula ($C_{28}H_{38}O_{17}$?); and there is no doubt that the *mimotannic acid* or tannin of the catechu is a distinct variety, although, from its proneness to change, the true composition of this substance is uncertain. Kino, valonia (the acorn-cups of the *Quercus agrifolia*), and divi-divi (the pod of the legume of *Casalpinia coriaria*), all contain powerfully astringent compounds which, according to Stenhouse, are distinct from gallotannic acid.

(1331) GALLOTANNIC ACID; *Tannic acid* ($C_{27}H_{22}O_{17}$; Strecker).—This acid is obtained in a state of purity from the gall nut, an excrescence produced upon the leaves of a species of oak (*Quercus infectoria*), by the puncture of a small hymenopterous insect. The gall nut contains as much as two-thirds of its weight of tannic acid, and about two per cent. of gallic acid (Guibourt). In order to extract the tannic acid, Pelouze directs the gall nuts to be reduced to powder, and digested with about an equal weight of washed ether; the decanted liquid separates, on standing, into two portions, the denser of which is of a yellow colour, and consists of a concentrated aqueous solution of tannic acid; the other portion is of a greenish colour, and is composed of ether holding gallic acid and colouring matter in solution. The yellow solution, when evaporated to dryness, yields a porous, pale buff-coloured residue of amorphous gallotannic acid. According to Stenhouse the tannic acid of sumach is identical with that of the gall nut, but it is not readily obtained in a pure form. Gallotannic acid is freely soluble in water; it reddens litmus paper,

and dissolves the carbonates with effervescence. It has a purely and intensely astringent taste; it is soluble in dilute alcohol, but sparingly so in ether. Its diluted aqueous solution absorbs oxygen from the air slowly, and is converted into gallic acid; this process is favoured by the presence of a particular ferment which is contained in the gall nut. A solution of tannic acid in water is coagulated by potassic chloride, and by many other salts. Sulphuric, hydrochloric, phosphoric, and some other acids also diminish its solubility, and precipitate it from a concentrated aqueous solution. Nitric acid converts it into oxalic and saccharic acids. If boiled with dilute sulphuric, or with hydrochloric acid, it unites with the elements of water and is converted into sugar and gallic acid (Strecker); the latter crystallizes on cooling, whilst the glucose remains in solution:—



A boiling concentrated solution of potash also decomposes tannic acid, and occasions the formation of gallic acid. If air be admitted to the mixture, the acid last named is in turn decomposed into a black ulmin-like substance.

Gallotannates.—The composition of these salts is but imperfectly known, and there is considerable uncertainty whether the acid should be regarded as dibasic or as tribasic. A solution of gallotannic acid occasions a violet-black precipitate in solutions of the ferric salts. It also causes precipitates in the solutions of the salts of morphia, quinia, brucia, and many other vegetable bases; these precipitates consist of gallotannates of the bases, and are readily soluble in acetic acid. The gallotannates of lead and antimony are white and insoluble in water. Those of the alkali-metals are soluble; their solutions have an astringent taste, and do not precipitate gelatin until some acid is added to liberate the gallotannic acid from the base. If the solutions of these salts be exposed to the air, especially if the base be in excess, they rapidly become brown, and are decomposed with absorption of oxygen. None of the gallotannates can be obtained in crystals.

The colouring matter of ordinary writing ink is gallotannate of iron. Various recipes are given for its preparation: the following furnishes a very good ink:—Digest three quarters of a pound of bruised nut galls in a gallon of cold water, then add six ounces of ferrous sulphate with an equal weight of gum arabic, and four or five drops of kreosote to prevent the ink from becoming mouldy: let this mixture digest at ordinary temperatures for two or three

weeks with occasional agitation; then allow it to settle, and decant for use. Oxalic acid and chlorine water readily discharge the colour of writing ink, and they may be employed to remove ink stains from linen. An ink-spot when washed with an alkaline soap becomes yellow, forming what is familiarly known as an iron-mould. This yellow stain is due to ferric oxide, which constitutes the basis of the ink, and which has attached itself to the cloth, whilst the alkali of the soap has removed the tannic acid.

The most remarkable compound of tannic acid, however, is that which it forms with *gelatin*, which constitutes the basis of *leather*. The principles of the manufacture of this important substance will be considered (1664) after the properties of gelatin have been described. When a solution of gelatin or isinglass is added to an aqueous infusion of any vegetable containing tannic acid, a copious gelatinous precipitate occurs, which is soluble in excess of gelatin if the liquid be boiled. An excess of tannic acid prevents the re-resolution of the compound. If a piece of raw hide freed from hair, be immersed in a solution of tannic acid, the gelatinous tissue gradually combines with the acid, and retains it in the form of leather, the supernatant liquid being ultimately completely freed from all traces of tannin, if the piece of skin be of sufficient size.

When gallotannic acid is subjected to a temperature of about 617° (325° C.), it is decomposed, and yields pyrogallic and metagallic acids (1333, 1334), whilst water and carbonic anhydride are expelled. The formation of pyrogallic acid appears to be characteristic of gallotannic acid, since the other varieties of tannin do not yield this compound (Stenhouse).

(1332) *Mimotannic Acid*.—The different species of catechu and of kino, although derived from trees belonging to several different natural families, appear to contain the same modification of the astringent principle, which, as already stated, differs in some essential particulars from the gallotannic acid. Formerly, kino and catechu were seldom employed in this country except for medicinal purposes; but of late years they have been extensively used by the dyer and the tanner, and have thus acquired considerable importance, both commercially and chemically.

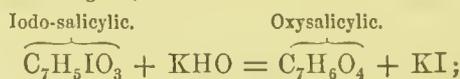
The essential constituents of catechu are *mimotannic acid* and *catechin*, which are mixed with a brown substance, resulting from the oxidation of both these bodies.

Mimotannic acid is sparingly soluble in dilute sulphuric acid, although freely soluble in water. If a concentrated aqueous infusion of catechu be mixed with a small quantity of dilute sulphuric acid, a precipitate occurs, at first consisting

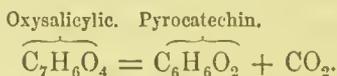
chiefly of colouring matter; this may be removed, and on then gradually adding concentrated sulphuric acid so long as it occasions a precipitate, mimotannic acid is thrown down: this precipitate may be collected on a filter, washed with dilute sulphuric acid, pressed between folds of blotting-paper, and dissolved in water. The excess of sulphuric acid is then removed by digestion with plumbic carbonate; and the filtered liquid, when evaporated *in vacuo*, furnishes mimotannic acid nearly pure.

This substance is distinguished from gallotannic acid, by yielding a greenish grey precipitate with the ferric salts; and by not precipitating a solution of tartar emetic: when subjected to heat it does not furnish pyrogallic acid. Its solution absorbs oxygen and becomes of a dark red colour, leaving, when evaporated, a substance no longer completely soluble in water. Under these circumstances, according to Delffs, a certain quantity of catechin is formed, and remains in a crystalline condition.

Catechin ($C_{20}H_{18}O_6, H_2O$? Zwenger) is contained in the portion of catechu which is not soluble in cold water; it is soluble in three or four parts of boiling water, or of boiling alcohol; and when pure is deposited in minute colourless crystals. The caustic alkalies immediately attack it, causing it to absorb oxygen, when it becomes first yellow, then red, and finally black. Catechin precipitates ferric chloride of a dark-green colour. It is soluble in the dilute acids: when treated with oil of vitriol it gives a purple solution: nitric acid converts it into oxalic acid. Catechin is fusible at $422^{\circ}6$ ($217^{\circ}C.$); at a higher temperature it is decomposed, and amongst other products yields a crystallizable substance termed *pyrocatechin*, or *oxyphenic acid* ($C_6H_6O_2$). Lautemann has obtained pyrocatechin artificially by decomposing moniodo-salicylic acid by means of an alkali (*Lieb. Annal.*, cxx. 312):—



and on heating—



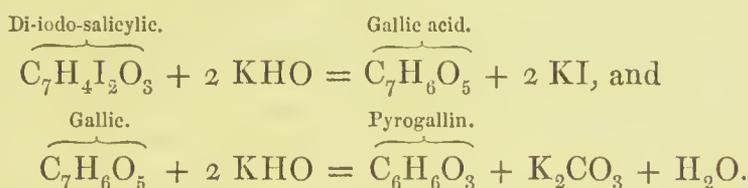
Moritannic acid ($C_{18}H_{16}O_{10}$; the tannin of the *Morus tinctoria*, the yellow dye called *fustic*) yields the same product when submitted to distillation.

It has been suggested that the different varieties of tannic acid may be homologous terms of the same series; but the facility with which they undergo change renders their investigation a matter of great difficulty; and the accuracy of the formulæ assigned to these different compounds, with the exception of that of gallotannic acid, must be regarded as very doubtful.

6. Gallic Acid and its Derivatives.

(1333) GALLIC ACID ($H_3C_7H_3O_5, H_2O = 170 + 18$).—This acid exists ready formed in the gall nut, in sumach, in valonia, and in a large number of other astringent vegetables, although the quantity in each is but small. It may readily be obtained by allowing an infusion of gall nuts, or the powdered galls moistened freely with water, to stand in a warm place for some weeks, exposed to the air: it quickly becomes mouldy, absorbs oxygen, and emits carbonic anhydride, owing to the occurrence of a species of fermentation, during which abundance of gallic acid is deposited in the form of crystals. The acid must be purified by digestion

with animal chareoal and re-crystallization from boiling water. Gallie acid is also deposited from infusion of gall nuts, if kept in vessels from which the air is excluded; but in this ease no evolution of gas ooeurs; the exaet stages of these proecesses of fermentation have not been elearly made out. Gallie acid may likewise be obtained by boiling tannie acid with dilute sulphurie or hydroehlorie acid, in which ease water is assimilated and glueose is set at liberty (1331). Lautemann, by eonverting salieylie acid into di-iodo-salieylie acid, and treating this eompound with potassie earbonate, has sneeceeded in obtaining gallie (dioxysalieylie) acid: when eaustie potash was used a good deal of the acid was decomposed and pyrogallin was formed:—

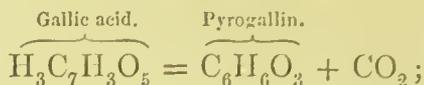


The acid crystallizes either in the form of delicate silky needles, or in brilliant oblique rhomboidal prisms, which require about 100 parts of cold water for their solution, but only 3 parts of boiling water: they are freely soluble in alcohol, but only sparingly so in ether. When dried at 248° (120° C.) they lose 9.5 per cent., or one atom of water.

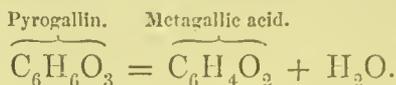
Gallates.—According to Streeker, gallie acid is tribasie, and it forms three classes of salts, the general formulæ of which are $\text{MH}_2\text{C}_7\text{H}_3\text{O}_5$; $\text{M}_2\text{HC}_7\text{H}_3\text{O}_5$; and $\text{M}_3\text{C}_7\text{H}_3\text{O}_5$. Besides these salts there are salts with an excess of acid and with excess of base; thus an acid salt of potassium [$2(\text{KH}_2\text{C}_7\text{H}_3\text{O}_5), \text{H}_3\text{C}_7\text{H}_3\text{O}_5, \text{H}_2\text{O}$] may be obtained by adding an alcoholic solution of potash to an alcoholic solution of gallie acid. The gallates of the alkalis speedily absorb oxygen, and become brown when their solutions are exposed to the air, especially if an excess of base be present. Nearly all the gallates of the heavy metals are insoluble. If an excess of gallie acid be added to a plumbic salt, the precipitate is at first white and amorphous, but it gradually becomes crystalline if left in contact with the liquid. But the most characteristic reaction of this acid is the formation of a deep bluish black solution, when added to a ferric salt: if the solutions be free from acid, and particularly if a solution of calcie earbonate in earbonic acid be added, the reaction is one of extreme delicacy. The salts of gallie acid do not cause a precipitate in solutions of gelatin.

When gallie acid is exposed to a temperature of from 410° to

419° (210° to 215° C.) it is wholly volatilized, and is converted into pyrogallin and carbonic anhydride:—



but if the temperature be allowed to reach 482° (250° C.) the pyrogallin in its turn suffers decomposition; water is expelled, and a dark ulmin-like body is formed, termed *metagallic acid*, which is insoluble in water, but soluble in alkaline solutions:—



(1334) *Pyrogallin* or *Pyrogallic Acid* ($\text{C}_6\text{H}_6\text{O}_3$).—This substance can scarcely be said to possess acid properties. It may be obtained by the sublimation of gallie acid, or of any vegetable extract which contains gallotannic acid. The extract may be placed in a shallow iron pan, which is covered with a sheet of filtering paper, over which a cone of writing paper is fastened; on applying a regulated sand heat, the acid is decomposed and the pyrogallin is converted into vapour; it passes through the bibulous paper, and rises into the chamber formed by the paper cone, where it is condensed, and is prevented from falling back into the pan beneath, by the interposed sheet of filtering paper. This method of sublimation, contrived by Mohr, is applicable in many other cases of a similar kind. Liebig mixes well-dried gallie acid with twice its weight of coarsely powdered pumice-stone, and heats the mixture in a retort, through which a current of dry carbonic anhydride is maintained:—31 or 32 parts of pyrogallin are thus obtained for every 100 parts of gallie acid employed.

Sublimed pyrogallin forms voluminous brilliant plates, which are freely soluble in water, alcohol, and ether: the solution has a bitterish taste and does not redden litmus paper. When heated to about 239° (115° C.) it melts; and when further heated it emits a colourless irritating vapour. Pyrogallin may be preserved unchanged whilst dry, but its solution quickly becomes brown, and absorbs oxygen; and if a free alkali be added, the absorption of oxygen is so rapid, as to afford a valuable method of removing free oxygen from gaseous mixtures (349 note).

The alkaline solutions of pyrogallin rapidly assume an intense reddish brown colour: this brown solution, according to Stenhouse (*Liebig's Ann.* xlv. 6), contains acetate and carbonate of the basyl. When pyrogallin is dropped into milk of lime it produces a beautiful purplish red colour, which soon becomes of a dingy brown: this reaction is very characteristic. Pyrogallin, on account

of the facility with which it absorbs oxygen, decomposes most of the salts of silver, of gold, and of platinum; but it forms a definite compound with plumbic oxide, and dissolves freshly precipitated alumina. If a solution of pyrogallin be added to a boiling solution of tartar emetic, sparingly soluble pearly crystals ($\text{SbO}, \text{C}_6\text{H}_5\text{O}_3$) are deposited. With ferrous sulphate, free from ferric salt, pyrogallin gives a deep indigo-blue solution, which becomes green by the action of air: with ferric salts it forms a bright red solution.

Pyrogallin is now extensively employed in photographic operations for the purpose of developing the latent image upon the argentiferous collodion film after it has been exposed to the action of light (127 h).

(1335) *Ellagic Acid* [$\text{HC}_7\text{H}_2\text{O}_4, \text{H}_2\text{O}$; or if dried at 239° (115° C.) $\text{HC}_7\text{H}_2\text{O}_4$].—During the preparation of gallic acid from gall nuts a quantity of a grey crystalline powder, termed *ellagic acid*, is formed. This substance is insoluble in water, but soluble in the alkalis; with potassium it forms a flaky salt which is but sparingly soluble: the solution of this salt speedily absorbs oxygen from the air, and becomes of a blood-red colour. When treated with a solution of ferric chloride, ellagic acid is gradually dissolved and forms a deep blue liquid. The most singular circumstance in connexion with this body is the discovery by Wöhler and Merklein that it is a constituent of certain kinds of oriental bezoars. These bezoars are intestinal concretions which occur in the wild goats, antelopes, and deer of the countries of Central Asia: they are brittle, ovoid, or reniform masses of a dark olive-green colour, polished upon the surface, and in size seldom exceeding a pigeon's egg; when broken, they are usually found to have been deposited in concentric layers upon some foreign nucleus: they are not fusible like the lithofellic bezoars (1701).

Concentrated sulphuric acid dissolves ellagic acid, and precipitates it, unaltered, on dilution.

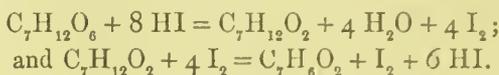
Rufigallic or *Parellagic Acid* ($\text{C}_7\text{H}_4\text{O}_4, \text{H}_2\text{O}$).—If the crystals of gallic acid be dissolved in five times their weight of oil of vitriol, a crimson solution is formed, which, if allowed to fall drop by drop into water, deposits a reddish-brown substance, partly in flocculi and partly in crystals. The crystalline portion, or *rufigallic acid*, is insoluble in water, but soluble in solutions of the alkalis. Its molecule contains 1 of H_2O less than the molecule of gallic acid. Rufigallic acid, when heated, yields a sublimate consisting of fine red prisms, resembling those of alizarin. If a piece of calico which has been moistened with alum, or with a salt of iron, be boiled with rufigallic acid, it becomes dyed with the same tints as if madder had been used, but the colours are less brilliant.

7. Quinic Acid and its Derivatives.

(1336) QUINIC OR KINIC ACID ($\text{H}, \text{C}_7\text{H}_{11}\text{O}_6$).—The bark of the cinchonas contains a peculiar modification of tannic acid, termed the quinotannic, and besides this, it furnishes the remarkable acid to which the name of *quinic acid* has been given. Quinic acid appears to exist in the bark in combination with calcium and with the organic bases of the bark. If an aqueous decoction of cinchona bark be mixed with milk of lime until it assumes a feebly alkaline reaction, the vegetable bases and the tannic acid are precipitated, and calcic quinate remains in the liquid: this salt may be crystallized from the mother-liquor by evaporation, and decomposed by the cautious addition of oxalic or of

sulphuric acid. The quinic acid may then be obtained in crystals from the solution.

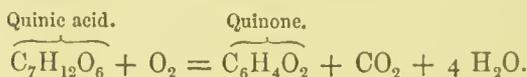
Quinic acid crystallizes in colourless, oblique rhombic prisms, which have a strongly acid taste; they are freely soluble in boiling water, less so in cold water, still less so in alcohol, and are very sparingly soluble in ether. When heated to 311° (155° C.) the acid fuses, and at a higher temperature yields a complicated mixture containing amongst other matters, benzol, benzoic acid, carbonic anhydride, salicylic acid, and a colourless substance termed hydroquinone. Lautemann (*Liebig's Annal.*, cxxv. 9) has shown that by the action of hydriodic acid quinic may be converted into benzoic acid:—



When swallowed, quinic acid is converted into hippuric acid, and escapes as such by the kidneys.

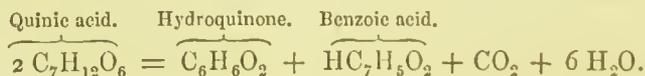
Quinates.—Nearly all these salts are soluble in water, with the exception of basic plumbic quinate ($C_7Pb''_2H_8O_6$), which is obtained by adding a solution of basic plumbic acetate to a neutral quinate. It is remarkable that in this salt 4 atoms of the hydrogen of the acid appear to have been displaced by lead. Quinic acid also forms a basic salt with copper ($C_7Cu''H_{10}O_6, 2 H_2O$), which may be obtained in brilliant green, sparingly soluble crystals.

(1337) *Quinone* or *Kinone* ($C_6H_4O_2$).—When one part of quinic acid is heated with four parts of finely powdered black manganese oxide and one part of sulphuric acid diluted with an equal weight of water, a beautiful yellow crystalline compound is sublimed, and becomes condensed in the neck of the retort in long needles; to this substance the name of *quinone* has been given:—



It may also be obtained from the aqueous extract of coffee by treating it in a similar manner. Hofmann has likewise obtained quinone by treating β phenylene diamine [$(C_{12}H_6N_2)$ the base obtained by reducing β nitraniline with acetic acid and iron] with sulphuric acid and black manganese oxide. Quinone fuses at 212° . It is sparingly soluble in water, but is dissolved more freely by alcohol and by ether.*

Hydroquinone ($C_6H_6O_2$).—When quinone is treated with reducing agents, such as sulphurous acid or stannous chloride, it is first converted into a green compound, but it ultimately furnishes a colourless body, termed *hydroquinone*. This substance, mixed with benzoic acid, is the principal product of the dry distillation of quinic acid:—



But the simplest plan of preparing it consists in suspending quinone in water and transmitting gaseous sulphurous anhydride until the quinone is dissolved;

* The name *umbelliferone* has been given to a beautifully crystallizable body isomeric with quinone, which was obtained by Sommer by distilling the alcoholic extract of the gum resins of the *Umbelliferae*, such as galbanum, sagapenum, assafoetida, opopanax. It forms colourless rhombic prisms, sparingly soluble in cold water, but readily so in boiling water, alcohol, and ether. It fuses at 464° (240° C.); and sublimes unaltered considerably below this point. It is not decomposed by strong sulphuric acid, but if fused with caustic potash, furnishes resorcin ($C_6H_6O_2$), a homologue of orcin.

by evaporating this solution, crystals of hydroquinone are obtained, whilst the liquid contains sulphuric acid. Hydroquinone forms six-sided colourless prisms, which are very soluble in water, alcohol, and ether. It is without odour, and has a sweetish taste; it fuses readily, and may be sublimed in brilliant plates, resembling those of benzoic acid. It is isomeric with pyrocatechin or oxyphenic acid (1558) and with resorcin (1530).

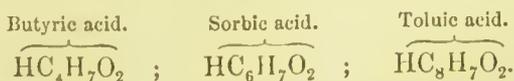
The action of oxidizing agents upon hydroquinone is remarkable. When its solution is mixed with a solution of ferric chloride, the liquid immediately assumes a deep blackish-red colour, and in a few moments it becomes filled with magnificent green acicular crystals, which have a metallic lustre. These crystals consist of a combination of quinone with hydroquinone, which has been called *green hydroquinone* ($C_6H_4O_2 \cdot C_6H_6O_2$). Chlorine, nitric acid, argentic nitrate, and potassic chromate, when mixed with a solution of hydroquinone, also occasion the formation of the same compound: the same substance is likewise formed by mixing a solution of quinone with one of hydroquinone. This beautiful compound fuses on the application of a gentle heat; it is partially decomposed by a further elevation of temperature, and emits vapour of quinone. It is freely soluble in boiling water, and sparingly so in cold water; the solution has a styptic taste. Alcohol and ether dissolve it readily, and form yellow solutions.

Both quinone and hydroquinone yield several substitution compounds with chlorine, and with sulphur.

Perchloroquinone, or *chloranil* ($C_6Cl_4O_2$).—Of the chlorinated derivatives of quinone, the substance which has been designated *chloranil* is the most interesting, since through this body the relation of quinone to the phenic, salicylic, and indigo groups of compounds is indicated. Perchloroquinone may be produced by the action of a mixture of potassic chlorate and hydrochloric acid upon quinone, and upon a variety of other substances—viz., on aniline, on carbolic and carbazotic acid of the phenyl series; on salicin, salicyl hydride, and salicylic acid, of the salicyl group; and on isatin, and its chlorinated derivatives in the indigo group. The easiest method of obtaining it consists in preparing a warm dilute solution of salicin acidulated with hydrochloric acid, and adding powdered potassic chlorate in small quantities at a time. A brisk reaction occurs on each addition of the chlorate, and a heavy orange-coloured oil is formed, which solidifies on cooling. This solid mass is perchloroquinone; it may be purified by crystallization from boiling alcohol. Perchloroquinone forms pale yellow flakes of pearly and metallic lustre. It may be sublimed unaltered by the application of a gentle heat. It is insoluble in cold water, and is but sparingly soluble in cold alcohol. Ether dissolves it rather more freely. A warm dilute solution of potash dissolves perchloroquinone readily, giving a purple liquid, which on cooling deposits scales of potassic *dichloroquinonate* ($K_2C_6Cl_2O_4 \cdot H_2O$).

8 & 9. Sorbic and Parasorbic Acids.

(1338) Hofmann has pointed out the existence of an acid derived from the berries of the service-tree, *Sorbus aucuparia* (*Q. J. Chem. Soc.*, xii. 43), which he has termed sorbic acid ($HC_6H_7O_2$), and which is one of a group intermediate between the fatty and the aromatic acids. If we compare together the terms of the fatty and aromatic series which contain an equal number of atoms of hydrogen, the new acid will contain a number of atoms of carbon intermediate between them—*e.g.*, the three corresponding acids in each group are:—



The general formula of the group of fatty acids being $HC_nH_{2n-1}O_2$, that of

the sorbic $\text{HC}_n\text{H}_{2n-5}\text{O}_2$, that of the benzoic group is $\text{HC}_n\text{H}_{2n-5}\text{O}_2$. We may confidently anticipate the discovery of aldehyds, alcohols, and other acids of this family from the labours of future inquirers.

Parasorbic Acid ($\text{HC}_6\text{H}_7\text{O}_2$). *Sp. gr. of liq.* 1.0681; *Boil. pt.* 429°.8 (221° C.).—If the juice of the unripe berries of the mountain-ash be partially neutralized with lime and submitted to distillation, an acid liquid passes over: after saturating this with sodic carbonate, concentrating the solution by evaporation and decomposing it by the addition of sulphuric acid somewhat diluted, a brownish oil rises to the surface of the liquid: it may be purified by solution in ether, and redistillation after the ether has been allowed to evaporate.

This oil has a peculiar, powerful, somewhat pungent aromatic odour: when pure, it is colourless, is somewhat soluble in water, and abundantly so in alcohol and ether. It possesses the properties of an acid, which Hofmann calls *parasorbic*; it is readily soluble in solutions of the alkalies and alkaline earths.

On heating this oil gently with solid caustic potash, a transformation of the acid occurs analogous to that of oleic acid by the agency of peroxide of nitrogen. A new isomeric acid is formed termed sorbic acid. When the potassium salt is decomposed by hydrochloric acid, sorbic acid is set at liberty, furnishing an oil which solidifies rapidly into a hard crystalline substance. A similar transformation of parasorbic acid occurs when the oil is boiled for a short time with concentrated hydrochloric acid. Oil of vitriol dissolves parasorbic acid, and on dilution, the substance which is separated gradually becomes crystallized as sorbic acid.

Sorbic Acid [$(\text{HC}_6\text{H}_7\text{O}_2)$]; *Fusing pt.* 274° (134°.5 C.) as thus obtained is nearly insoluble in cold water, but moderately soluble in boiling water. Ether and alcohol both dissolve it very readily. It may be obtained crystallized in magnificent white needles by dissolving it in a mixture of 1 volume of alcohol and 2 volumes of water by the aid of heat, and allowing the solution to cool. On the application of heat the acid fuses, and at a higher temperature may be distilled unaltered.

Potassic and sodic sorbates are very soluble, and crystallize with difficulty. Ammonic sorbate is also very soluble, but crystallizes in slender needles. The salts of calcium and barium are less soluble, and crystallize in anhydrous silvery scales on adding alcohol to their boiling aqueous solutions.

CHAPTER VI.

AMIDES, AND ORGANIC BASES.

§ I. AMIDES AND THEIR VARIETIES.

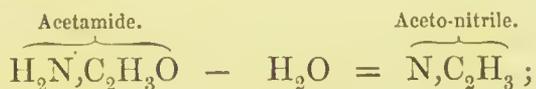
(1339) *Amides*.—It has been already stated (371), that under certain circumstances a portion of the hydrogen of ammonia may be displaced by potassium, and a compound may be formed consisting of KH_2N , which has been termed *potassiumide*. When ammonic oxalate is submitted to distillation, a white sublimate is obtained (610, *note*), in which the elements of ammonic oxalate, minus 2 atoms of water, are present; to this sublimate, Dumas,

by whom it was discovered, gave the name of *oxamide*. The following equation represents the relation which exists between oxamide and ammoniac oxalate :—

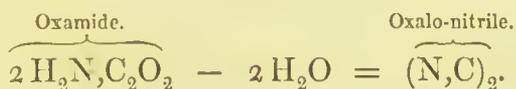


Now it is found that other salts of ammonium, when submitted to dry distillation, or otherwise deprived of water, yield compounds analogous to oxamide. When one molecule of an ammonium salt of a monobasic acid loses one atom of water, or when 1 molecule of a neutral ammonium salt of a dibasic acid loses 2 atoms of water, the resulting compound is called an *amide*; the amides obtained from the dibasic acids being further distinguished as *diamides*. It has been proposed to account for the formation of these compounds by the hypothesis, that they contain a certain hydride of nitrogen, which has not hitherto been procured in a separate form, but to which the composition H_2N , and the name of *amidogen* (371) has been assigned.

(1340) *Nitriles*.—But the amides themselves also admit of being deprived of water: and when a molecule of the amide of a monobasic acid has thus been made to lose an additional atom of water, it yields a compound belonging to a class known under the generic term of *nitriles*. Acetamide, less one atom of water, yields aceto-nitrile :—

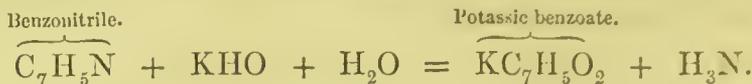


and, in like manner, oxamide gives oxalo-nitrile :—

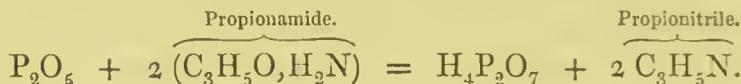
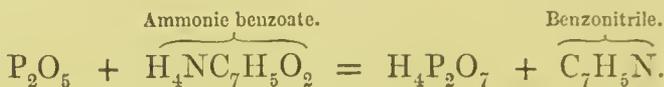


It is worthy of remark, that oxalonitrile has the same composition as cyanogen, and is not only metameric, but also identical with it; so that cyanogen admits of being regarded as the nitrile of oxalic acid; and thus a certain analogy may be traced between cyanogen and the products obtained by the dehydration of the ammonium salts; the nitriles of the fatty acids of the type $\text{HC}_n\text{H}_{2n-1}\text{O}_2$, being in fact identical with one class of the hydrocyanic ethers (1149). These nitriles, when fused with potassium, yield potassic cyanide, and disengage hydrogen mixed with gaseous hydrocarbons. The nitriles, when treated with an alkali, do not reproduce hydrocyanic acid, and their corresponding alcohol; but they recombine with the elements of water, and form ammonia, and a salt of the original acid from which the nitrile

was obtained. For instance, benzonitrile when boiled with a solution of potash, yields potassic benzoate and ammonia:—

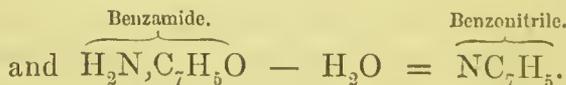
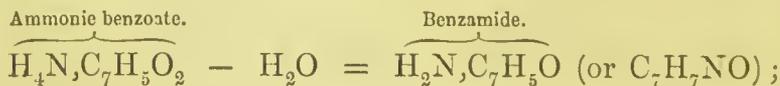


The nitriles may be obtained from the corresponding ammonium salts, or from their amides, by the action of an excess of phosphoric anhydride, or of phosphoric chloride:—in this way ammonic benzoate may be converted into benzonitrile, since the latter contains the elements of ammonic benzoate deprived of 2 atoms of water; the hydrogen being supplied from the elements of the ammonium, whilst the oxygen is derived from those of the acid:—



None of the nitriles hitherto procured contain oxygen, since all the salts which at present are known to yield them are formed either from monobasic acids of the form $(\text{HC}_x\text{H}_y\text{O}_2)$, or from dibasic acids of the form $(\text{H}_2\text{C}_x\text{H}_y\text{O}_4)$.

The relations subsisting between ammonic benzoate, benzamide, and benzonitrile, will exhibit the nature of the connexion between the ammonium salt, the amide, and the nitrile of a monobasic acid:—

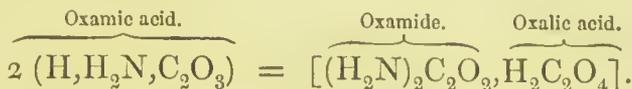


(1341) *Amidated Acids.*—If, instead of operating upon a *normal* ammonium salt obtained from either a monobasic or a dibasic acid, any of the *acid* salts formed by ammonium with the dibasic acids be subjected to dehydration, a body is produced belonging to the class of *amidic*, or *amidated acids*. Balard, in distilling the acid (or hydric) ammonic oxalate, thus obtained an azotised acid, which has been termed oxamic acid:—

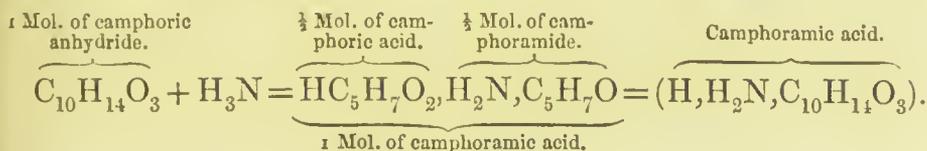


This substance may serve as the type of a numerous class of

compound acids, formed in a similar manner. The ammonium loses hydrogen, and the portion of the acid attached to the ammonium of the original salt loses oxygen, whilst that portion of acid which was attached to basylous hydrogen remains unaltered; so that oxamic acid may be viewed as a compound of unchanged oxalic acid and of oxamide:—

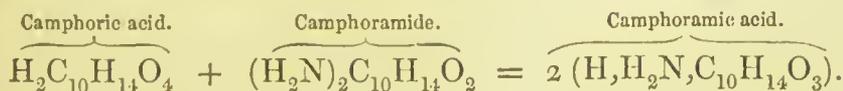


The amidic acids may also be obtained by acting upon the anhydride of a dibasic acid (1270) with dry ammonia in excess: the two bodies combine together, but the compound which is produced is found on examination to give evidence of the presence of but one half of the ammonia in the form of an ordinary ammonium salt; the second half having united with the elements of the acid to produce a new compound acid, which is the amidated acid of the one originally employed (Laurent). For instance, 1 molecule of camphoric anhydride when acted upon by 1 of ammonia, yields 1 of camphoramidic acid; the decomposition being supposed to consist in the conversion of one half of the molecule of camphoric anhydride into camphoramidic acid, while water is given off and enters into combination with the other half of the acid; these two bodies, camphoramidic acid and camphoric acid, then unite and form the new acid:—



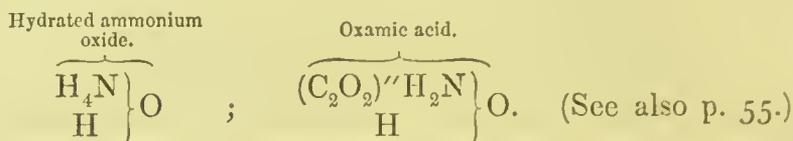
This amidic acid may be converted into ammoniac camphoramate by causing it to unite with a second atom of ammonia.

The amidic acids may therefore be viewed as monobasic compounds derived from dibasic acids, in which one half of the group composing the original dibasic acid is displaced by one half of the group which forms the amide of the acid; the combination of 1 molecule of the original dibasic acid with 1 of the amide furnishing 2 molecules of the monobasic amidic acid. To take again the case of the camphoric acid:—

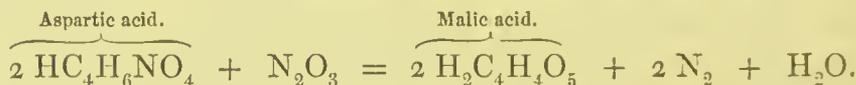


When the aqueous solutions of the amidic acids are boiled, they quickly unite with the elements of water, and become reconverted into acid ammonium salts.

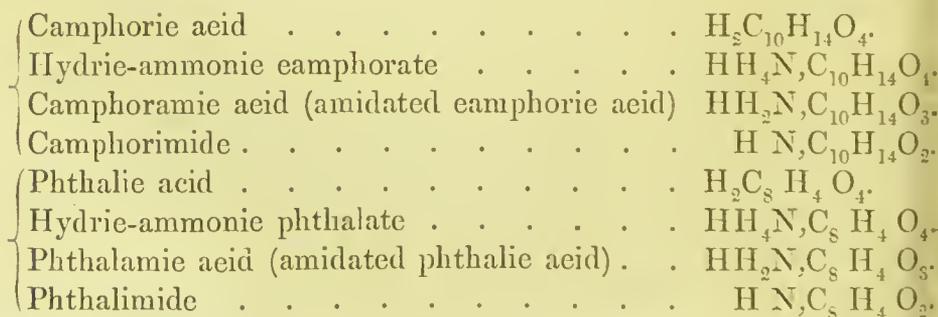
Hofmann regards the amidic acids as bodies formed upon the type of hydrated ammonium oxide, a substance too unstable to exist by itself, but acquiring permanence when two atoms of its hydrogen have been displaced by the radicle of a dibasic acid. Thus we may compare oxamic acid with hydrated ammonium oxide:—



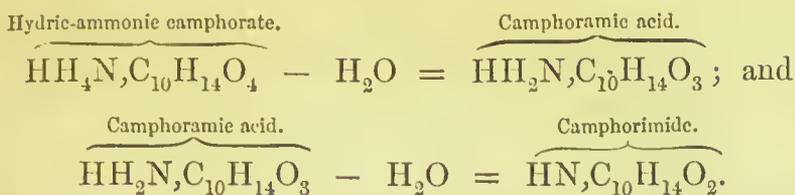
The action of nitrous anhydride (N_2O_3) upon the amidated acids is characteristic: mutual decomposition occurs, nitrogen and water are liberated, and the original acid from which the amidated compound was derived is reproduced. Aspartic acid (1317), for example, may thus be reconverted into malic acid:—



(1342) *Imides*.—Intermediate between the amides and the nitriles there is a third class of bodies, the *imides*, which contain nitrogen, and in which, if we are consistent, the existence of a body termed *imidogen* HN (or ammonia less two atoms of hydrogen), must be assumed to exist. These compounds are not numerous, but several of them are well known. They are obtained by a process of dehydration from certain acid ammonium salts, and from the amidated acids procurable from these salts: succinic, camphoric, and phthalic acids, for instance, each yield imidic compounds. The relation of these bodies to their respective acids will be seen by the following comparison:—



Hence it will be perceived, that the imides are bodies formed from the amidic acids by depriving the molecule of these compounds of one atom of water, just as the amidic acids are themselves obtained from the acid or hydric ammonium salts by depriving the molecule of the latter of an atom of water:—



The theory of the existence of amidogen and imidogen as distinct organic groups or radicles in these different bodies, does not, upon a general view of the question, appear to have any strong probability. It was, indeed, proposed merely as a temporary expedient for representing the facts. The different groups designated as amides, imides, and nitriles, must rather be regarded as *residues*, the results of successive stages of dehydration. The terms themselves may, however, be conveniently retained, provided that their use be not taken to imply an adhesion to the theory in accordance with which these names were framed.

We may sum up the foregoing facts in the following manner. The compounds which correspond to the normal ammonium salts are:—

1. The *amides*, produced by the combination of 1 molecule of the normal monobasic acid with 1 of ammonia, and the elimination of one atom of water.

2. The *diamides*, produced by the combination of 1 molecule of the normal dibasic acid with 2 molecules of ammonia, attended by the separation of two atoms of water.

3. The *nitriles*, produced by the combination of 1 molecule of a normal monobasic acid and 1 of ammonia, with elimination of 2 H₂O; or from 1 molecule of a normal dibasic acid and 2 molecules of ammonia, with elimination of 4 H₂O.

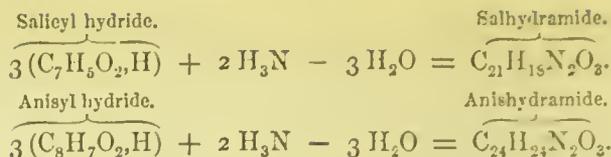
The compounds which correspond to the acid or hydric ammonium salts are:—

4. *Amidic acids*, formed from 1 molecule of a normal dibasic acid and 1 of ammonia, with separation of H₂O.

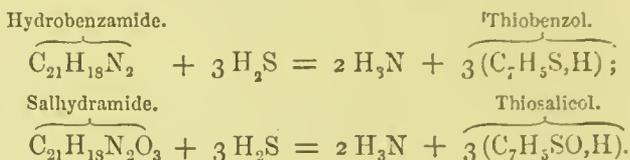
5. *Imides*, formed from 1 molecule of a normal dibasic acid and 1 of ammonia, with elimination of 2 H₂O.

(1343) *Hydrimates*.—Besides the varieties of amides already mentioned, a particular class of compounds is formed by the action of ammonia upon certain volatile oils which are indeed the aldehyds of the aromatic acids. These bodies, termed *hydrimates*, are furnished by the union of 3 molecules of the volatile oil and 2 molecules of ammonia, while water is separated in the proportion of 3 H₂O. Compounds of this kind are formed with the essential oil of bitter almonds, of spiræa, of cinnamon, of cumin, and of anise; as for example:—



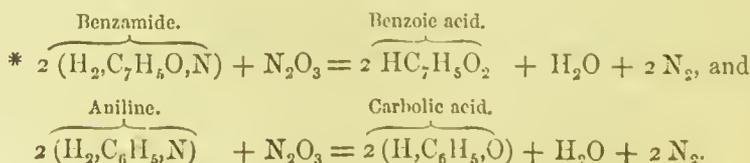


Sulphuretted hydrogen, in acting upon the hydranides, removes the elements of ammonia, and converts them into bodies analogous to the essences from which they were originally obtained, but the new essences contain as many atoms of sulphur as they previously possessed of oxygen; for example, thiobenzol is obtained from hydrobenzamide, and thiosalicol from salhydramide:—



(1344) *Theory of the Amides.*—The amides, ever since their discovery, have offered interesting subjects of investigation and speculation to the chemist. They are substances which, although derived from ammonia, generally exhibit no basic power, and yet in certain cases they can be converted into compounds which possess all the properties of powerful alkalis. Although this subject is somewhat abstruse, we shall enter into it in some detail, in order to furnish some idea of the number and variety of the products which may be obtained by the methods of substitution from a body apparently so simple as ammonia, as well as to exemplify the great variety of methods in which it is possible and even necessary to pursue researches of this description.

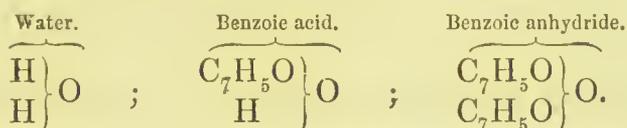
The investigations of Gerhardt and Chiozza (*Ann. de Chimie*, III. xlvi. 129) have shown that the amides bear the same relation to their respective acids, that the volatile alkalis, methyllia, ethyllia, &c., do to the alcohols from which they are formed. The amides, when treated with nitrous anhydride, yield nitrogen and the acid from which the amide was obtained; and, under similar treatment, the volatile alkalis of the aromatic alcohols yield nitrogen and their corresponding alcohol.* Upon this view, therefore, the amides are compounds derived by substitution from ammonia, upon which as a type they are founded; the ordinary amides of the monobasic acids, such as benzamide, being ammonia in which the basic character is neutralized



by the substitution of an electro-negative radicle (such as benzoyl) for one of its atoms of hydrogen: for instance,

ammonia being $\left. \begin{array}{c} \text{H} \\ \text{H} \\ \text{H} \end{array} \right\} \text{N}$, benzamide would be $\left. \begin{array}{c} \text{C}_7\text{H}_5\text{O} \\ \text{H} \\ \text{H} \end{array} \right\} \text{N}$; and $(\text{C}_7\text{H}_7\text{ON})$, or

starting from this idea, Gerhardt was led to effect upon the amides a series of substitutions similar to those performed by Hofmann with ethylia and its homologues. In this manner he was enabled by double decomposition to obtain amides, in which one atom or two atoms of hydrogen were displaced by certain electro-negative bodies; these electro-negative bodies being compounds which when substituted for either one half or both halves of the hydrogen in the atom of water, furnish in one case, the normal acids; in the other, the anhydrides (1268). Benzoyl ($\text{C}_7\text{H}_5\text{O}$), for instance, when thus substituted successively for hydrogen, yields first benzoic acid, then benzoic anhydride:—

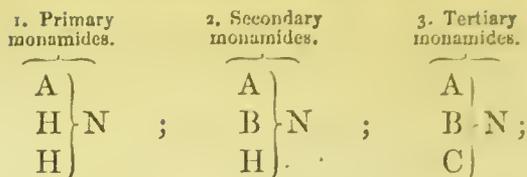


The subject has been rapidly extended in the hands of other chemists, and an admirable summary of the whole has been given by Hofmann (*Q. J. Chem. Soc.*, xii. 62).

It has been already explained, that the various compounds formed upon a certain type may possess properties in which they gradually differ from those that precede and from those that follow them in the series; these differences depending upon the nature and number of atoms of the elements or compounds which are introduced by processes of substitution into the prototype of the series. It becomes, therefore, quite possible to obtain compounds formed upon the type or plan of an eminently basic substance like ammonia, which, nevertheless, may possess neutral or even well-marked acid characters. In this manner various classes of amides have been formed by substitution, which may be distinguished thus:—

A. *Monamides*; B. *Diamides*; C. *Triamides*; formed respectively from one, from two, or from three atoms of ammonia. Each class admits of several subdivisions.

(1345) A. *Monamides*.—These are amides derived from a single atom of ammonia. They may be subdivided into three groups, according to the number of atoms of hydrogen in the ammonia which have been displaced by the electro-negative group. For instance, we have—



where A, B, and C represent the electro-negative groups by which the hydrogen is displaced.

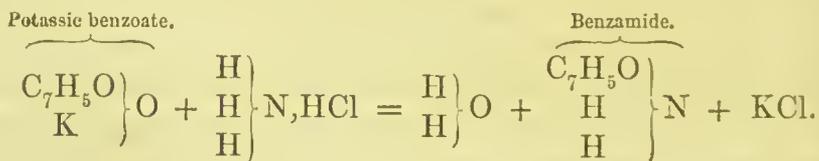
The primary and secondary monamides are crystalline fusible bodies, which for the most part are volatile without decomposition at high temperatures. The tertiary monamides are in many cases liquid at ordinary temperatures, but they may be volatilized unaltered.

a. Primary Monamides.—These amides, like acetamide, $(\text{C}_2\text{H}_5\text{ON}) = \begin{array}{c} \text{C}_2\text{H}_3\text{O} \\ \text{H} \\ \text{H} \end{array} \text{N}$, represent a molecule of ammonia, in which a single atom of hydrogen is displaced by an equivalent organic radicle.*

The primary monamides may be prepared by various methods:—

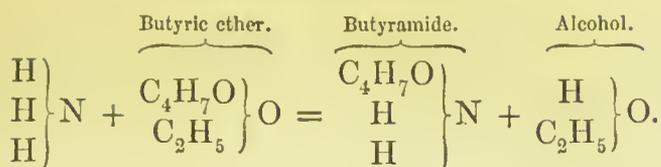
1. They may be obtained by the simple distillation of the ammonium salts, in the manner practised by Dumas for procuring oxamide from ammonic oxalate.

2. A better process consists in submitting to distillation a mixture of the potassium salt with ammonia hydrochlorate:—



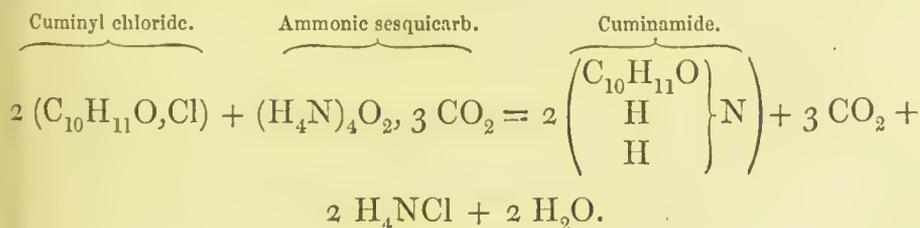
3. Liebig, in the preparation of the amides, takes advantage of the reaction occasioned by mixing the compound ethers with ammonia, which may be employed in the form either of an aqueous or of an alcoholic solution. The result of this decomposition is the formation of an alcohol, and of the amide of the acid contained in the ether; for example:—

* If a normal monobasic acid be defined to be an acid representing a molecule of water $\begin{array}{c} \text{H} \\ \text{H} \end{array} \text{O}$, in which 1 atom of hydrogen is displaced by an electro-negative radicle (acetic acid being $\begin{array}{c} \text{C}_2\text{H}_3\text{O} \\ \text{H} \end{array} \text{O}$), the primary amide is the amide derived from the normal ammonium salt of such an acid by the abstraction of an atom of water.

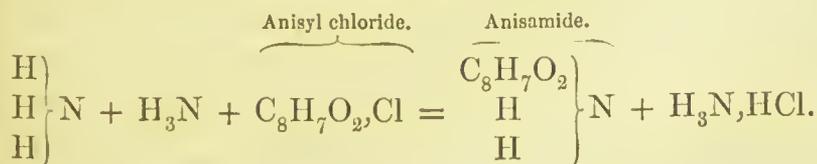


This method is far superior to the first; it is of more general application, and the results which it yields are perfectly definite, being produced by a specific mode of double decomposition. Sometimes the reaction does not occur immediately; it may in such cases be facilitated by inclosing the ammonia and ether in a sealed tube, and exposing the mixture for some hours to a temperature of from 212° to 266° (100° to 130°C). In this manner benzamide is obtained speedily, although it requires many weeks at the ordinary temperature to effect the decomposition.

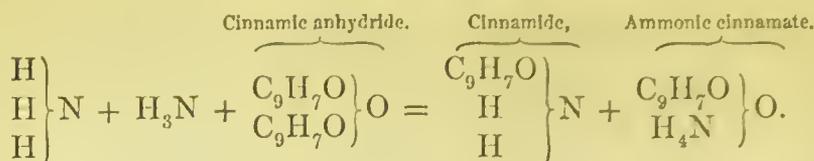
4. Gerhardt and Chiozza prepare many of the amides with facility, by treating the solid ammoniac sesquicarbonate with the oxychlorides (1267) corresponding to the anhydrides of those acids of which the amides are required. This process is very advantageous when applied to the preparation of amides which are insoluble or sparingly soluble in water, such as benzamide and cuminamide: all that is required in the performance of the operation is to triturate the ammoniac sesquicarbonate in a mortar with the oxychloride; after which the amide is formed by gently warming the mass: carbonic anhydride escapes with effervescence, and the sal-ammoniac and excess of sesquicarbonate are removed by washing with water. Cuminamide, for instance, is formed by the following reaction:—



Gaseous ammonia may be advantageously substituted in many cases for the sesquicarbonate; for example:—



5. In a similar manner the anhydrides of the monobasic acids are converted into monamides and a normal salt of the acid, by the action of ammonia:—



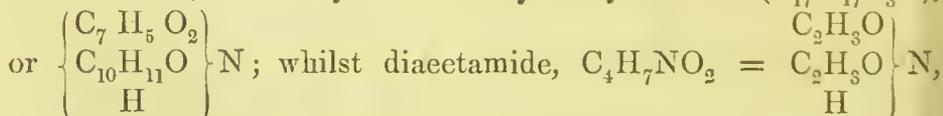
The monamides of acetic, propionic, butyric, valeric, and of a few other acids are freely soluble in water, and have a sweet taste; but the amides, as a class, are only sparingly soluble. Those which are soluble in water are also generally dissolved by both alcohol and ether. By long boiling with water most of them become dissolved, and converted into ordinary ammonium salts, by the assumption of the elements of water. This change is greatly accelerated by the addition of even a minute quantity of any free acid. The presence of a free alkali produces a like transformation; if potash or soda be the base employed, salts of these alkalies are formed, whilst ammonia is liberated; this change occurs very slowly at ordinary temperatures, but it takes place rapidly at the boiling point.

β . *Secondary Monamides.*—In these the displacement of hydrogen in the molecule of ammonia extends to two atoms. This class may be subdivided into two groups, according to the mode in which the substitution of hydrogen takes place: for instance we have

(a) Substitution of two atoms of a monatomic acid radicle belonging either to the same acid or to two different acids; and

(b) Substitution of a monatomic acid radicle, and of a monatomic alcohol radicle (secondary mixed monamides).

a. As an example of displacement by two different monatomic acid radicles, we may take eumylsalicylamide* ($\text{C}_{17}\text{H}_{17}\text{O}_3\text{N}$),

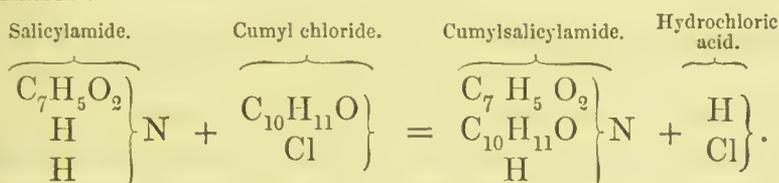


offers an instance of displacement of two atoms of hydrogen by two of the same monatomic radicle.

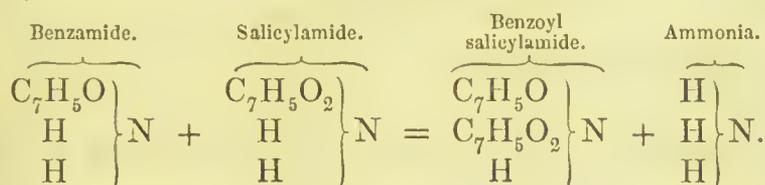
1. This subdivision of the secondary monamides may be prepared by heating the primary monamides to a certain temperature with an equivalent quantity of the electro-negative oxychloride: hydrochloric acid escapes in abundance, and the secondary mon-

* The inharmonious and unwieldy names employed to designate these complicated substitution-products are apt to discourage the learner; but in the present state of chemical nomenclature they are almost necessary, for the purpose of pointing out the parentage and relationship of the bodies which they represent; since the compounds themselves have little or no intrinsic interest, the relations indicated being, in most cases, the really important circumstances.

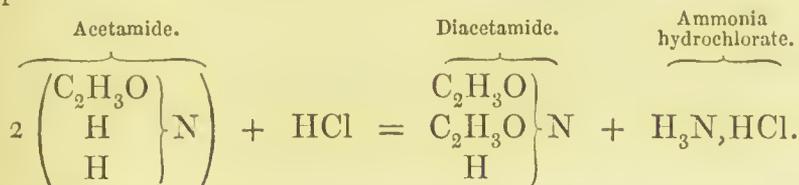
amide is found in the residue. Care must be taken to prevent the temperature from rising too high, otherwise nitriles are apt to be formed. If the products of the reaction assume a viscous condition, they must not be dissolved whilst in this state, but must be allowed to become solid; their solidification may often be effected by the addition of a few drops of ether. The formation of cumylsalicylamide by treating cumyl chloride with salicylamide, offers an instance of the formation of a secondary monamide in this manner:—



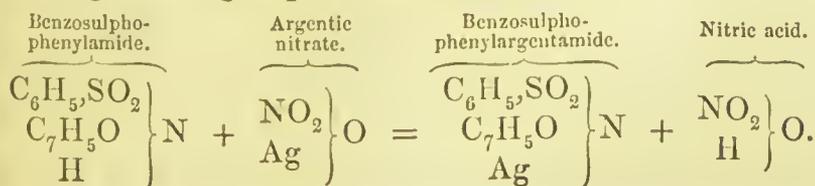
2. Sometimes new amides may be obtained by heating together two primary amides in equivalent proportions; ammonia is then disengaged, and a secondary amide is formed. For example:—



3. In other cases they may be obtained by the action of one atom of hydrochloric acid upon two atoms of a monamide; for example:—

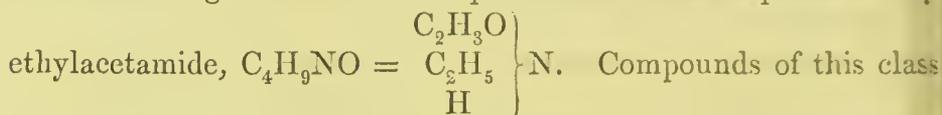


The members of the first subdivision of the secondary monamides possess the acid character more strongly than the primary monamides; and they frequently form metallic salts, those which contain silver being the salts most readily procured. For example, benzosulphophenylamide, when dissolved in boiling water by the aid of a few drops of ammonia, and mixed with a boiling solution of argentic nitrate, yields a compound in which silver takes the place of hydrogen in the original amide, the new silver salt crystallizing out in groups of colourless needles.



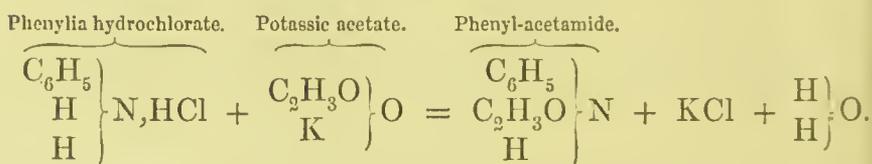
The prolonged action of the acids and alkalis, especially if aided by heat, expels the nitrogen of these secondary monamides in the form of ammonia, and liberates the acids corresponding to the electro-negative radicles present in the compound.

b. The second subdivision of the secondary monamides, in which one atom of hydrogen is displaced by a monacid radicle, and the second atom of hydrogen by an equivalent alcohol radicle, contains a large number of compounds which are represented by

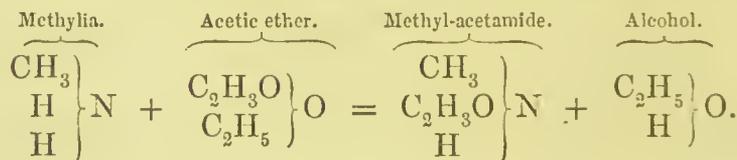


may be formed by submitting the primary monammonias to the several processes which when applied to ammonia furnish the alcohol bases (1373), as well as by the following methods:—

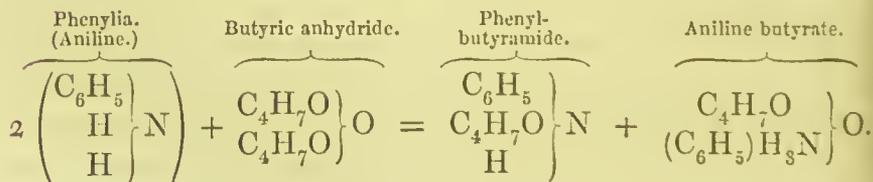
1. *Distillation of the Salts of the Organic Acids with those of the Alcohol Bases.*



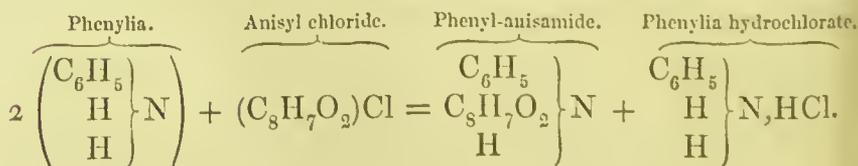
2. *Treatment of the Alcohol Bases with Compound Ethers.*



3. *Action of the Anhydrides on the Alcohol Bases.*



4. *Action of Oxychlorides on the Alcohol Bases.*



The prolonged action of acids and of alkalis upon this class o

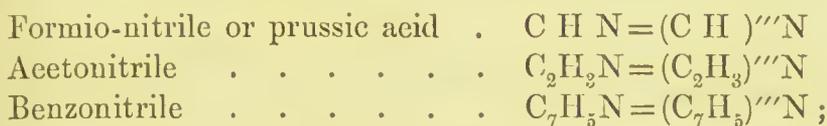
mixed monamides in the presence of water gives rise to the reproduction of the acid and the base from which they were derived.

γ . *Tertiary Monamides*.—In these bodies the three atoms of hydrogen in ammonia are displaced by a corresponding number of radicles, one of which at least must be of an electro-negative character. This class may be divided into several groups, in which the following substitutions occur respectively:—

(a) Substitution of each atom of hydrogen by one of a monacid radicle;

(b) Substitution of two atoms of hydrogen by acid radicles, and of the third atom of hydrogen by one atom of an alcohol radicle.

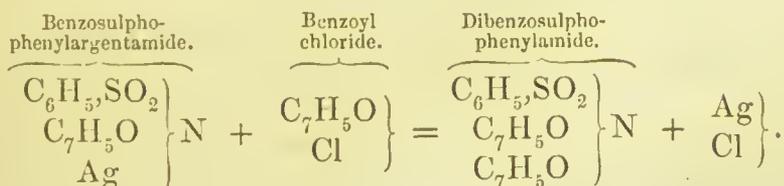
Hofmann regards the nitriles as belonging to the group of tertiary monamides in which the three atoms of hydrogen in the typical molecule of ammonia have been displaced by a *tribasic* acid radicle, and thus he represents the following compounds:—



but this mode of regarding the nitriles requires experimental confirmation.

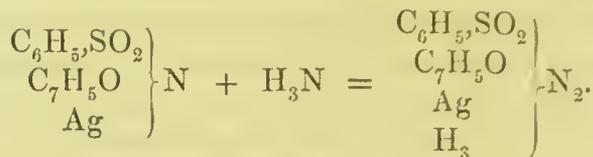
a. Tertiary monamides containing one atom of an acid radicle and two atoms of an alcohol radicle could doubtless be obtained by the action of the hydriodic ethers in excess upon the primary monammonias, or by the action of the electro-negative oxychlorides upon the secondary monammonias.

The members of the first subdivision of the tertiary monamides are readily prepared from the silver salts of the secondary monamides; for they are attacked by the negative oxychlorides even without the aid of heat, double decomposition occurring, whilst argentic chloride is formed, and an organic radicle takes the place of the silver in the amide. Benzosulphophenylargentamide is thus, by the action of benzoyl chloride, readily converted into dibenzosulphophenylamide:—

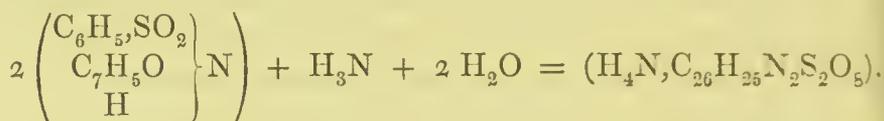


When the silver salt of a secondary monamide, such as the one referred to in the last equation, is treated with ammonia, it is commonly dissolved without fixing the elements of water, but

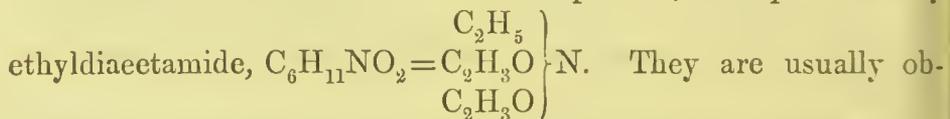
it combines with the ammonia and forms a diamide—that is to say, an amide derived from two molecules of ammonia; for example:—



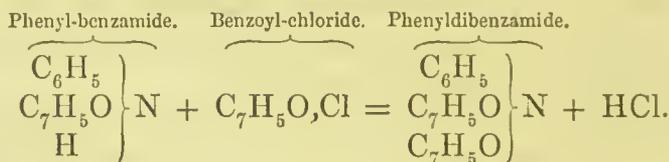
The other secondary and tertiary monamides when treated with ammonia have the power of fixing the elements both of ammonia and of water so as to form amidated acids, or rather salts of ammonium with amidated acids. Thus, for instance, benzo-sulphophenylamide may be transformed by ammonia into ammoniac benzosulphophenylamate:—



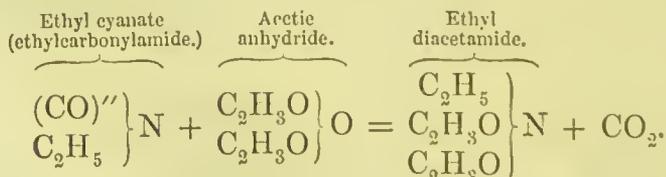
b. Tertiary monamides of the second variety, in which two acid radicles and one alcohol radicle are present, are represented by



They are usually obtained by acting upon the appropriate secondary monamide by an electro-negative oxychloride:—



Ethyldiacetamide has been obtained by acting upon ethyl cyanate with acetic anhydride, a process which Hofmann considers as admitting of general application, and which he regards as the action of an anhydride upon a tertiary monammonia:—



The action of the alkalis upon these compounds reproduces the monammonia and a salt of the acid from which the amide is derived.

In a few instances metallic radicles occupy the place of the organic radicles in the amides. A primary monamide of this kind is ob-

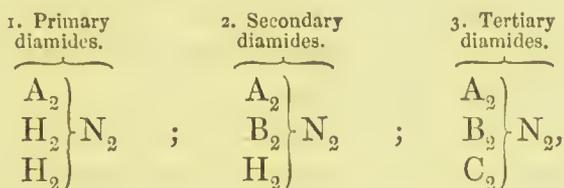
tained by heating potassium in ammonia, $2 \left(\begin{array}{c} \text{H} \\ \text{H} \end{array} \right) \text{N} + \text{K}_2 = 2 \left(\begin{array}{c} \text{K} \\ \text{H} \end{array} \right) \text{N} +$

H_2 ; and a similar compound of zinc is obtained by treating zinc-ethyl

with ammonia, $2 \left(\begin{array}{c} \text{H} \\ \text{H} \end{array} \right) \text{N} + \left(\begin{array}{c} \text{C}_2\text{H}_5 \\ \text{Zn} \end{array} \right)_2 = \left(\begin{array}{c} \text{Zn} \\ \text{H}_2 \end{array} \right) \text{N}_2 + 2 \left(\begin{array}{c} \text{C}_2\text{H}_5 \\ \text{H} \end{array} \right)$. An in-

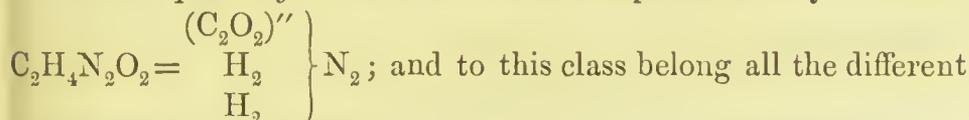
stance of a tertiary metallic monamide is afforded in the case of copper, $(\text{Cu})'_3\text{N}$, *tricuprosamide*: such metallic amides are obtained by submitting the metallic oxides to the action of gaseous ammonia; $4 \text{H}_3\text{N} + 6 \text{CuO} = 2 [(\text{Cu})'_3\text{N}] + 6 \text{H}_2\text{O} + \text{N}_2$.

(1346) B. *Diamides*.—These compounds are derived from two atoms of ammonia, and like the monamides, may be subdivided into three principal groups, viz. —



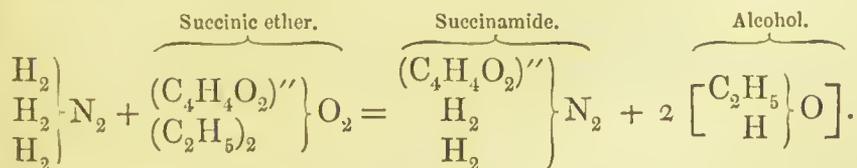
according as 2, 4, or 6 atoms of the hydrogen of the typical group have been displaced by a corresponding number of atoms of the substitution radicle. The last two of these principal groups again admit of various subdivisions.

a. *The primary diamides* are well represented by oxamide

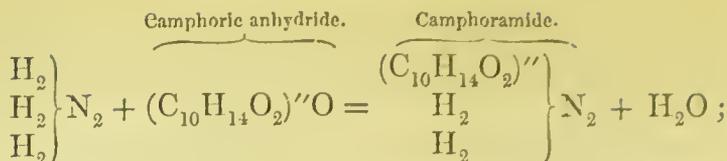


varieties of urea (1604).

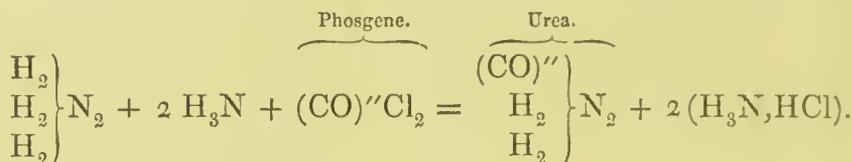
These diamides may in many instances be prepared by distilling the normal ammonium salt, as was originally practised in the case of oxamide itself. A better method consists in decomposing the dibasic ether either by an alcoholic or an aqueous solution of ammonia in excess; for example:—



The primary diamides may also be obtained by the action of ammonia on the anhydrides of the dibasic acids; for example:—



and it is probable that the action of ammonia on the oxyehlorides of the dibasic acids would also yield the corresponding diamides, as in the formation of urea (carbamide) from ammonia and phosgene gas (carbonyl chloride):—



The primary diamides are generally decomposed in great measure when submitted to distillation. They are converted by digestion with acids or with alkalis into ammonia and the dibasic acids from which they are derived.

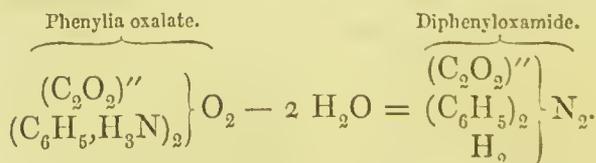
β . *a.* The secondary diamides contain the bodies often described as imides, (1342), 4 atoms of hydrogen in the typical diammonia group being displaced by 2 atoms of the radicle of a dibasic acid.

b. A second group of the secondary diamides contains one atom of the radicle of a dibasic acid, and two atoms of a monobasic alcohol radicle, or some corresponding hydrocarbon: diphenylsue-

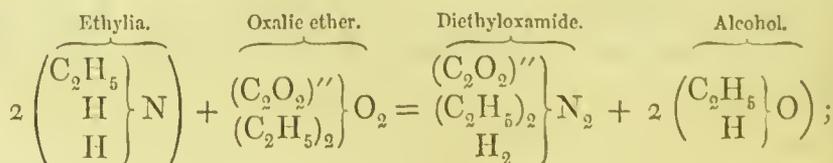
einamide ($\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2$) is an example of this class, $\left. \begin{array}{l} (\text{C}_4\text{H}_4\text{O}_2)'' \\ (\text{C}_6\text{H}_5)_2 \\ \text{H}_2 \end{array} \right\} \text{N}_2$.

The diamides of this subdivision are obtained from alcohol bases by processes which, if applied to ammonia, would furnish primary diamides; for example:—

1. By distillation of the normal salts which the alcohol bases form with dibasic acids:—

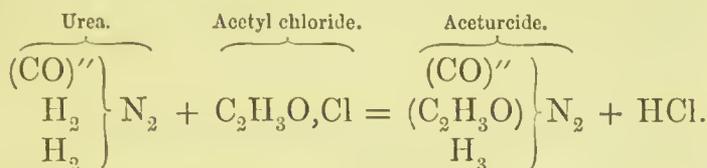


2. By the action of alcohol bases upon normal dibasic ethers:—

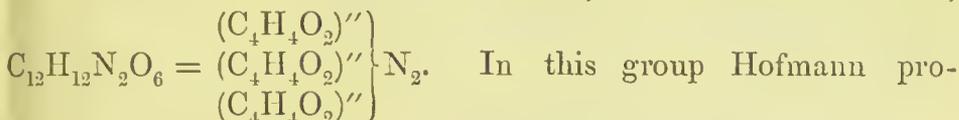


as well as by the action of the alcohol bases upon the anhydrides and oxychlorides of the dibasic acids.

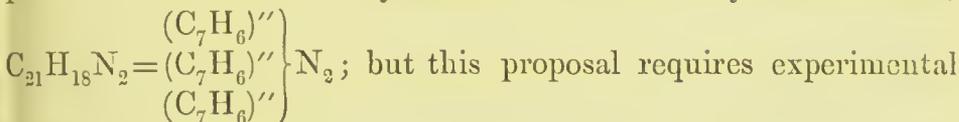
The ureides (1605) belong to this subdivision of secondary diamides. They are obtained by the action of an oxychloride of a monobasic acid upon one of the varieties of urea; for example:—



γ. *The tertiary diamides* contain bodies derived from three atoms of the radicle of a dibasic acid, such as trisuccinamide,

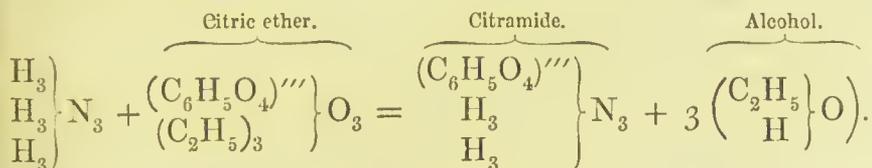


poses to include the hydramides, such as hydrobenzamide,

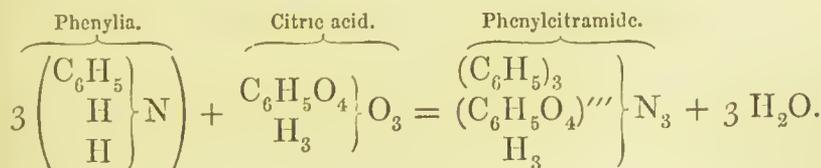


support. An instance of a metallic tertiary diamide is seen in *trimercuramide* $\text{Hg}''_3\text{N}_2$.

(1347) C. *Triamides*.—These compounds are derived from three atoms of ammonia; but they have not been extensively studied. Citryltriamide or citramide affords an example of a *primary triamide*. It may be obtained by the action of ammonia upon citric ether:—



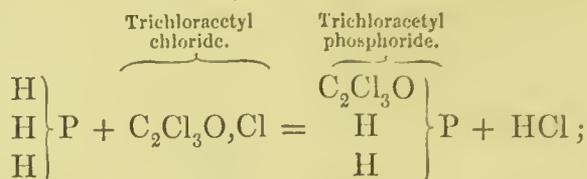
As an instance of a *secondary triamide*, phenylcitramide may be given; it may be obtained by acting upon phenylia (aniline) with citric acid:—



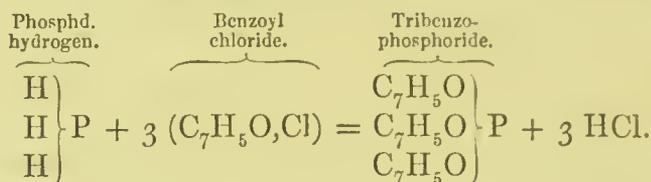
Phosphorides, Arsides, Stibides.

There is every reason to anticipate the formation of a class of compounds corresponding to the amides, in which phosphorus, arsenicum, or antimony occupies the place of the nitrogen of the

amides. Indeed, a *primary monophosphoride*, corresponding to a primary monamide, may be obtained by acting upon phosphuretted hydrogen with trichloroacetyl chloride:—



and a *tertiary monophosphoride*, corresponding to a tertiary monamide, has been obtained by acting upon phosphuretted hydrogen with benzoyl chloride:—



The organic radicles in these compounds often have their place supplied by the metals. They are generally formed by the action of phosphuretted, arseniuretted, or antimonuretted hydrogen upon solutions of the metallic salts. Thus a diphosphoride, *tricupricphosphide*, Cu_3P_2 , is obtained from cupric nitrate and phosphuretted hydrogen; $2 \text{H}_3\text{P} + 3 (\text{Cu}_2\text{NO}_3) = \text{Cu}_3\text{P}_2 + 6 \text{HNO}_3$; and a diarside, *tricuprarside* (Cu_3As_2) from cupric chloride and arseniuretted hydrogen; $2 \text{H}_3\text{As} + 3 \text{CuCl}_2 = \text{Cu}_3\text{As}_2 + 6 \text{HCl}$; and a monostibide, *triargenticstibide* (Ag_3Sb) from argentic nitrate and antimonuretted hydrogen; $\text{H}_3\text{Sb} + 3 (\text{AgNO}_3) = \text{Ag}_3\text{Sb} + 3 (\text{HNO}_3)$.

For a masterly discussion of the subject of amides and compound bases the reader is referred to Hofmann's paper on *Ammonia and its Derivatives* (Q. J. Chem. Soc., xi. 252).

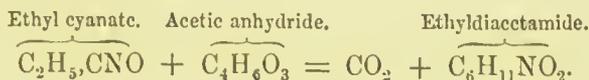
The description of a few of the more interesting compounds belonging to the different classes of amides will suffice to give an idea of the general properties of these substances.

(a) *Monamides, or Amides of the Monobasic Acids.*

(1348) *Acetamide* $\left[\begin{array}{c} \text{C}_2\text{H}_3\text{O} \\ \text{H}_2 \end{array} \right\} \text{N} = \text{C}_2\text{H}_5\text{NO}$]; *Fusing pt.* $172^\circ.4$ (78°C.); *Boil. pt.* $429^\circ.8$ (221°C.).—This compound is obtained in abundance by exposing acetic ether with an equal volume of aqueous solution of ammonia, under pressure, for six hours to a temperature of 248° or 257° (120° or 125°C.), then distilling the residue and collecting the distillate after the boiling point has risen to 43° . Acetamide forms a white solid which crystallizes in pearly leaflets after fusion. It is soluble in water, and has a cooling sweetish taste. When distilled with phosphoric anhydride its molecule loses one atom of water, and becomes converted into acetonitrile. If acetic ether be decomposed by admixture with ethylia and exposure to heat in sealed tubes, it forms a corresponding com-

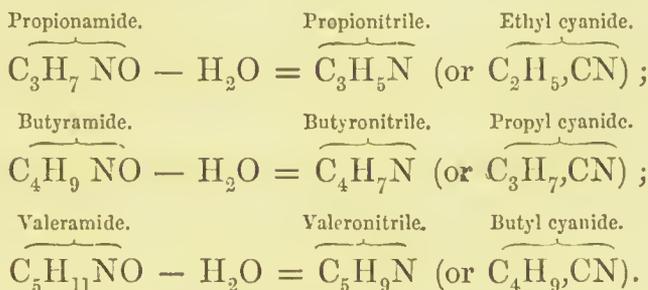
pond, *ethylacetamide* or *aceto-ethylide*, $C_4H_9NO = \left. \begin{array}{l} C_2H_3O \\ C_2H_5 \\ H \end{array} \right\} N$, in which one of the remaining typical atoms of hydrogen is displaced by ethyl.

Ethylidiacetamide [$C_6H_{11}NO_2 = 2 \left(\begin{array}{l} C_2H_3O \\ C_2H_5 \end{array} \right) \left. \vphantom{\begin{array}{l} C_2H_3O \\ C_2H_5 \end{array}} \right\} N$; *Boil. pt.* 377°·6 (192° C.)] is a limpid, colourless, neutral liquid, which is obtained by heating cyanic ether with acetic anhydride to about 392° (200° C.) in a sealed tube. Carbonic anhydride escapes on opening the tube when cold:—

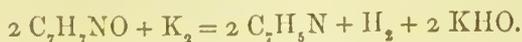


Trichloracetamide [$C_2H_2Cl_3NO = \left. \begin{array}{l} C_2Cl_3O \\ H_2 \end{array} \right\} N$; *Fusing pt.* 275° (135° C.)] is the compound procured by decomposing trichloroacetic ether with ammonia; but it is also obtained by acting upon several other perchlorinated ethylic ethers, such as the perchlorinated formic, carbonic, oxalic, and succinic ethers: perchloraldehyd likewise yields it when treated with ammonia. It is a crystallizable compound with a sweet taste; it is very soluble in alcohol and in ether.

(1349) *Propionamide* (C_3H_7NO), *Butyramide* (C_4H_9NO), and *Valeramide* ($C_5H_{11}NO$) may all be obtained by the action of ammonia, aided by heat, upon their respective ethers. They are fusible, volatile compounds, which may be sublimed without decomposition; they are soluble in water, alcohol, and ether. When distilled with phosphoric anhydride, they lose the elements of one atom of water, and yield the nitriles of the acid, or the hydrocyanic ether of the alcohol below them:—

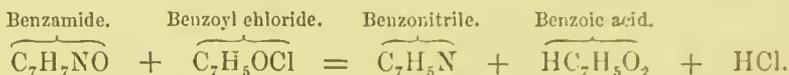


(1350) *Benzamide* [C_7H_7NO ; *Fusing pt.* 239° (115° C.)] is a white solid, which may be sublimed without undergoing decomposition. It is sparingly soluble in cold water; boiling water dissolves it easily, and deposits it, on cooling, in acicular crystals. It is still more readily dissolved by alcohol and by ether, from which it crystallizes in right rhombic prisms. When boiled with free acid or alkali, it is quickly converted into ammoniac benzoate. Benzamide is most easily obtained by the action of dry ammoniacal gas upon benzoyl chloride; in which case the change is accompanied by the formation of benzonitrile. It may also be procured by heating an alcoholic solution of ammonia with benzoic ether for some hours in a sealed tube. When boiled with mercuric oxide, water is separated, and *mercuric-benzamide* is obtained; $2 C_7H_7NO + HgO = C_{14}H_{12}HgN_2O_2 + H_2O$. Mercuric-benzamide may be viewed as a diamide $\left. \begin{array}{l} (C_7H_5O)_2 \\ Hg'' \\ H_2 \end{array} \right\} N_2$, or two atoms of benzamide in which half the remaining typical hydrogen has been displaced by mercury. Benzamide, when heated with potassium, loses oxygen; hydrogen is eliminated, and benzonitrile is formed:—



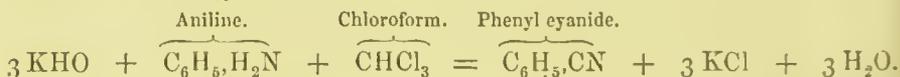
(b) *Nitriles.*

(1351) *Benzonitrile* (C_7H_5N); *Sp. gr. of liq.* 1.007; *of vap.* 3.70; *Rel. wt.* 51.5; *Boil. pt.* $375^{\circ}.8$ ($191^{\circ} C.$).—This substance is a colourless oil, with a powerful odour of bitter almonds. It is sparingly soluble in water, but is miscible with alcohol and ether in all proportions. When heated it emits an inflammable vapour, which burns with a smoky flame. Benzonitrile may be obtained by the dry distillation of ammoniac benzoate, or of benzamide; and still more readily by mixing either of these bodies with phosphoric anhydride in excess before proceeding to the distillation; the distillate when washed with hydrochloric acid, and redistilled, is pure benzonitrile. Benzamide also yields benzonitrile when treated with benzoyl chloride:—



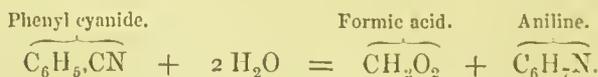
Benzonitrile, when boiled with alkalis, or with concentrated acids, is converted into benzoic acid and ammonia, with assimilation of the elements of water.

Phenyl cyanide (C_6H_5CN); *Boil. pt.* $332^{\circ}.6$ ($167^{\circ} C.$).—Isomeric with benzonitrile, but quite different from it in properties, is phenyl cyanide, obtained by Hofmann from the reaction of caustic potash on an alcoholic solution of aniline and chloroform (1149a):—



It is a mobile liquid, exhibiting a greenish colour in transmitted light and a beautiful blue by reflected light. The odour of this cyanide is powerfully aromatic, with a peculiar bitter taste, and it produces a constriction of the fauces characteristic of hydrocyanic acid. It cannot be distilled without undergoing partial decomposition, the distillate yielding a brown mass which is crystalline and destitute of odour.

Phenyl cyanide combines readily with other cyanides: the compound with argentic cyanide is particularly beautiful. Alkalis have but little action on phenyl cyanide, but contact with dilute acids speedily decomposes it with assimilation of the elements of water:—



Cumionitrile [$C_{10}H_{11}N$; *Sp. gr. of liq.* 0.765; *Boil. pt.* $462^{\circ}.2$ ($239^{\circ} C.$)] may be obtained from ammoniac cuminate, as a liquid with a fragrant odour, by methods similar to those employed in preparing benzonitrile.

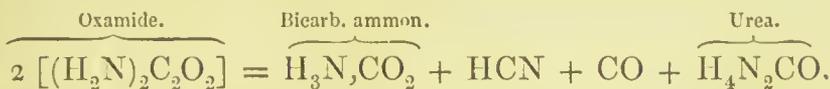
The nitriles of the fatty acids are identical with one class of the hydrocyanic ethers of the alcohol in the series immediately below that of the acid from which they are obtained (1149).

(c) *Diamides—Amides of Dibasic Acids.*

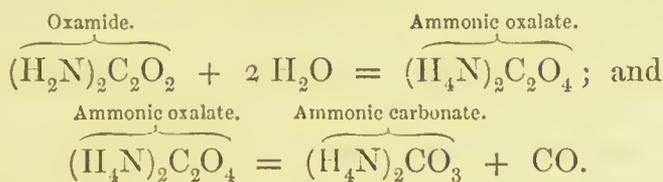
(1352) The dibasic acids give rise to the formation of diamides; that is to say, to amides, each molecule of which is formed from 2 molecules of ammonia. We shall examine those of two acids only, viz., the amides of oxalic acid, and those of succinic acid. The latter afford an instructive illustration of the preparation and properties of primary, secondary, and tertiary diamides, from the same acid.

(1353) *Oxamide* $[(\text{H}_2\text{N})_2\text{C}_2\text{O}_2, \text{ or } \left. \begin{array}{c} (\text{C}_2\text{O}_2)'' \\ \text{H}_2 \\ \text{H}_2 \end{array} \right\} \text{N}_2.]$ —This interest-

ing compound is most readily obtained by decomposing oxalic ether by an aqueous or an alcoholic solution of ammonia. It may also be procured, though less advantageously, by distilling ammoniac oxalate, when it condenses in the neck of the retort and in the receiver in the form of white flocculi. Oxamide is a light tasteless powder, which is insoluble in cold water, but soluble to a small extent in boiling water, from which it is deposited on cooling in crystalline flakes. The solution is neutral, and gives no precipitate with salts of calcium. It is insoluble in alcohol. It may be sublimed in an open tube, though with difficulty. When its vapour is transmitted through a red-hot tube, it is decomposed, according to Liebig, into bicarbonate of ammonia, hydrocyanic acid, carbonic oxide, and urea:—



When oxamide is heated to 436° ($224^\circ\cdot5$ C.), in a sealed tube with water, it becomes transformed into ammoniac oxalate. The same change is effected by boiling oxamide with dilute acids or alkalis. If heated alone in closed vessels to 590° (310° C.), it is converted into a mixture of cyanogen, carbonic oxide, and ammoniac carbonate. Oxamide, in fact, contains the elements of cyanogen and water; $(\text{H}_2\text{N})_2\text{C}_2\text{O}_2 = (\text{CN})_2 + 2\text{H}_2\text{O}$; but the water reacting upon a portion of oxamide, converts it into ammoniac oxalate, and this, by the action of heat, is resolved into ammoniac carbonate and carbonic oxide:—

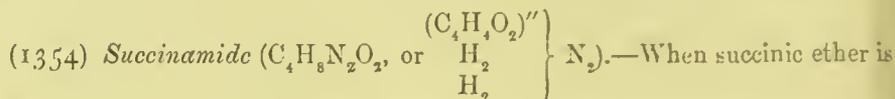
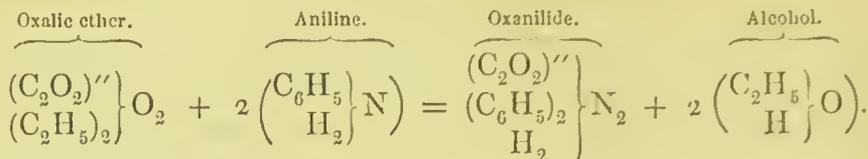


When oxamide is boiled with mercuric oxide, the two bodies enter into combination, and form a white heavy powder, $\text{HgO}, [(\text{H}_2\text{N})_2\text{C}_2\text{O}_2]_2$.

If oxalic ether be decomposed by the alcohol alkalis, such as ethylia, methylia, and amylium, or by other bases, such as aniline, compounds are obtained corresponding to oxamide: for example, ethylia, when made to act upon oxalic ether, yields diethyl-

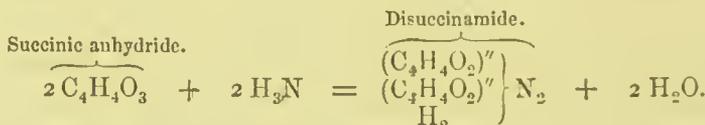
amide, $(\text{C}_6\text{H}_{12}\text{N}_2\text{O}_2)$, or $\left. \begin{array}{c} (\text{C}_2\text{O}_2)'' \\ (\text{C}_2\text{H}_5)_2 \\ \text{H}_2 \end{array} \right\} \text{N}_2$; and aniline, under similar

circumstances, if heated in a closed tube to 320° (160° C.), produces diphenyloxamide (oxanilide), $C_{14}H_{12}N_2O_2$:—



mixed with twice its volume of a concentrated solution of ammonia, alcohol is liberated, and succinamide is deposited in the form of a granular crystalline compound. It is nearly insoluble in cold water, but is dissolved by boiling water in considerable quantity. Alcohol and ether do not dissolve it.

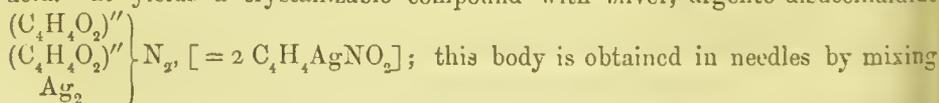
Disuccinamide, or *succinimide* [$(C_4H_4O_2)''_2H_2N_2, 2H_2O$]; *Fusing pt.* 257° (125° C.).—The simplest method of procuring this compound consists in neutralizing a solution of succinic acid with ammonia, evaporating to dryness, and submitting the residue to distillation. It may also be obtained by causing dry ammonia to react upon succinic anhydride; during this reaction water is formed, and a considerable elevation of temperature occurs :—



When succinamide is heated, ammonia is evolved, and disuccinamide is formed :—



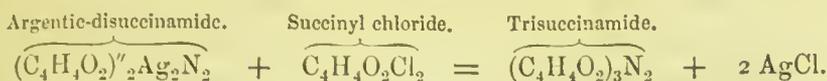
At a temperature above 401° (205° C.), it sublimes without decomposition, and may be purified, by crystallization, from its solution in boiling water, which on cooling deposits it in beautiful, efflorescent, rhombic tables. It is freely soluble in water, and the solution has a feebly acid reaction; alcohol also dissolves it, but it is insoluble in ether. Disuccinamide is metameric with succinamic acid. It yields a crystallizable compound with silver, argento-disuccinamide



a boiling concentrated alcoholic solution of disuccinamide, rendered slightly alkaline by ammonia, with a hot alcoholic solution of argentic nitrate: the salt is deposited as the liquid cools. It is not decomposed by potash in the cold, but on the application of heat to the mixture ammonia is evolved. Argentic-disuccinamide is freely soluble in ammonia, and if the solution so obtained be left to spontaneous evaporation, a syrupy alkaline liquid is left, which gradually becomes converted into a mass of rectangular prisms [$2 C_4H_4AgNO_2, 2 H_2N$], from which potash immediately liberates ammonia. Argentic-disuccinamide is decomposed with explosion when suddenly heated: it is isomeric with argentic succinamate, into which it is converted if its ammoniacal solution be boiled for some time; it then becomes much more soluble, and is no longer explosive.

Trisuccinamide [$(C_4H_4O_2)''_3N_2$]; *Fusing pt.* $181^{\circ}.4$ (85° C.).—When 10 parts of succinyl chloride (1302) are dissolved in twice their volume of ether, and mixed with 27 parts of argentic-disuccinamide, an immediate reaction

occurs, sufficient heat is emitted to volatilize the ether, and argentic chloride is formed:—



Boiling ether dissolves it under pressure, and on cooling deposits it in small crystals. Water and alcohol decompose this compound, alcohol converting it into disuccinamide without the formation of succinic ether.

(d) *Amidated Acids.*

(1355) A single instance will sufficiently illustrate the nature of these bodies, after what has been already stated of their general properties: but the existence of this class of substances is not confined to the compounds of organic chemistry, since both sulphuric and carbonic acids yield amidated acids, viz., the sulphamic and carbamic acids; these bodies being produced by the reaction of dry ammonia upon sulphuric and carbonic anhydrides; the compounds to which the term of ammonides was applied (610) being supposed by Laurent and Gerhardt to be amidated salts of ammonium.

(1356) *Oxamic Acid* ($\text{H}_2\text{H}_2\text{N}_2\text{C}_2\text{O}_3$).—When hydric ammonic oxalate [$(\text{H}_4\text{N}, \text{H}_2\text{C}_2\text{O}_4), \text{H}_2\text{O}$] is exposed to a carefully regulated heat, it loses its water of crystallization, and begins to undergo decomposition at a temperature of about 428° (220°C.), giving off water, carbonic acid, formic acid, and carbonic oxide. The residue in the retort, if not heated too strongly, consists of oxamide and an acid substance soluble in water. This soluble compound is oxamic acid. It may be neutralized by baryta water, or by lime water, and yields crystalline salts of these bases on evaporating the solution. If its aqueous solution be boiled, it is reconverted into hydric ammonic oxalate, $\text{H}_2\text{H}_2\text{NC}_2\text{O}_3 + \text{H}_2\text{O} = \text{HH}_4\text{NC}_2\text{O}_4$. Oxamic acid may be still more readily prepared by decomposing an alcoholic solution of oxalic ether by an alcoholic solution of ammonia in excess; oxamide is formed, and in a day or two the liquid deposits crystals of oxamic ether ($\text{C}_2\text{H}_5, \text{H}_2\text{NC}_2\text{O}_3$) mixed with those of ammonic oxamate. The latter may be separated from the oxamic ether by dissolving the mixture of the two substances in hot alcohol, adding an alcoholic solution of calcic chloride, and separating the sparingly soluble calcic oxamate by filtration.

A large number of dibasic acids form compounds analogous to oxamic acid, such as the following:—



| | |
|----------------------------|--|
| Tartramie acid | $\text{HH}_2\text{N}, \text{C}_4\text{H}_4\text{O}_6.$ |
| Malamie acid | $\text{HH}_2\text{N}, \text{C}_4\text{H}_4\text{O}_4.$ |
| Phthalamie acid | $\text{HH}_2\text{N}, \text{C}_8\text{H}_4\text{O}_3.$ |
| Camphoramie acid | $\text{HH}_2\text{N}, \text{C}_{10}\text{H}_{14}\text{O}_3.$ |

The amido-acids, of which amido-benzoic is the representative, will be considered hereafter (1436, 1614).

§ II. THE ORGANIC BASES.

(1357) The ALKALOIDS, or *organic alkalies*, are not less numerous than the organic acids; they form a natural group of high interest to the chemist, not only on account of their remarkable composition, but also from their powerful effects as medicinal or poisonous agents upon the animal economy.

In the majority of instances the natural organic bases are derived from the vegetable kingdom, and constitute the active principle of the plant that contains them. They always occur in combination with some acid, which is also frequently of organic origin, and peculiar to the plant or family of plants in which it is found. In many cases the alkaloids which occur in one species of a natural family are found also in several of the other members of the same family.

The vegetable bases when in solution have generally a decidedly alkaline reaction upon test papers, and for the most part they completely neutralize the acids, forming definite and well-crystallized salts.* They obey the usual law of bases when their salts are submitted to electrolytic analysis; since under these circumstances the base is liberated at the platinode of the voltaic battery. Most of these bases are dissolved sparingly by water, but are more freely soluble in alcohol, especially when it is at a boiling temperature; the alcoholic solutions as they cool generally deposit the alkaloids in the crystalline form. Some of these bases occur in two isomeric conditions, one of which is crystallizable, and the other amorphous; both forms combine with acids

* It is much to be regretted that a uniform system of nomenclature has not been adopted for these compounds; that the termination *ia*, for example, as in morphia and strychnia, has not been appropriated to the bases, to indicate their analogy with ammonia: the termination *ine*, might then have been restricted to the neutral principles. Both these terminations are now attached indifferently, by many writers, to the bases, and it might be attended with inconvenience were the attempt uniformly made to alter the termination familiarized by usage. In this work I have generally indicated the neutral bodies, such as salicin, amygdalin, &c., by the termination *in*, reserving the ending, *ine*, for those which have basic properties, in cases where that in *ia* could not well be used.

in the same proportion, but the crystalline variety alone yields crystalline salts.

The organic bases may be subdivided into two well-marked classes:—1st. Those which like aniline (C_6H_7N), do not contain oxygen:—and 2nd. Those which, like quinia ($C_{20}H_{24}N_2O_2, 3H_2O$), do contain it. The bases of the first class are oily and volatile; they absorb oxygen rapidly from the air: this class has recently been augmented by the formation of numerous artificial alkaloids, many of which closely resemble aniline in properties, and may, like aniline, be regarded as derivatives of ammonia. Less is known of the derivation and rational composition of the second and more complicated class, or oxidized bases.

All of the volatile bases have a powerful odour; they may be distilled either alone or with the vapour of water, without undergoing decomposition. Advantage is taken of this property in their preparation or extraction; it is sufficient to digest the plant containing them in a weak alkaline ley, and to submit the mixture to distillation. A portion of ammonia always comes over with the condensed products, which are neutralized by sulphuric acid, then evaporated, and afterwards digested with alcohol. This menstruum leaves the ammoniac sulphate, but dissolves the sulphate of the organic base, which may be purified by recrystallization. If this salt be agitated with a mixture of equal parts of a strong solution of caustic potash and ether, the mixture separates on standing into two layers, the upper one consisting of an ethereal solution of the volatile base. If this ethereal solution be decanted, and placed in a retort and distilled, the ether is first expelled, and the base may afterwards be obtained in a state of purity in the last portions which pass over.

The general process of extracting the alkaloids which are not volatile is simple. The rasped or powdered vegetable is digested with dilute sulphuric or hydrochloric acid, by which the organic salt of the alkaloid is decomposed, and a more soluble sulphate or hydrochlorate is formed. To the filtered solution, ammonia, magnesia, or sodic hydric carbonate ($NaHCO_3$) is added, by which a copious precipitate of the impure alkaloid is occasioned; and this, if magnesia be used, is mingled with the excess of this earth, and often with an insoluble compound of the organic acid with magnesium. The precipitate is treated with boiling alcohol, from which, on cooling, the alkali generally crystallizes: it is redissolved in sulphuric or hydrochloric acid, digested with animal charcoal, and the salt is purified by recrystallization. Animal

ehareoal, though it perfectly removes the colour, has in many cases, however, the serious disadvantage of retaining also a large proportion of the salt of the organic alkali; and if a great excess of ehareoal be used, almost the whole of the salt may be withdrawn from the solution.

In the search for an organic base in cases of suspected poisoning by one of these substances, Stas recommends the adoption of the following method (*Chem. Gaz.*, 1852, 350):—To the contents of the stomach add twice their weight of pure concentrated alcohol, then from 10 to 30 grains of tartaric acid, and heat the mixture in a flask to 158° or 167° (70° to 75° C.); allow it to cool completely; filter, and wash the residue with strong alcohol. Evaporate the filtrate *in vacuo* or in a current of air at a temperature not exceeding 90° (32° C.), filtering the solution if any fat separates; treat the dry residue with cold absolute alcohol; evaporate *in vacuo*; dissolve the acid residue in a few drops of water, adding hydric-potassic or hydric-sodic carbonate (bicarbonate) till it ceases to produce effervescence; then agitate with four or five times its bulk of pure ether. When clear, allow a portion of this ethereal solution to evaporate spontaneously in a very dry place: in this way the base is obtained in a state of purity sufficient to allow of its examination by its characteristic reagents. If sulphuric acid be added to the ethereal solution, the sulphates of the following volatile bases may be separated in the crystalline form—ammonia, tetrylia, nicotylia, aniline, quinoline, and picoline; conylia sulphate is slightly soluble in ether. Stas states that he has thus successfully isolated morphia, codeia, strychnia, brucia, veratria, emetia, atropia, hyoseyama, aconitina, and colchicinia, all of which, when uncombined with acid, are sufficiently soluble in ether to admit of extraction by the foregoing method.

Many of the organic bases are also dissolved by chloroform, which may often be advantageously substituted for ether in Stas's process. The liquid is filtered if necessary, and agitated with about one-thirtieth of its bulk of chloroform; the chloroform speedily separates in the form of a heavy oily layer, which can be decanted: it will be found to contain nearly the whole of the base, which may afterwards be purified by the usual methods. The following bases are especially soluble in chloroform—viz., veratria, quinia, brucia, strychnia, atropia, and nareotine; cinchonina is but sparingly soluble, and morphia still less so.

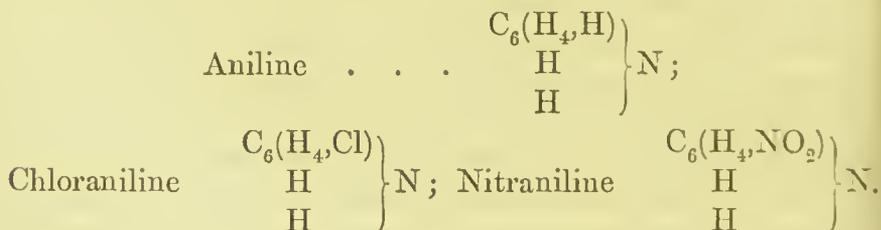
(1358) *Nature of the Organic Bases.*—The composition of the vegetable alkalies is remarkable; all of them contain nitrogen, and in the greater number each atom of base includes one atom

of nitrogen. Berzelius regarded ammonia as the body which confers upon them their basic character: and he considered them to be compounds of ammonia with a variety of neutral principles, which in most cases are not susceptible of isolation; the union of the neutral principle or *colligate* with the ammonia being of the same intimate nature as that of alcohol with sulphuric acid in the ethylsulphuric acid, where neither of the constituents exhibits its ordinary characters. Thus quinia ($C_{20}H_{12}NO_2 \cdot 3HO$; halving the formula now adopted) was represented by Berzelius as $(C_{20}H_9O_2, H_4NO)2HO$, or as a compound of the colligate, $C_{20}H_9O_2$, with oxide of ammonium and water of crystallization. This mode of viewing the composition of certain vegetable bases acquired some support from the discovery that, by the direct union of ammonia with a limited class of neutral substances, such as oil of mustard, and oil of bitter almonds, a number of basic compounds may be obtained, which present a striking analogy both in composition and properties to many of the organic bases produced by living plants; but this theory of Berzelius is now generally abandoned.

A different view was proposed several years ago by Liebig, who, finding that these bases gave no evidence of the presence of ammonia ready formed within them, suggested that they might be compounds containing H_2N , or amidogen; and that they might be derivatives from ammonia, in which an atom of hydrogen had been displaced by an equivalent organic group: he even predicted that if it should be found possible to displace this atom of hydrogen by ethyl, or by some other electro-positive hydrocarbon, a powerful volatile base would probably be obtained. This sagacious conjecture has since been fully verified by the discoveries of Wurtz and Hofmann, who have succeeded in obtaining the very compounds anticipated by Liebig; and Hofmann, as we have already seen, has extended the process of substitution much further. Liebig's view, with the extension and modifications required by the progress of discovery in this direction, admits in many instances of being happily applied to the natural vegetable bases; since these bodies themselves can be subjected to operations analogous to those which are applied in the formation of the alcohol bases; and portions of the hydrogen which they contain may thus be displaced by basic hydrocarbons. For instance, conylin $[(C_8H_{14})''H,N]$ may be converted into ethylconylin $[(C_8H_{14})''C_2H_5,N]$ by displacing an atom of hydrogen by an equivalent of ethyl. The number of exchangeable atoms of hydrogen in the different bases depends upon the

molecular constitution of the particular base under experiment (1373, 1375).

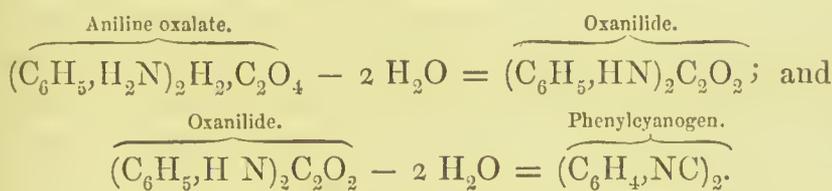
But the hydrocarbons either originally existing in the base or subsequently introduced into it, may also experience a change in their components by a species of secondary substitution by chlorine or bromine, whilst the general basic properties of the compound remain unchanged. Aniline (C_6H_5, H_2N), for example, may be represented as ammonia in which one atom of its hydrogen is displaced by C_6H_5 (phenyl); but aniline may lose a part of its hydrogen, and receive chlorine in its place, without having its basic character destroyed, becoming chloraniline (C_6H_4Cl, H_2N); and even NO_2 may be substituted for a portion of the hydrogen in aniline, while the new body (nitraniline, $C_6H_4NO_2, H_2N$) still retains its power of forming salts with acids. Nitraniline affords an instance of the artificial formation of a monobasic alkaloid containing two atoms of nitrogen; and examples of the occurrence of bases which contain more than one atom of nitrogen without any corresponding increase in basic power are not wanting among the products of organic nature. The relations of aniline to chloraniline and nitraniline may be represented in the following manner:



Hofmann, in the course of his researches upon aniline, discovered another method of combination which is worthy of remark, since it explains a second mode in which an additional atom of nitrogen may be introduced into the alkaloid without increasing its basic power:—cyanogen unites directly with aniline, forming a body, the composition of which is represented by $C_7H_7N_2$, but which is evidently not aniline hydrocyanate, for this would be represented by the formula C_6H_7N, HCN , or $(C_7H_5N_2)$; nor is it a substitution-product formed by the displacement of 1 atom of hydrogen by an equivalent of cyanogen; but a new body, *cyani-line*, which possesses basic properties, and enters into combination with acids in the proportion of one equivalent of acid to each atom of aniline which the new base contains.*

* Bases will be described hereafter, which, like guanidine and methyluramine (1610), appear to be formed upon the polyatomic type, and are derived from 2 or 3 atoms of ammonia united into one group.

It is evident that changes such as these affect that portion only of the compound which, like C_6H_5 in aniline, has been introduced into the ammonia by substitution; the compound retaining the basic power which it originally derived from the ammonia, upon the type of which it has been constructed. When this type is destroyed, the basic power of the compound disappears. For example, just as an atom of ammoniac oxalate by the abstraction of the elements of two atoms of water, loses its saline character, and becomes converted into an indifferent insoluble body, oxamide,—and this by the further abstraction of two more atoms of water furnishes cyanogen (1339); so the atom of aniline oxalate, by losing two atoms of water, becomes oxanilide; and by abstraction of two more atoms of water becomes oxanilo-nitrile, or phenylcyanogen, which still retains an atom of nitrogen intimately combined both with carbon and hydrogen, but which has lost its relationship or homology with ammonia, and with it has also lost its basic character. For instance:—



(1359) *Analogy of Organic Bases with Ammonia.*—The remarkable parallelism in properties of the salts of the organic bases with those of ammonia, will be rendered still more evident by the following additional particulars:—

Many of these bases may be obtained, like ammonia, in the anhydrous state: such, for instance, are cinchonia $C_{20}H_{24}N_2O$, and strychnia $C_{21}H_{22}N_2O_2$; and the same is true almost without exception with the aniline class. These anhydrous bases combine directly, like ammonia, with hydrochloric acid and the corresponding halogen acids, and do not require any addition of the elements of water; cinchonia hydrochlorate, for example, consists of $(C_{20}H_{24}N_2O, 2 HCl)$; and, as is the case also with ammonia, whenever these bases unite with the oxyacids, the basylous hydrogen of the normal acid unites with the organic alkali, and no separation of water occurs. Cinchonia sulphate, for instance, which contains $(C_{20}H_{24}N_2O, H_2SO_4, 4 H_2O)$, loses its 4 atoms of water by crystallization by heat, but the hydrogen of the acid cannot be expelled in the form of water without decomposing the salt. The double salts which the organic bases form, also closely resemble the corresponding compounds of ammonia:—for example, with platinum chloride they yield yellow crystalline double chlorides of sparing

solubility. These compounds are of considerable importance to the chemist, since they furnish him with very accurate means of determining the combining number of the organic base. Anrie chloride likewise forms with them similar compounds, which Hofmann has proposed to employ for the same purpose. Most of the organic bases also furnish nearly insoluble white precipitates when their solutions are mixed with one of corrosive sublimate, or with a solution of mercuric iodide in potassic iodide. They yield extremely insoluble compounds with sodic phosphomolybdate; and a solution of ferric sulphate, when mixed with one of quinia sulphate, yields by spontaneous evaporation crystals having the octahedral form of alum (Will). Octahedral crystals are also obtained when a solution of sulphate of conylin, which is an analogue of ammonia, is mixed with one of aluminic sulphate, and left to spontaneous evaporation.

In addition to these compounds there are some others peculiar to this class of bodies. Solutions of salts of the vegetable bases for the most part, when mixed with potassic diiodide (KI_2), yield precipitates insoluble in water, but soluble in boiling alcohol, from which they crystallize on cooling. It has been proposed to use these compounds in determining the bases quantitatively for the purposes of analysis. With this object the precipitate formed by the diiodide is placed in very dilute sulphuric acid, and treated with fragments of zinc; zincic iodide and hydriodate of the base are dissolved; and on the addition of ammonia in excess, the organic alkali is precipitated, whilst the zinc is retained in solution. In some cases it is found preferable to throw down both the zinc and the alkaloid by means of ammoniac carbonate; the precipitate after washing with water is treated with boiling alcohol, which dissolves out the alkaloid, leaving the zincic carbonate; and on evaporating the alcoholic solution, the alkali is obtained in a state of purity.

Nearly all the organic bases form insoluble curdy precipitates with gallo-tannic acid; indeed, this acid is one of the most complete precipitants of the organic bases. These gallotannates, when heated, melt to a resinous mass, and are soluble to some extent in boiling water: they are also dissolved freely by boiling alcohol.

The action of tartaric acid upon the alkaloids is analogous to that which it exerts on many of the inorganic bases; for instance, the tartrates of iron, copper, and some other metals, are not precipitated by the addition of the alkalies to their aqueous solutions; but plumbic tartrate is decomposed with separation of the metallic oxide. So it is with many of the organic bases; the tartrates of

brucia, quinia, and morphia, are not precipitated by an excess of caustic potash or soda; by converting these organic bases into tartrates, and adding an excess of an alkaline solution, they may be separated from strychnia, cinchonia, and narcotine, the tartrates of which are decomposed in the usual way on the addition of potash or of ammonia.

The greater number of the natural organic bases, when in solution, produce the phenomenon of left-handed rotation on a ray of polarized light. The artificial bases in general do not possess the power of affecting a polarized ray (Laurent). The left-handed rotation exerted by narcotine becomes right-handed when this base is combined with acids; and, generally speaking, the effect of the addition of an acid to a base is to reduce its power of rotation, though with quinia the rotatory power is exalted by the addition of an acid.

Artificial Formation of Organic Bases.

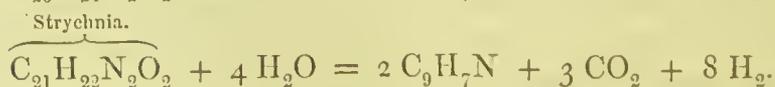
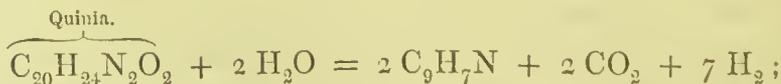
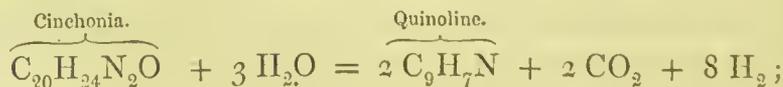
(1360) It has already been stated that many organic bases may be prepared by artificial means. All attempts at obtaining those which occur naturally in plants have, however, hitherto been unsuccessful. The following are the principal processes resorted to for the purpose of preparing organic bases artificially:—

1. By destructive distillation of organic bodies containing nitrogen.
2. By distillation of the organic alkalies with caustic potash (Gerhardt).
3. By distillation of the cyanic and cyanuric ethers with potash ley (Wurtz), when they break up into carbonic acid, with formation of an amide base.
4. By combination of ammonia with certain volatile oils, and subsequent moderate heating of the product with solution of potash (Fownes).
5. By reduction of nitrous derivatives of the hydrocarbons by means of sulphuretted hydrogen (Zinin).
6. By the reduction of the hydrocyanic ethers (the nitriles of the monobasic fatty acids) by nascent hydrogen (Mendius).
7. By substitution of the alcohol radicles for hydrogen in ammonia, during the action of hydrobromic or hydriodic ethers upon ammonia (Hofmann).
8. By substitution of the alcohol radicles for hydrogen in phosphuretted, arseniuretted, and antimoniuretted hydrogen, by means of processes analogous to those last mentioned.

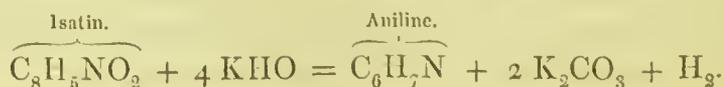
1. *Destructive Distillation of Substances containing Nitrogen.*—

This method constitutes the foundation of the manufacture of ammonia, which is always the principal basic substance thus furnished; but since the ammonia is, during this operation, brought into contact with hydrocarbons and with other products of distillation, in their nascent state, the elements of the ammonia react upon these bodies, and produce a small quantity of other bases, homologous with ammonia, or derivable from it by substitution. In the preparation of coal-gas, for instance, four, at least, of these compounds come over along with the coal-tar: these are aniline, or kyanol (C_6H_7N); picoline, a base metameric with aniline; quinoline, or leukol (C_9H_7N); and pyridine (C_5H_5N). Stenhouse has shown that when vegetable matters rich in nitrogen, such as the seeds of the *Leguminosæ* and of the *Cerealia*, are distilled in a similar way in vessels excluded from the air, in addition to ammonia, large quantities of volatile oily bases come over, the nature of which varies with that of the compound distilled (*Phil. Trans.*, 1850): and the destructive distillation of bones furnishes an empyreumatic oily liquid, known as *Dippel's oil*, which contains a variety of analogous bases.

2. *Action of Potash on Organic Bodies.*—Sometimes the azotised matters, instead of being distilled alone, are mixed with caustic potash, and submitted to the action of heat. In this way aniline is obtained abundantly from indigo, and quinoline from quinia and cinchonia; quinoline is also procured by similar means, though in smaller proportion, from strychnia. Greville Williams finds that some other volatile bases, including pyridine and several of its homologues, are formed at the same time. Although, therefore, the following equations do not represent the whole of the reaction which occurs under these circumstances, they will serve to point out the simple relation between quinoline and the complex bases which furnish it by distillation:—

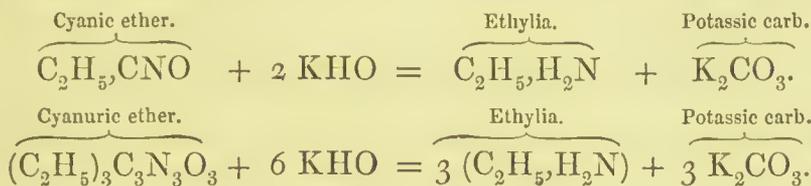


In like manner aniline is obtained from isatin:—

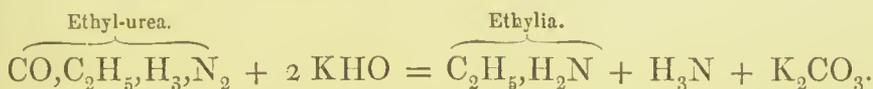


The carbonic acid produced during these operations remains in combination with the potassium, whilst the hydrogen escapes.

3. It was by distilling the cyanic and cyanuric ethers with caustic potash that Wurtz discovered the remarkable bases, methylyia, ethylyia, and amylyia; the reaction being analogous in all these cases (1164):—

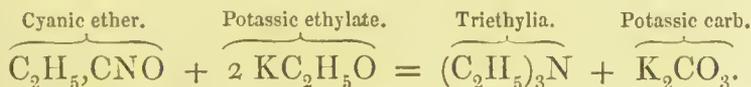


In a similar manner the substitution-products of urea which contain the radicles of the alcohols (1604), furnish analogous results when treated with caustic potash, whilst ammonia is also formed: in this, as in the case of the cyanic ethers, 2 atoms of hydrogen in the potassic hydrate are exchanged for 1 atom of carbonic oxide in the urea:—



The distillation of the cyanic ethers yields only primary monammonias, and is particularly applicable to the preparation of this class of compounds; since no secondary or tertiary monammonias are formed, as is always the case when the bases are procured by Hofmann's method of decomposing ammonia, by the bromides or iodides of the ethyl radicles.

If potassic ethylate ($\text{KC}_2\text{H}_5\text{O}$, potassium-alcohol) be substituted for caustic potash, a more advanced substitution-product may be obtained:—

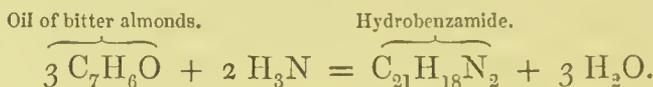


4. Another process consists in combining ammonia with the aldehyds. This may be effected by distilling the combinations of the aldehyds with hydric-ammonie sulphite, along with the hydrated alkalies or with soda-lime. Thus the compound with acetic aldehyd furnishes dimethylyia ($\text{C}_2\text{H}_7\text{N}$); that of œnanthylic aldehyd, trihexylyia ($\text{C}_{18}\text{H}_{39}\text{N}$); and that of oil of cinnamon, triphenylyia ($\text{C}_{18}\text{H}_{15}\text{N}$; Hofmann). These decompositions cannot be represented by a general equation. Certain of the volatile oils which possess the properties of aldehyds, also combine with ammonia when digested with it. The compound obtained in this manner exhibits in some cases, without further treatment, the properties of an alkaline base; but in other instances a neutral body is formed,

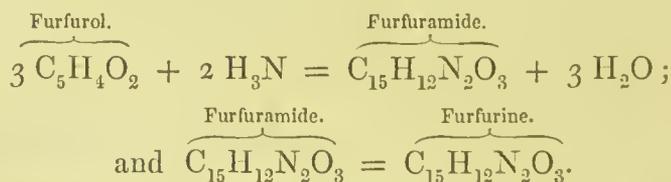
which, when heated with a solution of potash, is converted into an isomeric substance, possessed of basic powers. An example of the first kind occurs when the oil of mustard is treated with ammonia: it thus forms a powerful crystalline base, which, when mixed with acids, at once unites with them, and furnishes crystallizable salts:—



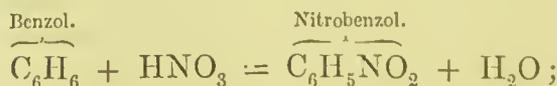
or the sulphuretted urea of the allyl series: whilst an instance of the second kind is afforded by bitter almond oil, which, on uniting with ammonia in the proportion of 3 atoms of the oil and 2 atoms of ammonia, loses 3 atoms of water, and forms the neutral body, hydrobenzamide:—



When the crystals of hydrobenzamide are boiled with a solution of caustic potash for some hours, they are gradually converted into benzoline (amarine), an alkaline body insoluble in water, which has the same composition as hydrobenzamide, and forms beautiful salts with acids. In a similar manner Fownes prepared furfureine by acting with potash on the compound of furfurol and ammonia:—

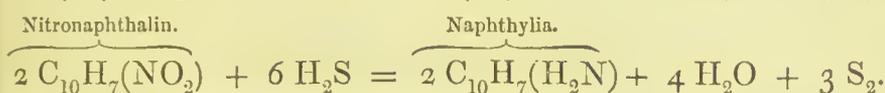
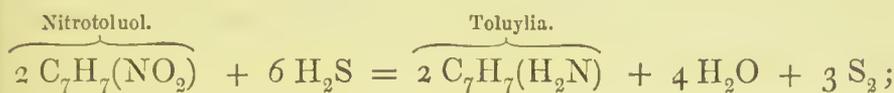
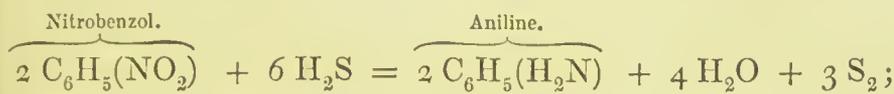


5. A fifth process for obtaining organic bases artificially is the remarkable one invented by Zinin. Many compounds of carbon and hydrogen, such as benzol, toluol, and naphthalin, when treated with strong nitric acid, lose an atom of hydrogen, whilst an atom of nitroxyl (NO_2) takes its place. In this way benzol is converted into nitrobenzol:—

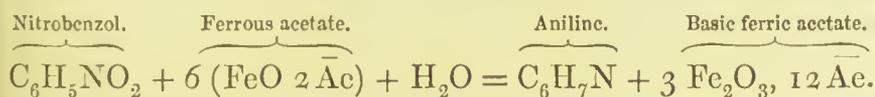


In like manner, toluol (C_7H_8) may be converted into nitrotoluol ($\text{C}_7\text{H}_7\text{NO}_2$), and naphthalin (C_{10}H_8) into nitronaphthalin ($\text{C}_{10}\text{H}_7\text{NO}_2$). These new compounds are soluble in alcohol; and Zinin found that, after saturating the alcoholic solution with dry ammoniacal gas, and then transmitting sulphuretted hydrogen, the solution, if left to itself, deposits sulphur: water is formed at the same time, whilst

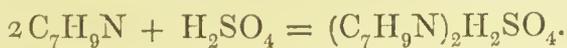
the whole of the oxygen is removed from the original compound, and a new substance, possessed of basic characters, is found in the solution. This substance in many instances may be obtained in crystals on evaporation. Nitrobenzol is thus converted into aniline (phenylia), nitrotoluol into toluylia, and nitronaphthalin into naphthylia; as represented in the following equations:—



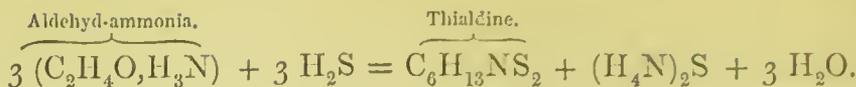
In each case the whole of the sulphur is precipitated, while 2 atoms of hydrogen enter into the combination instead of the 2 of oxygen which are removed, or a substitution of amidogen for nitroxyl is effected. The object of adding ammonia in the first instance is merely to retain the sulphuretted hydrogen in solution, so that the reaction may have time to take place. A large number of new bases have already been formed by this process, and numbers of others will, no doubt, be discovered. Béchamp has shown that by treating nitrobenzol, and other nitrous derivatives of the hydrocarbons, with ferrous acetate, they are reduced; the ferrous salt becomes converted into a ferric salt, and is most of it precipitated in the form of a basic ferric acetate, whilst an organic base is formed; this method is even preferable to Zinin's:—



All the bases thus procured are destitute of oxygen; they resemble ammonia in their mode of combination with oxyacids; direct union of the acid and base occurs unattended by any separation of water: the formation of toluylia sulphate, for instance, may be represented by the annexed equation:—

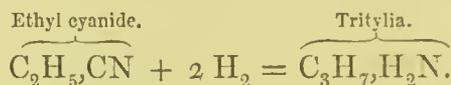


Liebig and Wöhler have also formed two bases, termed *thialdine* ($\text{C}_6\text{H}_{13}\text{NS}_2$), and *selenaldine* ($\text{C}_6\text{H}_{13}\text{NSe}_2$), in which sulphur and selenium are constituent elements. They are procured by the reducing agency of sulphuretted hydrogen and seleniuretted hydrogen respectively, upon an aqueous solution of 3 atoms of aldehyd-ammonia: thus in the case of thialdine:—



These alkalis belong to the group of nitrile bases (1375).

6. The primary monammonias may also be obtained by reducing the hydrocyanic ethers by nascent hydrogen. The base which is formed in this case is not that of the alcohol originally employed, but that of its next superior term in the series; for example, if ethyl cyanide be mixed with alcohol, and hydrochloric acid and zinc be added, tritylia is formed, and combines with the excess of acid:—



7 and 8. These important processes admit of various modifications, which will be considered when speaking of the numerous bases which have been obtained by their application (1373 *et seq.*).

9. In a few instances new bases are formed by processes of oxidation from other bases, as eotarnine from narcotine (1399), cacotheline from brucia (1404), and methyluramine from kreatine (1610).

10. Lastly, the formation of organic bases has been observed during processes of fermentation and putrefaction;—the putrefaction of wheaten flour, for example, furnishing trimethyilia, ethyilia, and amyilia.

(1361) The following order will be observed in the description of such of the organic bases as, from their important applications, their bearing upon other groups, or from the mode of their formation, seem to be most worthy of notice:—

A. Artificial Bases.

1. Volatile bases which do not contain oxygen:—
 - a. Aniline series $(\text{C}_n\text{H}_{2n-7})'\text{H}_2\text{N}$;
 - b. Pyridine series $(\text{C}_n\text{H}_{2n-5})'''\text{N}$;
 - c. Quinoline series $(\text{C}_n\text{H}_{2n-11})'''\text{N}$;
2. Bases obtained by the action of ammonia on derivatives of the alcohols.
3. Bases derived from phosphuretted, arseniuretted, and anti-moniuretted hydrogen.
4. Polyatomic bases.
5. Bases obtained by the action of ammonia upon certain essential oils.

B. *Natural Bases.*

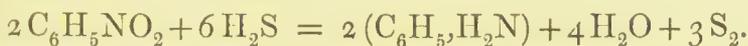
1. Volatile oily bases destitute of oxygen :—
Conylia ;—Nicotylia ;—Sparteia.
2. Oxidized bases :—
 - a. Bases from the cinchonas ;
 - b. Bases from opium ;
 - c. Bases from pepper ;
 - d. Bases from the strychnos tribe ;
 - e. Other less known bases ;
 - f. Caffeine and theobromine.

A. ARTIFICIAL BASES.

1. *Volatile Bases which do not contain Oxygen.*a. *Aniline Series* $(C_nH_{2n-7})'H_2N$.

(1362) ANILINE, *Kyanol*, *Phenylamine*, or *Phenylia* (C_6H_5, H_2N = 93) ; *Sp. gr. of liq.* 1·020 ; *of vap.* 3·210 ; *Rel. wt.* 46·5 ; *boil. pt.* 359°·6 (182° C.).—This remarkable base may be prepared from several sources, and by a variety of reactions :—

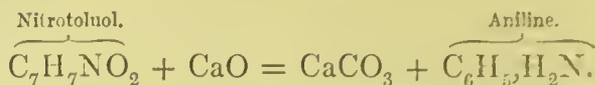
1. It is contained in small quantity among the products of the destructive distillation of coal in the process of gas-making.
2. Nitrobenzol is converted by ammoniac sulph-hydride into aniline and water, sulphuretted hydrogen being decomposed, whilst sulphur is deposited :—



A similar reduction takes place under the influence of a mixture of zinc and hydrochloric acid, or of iron and acetic acid. Aniline is now manufactured on a large scale for the dyer by the following process (Hofmann, *Jury report, Class II. Section A.*, 1862, p. 123.—To a mixture consisting of about equal weights of nitrobenzol and strong acetic acid, iron filings or borings are gradually added, taking care that the temperature does not rise too high. The semi-solid mass, which consists chiefly of ferrous acetate and aniline acetate, is distilled either alone or with the addition of lime in iron cylinders, which are gradually raised to a red heat. A mixture consisting chiefly of aniline, acetone, and unchanged nitrobenzol comes over. The product is redistilled, and the portions which distil between 347° and 374° (175° and 190° C.) furnish aniline sufficiently pure for commercial purposes.

3. It is also furnished by the distillation, with lime, of nitro-toluol, or of its metamerides, salicylamide and anthranilic acid,

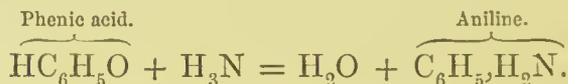
all of which substances furnish aniline and a carbonate; for example:—



The product from salicylamide is always accompanied by carbolic acid ($\text{C}_6\text{H}_6\text{O}$).

4. One of the methods by which aniline is easily procured consists in submitting to distillation a mixture of a concentrated solution of caustic potash with finely-powdered indigo, obtained from the *Indigofera anil* amongst other plants, whence the name aniline is derived: the mass swells up greatly, and water holding ammonia in solution passes over, accompanied by aniline in the form of a brownish oil. This oil, when re-distilled, furnishes pure aniline, amounting to nearly one-fifth of the weight of the indigo.

5. Hofmann represents aniline as *phenylia*, or a derivative of ammonia, in which 1 atom of hydrogen is displaced by its equivalent of a hydrocarbon C_6H_5 , termed phenyl; and it is a portion of the hydrogen of the phenyl which may also be displaced by chlorine, bromine, or nitroxyl (p. 489).* Aniline may be procured by heating carbolic (phenic) acid in a sealed tube with ammonia:—



The history of aniline affords one of the most remarkable instances of the value of scientific chemical research when perseveringly and skilfully applied, for at first few substances seemed to promise less; and the gigantic manufacturing industry at present connected with this compound in its application as a tinctorial agent offers a singular contrast to the early experiments upon this body when a few ounces of the base furnished a supply which exceeded the most sanguine expectations of the original discoverers of the body.

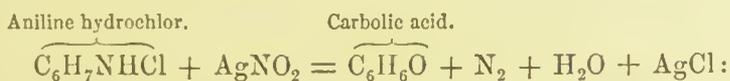
Aniline is a nearly colourless, limpid liquid, of an agreeable vinous odour, and an aromatic burning taste. It is very acrid and poisonous. Aniline remains fluid at -4° (-20°C.). When

* *Diphenyl* (C_6H_5)₂ [*Fusing pt.* 140° (60°C.); *Boil. pt.* 464° (240°C.)] or phenyl phenylide may be procured by decomposing bromobenzol by sodium; $2 (\text{C}_6\text{H}_5\text{Br}) + \text{Na}_2 = (\text{C}_6\text{H}_5)_2 + 2 \text{NaBr}$; and it is one of the products obtained by decomposing benzol vapour by passing it through a red-hot tube; $2 \text{C}_6\text{H}_6 = (\text{C}_6\text{H}_5)_2 + \text{H}_2$. It is a solid, which crystallizes in pearly scales from its alcoholic solution.

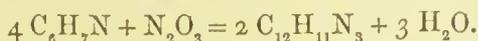
dropped upon paper it produces a greasy stain, which, owing to the volatility of the base, speedily disappears. Aniline is a non-conductor of electricity; it refracts light powerfully. When exposed to the air it absorbs oxygen rapidly, and becomes converted into a brown resinous mass; it is therefore necessary to distil it in a current of hydrogen, or of carbonic anhydride. It also distils over easily along with the vapour of water, when solutions of its salts are mixed with an excess of potash and submitted to distillation. Aniline is heavier than water, in which it is soluble to a considerable extent; but on saturating the liquid with certain salts, such as sodic chloride or magnesian sulphate, the aniline is separated. Aniline has little or no action on test-papers; it may be dissolved in unlimited quantity by alcohol, ether, and wood spirit.

Most of the salts of aniline crystallize readily. They are colourless, but if exposed to the air while moist, they become rose-coloured. If a slip of deal be plunged into a solution of any of these salts, it gradually acquires an intense yellow colour. If an aqueous solution of a salt of aniline be mixed with a solution of chloride of lime, a deep blue colour is produced, which gradually passes into a dirty red. With chromic acid these salts strike a green, a blue, or a black colour, according to the degree of concentration of the solutions. The methods of procuring these colours will be considered after the salts of aniline itself have been described. Aniline produces a white precipitate in a solution of corrosive sublimate, and a green crystalline precipitate in one of eupric chloride. Both precipitates contain aniline in combination with the metallic chlorides.

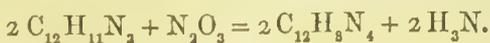
When a solution of aniline hydrochlorate is mixed with one of argentic nitrite, nitrogen escapes in abundance, whilst carbolic acid is separated in oily drops; this decomposition is due to the reaction of nitrous acid on aniline, which may be thus represented:—



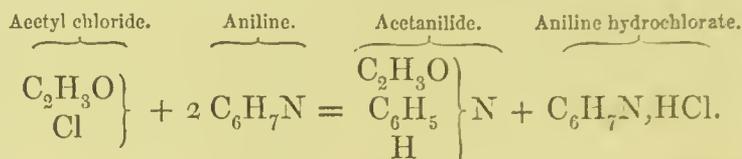
but when nitrous anhydride is passed into an alcoholic solution of aniline, 2 atoms of the base become united into 1; 3 atoms of hydrogen becoming exchanged for 1 atom of nitrogen, and a new base, *azodiphenyldiamine*, $\text{C}_{12}\text{H}_{11}\text{N}_3$, is formed:—



If azodiphenyldiamine be again subjected to the action of nitrous anhydride, it undergoes an analogous change, 3 more atoms of hydrogen being exchanged for 1 of nitrogen, and a new compound, of dangerously explosive properties, is formed (Griess), *azodiphenyldiamine*, $\text{C}_{12}\text{H}_8\text{N}_4$:—



Aniline acts powerfully upon the hydriodic ethers of the different alcohols, in the manner hereafter to be explained (p. 501), and yields derived bases, such as ethylaniline $[(C_2H_5, C_6H_5, H)N]$. When mixed with the oxychlorides, or with the anhydrides of the organic acids, aniline yields compounds which correspond with the amides. With acetyl chloride, for instance, it produces acetanilide, and aniline hydrochlorate:—



Acetanilide $[(C_6H_5, HN, C_2H_3O)]$; *Fusing pt.* $233^{\circ}6$ ($112^{\circ}C.$) may be taken as the representative of the class of anilides. It may be prepared by acting upon aniline with acetyl chloride, which is to be added drop by drop to the aniline as long as decomposition ensues. Aniline hydrochlorate is formed, and may be removed by washing the product with water; acetanilide remains in the form of a yellowish sticky mass of resinoid appearance, which may be obtained in colourless brilliant prismatic crystals, by dissolving it in hot water, and allowing the liquid to cool; alcohol and ether also dissolve it. A still easier method of preparing it consists in heating aniline with glacial acetic acid for some hours, and allowing the vapours as they condense to fall back again into the flask (G. Williams). Acetanilide melts readily to a yellowish oily-looking liquid, which, on cooling, solidifies to a crystalline mass. It may be distilled without decomposition. When fused with caustic potash, aniline is liberated.

(1363) Aniline forms anilidated acids, anilides, dianilides, and aniles. The aniles correspond to the imides of the ammonia group; they contain the elements of 1 molecule of a dibasic acid and 1 of aniline, minus water, in the proportion of $2 H_2O$. The anilidated acids, which correspond to the amidated acids, are formed from 1 molecule of a dibasic acid and 1 of aniline, with the separation of H_2O . The compounds enumerated in the following list afford examples of each of these classes of substances:—

Anilides.

| | |
|-------------------------|------------------------|
| Formanilide | C_6H_5, HN, CHO |
| Acetanilide | C_6H_5, HN, C_2H_3O |
| Benzanilide | C_6H_5, HN, C_7H_5O |
| Cinnamanilide | $C_6H_5, HN, C_9H_7O.$ |

Dianilides.

| | |
|-------------------------|-------------------------------------|
| Oxanilide | $(C_6H_5)_2, H_2N_2, C_2O_2$ |
| Succinanilide | $(C_6H_5)_2, H_2N_2, C_4H_4O_2$ |
| Suberanilide | $(C_6H_5)_2, H_2N_2, C_8H_{12}O_2.$ |

Anilidated Acids.

| | |
|------------------------------|--|
| Sulphanilie acid | $\text{HC}_6\text{H}_5, \text{HN}, \text{SO}_3$ |
| Oxanilie acid | $\text{HC}_6\text{H}_5, \text{HN}, \text{C}_2\text{O}_3$ |
| Succinanilie acid | $\text{HC}_6\text{H}_5, \text{HN}, \text{C}_4\text{H}_4\text{O}_3$ |
| Camphoranilie acid | $\text{HC}_6\text{H}_5, \text{HN}, \text{C}_{10}\text{H}_{14}\text{O}_3$ |

Aniles.

| | |
|------------------------|--|
| Succinanile | $\text{C}_6\text{H}_5\text{N}, \text{C}_4\text{H}_4\text{O}_2$ |
| Camphoranile | $\text{C}_6\text{H}_5\text{N}, \text{C}_{10}\text{H}_{14}\text{O}_2$ |

Aniline combines directly with cyanogen, and forms a feeble base, termed *cyaniline* ($\text{C}_7\text{H}_7\text{N}_2$), which is easily obtained by transmitting a current of cyanogen in excess through a solution of aniline in alcohol; it contains the elements of 1 atom of aniline with 1 of cyanogen. It may be procured in beautiful white pearly crystals by recrystallization from hot alcohol: when united with acids it is very unstable.

Aniline is remarkable as yielding compounds possessed of basic properties, when portions of the hydrogen in its phenyl radicle are displaced by chlorine or by bromine. The first two of these compounds are best obtained by decomposing chlorisatin and dichlorisatin, by means of caustic potash (p. 69). Trichloraniline is procured by acting upon aniline by means of chlorine, which converts the aniline at first into a purple compound, and then into a sticky tar-like mass; a quantity of trichlorophenic acid ($\text{HC}_6\text{H}_2\text{Cl}_3\text{O}$) is formed at the same time, but the trichloraniline may be obtained in a state of purity by distilling the mixture with a solution of potash, which retains the acid, while trichloraniline passes over and is condensed in delicate needles.

Chloraniline ($\text{C}_6\text{H}_4\text{Cl}, \text{H}_2\text{N}$) is a weaker base than aniline, and is obtained in white, fusible, volatilizable, crystalline needles: its salts have a strong disposition to crystallize; and, like those of aniline, they impart a yellow colour to a slip of deal. *Dichloraniline* ($\text{C}_6\text{H}_3\text{Cl}_2, \text{H}_2\text{N}$) is still less basic in its characters than the foregoing substance; and *trichloraniline* ($\text{C}_6\text{H}_2\text{Cl}_3, \text{H}_2\text{N}$) is a volatile crystalline compound, which is entirely devoid of basic properties. The corresponding compounds with bromine closely resemble the chlorinated forms of aniline in general properties.

The action of chlorine in these cases is very interesting: although the introduction of a single atom of this body into the molecule of aniline does not destroy the basic character, yet the electro-negative power of chlorine is exhibited in the diminution of the basic energy possessed by the new group, as compared with that of aniline; each successive addition of chlorine

weakening the basic property, until it disappears altogether in trichloraniline.

Hofmann, by whom these bases were discovered, has also succeeded, in conjunction with Muspratt, in preparing a yellow crystalline nitroxyl compound which fuses at $226^{\circ}\cdot4$ (108° C.), and may be sublimed unaltered. This substance is termed *a nitraniline*, ($C_6H_4NO_2, H_2N$); it is procured by the reduction of dinitrobenzol by means of ammoniac sulph-hydride. This body also forms salts with acids; it contains an atom of nitroxyl (NO_2) in the place of an atom of hydrogen. Its basic properties are, however, very feeble. A metameric crystalline form, β *nitraniline*, fusing at $285^{\circ}\cdot8$ (141° C.), was discovered by Arppe: it is a product of the decomposition of the nitranile of pyrotartaric acid.

(1364) *Aniline Dyes*.—Perkin has obtained from aniline a beautiful violet colour, now extensively employed as a dye-stuff, giving a tint known as *Mauve*. In order to prepare it he directs (*Chem. News*, June 8th, 1861) cold dilute solutions of aniline sulphate and potassic dichromate to be thoroughly mixed in equivalent proportions, and allowed to stand for 10 or 12 hours, or until the reaction is complete. The black precipitate is washed upon a filter till free from potassic sulphate. It is next dried, and digested in cold coal-tar naphtha, so long as any brown colour is taken up. The residue is then dissolved in alcohol, and on evaporation is left tolerably pure, but it seldom amounts to more than 5 per cent. of the aniline employed. Aniline violet is but sparingly soluble in cold water, to which it imparts a deep violet colour. Hot water, and water slightly acidulated, dissolve it more freely; alkalies precipitate it. With corrosive sublimate and with tannin it forms insoluble blue or violet compounds. Oil of vitriol, and Nordhausen sulphuric acid dissolve it, forming a dirty green solution, which becomes blue on dilution, and on further dilution resumes its original violet. Fuming nitric acid destroys it, as also does chlorine; concentrated alcoholic solution of potash does not decompose it. Aniline violet appears to be the most stable of the aniline dyes. By the use of glacial acetic acid as the solvent, Sehenrer Kestner has obtained the colouring matter crystallized in fine prisms. From this compound, which is a sulphate, the base *mauveine* ($C_{27}H_{24}N_4$) has been obtained. Silk is readily dyed with aniline violet by diluting the alcoholic solution of the colouring matter with hot water acidulated with tartaric acid. The silk is dyed by immersion in this liquid after dilution with cold water to the requisite extent.

Wool takes aniline violet readily from its aqueous but not acidulated solutions, at a temperature ranging from 122° to 140° (50° to 60° C.). Perkin uses tannin as a mordant for fixing the colour upon cotton and calicoes, working in acid solutions of the

colouring matter ; a basic lead salt may also be used as a mordant. In calico-printing the colours are usually mixed with albumin, which by coagulation at a steam heat fixes the colour on the fibre.

When treated with lead dioxide and sulphuric acid, aniline furnishes a delicate rose colour, the *roseine* of D. Price.

(1365) *Rosaniline, Aniline-red, or Magenta* ($C_{20}H_{19}N_3, H_2O$) is another extremely beautiful colouring matter, obtainable by oxidation from aniline. If anhydrous stannic chloride be gradually added to excess of aniline, the two bodies combine. When the pasty mass thus formed is heated gradually, stirring all the time, it becomes brown, and near its boiling point almost black, but it is of a rich crimson when viewed in thin layers. The temperature is kept up for some time. It is then well boiled with a large quantity of water, which gradually dissolves out the colouring matter, leaving the tin as a stannous salt. On saturating the solution with common salt, the colouring matter is separated as a mass of pitchy consistence. It may be purified from adhering resin by means of benzol. Many other bodies of feeble oxidizing power, such as corrosive sublimate, mercuric nitrate, arsenic acid, &c., may be substituted for stannic chloride in the preparation of magenta. The process, however, which is now usually adopted in the preparation of aniline-red, consists in mixing 20 parts of syrupy arsenic acid (sp. gr. 1.860) with 12 of commercial aniline (a mixture of aniline and toluidine), when a considerable evolution of heat takes place: the mixture is heated in an iron retort to a temperature ranging between 302° and 338° (150° and 170° C.). A good deal of aniline mixed with water distils over during the operation, which occupies four or five hours, and is complete as soon as a portion of the mass on cooling exhibits a brilliant colour and a bronze lustre. The melted mass is poured upon an iron plate, and when cold is broken up and digested with twice its weight of hydrochloric acid in iron tanks, heated by the injection of steam under pressure. An intensely red liquid is thus obtained. It is filtered off through woollen strainers from the undissolved portion, and treated with an excess of sodic carbonate in solution. The colouring matter is thus precipitated in flakes, which by the injection of steam are carried to the surface and skimmed off. It is then placed in a large volume of water in iron tanks, and heated as before by the injection of steam. A large proportion of the compound enters into solution, the hot liquid is again filtered, and beautiful green crystals of a brilliant coppery lustre are deposited as the liquid cools.

The red colouring matter obtained in this way is the hydro-

chlorate of a base to which Hofmann has given the name of *Rosaniline*; it is probably a hydrated triammonia, of the composition $C_{20}H_{19}N_3 \cdot H_2O$. Each atom of this base is capable of combining with one, two, or three atoms of a monobasic acid. Rosaniline when pure is colourless. It is sparingly soluble in water, insoluble in ether, slightly soluble in ammonia, and more soluble in alcohol, to which it gives a deep red colour. When exposed to the air the base rapidly becomes rose-coloured, and eventually deep red, owing to the absorption of carbonic acid. Its basic powers are considerable: most of its salts with one equivalent of acid crystallize readily, and possess in solution the magnificent red colour which is so highly prized. In the solid form they have a green metallic reflection, this green colour being exactly complementary to the red tint which they impart to silk. When viewed by transmitted light they are of an intense red colour, which in a mass of only moderate thickness seems opaque. The salts which rosaniline forms with three equivalents of the stronger acids are yellowish brown, both when solid and in solution. They are much more soluble than the monacid salts, though many of them crystallize without difficulty.

The *mono-hydrochlorate* ($C_{20}H_{19}N_3 \cdot HCl$), which is one of the commercial salts, is anhydrous, somewhat hygroscopic, and crystallizes in groups of well-defined rhombic plates, of a red colour and characteristic green lustre. It is sparingly soluble in water, more soluble in alcohol, and more soluble in dilute hydrochloric acid than in water. If the hot concentrated solution be mixed with an excess of strong hydrochloric acid, it solidifies on cooling into a network of brown-red crystals, the triacid hydrochlorate ($C_{20}H_{19}N_3 \cdot 3 HCl$); this salt is decomposed by water, and must be dried *in vacuo* over quicklime. If dried at 212° it gradually loses two-thirds of its acid, becoming first indigo blue, and finally it is reconverted into the green monacid salt.

The *acetate* ($C_{20}H_{19}N_3 \cdot C_2H_4O_2$) is one of the finest of the rosaniline salts; but the brilliant green lustre fades by exposure to light, and the crystals assume a dark reddish-brown tint. The salt is freely soluble both in water and in alcohol.

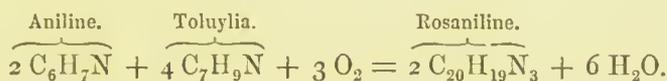
The *tannate* forms a carmine lake quite insoluble in water, but soluble in alcohol and in acetic acid. It is important as being the material produced on calico dyed red by aniline colours; and this salt, from its insolubility, furnishes the means of recovering the red dye from liquors too dilute to yield it to other precipitants.

A beautiful *green dye*, which preserves its hue by candlelight, is obtained by dissolving 1 part of rosaniline sulphate in 2 or 3 parts of sulphuric acid diluted with a fourth of its bulk of water, and adding from 2 to 4 parts of crude aldehyd. On gently warming the mixture, it becomes of a bluish green; the heating must be continued until the mixture becomes completely soluble, with a green colour, in acidulated water. It is then poured into boiling water, and immediately mixed with a hot solution of sodic hyposulphite, filtered, and the clear liquid precipitated by the addition of sodic carbonate. A beautiful green precipitate is obtained, but its composition is at present unknown. It dyes wool and silk of a brilliant green.

By the action of nitrous acid upon rosaniline, or its salts, a red dye is obtained, which imparts a beautiful orange red to silk or wool. Vogel calls it *zinalin*.

(1366) *Leucaniline* ($C_{20}H_{21}N_3$).—Rosaniline hydrochlorate when digested with zinc and excess of hydrochloric acid becomes decolorized; a new base, *leucaniline*, containing 2 more atoms of hydrogen than rosaniline, is produced. It is a colourless crystallizable substance, very sparingly soluble in water, furnishing colourless crystallizable salts. Oxidizing agents, such as barium dioxide, ferric or platonic chloride, and potassic chromate, reconvert its salts readily into beautiful red compounds of rosaniline.

The exact oxidizing reaction by which rosaniline is produced is not known; but Hofmann has shown that toluylia as well as aniline is required—a relation indicated in the following equation:—



It is evidently furnished by a process of oxidation of a mixture of aniline and toluylia, but a number of secondary products not at present investigated is always formed.

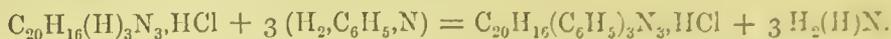
Amongst these is a yellow colouring matter, also basic in properties, to which Hofmann has given the name of *chrysaniline*, with a formula $C_{20}H_{17}N_3$: it forms a sparingly soluble orange-red nitrate. This base furnishes two series of salts, represented by the two hydrochlorates ($C_{20}H_{17}N_3.HCl$) and ($C_{20}H_{17}N_3, 2 HCl$). Chrysaniline contains 2 atoms of hydrogen less than rosaniline, so that the three bases may stand in isologous relation to each other; as follows:—

| | |
|------------------------|-------------------|
| Chrysaniline | $C_{20}H_{17}N_3$ |
| Rosaniline | $C_{20}H_{19}N_3$ |
| Leucaniline | $C_{20}H_{21}N_3$ |

Triphenyl rosaniline, [$C_{20}H_{16}(C_6H_5)_3N_3.H_2O$].—A beautiful blue colour may also be obtained from aniline by a modification of the method of Girard and De Laire. Rosaniline acetate is heated for an hour or more to a temperature of 338° (170° C.), with three times its weight of aniline. A copious evolution of ammonia occurs: when the blue colour is fully developed, the mass is purified by solution in oil of vitriol by digestion at 302° (150° C.; Nicholson), and on dilution is precipitated. This blue colour is a compound of a new base with sulphuric acid. Hofmann has analysed this base, and attributes to it a formula corresponding with triphenyl rosaniline, [$C_{20}H_{16}(C_6H_5)_3N_3.H_2O$] or $C_{38}H_{31}N_3.H_2O$. It may be obtained in a state of purity by dissolving one of its blue salts, such as the hydrochlorate, in alcohol, and filtering into an alcoholic solution of ammonia. The deep blue colour immediately disappears, a slightly reddish solution is obtained, and on dilution with water, the hydrated base is separated in white curdy flocculi, which, on drying *in vacuo*, remain colourless, or assume a slightly bluish tint, with an indistinctly crystalline appearance.

The monacid salts of this base furnish very pure and brilliant

blues. The conversion of rosaniline into the base of these blue salts may be thus represented :—



Hofmann finds that by treating rosaniline with the iodides of the alcohol radicles, such as ethyl iodide or amyl iodide, part of the hydrogen in the rosaniline may be displaced by a corresponding number of atoms of ethyl, or of amyl; and bases are obtained which yield beautiful colours when combined with 2 atoms of an acid, such as the hydriodic. The salts of the triethyl base $[\text{C}_{20}\text{H}_{16}(\text{C}_2\text{H}_5)_3\text{N}_3]$ furnish a highly-prized violet dye.

(1367) Several other oily bases have been discovered, homologous with aniline; they form a series, each member of which differs from the preceding one in containing one atom more of the hydrocarbon (CH_2). The bases of this class may be obtained from a series of hydrocarbons, of the form $(\text{C}_n\text{H}_{2n-6})$. These hydrocarbons when treated with nitric acid yield substitution-compounds, in which one atom of hydrogen is displaced by one of nitroxyl (NO_2); and from this nitro-compound, the corresponding base may be obtained by Zinin's process with ammoniac sulph-hydride, or by some other suitable reducing agent, 2 atoms of oxygen being removed, whilst 2 atoms of hydrogen are introduced into the compound, or what amounts to the same thing, a substitution of amidogen for nitroxyl is effected (page 483):—

| Hydrocarbon $(\text{C}_n\text{H}_{2n-6})$ | Nitro-substitute $(\text{C}_n\text{H}_{2n-7}\text{NO}_2)$ | Base $(\text{C}_n\text{H}_{2n-5}\text{N})$ |
|---|---|--|
| 1. Benzol . . . C_6H_6 | Nitrobenzol . . . $\text{C}_6\text{H}_5\text{NO}_2$ | Aniline . . . $\text{C}_6\text{H}_7\text{N}$ |
| 2. Toluol . . . C_7H_8 | Nitrotoluol . . . $\text{C}_7\text{H}_7\text{NO}_2$ | Toluylia . . . $\text{C}_7\text{H}_9\text{N}$ |
| 3. Xylol . . . C_8H_{10} | Nitroxylol . . . $\text{C}_8\text{H}_9\text{NO}_2$ | Xylylia . . . $\text{C}_8\text{H}_{11}\text{N}$ |
| 4. Cumol . . . C_9H_{12} | Nitrocumol . . . $\text{C}_9\text{H}_{11}\text{NO}_2$ | Cuminylia . . . $\text{C}_9\text{H}_{13}\text{N}$ |
| 5. Cymol . . . $\text{C}_{10}\text{H}_{14}$ | Nitrocymol . . . $\text{C}_{10}\text{H}_{13}\text{NO}_2$ | Cyminylia . . . $\text{C}_{10}\text{H}_{15}\text{N}$ |

These bases of the aniline series belong to the class of amidogen bases (1375), 1 atom of hydrogen having been displaced by the hydrocarbons, C_6H_5 ; C_7H_7 ; C_8H_9 , &c., but they still retain 2 atoms of hydrogen in a form susceptible of displacement by an equal number of atoms of the alcohol radicles (p. 505). Aniline may also be made to enter into the composition of various diammonias and triammonias.

Toluidine, or *toluylia*, $(\text{C}_7\text{H}_9\text{N})$ crystallizes in plates fusible at 104° (40° C.). Its basic powers are very feeble, but it furnishes crystalline salts.

Isomeric with toluylia is *benzylia* $(\text{CH}_3\text{C}_6\text{H}_5\text{HN})$, which may be regarded as phenyl-methylia; it is obtained mixed with *dibenzylia* $(\text{C}_7\text{H}_7)_2\text{HN}$, and *tribenzylia* $(\text{C}_7\text{H}_7)_3\text{N}$, by decomposing benzyl-chloride $\text{C}_7\text{H}_7\text{Cl}$ (1438), by means of alcoholic solution of

ammonia. It is a colourless liquid of considerable basic power, boiling at about $359^{\circ}6$ (182° C.).

Occasionally, in the manufacture of aniline, a beautiful crystalline polymeride of aniline, termed *paraniline* ($C_{12}H_{14}N_2$), has been obtained.

A number of diammonias and triammonias have been obtained by substitution from aniline, but at present they are unimportant.

b. Pyridine Series (C_nH_{2n-5})'''N.

(1368) A series of bases, however, exists, each member of which is metameric with one of those belonging to the aniline group: but in the alkalies of this class, none of the hydrogen admits of displacement by the alcohol radicles; consequently they must be regarded as belonging to Hofmann's subdivision of nitrile bases (1375). They boil at a lower temperature than the corresponding bases of the aniline series. These compounds have been principally investigated by Anderson, and by Greville Williams. They are furnished by the destructive distillation of a bituminous shale from Dorsetshire; and many of them are also contained in the products of the distillation of bones, and of pit-coal. The following table exhibits the metameric pairs of the aniline and pyridine groups:—

| Formula. | Aniline series. | | | | Pyridine series. | | | | |
|-----------------|-----------------|----------------|------|-----------------------------|------------------|----------------|-------|-------------------|---------|
| | Name of base. | Boiling Point. | | Specific gravity of liquid. | Name of base. | Boiling Point. | | Specific Gravity. | |
| | | ° F. | ° C. | | | ° F. | ° C. | Liquid at 32°. | Vapour. |
| C_5H_5N | Unknown . . | | | | Pyridine | 242.6 | 117 | 0.986 | 2.92 |
| C_6H_7N | Aniline . . | 359.8 | 182 | 1.080 | Picoline | 275 | 135 | 0.961 | 3.29 |
| C_7H_9N | Toluylia . . | 388.4 | 198 | | Lutidine | 310 | 154.5 | 0.946 | 3.839 |
| $C_8H_{11}N$ | Xylylia . . | 417.2 | 214 | | Collidine | 356 | 180 | 0.944 | |
| $C_9H_{13}N$ | Cuminylia . . | 437 | 225 | 0.952 | Parvoline | 370.4 | 188 | | |
| $C_{10}H_{15}N$ | Cyminyia . . | 482 | 250 | | Coridine | 411.8 | 211 | | |
| $C_{11}H_{17}N$ | | | | | Rubidine | 446 | 230. | | |
| $C_{12}H_{19}N$ | | | | | Viridine | 483.8 | 251 | | |

The bases of the pyridine series correspond to ammonia in which the 3 atoms of hydrogen have been displaced by 1 atom of a triad hydrocarbon, such as $(C_5H_5)'''$ or $(C_6H_7)'''$, equivalent to 3 atoms of hydrogen: none of the hydrogen in these hydrocarbons admits of displacement by the alcohol radicles, but Anderson has succeeded in obtaining from the pyridine series some remarkable bases into the composition of which platinum enters. These bases have the closest connexion with those obtained by the action of ammonium on the chlorides of platinum (973).

The two platinum bases from pyridine are, platinopyridine = $[(C_5H_3)_2Pt]^{vi}N_2$; platosopyridine = $(C_5H_3Pt)'''N$. In the first of these compounds 4 atoms of hydrogen in 2 atoms of the hydrocarbon C_5H_5 , appear to have been displaced by *one* atom of platinum, which here performs the function exerted by it in the *platinic* compounds; whilst in the second compound the 2 atoms of hydrogen in a single atom of the hydrocarbon are displaced by the atom of platinum, the metal here discharging the function exercised by it in the *platinous* compounds. Picoline yields similar compounds with platinum.

When the alkaloids of the pyridine group are treated with ethyl iodide, compounds are formed belonging to the class of ammonium bases (1375). Anderson has thus obtained *ethylpyridium* iodide $[(C_5H_5)'''(C_2H_5)N,I]$ and *ethylpicolium* iodide $[(C_6H_7)'''(C_2H_5)N,I]$. The hydrated oxides, procured by acting upon these compounds with argentic oxide, are not volatile, and are strongly basic.

(1369) *Pyridine* $[(C_5H_5)'''N = 79]$; *Sp. gr. of liq.* 0.9858; *of vap.* 2.92; *Rel. wt.* 39.5; *Boil. pt.* 242°.6 (117° C.).—This base is a colourless oil with a pungent smell; it is soluble in water in all proportions. It precipitates the oxides of iron, zinc, manganese, and aluminum from their salts, and forms a blue solution with the cupric salts when added to them in excess. Its simple salts crystallize with difficulty, but many of its double salts—particularly its double chlorides with platinum, gold, and copper—form well-defined crystals with facility. Pyridine, which derives its name from $\pi\bar{\nu}\rho$, fire, may be extracted from *Dippel's oil* (a product of the destructive distillation of bones) by treating it with hydrochloric acid, and distilling the hydrochloric solution with lime. The volatile bases which come over are submitted to fractionated distillation, collecting separately those parts which come over at about 240°.

(1370) *Picoline* $[(C_6H_7)'''N = 93]$; *Sp. gr. of liq.* 0.955; *of vap.* 3.29; *Rel. wt.* 46.5; *Boil. pt.* 275° (135° C.).—This base is the one best known of the series to which it belongs. It is usually extracted from coal tar or from *Dippel's oil* by a process similar to that employed for pyridine, collecting separately those portions of the distillate which come over at about 270°. The name picoline was suggested by the word *pix*, pitch. Picoline is a colourless, very mobile, oily liquid, of a penetrating odour. It is gradually volatilized by exposure to the air, and it does not, like aniline, become brown under these circumstances. By this fact, as well as by its lower boiling point and smaller density, picoline is at once distinguished from aniline. Picoline is soluble in water in all proportions. It is not coloured violet by chloride of lime, and is not affected by the addition of chromic acid to its solutions. The salts of picoline crystallize with difficulty, and many of them are deliquescent. The hydrochlorate forms deliquescent prisms.

Parapicoline $(C_{12}H_{14}N_2)$; *Sp. gr. of liq.* 1.077.—The effect of heating picoline for several hours with from $\frac{1}{8}$ th to $\frac{1}{4}$ th of its weight of sodium is remarkable. A hard, dark-brown resinous mass is obtained, which, when freed from the excess of sodium, and thrown into water, is gradually decomposed. An alkaline liquid is obtained containing soda and unchanged picoline, and a viscid dark-coloured oily base collects at the bottom. If this be washed and carefully distilled until the temperature rises to 379°.4 (193° C.), the water and picoline

are expelled with a little ammoniac carbonate. On continuing the distillation in a current of hydrogen at a temperature which must not be allowed to exceed 401° (205° C.), and rectifying the product a second time with similar precautions, a pale yellow viscid oily base, with a persistent characteristic empyreumatic odour, is obtained; it becomes brown by exposure to air. It is insoluble in water, but soluble in alcohol, ether, and the fixed and essential oils. With cupric sulphate it gives an emerald-green precipitate, soluble in hydrochloric acid, with which it forms a double salt. The salts of parapicoline exhibit but little tendency to crystallize. The principal point of interest is the fact that it is a polymeride of picoline, presenting the closest analogy with nicotylia. Owing to the facility with which it undergoes decomposition at temperatures near its boiling point, it has not been practicable to ascertain the density of its vapour, but there can be little doubt that the base is diatomic, saturating two atoms of a monobasic acid, and that a quantity of it represented by the formula given above would yield 2 volumes of vapour. The attempts made by Anderson to reconvert parapicoline into picoline were unsuccessful. (*Edinb. Phil. Trans.* xxi. 580.) Both picoline and parapicoline are isomeric with aniline.

c. Quinoline Series of Bases (C_nH_{2n-11})'''N.

(1371) In addition to the members of the aniline and pyridine series, coal tar contains a third series of bases of which quinoline is the most important member. Three bases of this class are at present known, viz.:—

| Base. | Formula. | Boiling Point. | | Specific Gravity. | | Rel. wt. H = 1. |
|-----------------|------------------------|----------------|---------------|-------------------|---------|--------------------|
| | | $^{\circ}$ F. | $^{\circ}$ C. | Liquid. | Vapour. | |
| Quinoline . . . | (C_9H_7)'''N | 462.2 | 239 | 1.081 | 4.519 | 64.5 |
| Lepidine . . . | ($C_{10}H_9$)'''N | 510 | 265.5 | 1.072 | 5.14 | 71.5 |
| Cryptidine . . | ($C_{11}H_{11}$)'''N | 525 ? | 274 ? | | | |

They combine with the hydriodic ethers, and form compounds corresponding to ammonium; quinoline, for instance, yields with ethyl iodide *ethyl-quinolium* iodide [$(C_9H_7)'''C_2H_5N, I$]. These compounds, therefore, like those of the pyridine group, belong to the class of nitrile bases.

(1372) *Quinoline*, or *Leukol* [$(C_9H_7)'''N = 129$]; *Sp. gr. of liq.* 1.081; *of vap.* 4.519; *Rel. wt.* 64.5; *Boil. pt.* $462^{\circ}.2$ (239° C.).—This alkali is readily obtained by decomposing cinchonia with caustic potash: the resinous mass which is separated under the name of quinoidine, during the preparation of the salts of quinia, also yields it by similar treatment. Fragments of caustic potash are placed in a tubulated retort, moistened with a few drops of water, and powdered cinchonia is added in small quantities at a time; on applying heat, the new base passes over, accompanied by free hydrogen; if the product be redistilled, an aqueous solution of ammonia with portions of the base pass over first, and the latter portions consist of nearly pure quinoline, which may be rendered anhydrous by a second rectification, after it has stood some days upon calcic chloride.

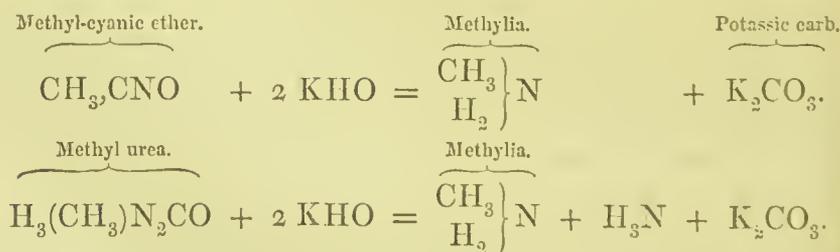
Quinoline is a colourless oil of high refracting power; it has a disagreeable penetrating odour, and a bitter acrid taste. It remains liquid at -4° (-20° C.)

When heated it burns with a smoky flame. When exposed to the air it becomes slowly converted into a resinous mass. If dropped upon paper it leaves a greasy stain, which quickly disappears. It is dissolved sparingly by water, but it is soluble in all proportions in alcohol, ether, wood spirit, and carbon disulphide, as well as in the fixed and essential oils. The nitrate, the oxalate, and the acid chromate of quinoline crystallize with facility; many double salts of quinoline, such as those which it forms with platinum, gold, palladium, and cadmium, may be obtained in beautiful crystals. The platinum salt is nearly insoluble in water.

Greville Williams, by boiling 1 part of quinoline for ten minutes with $1\frac{1}{2}$ of amyl iodide, obtained a mass of crystals which he dissolved by boiling with 6 parts of water, and then mixed with excess of ammonia and boiled for an hour: he thus separated a resinous substance which is readily soluble in alcohol, and furnishes a splendid, though fugitive, blue dye.

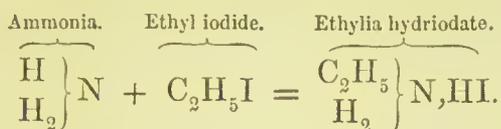
2. Bases obtained by the action of Ammonia upon Derivatives of the Alcohols.

(1373) ALLUSION has been already made (p. 75) to the remarkable manner in which the hydrogen in ammonia may be displaced by the hydrocarbons supposed to form the radicles of the alcohols; and in consequence of this kind of substitution, compounds are produced in which the basic character of the ammonia is fully preserved, and a new series of highly interesting bodies is obtained. The first bases of this description were produced by Wurtz, who found that when the cyanic ether, or its polymeride, the cyanuric ether of any of the alcohols, or the corresponding urea (1164), is distilled with caustic potash, a volatile base is obtained homologous with ammonia, but containing the radicle of the alcohol corresponding to the compound subjected to distillation; for example:—

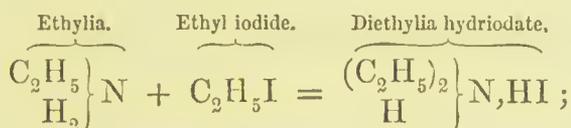


Hofmann (*Phil. Trans.*, 1850) found shortly afterwards that these bases may also be produced directly from ammonia, by acting upon this alkali by means of the hydriodic or the hydrobromic ethers of the different alcohols. He obtained this result by enclosing, in a long sealed tube, a mixture of a concentrated alcoholic solution of ammonia, and the bromide, or the iodide derived from the alcohol which he wished to examine. When this mixture is heated for some hours in a water-bath, combination occurs, and a hydrobromate or hydriodate of the new base is

formed. If, for instance, ethyl iodide is made to act upon a solution of ammonia, the following change occurs:—

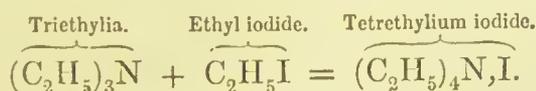


When the result of this reaction is distilled with caustic potash, ethylia is liberated, while water and potassic iodide are formed. Now, if ethylia be submitted in a sealed tube to a fresh portion of ethyl iodide, a second atom of hydrogen will be removed, and an additional equivalent of ethyl will be substituted for it, while the hydriodate of a new base (diethylia) is formed:—



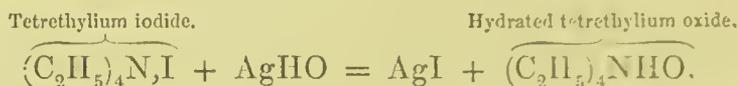
and if diethylia hydriodate be submitted to distillation with caustic potash, diethylia itself will be liberated. This base may in its turn be treated with a fresh portion of ethyl iodide, and so the third atom of hydrogen may be displaced by a third equivalent of ethyl, yielding a salt which, when distilled with potash, furnishes a third base, triethylia $(\text{C}_2\text{H}_5)_3\text{N}$.

Each of the alcohols may be made to furnish bases corresponding to each of the foregoing ethyl bases; for instance, by similar methods, a mixture of methyl iodide and ammonia can easily be made to yield methylia, dimethylia, and trimethylia; and from amyl iodide, amylium, diamylium, and triamylum may be formed. These bases are all homologous with ammonia, which they closely resemble in properties. But the action of ethyl iodide does not stop even here, for it is possible, by its means, to obtain a fourth series of bases homologous with the hypothetical body ammonium. (Hofmann, *Phil. Trans.*, 1851.) If, for example, a quantity of triethylia be heated in a tube with an additional quantity of ethyl iodide, the two bodies enter into combination, and a compound $[(\text{C}_2\text{H}_5)_4\text{N, I}]$, analogous to ammonium iodide $[(\text{H})_4\text{N, I}]$, is formed; all the 4 atoms of hydrogen in the ammonium having been displaced by a corresponding number of equivalents of ethyl:—

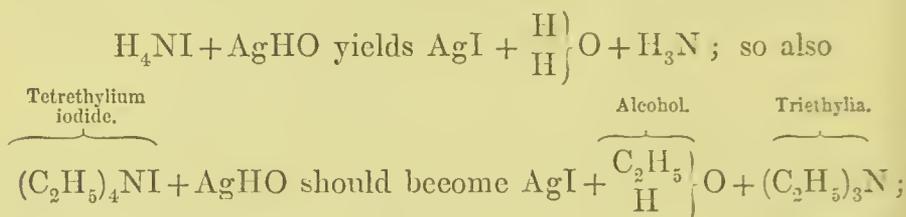


The iodide thus obtained is a crystalline substance. It is not possible to obtain the base tetraethylium $(\text{C}_2\text{H}_5)_4\text{N}$, in a separate form; since, like ammonium, it immediately undergoes decompo-

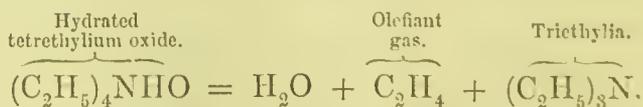
sition: nor can the base be liberated by the action of a solution of caustic potash; but if a solution of the iodide be treated with freshly precipitated argentic oxide, double decomposition ensues, argentic iodide is formed, and the hydrated tetrethylum oxide is liberated:—



It might have been anticipated that, under these circumstances, tetrethylum oxide would have been resolved into triethylia and alcohol, just as ammonium oxide becomes broken up into ammonia and water when similarly treated: thus, since



but such is not the case; for the new compound is very stable. On evaporation of the solution, the hydrate of the new base may be obtained in crystals, which, like those of caustic potash, absorb water and carbonic acid from the atmosphere, and possess the caustic action of potash, combined with a bitter taste like that of quinia. This base forms the type of a numerous class, which are analogous to it both in composition and in properties. Hydrated tetrethylum oxide in common with many others like it, such as the hydrated tetramethylum oxide $[(\text{CH}_3)_4\text{NHO}]$, is sufficiently powerful to saponify the oils, and to precipitate the metallic oxides from their salts, just as potash does. It forms crystallizable salts. These bases differ in a marked manner from such bases as ethylia, diethylia, and triethylia, all of which, like ammonia, are volatile without decomposition. The hydrated tetrethylum oxide, and others which resemble it, however, cannot be volatilized without undergoing decomposition, in which case they are converted into water, a hydrocarbon homologous with olefiant gas, and a volatile alkali corresponding to triethylia; for example:—



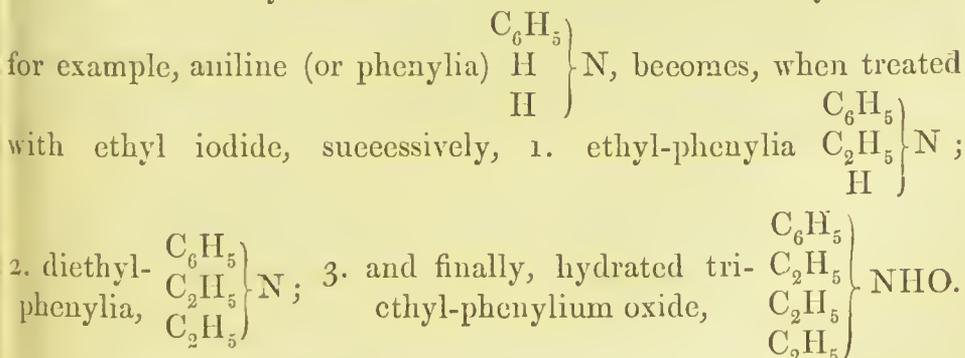
Ammonia is thus capable of originating two classes of bases, one set being volatile, and corresponding in properties to ammonia itself, and thence termed *ammonia bases*; the other set fixed,

resembling caustic potash in properties, and corresponding to hydrated ammonium oxide, and hence distinguished as *ammonium bases*.

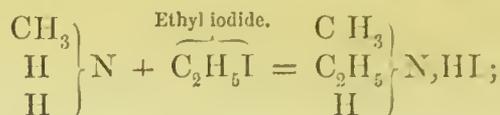
The successive stages of these reactions are usually less distinct than the foregoing statement would make it appear. Even during the first operation of the iodide of the alcohol radicle upon ammonia, a mixture of the secondary and tertiary bases, or even of the ammonium base, is observed; so that the isolation of a single base is not easy. The ammonium base may always be obtained pure with certainty by decomposing the product of the first operation with potash, and treating the mixed bases which come over on distillation, with fresh iodide, and repeating these operations successively two or three times. The whole of the distilled bases finally become converted into the ammonium base. The tertiary bases, like triethylia, may also easily be obtained pure, since, if the ammonium base be liberated from the iodide by means of argentic oxide, and be then distilled, the distillate furnishes the tertiary base in a pure state. The primary bases, such as ethylia, are best obtained pure by distilling the cyanic ether of the alcohol with caustic potash; but the secondary bases, like diethylia, are less readily procured in a pure form.

The ammonia bases in the free state precipitate many of the metallic oxides from solutions of their salts, and like the organic bases generally, furnish sparingly soluble crystalline double salts when their chlorides are mixed with platinic chloride.

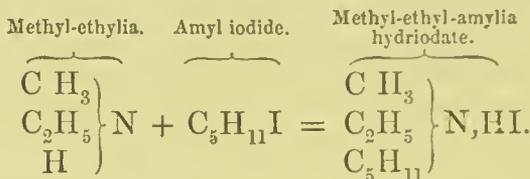
If in the preparation of these bases, by substitution from the iodides of the alcohol radicles, *phenylia* (C_6H_5, H_2N), or aniline, as it is commonly termed, be employed instead of ammonia, a corresponding series of bases may be obtained from it, in which the two remaining typical atoms of hydrogen in aniline may be successively displaced by one equivalent of one of the alcoholic radicles; and finally, the compound may be converted into an ammonium base by the action of another atom of ethyl iodide;



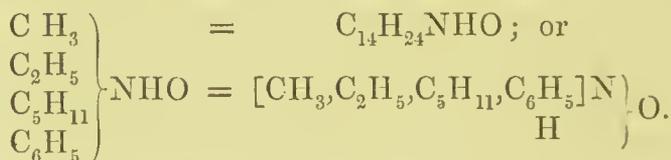
Hofmann, in the further investigation of this remarkable method of preparing artificial bases, found that each of the three atoms of hydrogen in ammonia may be displaced by a different alcohol radicle. For instance, it is possible to obtain, first, methylia, by the action of methyl iodide upon ammonia; then by acting upon methylia with ethyl iodide, the compound methyl-ethylia (corresponding to diethylia) is formed:—



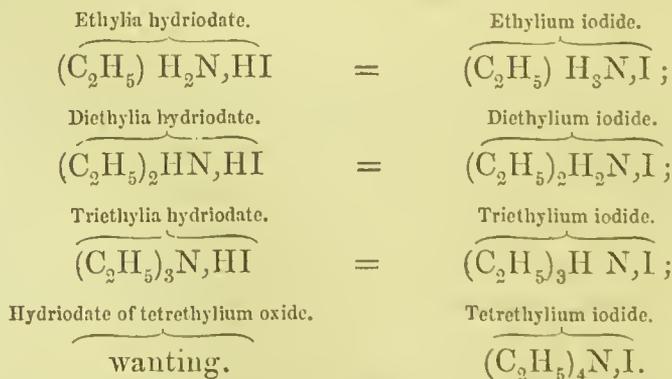
and on distilling this hydriodate of methyl-ethylia with caustic potash, the new base is liberated. Now, if methyl-ethylia be treated with amyl iodide, a compound corresponding to triethylia is formed, but containing, in the place of the three atoms of ethyl, three different alcohol radieles; for example:—



Hofmann even succeeded in obtaining a hydrated ammonium base, derived from aniline, containing 4 different hydrocarbon radieles, and to which the unwieldy name of hydrated methyl-ethyl-amyl-phenylum oxide must be assigned:—



It, of course, will not be overlooked that if the ordinary salts of ammonia are supposed to be compounds of ammonium, the salts of all the bases derived from ammonia ought to be considered from the same point of view:—If ammonia hydriodate be regarded as ammonium iodide, ethylia hydriodate should be ethylum iodide, and the composition and nomenclature of the ethyl bases would be simply translated thus (no hydriodates of the ammonium bases are known):—



In this work, however, for the sake of marking the distinction

between the volatile and the fixed bases, the termination *ium* will be reserved for such bases as are formed upon the type of hydrated ammonium oxide.

(1374) *Isomeric Bases*.—An important circumstance, in relation to the molecular constitution of ammonia, was elicited in the course of these investigations. Let the three atoms of hydrogen in ammonia be represented by the letters *h*, *H* and *H*; and

let $\left. \begin{array}{l} h \\ H \\ H \end{array} \right\} \text{N} = \text{ammonia}$:—it might be supposed that the three different

atoms of hydrogen *h*, *H*, and *H*, in the molecule of ammonia, might each have a different function to perform in the alkaline group. Suppose, then, that a substitution base were formed, in which the atom of hydrogen *h* were displaced by a radicle called

$\left. \begin{array}{l} X \\ H \\ H \end{array} \right\} \text{N}$; the other atoms of hydrogen, *H*

and *H*, admit of being displaced respectively by other radicles, *Y* and *Z*. Suppose, for example, that *X* represents phenyl (C_6H_5), *Y*, amyl, and *Z*, ethyl; the question is, whether the same compound will be formed indifferently when amyl is substituted for *H*, and ethyl for *H*, or when ethyl supplies the place of *H*, and amyl of *H*. Whether, in fact, there will be any perceptible dif-

ference if the compound be obtained in the form of $\left. \begin{array}{l} X \\ Y \\ Z \end{array} \right\} \text{N}$; or of $\left. \begin{array}{l} X \\ Z \\ Y \end{array} \right\} \text{N}$.

To decide this point Hofmann carefully compared the properties of phenyl-amyl-ethylia ($\text{C}_{13}\text{H}_{21}\text{N}$), prepared by acting upon phenyl-

amylia, $\left. \begin{array}{l} \text{C}_6\text{H}_5 \\ \text{C}_5\text{H}_{11} \\ \text{H} \end{array} \right\} \text{N}$, by ethyl bromide ($\text{C}_2\text{H}_5\text{Br}$), which would

yield $\left. \begin{array}{l} \text{C}_6\text{H}_5 \\ \text{C}_5\text{H}_{11} \\ \text{C}_2\text{H}_5 \end{array} \right\} \text{N}$, with the compound phenyl-ethyl-amylia, $\left. \begin{array}{l} \text{C}_6\text{H}_5 \\ \text{C}_2\text{H}_5 \\ \text{C}_5\text{H}_{11} \end{array} \right\} \text{N}$,

formed by decomposing phenyl-ethylia, $\left. \begin{array}{l} \text{C}_6\text{H}_5 \\ \text{C}_2\text{H}_5 \\ \text{H} \end{array} \right\} \text{N}$, with amyl bro-

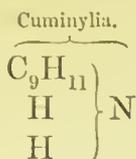
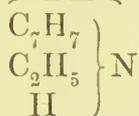
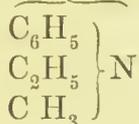
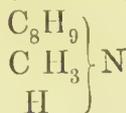
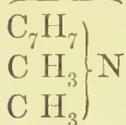
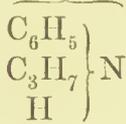
mide ($\text{C}_5\text{H}_{11}\text{Br}$); but the two substances comport themselves alike in all respects. The two bodies thus obtained are, therefore, not only isomeric, but identical, and the functions of the two atoms of hydrogen *H* and *H* in ammonia must be similar. The ease, however, is very different if alkalis be

compared together which have the same empirical formulæ, but which have been produced by the substitution of dissimilar alcohol radicles.

In order to render this evident, we may take for example the bases of the aniline series (1367).

Toluylia has the same composition as methyl-phenylia; xylylia as ethyl-phenylia, and euminylia as methyl-ethyl-phenylia. These pairs of substances are, however, only metameric, they are not identical. Toluylia is a fusible crystalline solid, which boils at $388^{\circ}\cdot 4$ (198° C.), and yields stable, sparingly soluble salts with most of the acids, including a beautiful crystallizable double salt with platinum chloride. Methyl-phenylia is an oily liquid which boils at $377^{\circ}\cdot 6$ (192° C.); its platinum salt is of a pale yellow colour, and begins to blacken almost immediately after its formation: all its salts are distinguished by their solubility, and the facility with which they are decomposed,—aniline being reproduced; whilst toluylia does not yield aniline under any known circumstances. The properties of euminylia and methyl-ethyl-phenylia, though both are liquid at ordinary temperatures, are not less distinct.

Further, it is possible to introduce an atom of ethyl into toluylia; one of the atoms of hydrogen which this base contains being readily eliminated when the alkali is treated with ethyl iodide. The ethyl-toluylia thus obtained is a third alkali isomeric or metameric with euminylia, yet possessed of properties quite distinct from it. Hence it is evident that three different bases are already known, all of which possess the empirical formula $C_9H_{13}N$; and there is no doubt that besides these, three other bases, each having the same empirical formula and the same combining proportion, could readily be obtained; yet each of these new bases would differ in constitution from the foregoing bases and from each other: they would also probably be found to differ in properties. The first of these new bases (methyl-xylylia) might be formed by substituting an atom of methyl for one of hydrogen in xylylia; the second (dimethyl-toluylia) would be formed by substituting 2 atoms of methyl in toluylia for its 2 remaining typical atoms of hydrogen; the third (propyl-phenylia) would be obtained by substituting propyl (C_3H_7) the radicle of propylic alcohol (C_3H_8O), for one of the typical atoms of hydrogen in aniline. The six bases metameric with euminylia would therefore have the composition which is represented in the following table:—

Known Bases.*Ethyl-toluylia.**Methyl-ethyl-phenyilia.**Bases not yet formed.**Methyl-xylylia.**Dimethyl-toluylia.**Propyl-phenyilia.*

The manner in which toluylia and other bases not derived from the alcohols admit of being attacked by the hydriodic and hydrobromic ethers shows that the action of these ethers upon the different bases affords a most important means of examining and dissecting these various compounds; and it has been found to be applicable to organic bases both of natural and artificial origin. Within the few years that have elapsed since Hofmann first showed the applicability of these reagents to this purpose, extensive use has been made of them in such examinations.

(1375) *Hofmann's Classification of Organic Bases.*—Hofmann originally proposed to classify the various monatomic bases which may be produced by these methods of substitution, under the heads of *amidogen*, *imidogen*, *nitrile*, and *ammonium* bases—a distinction still useful, although he has since termed the amidogen bases *primary monamines*, or *monammonias*, the imidogen bases *secondary monamines*, and the nitrile bases *tertiary monamines*. The bases, or *amines*, differ from the amides in the fact that they contain the basic radicals of the alcohols, whilst the corresponding amides (1345 *et seq.*) contain the acid radicals in the place of the hydrogen of the original molecule of ammonia. Amidogen bases, or primary monammonias, are those which may be regarded as still retaining two atoms of the hydrogen of the original ammonia, one atom only of hydrogen having been displaced by a hydrocarbon: they are more powerfully basic than the secondary and tertiary monammonias. In the imidogen bases, or secondary monammonias, the substitution has proceeded a step further, one atom of hydrogen of the original ammonia only being left; whilst in the nitrile bases, or tertiary monammonias, none of the typical hydrogen of the ammonia remains. In the ammonium bases a

| Ammonia Bases. | Amide, or Amidogen Bases. (Primary Monamines.) | Imide, or Imidogen Bases. (Secondary Monamines.) | Nitrile Bases. (Tertiary Monamines.) | Bases analogous to Hydrated Ammonium Oxide. (Ammonium bases.) |
|--|---|--|---|---|
| Ammonia (H ₃ N) | Methylia (C ₁ H ₅ N) | Dimethylia (C ₂ H ₇ N) | Trimethylia (C ₃ H ₉ N) | Hydrated tetramethylium oxide (C ₄ H ₁₂ NHO) |
| Ethylia (C ₂ H ₇ N) | Ethylia (C ₂ H ₇ N) | Diethylia (C ₄ H ₁₁ N) | Triethylia (C ₆ H ₁₅ N) | Hydrated tetraethylium oxide (C ₈ H ₂₀ NHO) |
| Anylia (C ₅ H ₁₃ N) | Anylia (C ₅ H ₁₃ N) | Diamylia (C ₁₀ H ₂₃ N) | Triamylia (C ₁₅ H ₃₃ N) | Hydrated tetramylium oxide (C ₂₀ H ₄₄ NHO) |
| Aniline (Phenylia C ₆ H ₇ N) | Aniline (Phenylia C ₆ H ₇ N) | Ethylphenylia, or ethylaniline (C ₈ H ₁₁ N) | Diethylphenylia, or Diethylaniline (C ₁₀ H ₁₅ N) | Hydrated triethylphenylium oxide (C ₁₂ H ₂₀ NHO) |
| Phosphuretted Hydrogen (H ₃ P) | Methylphenylia, or methylaniline (C ₇ H ₉ N) | Methylphenylia, or methylaniline (C ₇ H ₉ N) | Methyl-ethylphenylia, or methyl-ethyl-aniline (C ₉ H ₁₃ N) | Hydrated methyl-ethyl-amiylium oxide (C ₁₀ H ₂₄ NHO) |
| Arseniuretted Hydrogen (H ₃ As) | Chlorophenylia, or chloraniline (C ₆ H ₆ ClN) | Ethylchlorophenylia, or ethylchloraniline (C ₈ H ₁₀ ClN) | Diethylchlorophenylia, or diethylchloraniline (C ₁₀ H ₁₄ ClN) | Hydrated methyl-diethyl-amiylium oxide (C ₁₀ H ₂₄ NHO) |
| Antimoniuretted Hydrogen (H ₃ Sb) † | Toluylia (C ₇ H ₉ N) | Ethyltoluylia (C ₉ H ₁₃ N) | Dimethyltoluylia (C ₁₁ H ₁₇ N) | Hydrated methyl-ethyl-conylium oxide (C ₁₁ H ₂₃ NHO) |
| Conylia (C ₈ H ₁₆ N) | Conylia (C ₈ H ₁₆ N) | Methylconylia (C ₉ H ₁₇ N) | Methylconylia (C ₉ H ₁₇ N) | Hydrated methyl-ethyl-nicotylium oxide (C ₁₁ H ₂₃ NHO) |

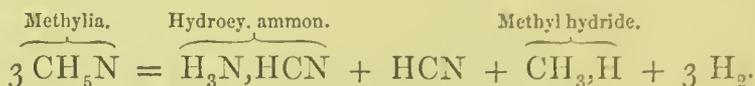
fourth equivalent of a hydrocarbon is superadded, and takes the place of the fourth atom of hydrogen theoretically assigned to ammonium. All the ammonium bases when separated from their salts retain the elements of water, and are only known in the form of hydrates. The table on the preceding page will afford an illustration of the mode of classifying the different bases upon Hofmann's method.

There can be no doubt that in certain cases, the organic alkalies, as they exist in the plant, are formed upon the type of ammonia: though in the present state of our knowledge upon this subject we are far from warranted in drawing the general conclusion that such is their constitution in all instances. The two bases last mentioned in the table, viz., conylia and nicotylia, are the natural volatile alkalies contained respectively in hemlock and in tobacco. On treating conylia with methyl iodide, two compounds were formed, the simpler of which may be considered as a tertiary base, and the more complicated one as an ammonium base; conylia itself being regarded as a secondary base in which the dyad group $(C_8H_{14})''$ has displaced 2 atoms of hydrogen, whilst nicotylia must be regarded as a diatomic tertiary base, formed upon the type of 2 molecules of ammonia, in which the 6 atoms of hydrogen in the ammonia have been displaced by the hexad group $(C_{10}H_{14})^{vi}$.

(1376) METHYLIA; *methylamine* $(CH_5N$ or $CH_3, H_2N=31)$; *Sp. gr. of vap.* 1.08; *Rel. wt.* 15.5.—This body is gaseous under ordinary circumstances, but may be condensed by a freezing mixture to a very mobile liquid, which is not solidified by exposure to a bath of solid carbonic anhydride and ether. It is colourless, has an intensely pungent odour of ammonia, and an extremely powerful alkaline reaction, producing dense white fumes when exposed to the vapour of hydrochloric acid; but it is distinguished from ammonia by its ready inflammability: it burns with a yellowish livid flame, and furnishes carbonic acid, water, and nitrogen, accompanied, if the supply of air be insufficient, with traces of cyanogen or of hydrocyanic acid. Methyilia is more soluble in water than any other known gas; at $55^{\circ}4$ (13° C.) water dissolves 1150 times its bulk, forming a powerfully alkaline solution with a very pungent ammoniacal odour, and a strongly caustic action upon the skin; when boiled, the alkali is expelled in the gaseous form. Solution of methyilia acts upon solutions of the metallic salts as ammonia would do, dissolving the precipitated oxides of zinc, silver, and copper; in the latter case forming

a deep blue liquid. The oxides of cadmium, cobalt, and nickel, are precipitated by methyilia, but are not redissolved by it.

When methyilia is passed through a porcelain tube heated to redness, it is decomposed; ammonia hydrocyanate, and a gaseous mixture of hydrocyanic acid, methyl hydride, and free hydrogen being formed:—



If potassium be heated in gaseous methyilia, potassic cyanide is formed, and hydrogen is liberated: $2 \text{ CH}_5\text{N} + \text{K}_2 = 2 \text{ KCN} + 5 \text{ H}_2$.

Preparation.—Methyilia is readily obtained by distilling the carefully dried hydrochlorate of the base with twice its weight of quicklime. The operation should be performed in a long tube, the lower half of which is filled with the mixture, and the upper half with caustic potash, in order to dry the gas completely; it may be collected in jars over mercury. Hydrochlorate of methyilia is best obtained for this purpose by distilling methyl cyanurate with caustic potash (1165), and saturating the distillate with hydrochloric acid; the residue when evaporated to dryness may be dissolved in boiling absolute alcohol, from which on cooling it crystallizes in large iridescent foliated deliquescent crystals: at a temperature a little above 212° it fuses, and when heated in an open vessel it volatilizes in dense white clouds, which may be condensed unchanged. This salt does not yield any amalgam similar to that of ammonium when decomposed by the voltaic battery in contact with mercury, nor when its concentrated solution is mixed with an amalgam of potassium.

Methyilia is likewise a frequent product of the destructive distillation of azotised substances; it is also present, amongst other bases, when many natural alkaloids—such as narcotine, morphia, codeia, and caffeine—are distilled with caustic potash.

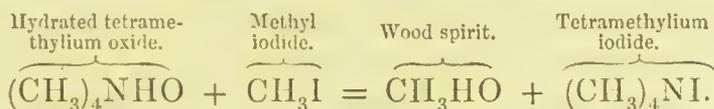
Most of the salts of methyilia are very soluble in water. Its hydrochlorate forms with platinic chloride a soluble compound, crystallizing in golden yellow scales, which are insoluble in alcohol.

Trimethyilia ($\text{C}_3\text{H}_9\text{N}$).—This alkali, which is metameric with propyilia (C_3H_7) H_2N , is found in considerable quantity in the roc of herrings. It has an extremely powerful and disagreeable fishy odour. It is also obtained by distilling ergot of rye with caustic potash; and it imparts to the *Chenopodium vulvaria* its peculiar odour. Trimethyilia is a very volatile liquid, which boils at about 41° (5° C.), and emits an inflammable vapour very soluble

in water. Methyl iodide immediately converts this base into a magma of crystals of tetramethylum iodide.

Tetramethylum Hydrated Oxide $[(\text{CH}_3)_4\text{NHO}]$.—The iodide of this base is the principal product formed by heating methyl iodide in excess with a solution of ammonia in wood spirit or in alcohol. Since tetramethylum iodide is sparingly soluble in cold water, it may be purified from the accompanying hydriodates of methyilia, dimethyilia, and trimethyilia, by crystallization from boiling water. Caustic potash does not liberate any of these ammonium bases from their salts; but the decomposition is easily effected by treating the aqueous solution of the salt with freshly precipitated argentic oxide. When tetramethylum iodide is treated with recently precipitated argentic oxide, silver iodide is formed, and hydrated tetramethylum oxide remains in solution; it may be obtained by evaporation *in vacuo*, over sulphuric acid, in crystals which are deliquescent, and attract carbonic acid. Its salts crystallize well, particularly the nitrate, which forms long brilliant needles. The chloride of platinum and tetramethylum $[(\text{C}_4\text{H}_{12}\text{NCl})_2\text{PtCl}_4]$ crystallizes in magnificent dark orange-coloured octahedra. This hydrated tetramethylum oxide when heated breaks up into trimethyilia and wood spirit $(\text{CH}_3)_4\text{N,HO} = (\text{CH}_3)_3\text{N} + \text{CH}_4\text{O}$. Tetramethylum iodide in like manner, when heated, breaks up into triethyilia and methyl iodide $(\text{CH}_3)_4\text{NI} = (\text{CH}_3)_3\text{N} + \text{CH}_3\text{I}$.

When the hydrated tetramethylum oxide is treated with an additional quantity of methyl iodide, no further combination of methyl with the base occurs; but double decomposition ensues, tetramethylum iodide is formed, and wood spirit is liberated:—



(1377) ETHYLIA, or *Ethylamine* $(\text{C}_2\text{H}_7\text{N}$, or $\text{C}_2\text{H}_5, \text{H}_2\text{N} = 45)$; *Sp. gr. of liq.* 0.696; *of vap.* 1.594; *Rel. wt.* 22.5; *Boil. pt.* $65^{\circ}6$ ($18^{\circ}6$ C.).—This base constitutes a volatile, mobile, colourless liquid, which emits an inflammable vapour of a pungent ammoniacal odour. It is miscible with water in all proportions, but, by prolonged boiling, the whole of the ethyilia may be expelled. Ethyilia produces results with solutions of metallic salts very similar to those of methyilia, from which, however, it may be distinguished by the power possessed by ethyilia of dissolving recently precipitated alumina. Wurtz has proposed to take advantage of this property as a means of separating alumina from ferric oxide, in the operation of analysis. Ethyilia displaces ammonia from its

salts if evaporated with them. It yields dense white fumes with vapours of hydrochloric acid.

Ethylia may be prepared in a manner similar to that directed for methylia, by acting upon cyanic or cyanuric ether with caustic potash. It may also be obtained by acting upon ethyl iodide with ammonia, in which case ethylia hydriodate is formed; the salts of ethylia do not generally crystallize with facility; they are soluble in water and in alcohol. The hydrochlorate forms colourless plates, which are fusible at $168^{\circ}\cdot 8$ (76° C.). The sulphate is deliquescent, and since it is soluble in alcohol it may readily be separated from ammonium sulphate, which is insoluble in this menstruum. The double salt with platinic chloride $[(C_2H_5)_3N, HCl]_2 PtCl_4$, crystallizes in yellow octahedra.

Diethylia $[C_4H_{11}N = (C_2H_5)_2HN$; *Boil. pt.* $134^{\circ}\cdot 6$ (57° C.)] is a colourless, volatile, inflammable liquid, powerfully alkaline, and very caustic. It may be obtained by treating ethylia with ethyl iodide in the manner already described (1373).

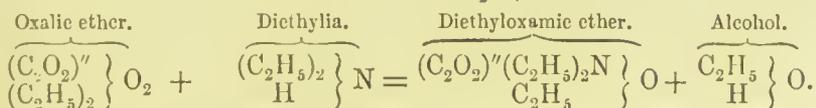
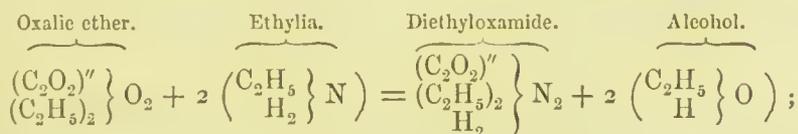
Triethylia $[C_6H_{15}N = (C_2H_5)_3N$; *Boil. pt.* $195^{\circ}\cdot 8$ (91° C.)] is also a soluble, volatile and powerful base, which forms a beautiful orange double salt with platinic chloride, crystallizing in large rhombic tables $[(C_2H_5)_3N, HCl]_2 PtCl_4$. Triethylia may be obtained from the foregoing base by the action of ethyl iodide upon it. The salts of tetrethylum are procured by continuing the action of ethyl iodide upon triethylia.

The *hydrated tetrethylum oxide* $[(C_2H_5)_4NHO]$ is a powerful base, perfectly analogous to the corresponding compound of tetramethylum. It may be obtained in solution by treating tetrethylum iodide with argentic oxide. If this solution be allowed to evaporate *in vacuo* over sulphuric acid, the base forms long hair-like needles, which are very deliquescent, and absorb carbonic acid with great avidity. A strong solution of the base may be boiled without undergoing decomposition, but if evaporated to dryness over the water-bath, it becomes decomposed as soon as the water is nearly all expelled. A solution of the base acts powerfully upon the cuticle, and it saponifies the fats as readily as potash, forming soft soaps. The tetrethylum oxide is not liberated from its iodide by the action of potash; on adding a solution of potash to one of the iodide of the base, a crystalline mass of the pure tetrethylum iodide is separated, as it is less soluble in alkaline liquids than in pure water: even when boiled with the concentrated solution of potash for some hours, no decomposition is effected; but it is decomposed with facility by the salts of silver, or by freshly precipitated argentic oxide. Analo-

gous reactions with potash and argentic oxide are found to occur with a large number of other ammonium bases. The hydrated tetrethylum oxide when heated breaks up, not into its alcohol and triethylia, like the methylum base, but into olefiant gas, water, and triethylia, which is in accordance with the usual mode of decomposition of these bases $(C_2H_5)_4N, HO = C_2H_4 + H_2O + (C_2H_5)_3N$.

The iodides of the ammonium bases combine with an additional quantity of iodine, and form crystallizable compounds which may be obtained by mixing a solution of iodine in alcohol with the alcoholic solution of the iodide of the base. The *triiodide of tetrethylum* $(C_2H_5)_4N, I_3$ crystallizes in dark violet brilliant prisms. The *pentiodide* $(C_2H_5)_4N, I_5$ forms tabular plates of a brilliant metallic lustre and a dark greenish-grey colour. These compounds are very sparingly soluble in water, and may be employed to separate the ammonium compounds from those of the ammonia series of alcohol bases. The iodine may be removed by treatment with sulphuretted hydrogen.

Hofmann finds that the mixed ethyl bases may be completely and readily separated when in their anhydrous form, by treating them with oxalic ether. Ethylia is thus converted into a beautiful sparingly soluble crystallized compound, *diethyloxamide*, with liberation of alcohol; diethylia furnishes *ethyloxamic ether*, an oily liquid which boils at a high temperature, alcohol being here also liberated from the oxalic ether; and triethylia remains unaltered:—



On distilling the result of the reaction of oxalic ether on the mixed anhydrous bases, triethylia passes over pure. The crystals of diethyloxamide are purified by crystallization from boiling water, and when decomposed by potash yield pure ethylia. The oily diethyloxamic ether when cooled to 32° deposits a few crystals of diethyloxamide; if decanted from these and distilled, and the portions collected which come over at 500° (260° C.), the product is pure diethyloxamic ether; and this when distilled with caustic potash furnishes pure diethylia.

Carey Lea takes advantage of the difference in the solubility of the carbazotates of the different ethyl bases to effect their separation.

Bases derived from other Alcohols.

(1378) *Tritylia*, or *Propylamine* (C_3H_7, H_2N) is isomeric with trimethylia; it is one of the bases obtained by Anderson during the destructive distillation of bones; and the same chemist has likewise procured from Dippel's oil another base, which he termed

petinine, but which corresponds to *tetrylia* or *butyria* (C_4H_9, H_2N), the alkali of tetryl alcohol; it also occurs mixed with amylium in the distillate when wool or flannel is distilled with caustic potash. These bases are liquid and volatile.

A series of bases corresponding to those from methylic and ethylic alcohols has also been obtained from fousel oil. Their basic powers are smaller than those of the ethyl and methyl series, and they present no particular points of interest. *Amylia* (C_5H_{11}, H_2N) is a very light, colourless, inflammable liquid, which boils at 203° (95° C.), and is of sp. gr. 0.750. It is soluble in water in all proportions. Horn when distilled with caustic potash was found by Limprieth to yield 4 or 5 per cent. of this base. Its salts crystallize readily.

(1379) The alcohol from castor oil (oetyl alcohol) also yields a well-marked base, *octylia* or *caprylia* (C_8H_{17}, H_2N); and even the alcohol of palmitic acid, ethal, has been made to yield a compound ammonia in which all the three atoms of hydrogen have given place to the hydrocarbon octyl, thus forming *tricetylia* [$C_{48}H_{99}N = (C_{16}H_{33})_3N$], which crystallizes in white fusible needles, freely soluble in boiling alcohol. Its salts are not soluble in water, but they crystallize readily from boiling alcohol and from ether.

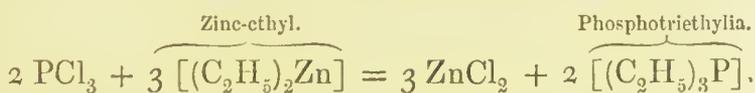
3. Alcohol Bases obtained from Phosphuretted, Arseniuretted, and Antimoniuretted Hydrogen.

(1380) The first column of the table of bases given (p. 506) includes three substances which do not possess basic properties, but which present the closest analogy in composition with ammonia; viz., phosphuretted, arseniuretted and antimonuretted hydrogen. Each of them contains three atoms of hydrogen, and one atom of its characteristic component; and they may be looked upon as analogues, or representatives of ammonia, in which the nitrogen has been displaced respectively by phosphorus, arsenium, and antimony. Widely as these three elements differ from nitrogen in their separate form, they yet exhibit a considerable analogy with it in their mode of entering into combination; all three of them forming not only corresponding compounds with three atoms of hydrogen, but, like nitrogen, all of them yielding with oxygen, anhydrides which contain five atoms of oxygen, and which when united with the elements of water furnish powerful acids (442).

Neither arseniuretted nor antimonuretted hydrogen exhibits any basic properties, and the only indication of basic power in the

ease of phosphuretted hydrogen consists in the formation of volatile crystalline bodies with hydrobromic and hydriodic acids (454); yet it has been shown by P. Thénard, that if the hydrogen of phosphuretted hydrogen be displaced by methyl or by ethyl, powerful bases may be procured, formed upon the type of ammonia, but containing phosphorus instead of nitrogen, and ethyl or methyl in the place of hydrogen. Hofmann and Cahours have investigated these compounds more minutely (*Phil. Trans.* 1857), and have described a method by which they may be obtained with certainty. The process introduced by the chemists last named, for the preparation of these phosphorised bases consists in mixing phosphorous chloride (PCl_3) with zinc-methyl, zinc-ethyl, &c., when zincic chloride is formed, whilst the new base is produced. Many of these bases have a most offensive odour, and the vapour of several of them when mixed with atmospheric air, or with oxygen, takes fire, especially if the temperature be slightly raised. Moreover, not only may phosphorised bases $(\text{CH}_3)_3\text{P}$; $(\text{C}_2\text{H}_5)_3\text{P}$; $(\text{C}_5\text{H}_{11})_3\text{P}$, &c., analogous to ammonia, be formed, but by treating these new bases with iodide of ethyl, of methyl, or of amyl, iodides of ammonium bases analogous to that of tetrethylum may be obtained; and by the action of argentic oxide upon these iodides, hydrates of the new ammonium bases may be procured.

(1381) *Phosphotriethylia*, or *Triethylphosphine* [$(\text{C}_2\text{H}_5)_3\text{P} = 118$]; *Sp. gr. of liq.* 0.812; *Boil. pt.* $260^{\circ}.6$ (127° C.).—This interesting compound is a colourless transparent liquid of high refracting power, insoluble in water, but freely soluble in alcohol and in ether. It has a benumbing odour, which, when largely diluted, greatly resembles that of hyacinths. The reaction by which it is formed may be represented by the following equation:—

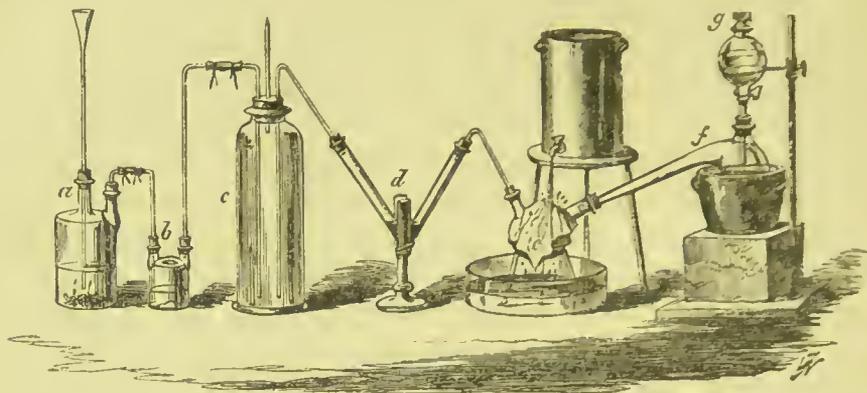


In order to prepare phosphotriethylia, the arrangement of apparatus represented in the annexed figure (Fig. 390) was adopted:—

a is a gas-bottle for generating carbonic anhydride; *b* a wash-bottle containing sulphuric acid; *c* a reservoir of carbonic anhydride; *d* a bent tube containing phosphorous chloride; *e* a receiver; *f* a retort containing a solution of zinc-ethyl in ether; *g* a reservoir for the phosphorous chloride, the supply being regulated by a glass stop-cock. The whole apparatus is first filled with dry gaseous carbonic anhydride. The tube in *c*, which at first was closed with a cap of caoutchouc, is opened, and the

etheral solution of zinc-ethyl is distilled into the retort, after which the globe with the phosphorous chloride is fixed in its place; this chloride is allowed to enter drop by drop, while the

FIG. 390.



retort is cooled by immersion in ice-cold water. The action is very violent. As soon as heat is no longer evolved by addition of the phosphorous chloride the decomposition is completed.

In the retort and the receiver are two layers of liquid: one a pale, heavy, straw-coloured viscid liquid, the compound of phosphotriethylia and zinc chloride; the other a colourless mobile fluid, which is a solution of phosphorous chloride in ether, and which may be poured off and used in a subsequent similar operation. In order to separate the phosphorus base, the compound is decomposed by means of caustic potash. For this purpose the mass in the retort is first diluted with water, then the retort is filled with hydrogen, and a concentrated solution of potash allowed to flow slowly into it. On subsequently distilling, in a very slow stream of hydrogen, phosphotriethylia passes over with the aqueous vapour, and forms a layer which floats on the top of the condensed water in the receiver.

Phosphotriethylia, by slow oxidation, is converted into a crystalline, volatile, very deliquescent mass, of a composition represented by the formula $[(C_2H_5)_3P, O]$; *Fusing pt.* $111^\circ.2$ (44° C.); *Boil. pt.* 464° (240° C.); *Sp. gr. of vap.* 4.60: it corresponds to the oxide of stibiotriethyl (1199).

Corresponding compounds, which contain sulphur $(C_2H_5)_3P, S$, and selenium, may also be formed by the direct action of sulphur or of selenium upon the phosphorous base. The *sulphide* of phosphotriethylia is a volatile substance which fuses at 203° (95° C.). It is soluble in hot water, from which it crystallizes in remarkably beautiful needles. It is also freely dissolved by hot alcohol, as well as by ether, and carbon disulphide. Chlorine,

bromine, and iodine likewise enter into direct combination with phosphotriethylia; two atoms of each of these elements combining with one atom of the base. Direct combination also occurs between phosphotriethylia and hydrochloric, hydrobromic, and hydriodic acids; the hydrochlorate having the composition represented by the formula $[(C_2H_5)_3P, HCl]$. Other monacid salts, such as the nitrate $[(C_2H_5)_3P, HNO_3]$, may be formed. These compounds may be crystallized, though with difficulty.

On treating phosphotriethylia with ethyl iodide, a very powerful and almost explosive reaction occurs, and the mixture, on cooling, yields a crystalline mass of *phosphotetrethylum* (tetrethyl-phosphonium) *iodide*, which, when decomposed by argentic oxide, yields a strongly alkaline solution of the hydrated oxide of the base $[(C_2H_5)_4PHO]$; it has a bitter phosphoric taste, and yields crystallizable deliquescent salts. When this hydrated base is heated, it gives off a compound of carbon and hydrogen, and at a higher temperature furnishes crystals of the oxide of phosphotriethylia $(C_2H_5)_3P, O$.

Both arsenic and antimony form with ethyl and methyl, and the other alcohol radicles, compounds which combine with oxygen, and possess basic properties as powerful as those of many of the metallic oxides (1191—1200).

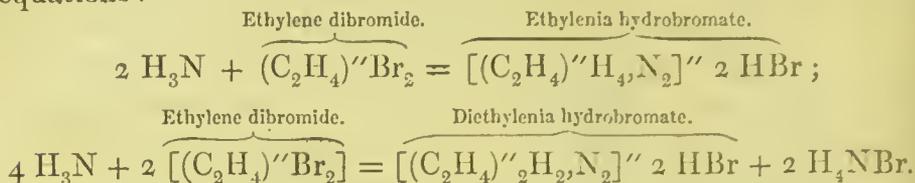
4. Polyatomic Bases.

(1382) Recent researches, especially those of Hofmann, have shown that, in addition to the monatomic bases, or bases formed upon the type of a single atom of ammonia, others may be obtained, which are produced by substitution from two, from three, or even from a still larger number of atoms of ammonia. So that we have diatomic and triatomic bases, or diammonias and triammonias formed from the diatomic and triatomic alcohols, just as the monammonias are from the monatomic alcohols.

When, for instance, ethylene dibromide is decomposed by ammonia, a complex reaction occurs; but among the products two substances are always present as hydrobromates; viz., ethylene-diamine, or *ethylenia*, and diethylene-diamine, or *diethylenia*.* Each of these bases is formed from two atoms of

* In studying these diamines or compounds on the type of diammonia, Hofmann found it far more advantageous to use phosphotriethylia than ammonia as the compound from which they were formed. The number of compounds obtainable from phosphotriethylia by substitution is much smaller than that

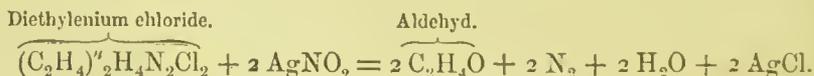
ammonia, and requires two atoms of a monobasic acid for its saturation. This formation may be illustrated by the subjoined equations:—



Hofmann has shown that there is no limit to the number of atoms of ammonia which may be thus welded into one, and he has indeed succeeded in grouping together as many as eight atoms of ammonia into one atom of a compound base. The mode in which he has effected this will be readily understood from the symbols of the compound given in the margin, in which eight atoms of ammonia are represented as all linked together into one molecule by the seven atoms of the dyad radicle ethylene.

(1383) Diethylene is a base which was discovered about the same time by Cloez and by Natanson, and was named *acetylia*; but its true nature was first explained by Hofmann.

Hydrated Diethylenium Oxide $[(\text{C}_2\text{H}_4)''_2\text{H}_4\text{N}_2\text{O}, \text{H}_2\text{O}]$.—When Dutch liquid ($\text{C}_2\text{H}_4\text{Cl}_2$) is heated for some hours to a temperature of 302° (150° C.) in a sealed tube, with about 5 times its bulk of a concentrated solution of ammonia, it is completely decomposed; a yellow liquid is formed, and crystals of ammoniac chloride are deposited in abundance: if these be separated by filtration through muslin, and the mother liquid be treated with argentic oxide, it yields a decidedly alkaline solution, which absorbs carbonic acid from the air. The new base thus obtained is not volatile, its salts have a feebly acid reaction, and do not crystallize. If its chloride be mixed with a solution of platinic chloride, it yields a wax-like mass, which has the composition of the double chloride of platinum and diethylenium $[(\text{C}_2\text{H}_4)''_2\text{H}_4\text{N}_2\text{Cl}_2, \text{PtCl}_4]$. Diethylenium chloride, if slightly acidulated with sulphuric acid and mixed with argentic nitrite, furnishes aldehyd in abundance:—

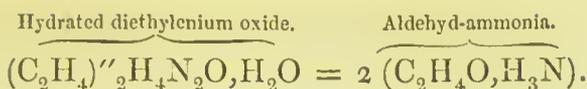


This reaction corresponds to that of nitrous acid on aniline, by which carboic acid ($\text{C}_6\text{H}_6\text{O}$) is reproduced, whilst nitrogen and water are liberated.

It may be remarked that hydrated diethylenium oxide is isomeric with aldehyd-ammonia, although so different from it in properties:—

obtainable from ammonia, inasmuch as the three displaceable atoms of hydrogen which ammonia contains have been already displaced in the phosphorus base.

When ammonia is acted upon by means of ethylene dibromide, compounds may be obtained in which the hydrogen may be successively displaced by the diatomic radicle $(\text{C}_2\text{H}_4)''$, and by the monatomic radicles $(\text{C}_2\text{H}_2)'$, $(\text{C}_2\text{H}_4\text{Br})'$, $(\text{C}_2\text{H}_5\text{O})'$. These different compounds are liable to be obtained mixed in every proportion (*Phil. Trans.*, 1860, p. 450), so that the difficulties of the investigation are sufficient to discourage even the most practised skill, and often to baffle all the resources of analysis.

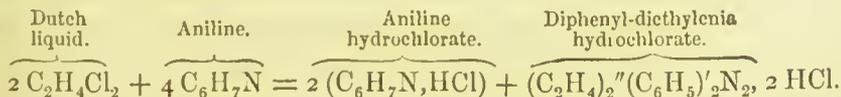


Diethylenia, or *Diethylene diamine* $(\text{C}_2\text{H}_4)''_2\text{H}_4\text{N}_2$; *Sp. gr. of liq.* 0.975; *of vap.* 1.522; *Rel. wt.* 43; *Boil. pt.* 338° (170° C.; Hofmann).—If an alcoholic solution of the hydrated diethylenium oxide be distilled to dryness in a retort, and the temperature be then raised to about 302° (150° C.), water again begins to escape, and at a temperature of 428° (220° C.) yellowish oily drops of diethylenia pass over. This body has a peculiar persistent odour, which is ammoniacal, and at the same time recalls that of aldehyd. It does not become solid at -13° (-25° C.). It is inflammable, and burns with a bluish-white flame. It is insoluble in ether, but freely soluble both in water and in alcohol. Sodium exerts no action upon diethylenia at ordinary temperatures. Dry reddened litmus-paper does not become blue even when immersed in it; but if the base be treated with acids, it forms salts which are identical with those of diethylenium oxide. If caustic potash be added to a solution of these salts, the liquid does not emit the odour of diethylenia, but exhibits the properties of a solution of hydrated diethylenium oxide. An aqueous solution of diethylenia produces in a solution of the salts of zinc, a white precipitate which is soluble in excess of the base. With cupric salts it gives a pale yellow precipitate, which is partially soluble if diethylenia be added in excess, forming a bright blue liquid. It occasions a white precipitate in solutions of the salts of silver, but the precipitate is readily dissolved by an excess of the base; and if the solution be gently warmed, a mirror-like coating of reduced silver is formed on the sides of the vessel.

It is remarkable that diethylenium oxide should be so permanent a body as to require a temperature of 302° (150° C.) for its decomposition, although the corresponding compound of ammonium undergoes decomposition at ordinary temperatures as soon as it is formed. Diethylenia corresponds exactly with two atoms of ammonia, and like it does not form salts until it has assimilated the elements of water.

(1384) *Ethylenia*, or *Ethylene diamine* $(\text{C}_2\text{H}_4)''\text{H}_4\text{N}_2$; *Boil. pt.* 253° 4 (123° C.); *Sp. gr. of vap.* 2.00; *Rel. wt.* 30.—Cloez believed that formyl (CH) entered into the composition of a base termed *formylia*, homologous with acetylia; but Hofmann has proved that this base contains one atom of hydrogen more than that required by such a formula, and that it is really as given above.

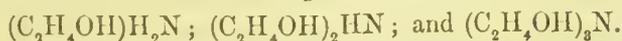
If diethylenia be treated with ethyl iodide, *diethyl-diethylenia* is obtained, a base which may be represented by the formula $(\text{C}_2\text{H}_4)''(\text{C}_2\text{H}_5)'_2\text{N}_2$. *Diphenyl-diethylenia* $(\text{C}_2\text{H}_4)''_2(\text{C}_6\text{H}_5)'_2\text{N}_2$ is procured by treating Dutch liquid with aniline instead of with ammonia:—



Corresponding bodies may be obtained by treating Dutch liquid, or ethylene dibromide, with methyilia, ethyilia, and other analogous bases.

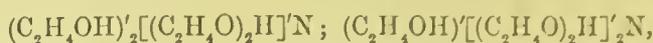
Diethylenia also produces compounds corresponding to the amides. For instance, when butyric ether is mixed with an alcoholic solution of diethylenia, crystals of *butyric diethylenamide* $\left. \begin{array}{l} (\text{C}_4\text{H}_7\text{O})' \\ (\text{C}_2\text{H}_4)'' \end{array} \right\}_2 \text{N}_2$ are formed.

(1385) Other bases containing oxygen were obtained by Wurtz by acting upon ammonia with successive quantities of ethylene oxide (1215); and these, though obtained from a diatomic alcohol, correspond to a single atom of ammonia:—



If the third of these bases be further acted upon by ethylene oxide, a fresh set

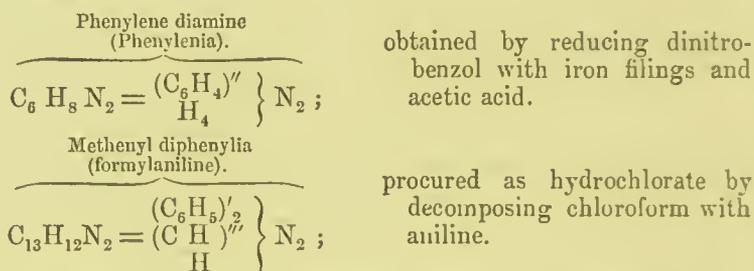
of bases may be obtained, corresponding to the condensed glycols, or polyethylene alcohols, such as—



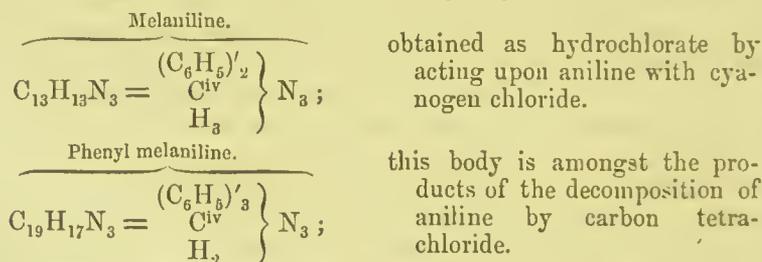
and so on.

At present little is known of these bases, but the existence of oxidized radicles within them has some interest, in relation to the as yet unknown constitution of many natural vegetable bases which contain oxygen.

A considerable number of diammonias and triammonias have been formed from aniline. Rosaniline has already been described (1365) as a triammonia; but its constitution has not yet been definitely ascertained, though its empirical formula is admitted to be correct. We cannot enter into a detailed description of these substances, but must refer the reader to the papers of Hofmann in the *Proceedings of the Royal Society*. Of the aniline *diammonias*, the following may be mentioned:—



And of the aniline *triammonias*, the following may be referred to, viz. :—



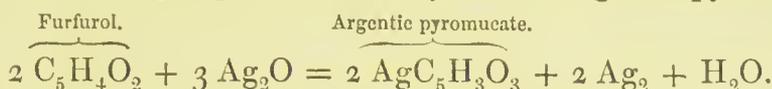
5. Bases produced by the action of Ammonia on certain Aldehyds among the Essential Oils.

(1386) During the process of obtaining formic acid by distilling bran or oatmeal with black manganese oxide and dilute sulphuric acid, a small quantity of an essential oil distils over, which may be purified by redistillation. To this body the name of *furfurol* (from *furfuri oleum*, oil of bran) [$C_5H_4O_2$; *Sp. gr. of liq.* 1.168; *of vap.* 3.34; *Rel. wt.* 48; *Boil. pt.* 323° (162° C.)] has been given. When pure it is colourless, but it quickly becomes brown by exposure to the air. It has a fragrant odour, somewhat resembling that of bitter almonds. It is dissolved by cold sulphuric acid, forming a beautiful purple liquid, from which on dilution with water the oil is separated unchanged.

Furfurol is best obtained by digesting the bran in a cold dilute solution of caustic potash to dissolve out the gluten and starch, washing well, and drying at

a gentle heat, then mixing it with half its weight of sulphuric acid, which must be first diluted with an equal bulk of water. The pasty mass thus obtained is distilled in a current of steam: the furfural comes over dissolved in the water, from which it may be recovered by distillation, collecting the first half only, and again submitting that to a like process of partial distillation.

Sehwanert (*Liebig's Annal.*, exvi. 260) has verified the conjecture of Gerhardt, that furfural is the aldehyd of pyromucic acid. Like the aldehyds it combines with hydric sodic sulphite. If an aqueous solution of furfural is boiled with freshly precipitated argentic oxide, metallic silver is deposited, and the hot filtrate on cooling deposits small crystals of argentic pyromucate.



In this way an atom of furfural, by combining with an atom of oxygen, becomes converted into pyromucic acid.

If furfural be mixed with a solution of ammonia in the cold, it is gradually converted into a solid, yellowish-white, insoluble mass, 3 molecules of furfural reacting upon 2 of ammonia, while 3 atoms of water are separated; $3 \text{C}_5\text{H}_4\text{O}_2 + 2 \text{H}_3\text{N} = \text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_3 + 3 \text{H}_2\text{O}$. This new compound belongs to the class of hydramides (1343); it has been termed *furfuramide*. Acids immediately decompose it; a salt of ammonium is formed, and the oil is set at liberty. When boiled with potash, however, no ammonia is evolved; the substance is completely dissolved, and the solution on cooling deposits long silky needles of a powerfully alkaline base which is isomeric with furfuramide (Fownes).

Furfuria, or *Furfurine* ($\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_3 = 268$), as this base has been named, is odorless and sparingly soluble in water; alcohol and ether dissolve it freely. It melts below 212° to an oily-looking liquid. It is dissolved by dilute acids, and completely neutralizes them; on adding ammonia to these solutions, the alkaloid is precipitated unchanged. Its salts have a bitter taste; they are said to have been used medicinally, with success, as substitutes for those of quinia (Gregory).

(1387) *Benzoline*, or *Amarine* ($\text{C}_{21}\text{H}_{15}\text{N}_2$).—When a solution of ammonia is allowed to remain for some days in contact with pure benzoyl hydride (essential oil of bitter almonds), a reaction occurs analogous to the foregoing one with furfural: the mixture gradually becomes converted into a crystalline mass of hydrobenzamide; this substance is soluble in alcohol, but insoluble in water. If boiled with a solution of potash it assumes the appearance of a resin, and becomes changed into *benzoline*, which is a base isomeric with hydrobenzamide. The same change occurs if hydrobenzamide be simply heated for some time to a temperature between 248° and 266° (120° and 130° C.). If the mass which is obtained by either of these methods be treated with boiling alcohol, it is dissolved, and the solution on cooling deposits the base in brilliant transparent four-sided prisms, which are fusible below 212° . Benzoline is nearly insoluble in

water, but it is readily dissolved by both alcohol and ether. Its salts, with the exception of the acetate, are sparingly soluble, and have an intensely bitter taste. When benzoline is submitted to destructive distillation, a new crystalline body, *pyrobenzoline* or *lophine* ($C_{21}H_{17}N_2$)? is formed, amongst other products.

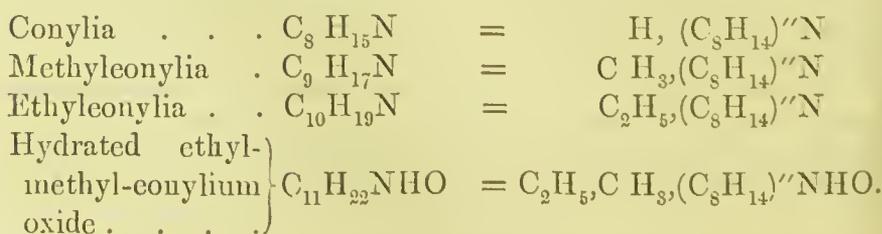
B. NATURAL BASES.

I. Volatile Oily Bases destitute of Oxygen.

The natural volatile bases may generally be extracted from the plant by digesting it in water slightly acidulated with sulphuric acid, adding to the decoction an excess of potash, and afterwards agitating with ether. The ether dissolves and separates the oily base, and on agitating this ethereal solution with water acidulated with sulphuric or hydrochloric acid, an aqueous solution of the salt of the organic base is obtained; by a second treatment of the solution with potash and ether, the base is obtained nearly pure.

(1388) *CONIA*, *Coniine*, or *Conylia* [$C_8H_{15}N = 125$; *Sp. gr.* of *liq.* 0.89; *Boil. pt.* $339^{\circ}.8$ (171° C.) Blyth], is the active principle of the hemlock (*Conium maculatum*); it pervades the whole plant, but is most easily procured from the seeds. As it is volatile, it is obtained by distilling hemlock seeds with water which contains a small quantity of potash in solution; conylia then passes over with the water in the form of a yellowish oil. When purified by redistillation, conylia is a colourless, transparent, volatile, oily liquid. It has a powerful, penetrating, most unpleasant and oppressive odour, like that of the fresh hemlock. A drop of it, when placed upon paper, produces a temporary greasy stain. It is soluble to some extent in water, but is much less so in hot than in cold water; ether and alcohol dissolve it freely. Its vapour is inflammable.

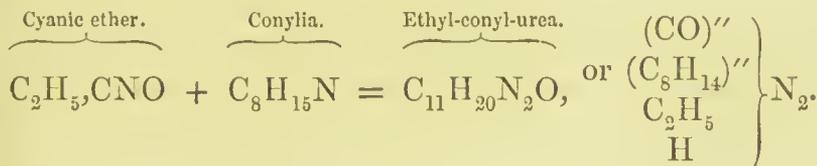
According to Kekulé and Planta there are two homologous varieties of conylia contained in the plant; viz., *conylia* ($C_8H_{15}N$), and *methylconylia* ($C_9H_{17}N$); when either of these bases is acted upon by iodide of ethyl or of methyl, new substitution bases are obtained, furnishing the following series of compounds:—



These experiments show that conylia contains the hydro-

carbon *conyl* (C_8H_{14}), but which has not yet been isolated, and that the alkaloid must be regarded as an imide or secondary base, from which ammonium bases may be procured.

When normal conylia ($C_8H_{15}N$) is exposed to the air, it absorbs oxygen rapidly: first becoming brown, and ultimately nearly solid. Conylia has a powerfully alkaline reaction; it neutralizes the acids perfectly, and precipitates many of the metallic oxides from their salts: in all its forms it is a most dangerous poison. Its salts crystallize with difficulty; if their solutions are evaporated in the air, they are decomposed, becoming red or violet in colour, and ultimately assuming a dark green or a blue tint. Strong sulphuric acid causes its compounds to become first of a purple-red colour, and then of an olive green. With nitric acid it gives a blood-red colour, fading into orange; butyric acid is one of the products of this reaction. Conylia unites with cyanic ether, and immediately forms a compound urea:—



Wertheim finds that hemlock contains, in addition to conylia, a small quantity of another base, *conhydrine* ($C_8H_{17}NO$; *Liebig's Annal.*, c. 328), which contains the elements of 1 atom more water than conylia, and which, by distillation with phosphoric anhydride, may be converted into conylia; the latter may be obtained from the phosphoric acid by treatment with potash. Conhydrine is much less poisonous than conylia. It may be sublimed in beautiful colourless needles, which are freely soluble in alcohol, and ether; it is strongly alkaline.

(1389) SPARTEIA ($C_{15}H_{26}N_2$); *Boil. pt.* $550^{\circ}.4$ ($288^{\circ} C.$).—In the *Spartium scoparium*, or common broom, Stenhouse discovered an oily base, to which he gave the name of *sparteine*. It possesses narcotic properties, is considerably heavier than water, and has a faint odour recalling that of aniline; when pure it is colourless, but it gradually becomes brown by exposure to the air. The experiments of Mills (*Journ. Chem. Soc.*, 1862, p. 1) have shown that sparteia is a tertiary diammonia or nitrile base ($C_{15}H_{26}$)^{vi} N_2 . With platonic chloride, and with corrosive sublimate, it forms double chlorides, which crystallize readily: but its other salts are obtained in crystals with difficulty. The hydrochlorate appears to undergo partial decomposition if boiled with excess of hydrochloric acid, and it emits an odour like that of mice. Both the base and its salts have an extremely bitter taste. The broom plant also furnishes a neutral, yellow, crystallizable principle, termed *scoparin* ($C_{10}H_{11}O_5$), to which its diuretic properties appear to be owing.

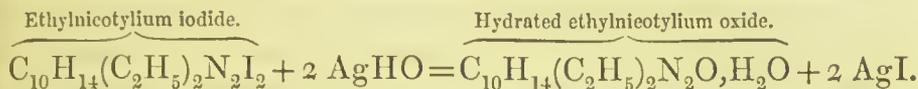
(1390) NICOTYLIA, or *Nicotine* [$(C_{10}H_{14})$ ^{vi} N_2 ; *Sp. gr. of liq.* 1.027 at $66^{\circ}.2$ ($19^{\circ} C.$); *of vap.* 5.607; *Rel. wt.* 81; *Boil. pt.* $480^{\circ}.2$ ($249^{\circ} C.$)].—This is another remarkable volatile base, which is destitute of oxygen. From the specific gravity of its vapour it is necessary to regard it as a diatomic base, the quantity

$C_{10}H_{14}N_2$, being equivalent to 2 volumes. It must therefore be formed upon the type of 2 atoms of ammonia, and it saturates 2 atoms of a monobasic acid. Nicotylia is the active principle of the tobacco plant (*Nicotiana tabacum*), in which it occurs in combination with malic and citric acids. It is also contained in the smoke of the burning leaves. Nicotylia is a limpid, colourless, oily liquid, with an extremely irritating and powerful odour of tobacco. It is very inflammable, and burns with a smoky flame. It may be distilled readily along with the vapours of water, or in a current of hydrogen gas; though its boiling point is as high as 480° . If exposed to the air it absorbs oxygen, becoming brown, and ultimately solid. Nicotylia is very soluble in water, and in the fixed oils; it is also soluble in all proportions in alcohol and in ether. Ether, if agitated with the aqueous solution, extracts the whole of the alkali; and the ethereal solution rises to the surface when the two liquids are left at rest. Nicotylia is extremely poisonous, a single drop of it being sufficient to kill a large dog. It exerts left-handed rotation on a polarized ray. Its solution forms a white precipitate in a solution of corrosive sublimate, as well as in one of plumbic acetate, and of both the chlorides of tin. The white precipitate which it occasions in solutions of the salts of zinc is soluble in excess of nicotylia. Cupric salts, with an excess of nicotylia yield a blue solution, like that which they furnish when supersaturated with ammonia.

Chlorine acts powerfully upon nicotylia, producing with it a blood-red liquid. Iodine forms with the alkali a crystallized combination [$C_{10}H_{14}N_2I_3$] which has a ruby-red colour: potash decomposes this compound, liberating pure nicotylia. The salts of nicotylia crystallize with difficulty: they are neutral, and are very soluble in water and in alcohol, but insoluble in ether, with the exception of the acetate. The proportion of this alkali varies greatly in different samples of tobacco. French tobacco contains 7 or 8 per cent.; Virginia 6 or 7 per cent.; and Maryland and Havannah, not more than 2 per cent., which is the proportion in ordinary snuff.

Nicotylia appears to belong to the class of diammonia tertiary or nitrile bases; the hydrocarbon *nicotyl* ($C_{10}H_{14}$)^{ri} which it contains, being equivalent in function to the 6 atoms of hydrogen in the 2 atoms of ammonia. This base enters into direct combination with ethyl iodide, and with methyl iodide; forming compounds which correspond to tetrethylum iodide; and when these compounds are treated with recently precipitated argentic

oxide, they yield a powerfully alkaline, inodorous, very bitter substance, which rapidly attracts carbonic acid from the air; for example:—



(Kekulé and Planta, Liebig's *Annal.*, lxxxvii. 1.)

The best process for preparing nicotylia is that employed by Schläesing. He evaporates the aqueous infusion of tobacco leaves to the consistence of syrup, and adds twice its volume of alcohol of sp. gr. 0.837. The liquid is thus separated into two layers; the upper one, which contains the salts of nicotylia, is decanted, concentrated by evaporation, mixed with a solution of potash, and agitated briskly with ether. The ether dissolves the liberated nicotylia and some fatty matters, and rises with them to the surface when the mixture is left at rest. In order to purify the alkali, powdered oxalic acid is added by degrees to the decanted ethereal solution. Nicotylia oxalate, being insoluble in ether, forms a dense syrupy layer at the bottom of the vessel. It is washed two or three times with pure ether; and the nicotylia is separated by the addition of a fresh quantity of solution of potash and ether. The ethereal solution is decanted into a retort, provided with the means of transmitting a current of dry hydrogen through it; the ether is then driven off, and the residue exposed for twenty-four hours to a temperature of 284° (140° C.), in order to expel the last traces of ammonia and ether; after which the temperature is raised to 356° (180° C.), when the nicotylia distils over in the current of hydrogen in a state of purity.

(1391) *Preparation of Snuff.*—A full account of this operation, as performed at the Imperial tobacco works in Paris, is given by Pelouze and Fremy (*Traité de Chimie*, 2nd ed., iv. 437). The following is an outline of the steps of the manufacture:—The stronger kinds of tobacco are those which are preferred for the preparation of snuff. The leaves are spread out in thin layers upon a stone pavement, and moistened with about a fifth of their weight of an aqueous solution of sodic chloride (sp. gr. 1.089). The moistened leaves are next cut into blocks, and are then piled up in large rectangular heaps, in quantities of 40 or 50 tons. These masses gradually enter into fermentation, and the temperature rises sometimes as high as 167° (75° C.), but usually it does not exceed 140° (60° C.). If the temperature be allowed to rise too high, some parts of the mass become black, as though they had been charred. Spring and autumn are the

seasons most favourable for the commencement of this operation, which requires careful watching to prevent the development of heat from becoming excessive. In about five or six months the temperature becomes stationary, or begins to decline; the heaps are then opened out, and the fermented mass is submitted to grinding. The pale brown and comparatively dry powder thus obtained is next mixed with about four-tenths of its weight of the solution of sodic chloride, and is passed through a sieve, to ensure a uniform moistening of the mass; after which it is packed in large oaken chests, capable of containing from 25 to 50 tons of the material. Here the snuff remains for nine or ten months, and undergoes a second fermentation, in the course of which the temperature in the centre of the mass rises to 122° or 131° (50° or 55° C.). During this process the snuff acquires its well-known dark colour, and the aroma is developed. The mass is, however, still far from uniform in quality throughout; it is therefore transferred to a second chest, in which operation all the different parts of the heap are thoroughly mixed together; after the lapse of two months, it is a second time turned over, and, sometimes, a third transfer is deemed requisite. When considered ripe, the contents of the various chests are mixed in a large room capable of containing 350 tons of snuff. Here it is left for about six weeks, to render the entire mass uniform in quality; and finally it is sifted into barrels for the market. The whole process of manufacture thus occupies from eighteen to twenty months. During the fermentation, about two-thirds of the nicotylia is destroyed. A small portion of this base appears to exist in snuff in the uncombined form; but the greater part of the portion still remaining is left in the form of acetate, a certain amount of acetic acid having become developed during the fermentation. A portion of the decomposed nicotylia undergoes conversion into carbonate of ammonium, which is partially retained by the snuff; and the gradual volatilization of this salt appears to favour the conversion of nicotylia into vapour, and thus to occasion the pungent odour for which snuff is valued. The proportion of citric and malic acids becomes diminished during the fermentation; so that ordinary snuff has an alkaline reaction. A certain quantity of a peculiar essential oil appears also to be developed during the operation; and to the variable proportion of this oil, much of the difference in the flavour of the several varieties of snuff is owing. The quantity of potassic nitrate which fresh tobacco contains, passes over, unaltered, into the snuff.

It may be remarked, that tobacco is one of the most exhausting crops which can be grown upon any soil, since it carries off an enormous amount of mineral constituents (the proportion of ash amounting to not less than 21 per cent. of the dry leaf). Among these constituents, nitric acid is found in quantity often exceeding 2 per cent. of the dry leaf; while the salts of potassium amount to more than a third of the saline residue.

It is probable that the active principle of henbane, or *Hyoscyamus niger*, is a volatile base, analogous to nicotylia; since a portion of some volatile base comes over when the plant is distilled with a solution of potash. Much of the alkaloid, however, is decomposed in this operation: its composition has not been determined.

2. Bases which contain Oxygen.

(a) Alkaloids of the Cinchonas.

(1392) In the bark of the different varieties of *Cinchona*, several well-characterized and important bases occur. They are all closely related to each other in composition, and are found in the bark in combination chiefly with quinic and quinotannic acids. The most abundant of these bodies are *cinchonina* and *quinina*, each of which is accompanied by, or is convertible into, two isomeric bases, termed respectively, *cinchonidine* and *cinchonine*, *quinidine* and *quinicine*. Besides these, a base termed *aricine*, or *cinchovatine*, has been found in the bark of *Cinchona ovata*. Both *cinchonina* and *quinina* form two classes of salts; one class of which has been regarded, until quite recently, as being basic, whilst the other was supposed to be normal: the common medicinal sulphate of *quinina*, for example, was viewed as the basic sulphate. Streeker has, however, shown that the formula of the base must be doubled, in which case this salt will be normal, whilst that formerly regarded as normal must be an acid salt. The salts which these bases form with the smaller proportion of acid are very sparingly soluble in water, but are readily dissolved on the addition of any free acid.

Quinia and *cinchonina*, as well as *cinchonidine*, appear to belong to Hofmann's class of nitrile bases; since, when treated with iodide of methyl, or of ethyl, they yield bases of the ammonium type. Hydrated *ethylquinium* oxide $[(C_{20}H_{24}N_2O_2)_2, (C_2H_5, HO)]$ is a powerful base, which attracts carbonic acid from the air: the *methylquinium* iodide consists of $(C_{20}H_{24}N_2O_2)CH_3I$. The iodide of the corresponding methylic derivatives of the metameric *cinchonina* and *cinchonidine* consists of $(C_{20}H_{24}N_2O)CH_3I$.

Induced by these and other circumstances, Strecker doubles the old formula of these alkaloids, representing quinia as $C_{20}H_{24}N_2O_2$.

Cinchonia and quinia, with their isomerides, are decomposed when distilled with caustic potash. Several volatile bases are formed, amongst which quinoline (1372) is the most abundant; and potassic formiate is left in the retort.

Cinchonia and its isomeric congeners are most abundant in the pale Peruvian bark, *Cinchona condaminea*. Quinia and its isomeric companions occur most abundantly in the yellow bark, or *C. calisaya*; whilst the red bark, *C. succirubra*, contains both classes of alkaloids.

Quinia, from its febrifuge and antiperiodic powers, is the most highly esteemed of these alkaloids for medicinal purposes; though it appears that quinidine possesses similar therapeutic virtues to a nearly equal extent.

(1393) 1. CINCHONIA [$C_{20}H_{24}N_2O = 308$; *Fusing pt.* 329° (165° C.)] crystallizes in large quadrilateral prisms, which are anhydrous; it is less soluble in alcohol than quinia, and is insoluble in ether. Cinchonia is dissolved by solutions of the alkalies and alkaline bicarbonates. At 329° it fuses to a colourless liquid, which becomes a crystalline mass on cooling; when heated further it is partially volatilized; but a portion at the same time undergoes decomposition. It may be sublimed readily in an atmosphere of hydrogen. Its salts are intensely bitter; they are precipitated by infusion of galls, as well as by solutions of the oxalates, tartrates, and gallates. Two atoms of the hydrogen in cinchonia admit of displacement by chlorine, and by bromine; the new compounds thus obtained retain basic powers.

Cinchonia sulphate [$(C_{20}H_{24}N_2O)_2H_2SO_4, 2H_2O = 714 + 36$] crystallizes in irregular prisms, which melt, like wax, at a little beyond 212° ; when gently heated it emits a phosphorescent light. If it be first moistened with water acidulated with sulphuric acid, it may be kept in a fused condition for some hours; during which time it gradually passes into cinchonine sulphate (Pasteur). If heated more strongly it is converted into a resinous mass of a beautiful red colour. The *acid sulphate* ($C_{20}H_{24}N_2O, H_2SO_4, 3H_2O$) is very soluble both in water and in alcohol; it crystallizes from a hot solution, in large, well-defined, rhombic octahedra. When cinchonia is dissolved in sulphuric acid, and heated with lead dioxide, it produces a red-coloured compound; when mixed with chlorine water and afterwards with ammonia, no green tint is produced, as occurs when quinia is similarly treated. Its salts

are generally more soluble both in alcohol and in water than those of quinia.

2. *Cinchonidine* ($C_{20}H_{24}N_2O$); *Fusing pt.* 347° (175° C.).—This alkali, which is isomeric with cinchonia, occurs naturally in certain varieties of cinchona bark; and may be obtained by the spontaneous evaporation of its alcoholic solution, in hard, brilliant, striated, rhomboidal prisms, which are anhydrous, and insoluble in ether. Its solution in absolute alcohol produces left-handed rotation upon a polarized ray; whilst cinchonia produces rotation to the right. Cinchonidine fuses at 347° , and at a higher temperature is decomposed, emitting an odour of oil of bitter almonds.

When the solutions of the salts of this base are mixed with the caustic alkalis, or with the carbonates or bicarbonates of these bases, they give a white precipitate of cinchonidine, which gradually becomes crystalline. Hydric disodic phosphate, corrosive sublimate, argentic nitrate, and ammoniac sulphocyanide, also give white precipitates in solutions of salts of cinchonidine. At a high temperature, the salts of cinchonidine pass into those of cinchonicine. *Cinchonidine sulphate* [$(C_{20}H_{24}N_2O)_2H_2SO_4$] crystallizes in stellate groups of silky needles, the solution of which is neutral to test papers. The hydrochlorate crystallizes in large, brilliant, rhomboidal prisms, soluble in about twenty-seven parts of water.

3. *Cinchonicine* is a third base, which has the same composition as the two foregoing ones. It is precipitated from its salts in the form of a resinous mass, which is freely soluble in alcohol. This solution causes right-handed rotation of a ray of polarized light. Cinchonicine is best prepared by the action of heat upon cinchonia sulphate, in the manner already mentioned.

(1394) 4. QUINIA ($C_{20}H_{24}N_2O_2, 3H_2O = 324 + 54$; Regnault), is most abundant in the yellow bark (*Cinchona calisaya*), in which it occurs mixed with cinchonia, and combined with quinic and quinotannic acids. The quantity of the alkaloids varies in different specimens of bark, but the two together generally amount to 3.5 or 4 per cent. In order to extract the bases, the pulverized bark is boiled with 8 or 10 times its weight of water acidulated with 1 per cent. of oil of vitriol, or with 2 per cent. of hydrochloric acid. The liquid is strained through a cloth, and the residue is boiled twice with acidulated water. When the strained liquors are cold, milk of lime, or sodic carbonate, is added in slight excess; the precipitate is submitted to pressure, and then treated with hot alcohol. If the proportion of cinchonia be considerable, it crystallizes as the liquid cools; and a fresh quantity is obtained by distilling off one-half of the alcohol from the residue, while the quinia remains in solution: the liquid is then neutralized with sulphuric acid. The separation of the two bases is afterwards completed by crystallizing the mixed sulphates from a slightly acid solution; quinia sulphate being much the less soluble of the two, crystallizes first. The quinia is then thrown down from its sulphate by adding ammonia. Cinchonia and cinchonidine may also be separated from quinia by means of ether, which dissolves the quinia, and leaves the cinchonia and cinchonidine.

Quinia may be obtained in crystals, though with some difficulty, by allowing its alcoholic solution to evaporate spontaneously in a cool place: silky needles are thus formed; they are dissolved much more readily by cold alcohol than the crystals of cinchonia. Quinia requires about 350 parts of water for its solution. By a heat of 240° ($115^{\circ}.5$ C.), 3 atoms of water are expelled, and at a little above this point the alkali fuses into a resinoid mass, which may be distilled in great part without decomposition. Quinia is also soluble both in the essential and in the fixed oils.

Quinia yields crystallizable salts; but when these salts are exposed in solution to a strong light, or when they are treated with an excess of acid, they pass into a resinoid amorphous condition, and constitute the principal part of the substance met with in the shops as *quinoidine*, which is also contained abundantly in the mother-liquors from which the salts of quinia have been crystallized. The employment of an excess of acid in extracting the alkali from the bark should be avoided, since it appears to increase the formation of this uncrystallizable substance. Quinoidine is a mixture of several basic compounds, among which are all the alkaloids of the cinchona bark. In some instances as much as 50 or 60 per cent. of crystallized quinidine has been extracted from it by treatment with ether. Pasteur considers that the production of quinoidine might be greatly diminished if more care were taken in drying the bark upon the spot where it is collected. Exposure to the sun's rays should be avoided, for it is found that direct sunlight has a remarkable influence in producing the change of the crystallizable alkaloids into the uncrystallizable form.

The salts of quinia have an intensely bitter taste; they give abundant precipitates with tincture of galls, with mercuric and with argentic nitrate,—also with gallic, tartaric, and oxalic acids, and their salts. If quinia be suspended in water, and chlorine be transmitted through the liquid, the alkali is dissolved, and the solution passes successively through various shades of rose, violet, and dark red. The following reaction is regarded as characteristic of quinia and its metamerides: when freshly prepared chlorine water is poured into a solution of one of the salts of this alkali, and then a few drops of solution of ammonia are added, a green colour is produced.

The presence of cinchonia in the salts of quinia may be detected in several ways; one of the best is that proposed by Liebig: 15 grains (1 grm.) of sulphate, or other salt of quinia

suspected to be impure, are placed in a test tube with 3 drachms (6 cub. centim.) of washed ether, and 30 drops (2 e. e.) of a solution of caustic ammonia are added. The mixture is briskly shaken, and, on standing, it separates into two layers, the upper one consisting of an ethereal solution of quinia, the lower one of an aqueous solution of ammoniac sulphate; the cinchonia being insoluble in either liquid floats upon the surface of the watery layer. The fraudulent admixture of salicin with the salts of quinia is detected by the addition of a few drops of oil of vitriol to the salt; if salicin be present it gives a red colour to the mixture.

Quinia sulphate, formerly supposed to be the *basic sulphate* $[(C_{20}H_{24}N_2O_2)_3H_2SO_4, 7H_2O = 746 + 126]$, is the salt employed in medicine: it crystallizes in snow-white, very light, bulky, efflorescent needles, which are sparingly soluble in water, but abundantly so in dilute sulphuric acid and in alcohol. The acidulated solution shows the phenomenon of fluorescence (110) in a striking manner. Quinia sulphate fuses easily on the application of heat, and emits a phosphorescent light. An *acid sulphate* $(C_{20}H_{24}N_2O_2, H_2SO_4, 7H_2O)$ may be obtained by dissolving the foregoing salt in sulphuric acid, and concentrating the liquid; it crystallizes in small needles, which are freely soluble in water and in alcohol.

A remarkable compound of iodine and quinia sulphate $(C_{20}H_{24}N_2O_2I_2, H_2SO_4, 5H_2O)$ has been described by Dr. Herapath. It may be obtained by dissolving the acid quinia sulphate in concentrated acetic acid, and adding to the heated liquid an alcoholic solution of iodine, drop by drop. After standing for a few hours, the salt is deposited in large flat rectangular plates, which when seen by reflected light are of a brilliant green colour, with a metallic lustre, like the wing-cases of the blistering beetle. When viewed by transmitted light they appear to be of a pale olive tint, but the light so transmitted is perfectly polarized; so that if a second plate cross the first at right angles, the whole of the light is as completely arrested by the overlapping portions, as it would be by two overlapping plates of tourmaline, the axes of which cross each other at right angles (119).

Quinia passes unchanged into the urine, and may readily be detected in this excretion from patients to whom it has been freely administered.

When a solution of quinia sulphate is boiled with one of potassic nitrite, nitrogen is evolved, and the liquid when mixed with ammonia deposits a white crystalline hydrate of a new base, *oxyquinia*, which, when dried at 302° (150° C.),

consists of $C_{20}H_{24}N_2O_3$; (Schutzenberger). It is much less bitter than quinia, and is fusible into a resinoid mass.

5. *Quinidine* [$C_{20}H_{24}N_2O_2, 2 H_2O$; *Fusing pt.* 320° (160° C.)] is a base isomeric with quinia. It is extracted from quinoidine by treatment with ether. The ethereal solution if left to spontaneous evaporation crystallizes with facility, in long rhombic efflorescent prisms. The solution of quinidine in absolute alcohol produces right-handed rotation of a polarized ray (Pasteur), whilst a similar solution of quinia produces rotation to the left (Bouchardat). Quinidine is much less soluble in water than quinia, for it requires about 1500 parts of cold water for solution; but it is much more soluble in ether than quinia. When heated, it loses its water of crystallization, and fuses at 320° . The acid quinidine sulphate is much less soluble than the corresponding salt of quinia; whilst the oxalate is freely soluble in water, and may thus be separated from the oxalate of quinia, which is sparingly soluble. Chlorine and ammonia produce a green coloration with the salts of quinidine, similar to that which they occasion with those of quinia.

6. *Quinicine* is produced by the action of heat upon the salts of quinia and quinidine. It is precipitated by alkalis in the form of a fluid resinoid mass, which combines readily with acids, and forms bitter uncrystallizable salts, endued with febrifuge properties. These salts are metameric with those of quinia. Quinicine is freely soluble in alcohol: the solution produces right-handed rotation of a ray of polarized light.

The relation of the cinchona alkalics to polarized light is remarkable, and may thus be exhibited:—

| | | |
|--------------|----------|----------------------------------|
| Quinia | produces | a powerful left-handed rotation, |
| Quinidine | ,, | a powerful right-handed ,, |
| Quinicine | ,, | a feeble right-handed ,, |
| Cinchonia | ,, | a powerful right-handed ,, |
| Cinchonidine | ,, | a powerful left-handed ,, |
| Cinchonicine | ,, | a feeble right-handed ,, |

Pasteur considers that quinia and cinchonidine each contain two active groups, one of which produces strong left-handed rotation, the other produces a feeble right-handed rotation. He also regards quinidine and cinchonia as each consisting of two groups; one of which exerts a powerful right-handed rotation, and the other a feeble left-handed rotation; and he supposes that in each of these bases, by the agency of heat, the more powerful group is rendered inert, whilst the weaker one remains unmodified, thus occasioning the effects observed in quinicine and cinchonicine.

7. *Aricine*, or *Cinchovatine* ($C_{25}H_{27}N_2O_4$; Manzini); *Fusing pt.* $370^\circ.4$ (188° C.).—This base is less abundant than the two alkalies just described. It has been found in a white variety of cinchona bark, and has been but incompletely examined. Aricine crystallizes in white needles, which are fusible, but not volatile: it is soluble in ether; with nitric acid it strikes an intense and characteristic green colour.

(b) *Alkaloids contained in Opium.*

(1395) *OPIMUM*, the inspissated milky juice of the *Papaveraceæ*, is a very complicated substance, the composition of which varies greatly even when it is not adulterated, as it often is very largely. Genuine Smyrna opium is the best variety, since it contains the largest proportion of morphia. The following constituents, with the exception of opianine, have been ascertained to exist in most kinds of opium:—

| | | | |
|---|---------------------------|----------------------|-------------------------------|
| | Meconic acid | $H_3 C_7 HO_7$, 3 | H_2O from 6 to 8 per cent. |
| { | 1. Morphia | $C_{17}H_{19}NO_3$, | H_2O from 6 to 12 per cent. |
| | 2. Codeia | $C_{18}H_{21}NO_3$, | H_2O less than 1 per cent. |
| | 3. Thebaia | $C_{19}H_{21}NO_3$ | ditto. |
| | 4. Papaverine | $C_{20}H_{21}NO_4$ | ditto. |
| | 5. Opianine | $C_{21}H_{21}NO_7$? | (from Egyptian opium). |
| | 6. Narcotine | $C_{22}H_{23}NO_7$ | from 6 to 8 per cent. |
| | 7. Narceia | $C_{23}H_{29}NO_9$ | |
| | 8. Cryptopia | $C_{23}H_{25}NO_5$ | |
| | Meconine | $C_{10}H_{10} O_4$ | |
| | Resinous matter | | |
| | Caoutchouc | | 4 or 5 per cent. |
| | Essential oil | | |
| | Mucilage or gum | | |

Many of the opium bases exhibit a very intimate relation to each other, although as yet the efforts of the chemist to transform them one into the other have met with limited success. Morphia, it will be observed, differs from codeia in containing one atom less of the hydrocarbon (CH_2), although the two bases do not exhibit the close resemblance usually observed between the contiguous members of a homologous series. Even if the relation were not one of ordinary homology, the action of methyl iodide upon morphia might cause the production of codeia, just as dimethylia is produced from methylia by similar treatment; but, instead of this, the action of methyl iodide upon morphia is attended with the formation of a new base of the ammonium class. Thebaia contains one atom more of carbon than codeia, and papaverine one atom more of carbonic oxide than thebaia, whilst opianine, if Gerhardt's interpretation of the results of Hinterberger be admitted, contains one atom of carbon and three of oxygen more than papaverine. Its composition corresponds with that of one of Matthiessen's new bases from narcotine. Opianine has hitherto only been found in Egyptian opium, and has been but imperfectly examined.

The opium alkalies, morphia, codeia, and papaverine, combine readily with iodine, and form crystallizable compounds containing three atoms of iodine to each atom of the alkali. Codeia also

unites with two atoms of cyanogen, and forms a new and distinct base, *cyanocodeia*. True substitution-compounds may also be obtained from codeia with the halogens, and with nitric acid, in which case one or more atoms of hydrogen are displaced by a corresponding number of atoms of chlorine, of bromine, or of nitroxyl (NO_2).

(1396) *Isolation of the Components of Opium*.—The separation of the opium bases from each other is a matter of considerable difficulty, and can only be performed satisfactorily when large masses of opium are acted upon. The following is an outline of the method to be adopted,—the morphia being first obtained by the process of Robertson and Gregory, and the mother-liquors being afterwards treated for the other alkalies upon Anderson's plan (*Trans. Roy. Soc. Ed.*, xx. 57, 347, and xxi. 204):—

1. *Meconic Acid*.—An aqueous infusion of opium is prepared by mixing several pounds of the drug with three times its weight of water, straining the solution through linen, and treating the residue two or three times with fresh portions of water. An acid liquid is thus obtained, which is to be concentrated by evaporation, and mixed with sufficient chalk to render it neutral; a solution of calcic chloride free from iron, containing a quantity of this salt equal to about one-twentieth of the weight of the opium employed, is then to be added. The precipitate which is thus occasioned consists of calcic meconate (1328), and must be separated by filtration.

2. *Narcotine*.—A large amount of narcotine remains in the portion of opium which is not soluble in water; it can be extracted by adding acetic acid to the mass, precipitating the filtered liquid by the addition of ammonia, and purifying the crude narcotine by digesting its solution in alcohol with animal charcoal, and re-crystallizing.

3. *Morphia*.—The clear liquor filtered from the calcic meconate is evaporated till it acquires the consistence of a thin syrup. On cooling, it becomes semi-solid, from the formation of crystals of morphia hydrochlorate; this salt may be purified by re-crystallization, after the strongly-coloured mother-liquor has been separated from it by pressure.

4. *Codeia*.—On further concentrating the mother-liquors from the morphia hydrochlorate, a fresh crop of crystals is separated, which consists of a mixture of the hydrochlorates of morphia and codeia. If this be dissolved in hot water, and supersaturated with ammonia, the morphia is precipitated, while codeia remains in solution, mixed with ammonia hydrochlorate. The hot aqueous solution is concentrated by evaporation, and, on the addition of

potash, the codeia is separated, partly in the form of an oil which gradually becomes solid, and partly in crystals which are deposited as the liquid cools.

The black mother-liquor from which the hydrochlorates of morphia and codeia have been separated, contains the whole of the remaining bases. It is to be diluted with water, and filtered from flocculi of resinous matter which are thus got rid of, and ammonia is then to be added so long as a precipitate is occasioned. This precipitate (A) contains a large proportion of narcotine and of resin, with small quantities of thebaia and papaverine. The filtrate (B) contains narceia and meconine.

5. *Narceia*.—To the filtered liquid (B) a solution of plumbic acetate is added, so long as it occasions a precipitate; a dirty brown colouring matter is thus thrown down, and is to be separated by filtration through a cloth; the excess of lead is to be removed by sulphuretted hydrogen, and the filtered liquid concentrated by evaporation to a syrup, which, on standing, becomes filled with voluminous silky crystals of narceia: these may be purified by a second crystallization.

6. *Meconine*.—The mother-liquor from the narceia is agitated with a fourth of its bulk of ether, and the ethereal solution is decanted; this process is repeated upon the aqueous portion, with fresh portions of ether, so long as the ether becomes coloured. The ethereal solutions are submitted to distillation, and, on the addition of water to the residuc, a resinoid substance is separated, from which hydrochloric acid extracts a portion of papaverine. The undissolved portion, when crystallized from its solution in boiling water, yields needles of meconine.

7. *Additional quantity of Narcotine*.—The precipitate (A) which was separated by ammonia from the mother-liquors of the morphia and codeia, is at first granular, but if left in the press it soon concretes into a resinoid mass; in order to prevent this agglomeration, it must without delay be broken up and diffused through water, strained, again pressed, and the washings repeated until they run off nearly colourless. A portion of the precipitate is then boiled with rectified spirit, and the liquid filtered while hot; crystals of narcotine are deposited as it cools. The spirituous solution is then boiled with a fresh portion of the precipitate, and the same process is repeated until the whole of the precipitate has been so treated; the narcotine obtained in this manner can be added to that already procured from the undissolved mass (2).

8. *Thebaia*.—The spirituous mother-liquor from which the

narcotine has crystallized, now contains resinous matter, besides still retaining some narcotine, and nearly all the papaverine and thebaia. The alcohol is distilled off, the bases are separated from the dark brown residuc by means of acetic acid, and the solution thus obtained is decanted from the undissolved portion. On adding an excess of basic plumbic acetate to the acetic solution, the whole of the papaverine, narcotine, and resin are precipitated. The excess of lead is next removed from the supernatant liquid, by the addition of sulphuric acid, and filtration; and, on then adding a slight excess of ammonia, impure thebaia is thrown down: it is purified by digestion with animal charcoal, and re-crystallization from alcohol.

9. *Papaverine*.—The greater part of the papaverine is contained in the precipitate which is separated from the acetic solution of thebaia by basic plumbic acetate. In order to isolate it, the precipitate is reduced to a fine powder, and boiled with alcohol. The alcohol is distilled off, and the dark brown residue is treated with dilute hydrochloric acid, and filtered from undissolved resin: the solution is then concentrated, and left to spontaneous evaporation; crystals of papaverine hydrochlorate are thus gradually formed, whilst the accompanying narcotine is retained in solution.

One of the greatest difficulties in the purification of the opium bases upon a small scale, arises from the presence of a peculiar resin in the drug; which, though not possessing the properties either of an acid or of a base, is readily soluble in dilute acids, and in solutions of potash, but sparingly so in ammonia. It is also soluble in alcohol, but insoluble in ether. It is fusible at a temperature considerably below that of boiling water. Aqueous solutions of opium contain it in considerable quantity, probably owing to the free acid which is present in the drug. On the addition of ammonia it is precipitated with the morphia and other bases; and, if the solution be heated, the resin fuses; thus occasioning the entire precipitate to agglomerate into a resinoid mass, which assumes the form of a brittle solid on cooling.

(1397) 1. MORPHIA ($C_{17}H_{19}NO_3, H_2O = 285 + 18$).—This base occurs in combination with meconic, and, sometimes, with sulphuric acid. It appears to be the principal sedative constituent of opium, of which it constitutes from one-seventh to one-sixteenth by weight. In large doses it acts as a powerful narcotic poison.

Properties.—Morphia (so called from Morpheus, in allusion to

its narcotic properties) crystallizes in short, rectangular prisms, with $1\text{H}_2\text{O}$. At a gentle heat the water is expelled, and the alkali melts into a resinoid substance, which solidifies into a radiated crystalline mass on cooling: by a higher heat it is partially sublimed, but most of it is decomposed. Morphia is soluble in about 1000 times its weight of cold, and in 400 of boiling water; the solution has a bitter taste, and changes the yellow colour of turmeric paper to brown. Boiling alcohol dissolves it abundantly, but it is insoluble in ether and in chloroform. Its alcoholic solution exerts a powerful rotation to the left upon a ray of polarized light. The fixed alkalies and alkaline earths dissolve morphia without change, and deposit it in crystals, as the solutions by exposure to the atmosphere absorb carbonic acid. Ammonia dissolves it more sparingly. Concentrated nitric acid, when applied to a crystal either of morphia or of one of its salts, produces a lemon yellow or orange colour; and, ultimately, oxalic acid is formed. A mixture of nitric and sulphuric acids colours morphia green. When morphia is mixed with iodic, or with periodic acid, iodine is liberated, which may be recognized by its brown colour, and by the blue which it yields on the addition of a solution of starch. A neutral solution of ferric chloride strikes with morphia a very characteristic blue colour, which is destroyed by an excess of acid. The salts of morphia give no precipitate with the gallates, but a copious curdy one with tannic acid and its salts. When morphia is heated to 401° (205°C .) with caustic potash, an alkaline liquid distils over, containing ethylia. The salts of morphia crystallize readily; they are very soluble in water, and in alcohol, but are not soluble in ether. They have a bitter, disagreeable taste. If their solution be mixed with tartaric acid, and supersaturated with hydric-sodic carbonate (NaHCO_3), no precipitate is formed.

Morphia appears to belong to the class of nitrile bases: since, when treated with iodide of ethyl, or of methyl, it yields salts of *ethylmorphium*, or of *methylmorphium*, corresponding to those of ammonium. Methylmorphium iodide has the composition $[\text{C}_{17}\text{H}_{19}(\text{CH}_3)\text{NO}_3, \text{I}, \text{H}_2\text{O}]$ (How).

Matthiessen and Wright have recently obtained a remarkable base from morphia, possessed of powerful emetic properties. One-tenth of a grain of the hydrochlorate of this base, if injected under the skin, produces vomiting in the course of from 4 to 10 minutes.

Apomorphia, ($\text{C}_{17}\text{H}_{17}\text{NO}_2$) as the base has been termed, contains the elements of H_2O less than morphia. It is easily procured by heating morphia with an excess of hydrochloric acid to 302° (150°C .) in a sealed tube for about 3 hours:—



Apomorphia in its reactions differs materially from morphia. With ferric chloride it gives a dark purple-anethyst coloration; with nitric acid a brucia red; with potassic dichromate and sulphuric acid a strychnia red.

Apomorphia itself is amorphous, but forms a crystalline hydrochlorate, $C_{17}H_{19}NO_3 \cdot HCl$. The base is somewhat soluble in ether and in water, more so in alcohol and in chloroform. (*Proc. Roy. Soc.* 1869).

Extraction of Morphia.—Several methods are in use for extracting morphia from opium. On the large scale, Robertson's process, as modified by Gregory, and already described, is generally adopted. One of the simplest and best plans, if the operation be upon a small scale, is that proposed by Mohr; it is founded on the solubility of morphia in lime water, and the insolubility of the other bases in this liquid:—Each pound of opium is digested in 3lb. of water, and boiled, and the liquid expressed from the undissolved portion, which is twice similarly treated; $\frac{1}{4}$ lb. of lime is boiled with 2lb. of water, and the mixed opium infusions are added, in small quantities at a time, to the milk of lime, which is kept boiling; the liquid is filtered from the residue containing undissolved lime, and the other opium alkalies: this residue is twice boiled up with fresh water. The filtered liquids are mixed, and evaporated down to two pints, again filtered, heated to boiling, and one ounce of powdered sal-ammoniac is added. By this means the lime is neutralized, and the ammonia, as it is liberated, is volatilized at the high temperature employed: morphia is precipitated immediately, and increases in quantity as the liquid cools. The morphia thus obtained is of a deep brown colour. It is, therefore, re-dissolved in hydrochloric acid, again treated with milk of lime, and a second time precipitated by sal-ammoniac. The alkaloid, if the solution be dilute, is now deposited in beautiful crystals.

The *Hydrochlorate* ($C_{17}H_{19}NO_3 \cdot HCl, 3 H_2O = 321.5 + 54$) is the most important salt of morphia; it crystallizes in silky needles, and is readily soluble in water, especially if it contain a little free hydrochloric acid. It is also dissolved freely by alcohol. The *Acetate* was formerly a good deal used in medicine, but it has the disadvantage of being slightly deliquescent, and of losing acid when its aqueous solution is evaporated. The *Sulphate* [$(C_{17}H_{19}NO_3)_2 H_2SO_4, 5 H_2O$] crystallizes in tufts of colourless prisms. The *Citrate* is said to form the basis of the sedative medicine known under the name of the *Black drop*.

(1398) 2. CODEIA ($C_{18}H_{21}NO_3, H_2O = 299 + 18$; Anderson); *Fusing pt.* 302° (150° C.).—Codeia (from $\kappa\acute{o}\delta\eta$, a poppy-head) appears, like morphia, to be one of the nitrile bases; since, when treated with ethyl iodide, and then with argentic oxide, it yields

a powerful alkaline base of the ammonium class. It is contained in opium only in small proportion, for it does not amount to more than from one-fifteenth to one-thirtieth of the quantity of morphia. It has a powerfully alkaline reaction, and is remarkable as being soluble in 80 parts of cold, and in 17 of boiling water: this solution throws down the oxides of lead, copper, iron, and several other metals, from a solution of their salts. If codeia be boiled with less water than is necessary for its solution, it melts beneath the liquid to an oily-looking fluid. Codeia crystallizes from its aqueous solution in bold rhombic octahedra. If heated alone, its hydrated crystals lose $1 \text{H}_2\text{O}$, and undergo fusion at 302° . Both ether and alcohol dissolve codeia freely: the ethereal solution, by spontaneous evaporation, yields fine anhydrous prisms of the alkali. Its solutions exert left-handed rotation on a ray of polarized light.

The caustic alkalis dissolve it but very sparingly: when distilled with potash, codeia yields ammonia, methyllia, tritylia, and some other compounds still higher in this series of alcohol bases. The salts of codeia are practically unimportant: they have been carefully examined by Anderson, and they appear to have a powerful narcotic action when taken medicinally: they are not turned red by nitric acid, nor blue by ferric chloride, but are precipitated by infusion of galls. The hydrochlorate crystallizes with great facility.

By acting upon codeia with hydrochloric acid Matthiessen and Wright have obtained a base which corresponds in all its properties to apomorphia; $\text{C}_{13}\text{H}_{21}\text{NO}_3, \text{HCl} + \text{HCl} = \text{C}_{17}\text{H}_{17}\text{NO}_2, \text{HCl} + \text{CH}_3\text{Cl} + \text{H}_2\text{O}$. (*Proc. Roy. Soc.* 1869).

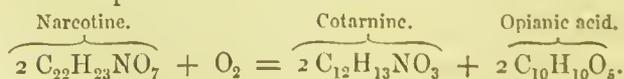
3. *Thebaia*, or *Paramorphia* ($\text{C}_{19}\text{H}_{21}\text{NO}_3$); *Fusing pt.* 257° (125°C).—This alkali crystallizes from its solution in alcohol or in ether, in square plates of silvery lustre, which have a styptic, acrid taste. It is poisonous when taken internally, and is said to produce tetanic symptoms, resembling those occasioned by strychnia. Thebaia is insoluble in alkaline liquids: concentrated sulphuric acid colours it of a deep red: its salts do not crystallize readily.

4. *Papaverine* ($\text{C}_{20}\text{H}_{21}\text{NO}_4$; Merck) is distinguished from the other opium bases except cryptopia by giving with concentrated sulphuric acid a deep blue colour. It is sparingly soluble in cold alcohol, and is deposited from a hot alcoholic solution in small confused crystals. It does not appear to exert any powerful effect upon the animal economy when taken internally.

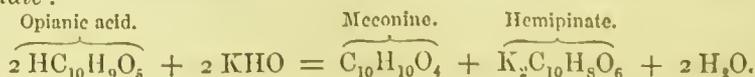
(1399) 5. *Narcotine* ($\text{C}_{22}\text{H}_{23}\text{NO}_7 = 413$; Matthiessen and Foster); *Fusing pt.* $339^\circ.8$ (171°C).—The quantity of narcotine in opium varies from 6 to 8 per cent.: this body can hardly be said to possess alkaline properties. It is nearly insoluble in water, but is freely soluble in alcohol, and still more so in ether and in chloroform; its ethereal solution, by spontaneous evaporation, yields it crystallized in acicular groups, or in colourless, brilliant right rhombic prisms; these crystals are soluble in the fatty and essential oils, but are insoluble in the caustic alkalis. Solutions of narcotine exert a powerful left-handed rotation upon polarized light: when the solution is acidulated, this rotatory

power is reversed, and becomes right-handed. At 340° narcotine fuses, and loses water, and by a higher temperature it is decomposed. Acids dissolve it freely, but the solutions are decomposed by the addition of a large bulk of water: they are precipitated of a bright yellow on the addition of infusion of galls. A mixture of concentrated sulphuric and nitric acids produces a blood-red colour with narcotine and its compounds. Narcotine is less active as a poison than morphia; but, when administered to a dog in a dose of 23 grains, it speedily produced death. The salts of narcotine have a more bitter taste than those of morphia: the chloride and acetate crystallize with difficulty: most of its other salts form gummy compounds, which do not crystallize. The double salts with platinum chloride and auric chloride are, however, easily procured in crystalline scales. Narcotine is contained largely in the portion of opium which remains undissolved when treated with water. If this residue be digested with acetic acid, and the solution be supersaturated with ammonia, narcotine mixed with colouring matter is thrown down: it may afterwards be purified by solution in alcohol, and treatment with animal charcoal. If any of the acid solutions of narcotine be saturated with sodic chloride, the liquid becomes turbid, and the narcotine is deposited, in the course of a few days, in crystalline masses. This property has sometimes been taken advantage of, in the separation of narcotine from morphia. When narcotine is distilled with concentrated hydriodic acid it yields rather more than its own weight of methyl iodide, or 3 atoms of the iodide for each atom of narcotine. This is indeed a convenient mode of procuring methyl iodide (Matthiessen and Foster).

Narcotine, under the oxidizing influence of platinum chloride, or of sulphuric acid and manganese dioxide, is decomposed, and gives rise to some very remarkable compounds (Wöhler, *Liebig's Annal.* l. 1; Blyth, *ib.* p. 29; Anderson, *Trans. Roy. Soc. Edin.* xx. 359). It appears to split up into a new base, termed *cotarnine* (this name being simply a transposition of the syllables of the word narcotine), and into opianic acid, or into products which are the result of the decomposition of opianic acid:—



If the oxidation be more energetic, the cotarnine is broken up into ethylia and *apophyllie acid* ($\text{H}_2\text{C}_{16}\text{H}_{13}\text{N}_2\text{O}_9$?), the latter name being given in consequence of its resemblance in appearance to the pearly crystals of the mineral apophyllite. Opianic acid when treated with potash ley yields *meconine* and potassic *hemipinate*:—

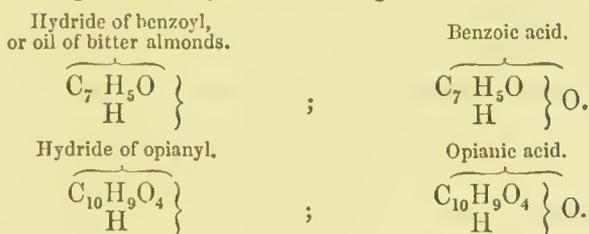


Cotarnine contains all the nitrogen of the narcotine. It forms fusible aci-

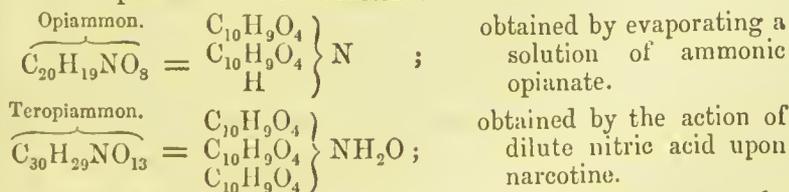
ular crystals, which are sparingly dissolved by water, or by a solution of potash: but they are freely soluble in alcohol, ether, and solution of ammonia. Cotarnine is readily obtained by boiling a solution of narcotine in hydrochloric acid, with platinic chloride: the liquid becomes of a blood-red colour, and red crystals of the double salt platinic chloride and cotarnine hydrochlorate $[(C_{12}H_{13}NO_3 \cdot HCl)_2PtCl_4]$ are deposited: the base is easily procured by decomposing the salt with an alkali.*

When narcotine is heated alone to about 400° , or by prolonged heating with water, it splits into meconine and cotarnine; the latter being immediately decomposed at the higher temperature; $C_{22}H_{23}NO_7 = C_{10}H_{10}O_4 + C_{12}H_{13}NO_3$. Matthiessen and Foster could find only one kind of narcotine as a natural product, contrary to the statement of Wertheim, although they examined narcotine from various sources. Matthiessen has however succeeded in procuring a series of bases homologous with true narcotine, $C_{22}H_{23}NO_7$; viz. $C_{21}H_{21}NO_7$; $C_{20}H_{19}NO_7$; and $C_{19}H_{17}NO_7$: these bases are susceptible of decompositions analogous to those of narcotine. The first of these may be obtained by heating narcotine for 2 hours in a sealed tube with excess of hydrochloric acid: one atom of hydrogen is thus substituted for one of methyl; $C_{22}H_{23}NO_7 + HCl = C_{21}H_{21}NO_7 + CH_3Cl$. If the mixture be heated for some days $(CH_3)_2$ is withdrawn, and H_2 substituted in the narcotine; and if instead of hydrochloric, fuming hydriodic acid be made use of, H_3 takes the place of $(CH_3)_3$, forming the lowest term of this series of bases that has yet been obtained.

6. *Meconine* ($C_{10}H_{10}O_4$) exists in opium, in small quantity. It may also be formed by digesting narcotine with water at 212° (100° C.), as well as by the action of caustic potash on opianic acid. This substance does not possess basic properties: it is freely soluble in boiling water, and crystallizes in white, inodorous, six-sided prisms, which are sparingly soluble in cold water, but are readily dissolved by alcohol and ether. It fuses at 194° (230° , Anderson), and may be distilled without alteration. It is soluble in concentrated sulphuric acid, and the liquid becomes purple when gently heated. Gerhardt considers this body to be a *hydride of opianyl*, which stands in the same relation to opianic acid that oil of bitter almonds does to benzoic acid (Gerhardt's opianyl being $C_{10}H_9O_4$), as is represented by the following formulæ:—



Gerhardt's opianyl ($C_{10}H_9O_4$) also appears to enter into the formation of two remarkable compounds, derived from ammonia, which present the composition of amides. They have been termed, respectively, *opiammon* and *teropiammon*: neither of them possesses basic characters:—



(1400) 7. *Narceia*, or *Narccine*.—Two substances appear to have been

* For details upon the products of oxidation of narcotine, *vide* Anderson, Wöhler, and Blyth, *loc. cit.*, and Matthiessen and Foster, *Phil. Trans.*, 1863, p. 345, 1867, p. 657, and *Procced. Roy. Soc.*, xvii. 337.

described under this name; one of these, obtained by Pelletier, having the composition ($C_{16}H_{19}NO_3$); the other examined by Anderson, being ($C_{23}H_{29}NO_3$). The latter is a feeble base, which is soluble in boiling water, and crystallizes from a hot solution as it cools, in delicate silky needles, which are soluble in alcohol, but insoluble in ether: at $197^{\circ}\cdot6$ (92° C.) it fuses, and at a somewhat higher temperature it becomes decomposed. It combines with the dilute acids, forming crystallizable salts. Concentrated sulphuric acid dissolves narceia with an intense red colour, which, when gently heated, passes into green. Iodine colours the base of a deep blue, which disappears on the addition of an alkali.

(c) *Alkali obtained from the Pepper Tribe.*

(1401) *Piperine* ($C_{17}H_{19}NO_3$; Streeker).—This is a substance which is isomeric with morphia; it is possessed of feebly basic properties. It is found in the common white and black pepper, and in long pepper. White pepper yields it easily when treated with alcohol, which extracts a resinous matter with the piperine, from which the latter may be freed by digestion in a solution of potash: the piperine which remains undissolved is recrystallized from alcohol, and furnishes colourless prisms, fusible at 212° . Piperine is nearly insoluble in cold water; it has an acrid taste, resembling that of pepper: the hydrochlorate is its most stable salt. Concentrated sulphuric acid dissolves piperine, with a red colour; but the base is precipitated unchanged, on dilution with water. Nitric acid acts powerfully on piperine, developing an odour of bitter almonds, whilst a brown resin rises to the surface. On evaporating the solution to dryness, a brown residue is left, which, when treated with potash, yields a magnificent blood-red liquid; and on distilling this mixture it furnishes *piperidine*, which is a powerfully alkaline base. The same base is also obtained when piperine is distilled with three times its weight of caustic potash, at a temperature not exceeding 320° (160° C.). The piperidine ($C_5H_{11}N$), being volatile, passes over, and a yellow, resinoid acid—*piperic acid* ($H C_{12}H_9O_4$; Streeker)—remains in combination with potassium; $C_{17}H_{19}NO_3 + KHO = KC_{12}H_9O_4 + C_5H_{11}N$.

Piperidine [$(C_5H_{10})^nH,N$]; *Sp. gr. of vap.* 2.982; *Rel. wt.* 42.5; *Boil. pt.* about $222^{\circ}\cdot8$ (106° C.).—This is a remarkable oily base, with a pungent odour, recalling both that of ammonia and that of pepper. It resembles ammonia in alkaline power, and precipitates many metallic oxides from their salts. It combines with the acids, neutralizing them, and forming well-crystallized salts: with cyanic acid it forms a compound urea, *piperyl-urea*; and, if heated with cyanic ether, piperidine forms a compound termed *ethyl-piperyl-urea*:—



Piperidine is a secondary or imide base, since one of its atoms of hydrogen may be displaced by ethyl or by methyl, on treating the base with iodide of ethyl

or of methyl; and *ethyl-piperidine*, by treatment with an additional quantity of the hydriodic ether, yields the iodide of an ethyl base corresponding to tetraethylam.

Capsicine is the name given to an alkaloid obtained from the *capsicum*, or Cayenne pepper. It has a burning taste; and as usually prepared, it presents a resinous appearance; but, when quite pure, it may be crystallized. It forms crystallizable salts with acetic, nitric, and sulphuric acids.

(d) *Alkaloids from the Strychnos Tribe.*

(1402) The fruit and bark of the *Strychnos nux vomica*, and other parts of several plants of this tribe, particularly the seeds of the *Strychnos ignatii*, contain two alkalies closely related to each other: both of them act as powerful poisons on the living frame, and speedily occasion death, amid violent tetanic convulsions: these bases are *strychnia* and *brucia*. They contain two atoms of nitrogen in each molecule of base. In the *nux vomica* they occur in combination with lactic acid, and a peculiar vegetable acid, termed *igasuric acid*. In order to extract them from this fruit, the following method may be adopted:—The rasped seeds are boiled with 4 times their weight of alcohol, acidulated with 1 per cent. of sulphuric acid. The alcoholic liquid is neutralized with lime in slight excess: the acid and colouring matters are thus precipitated, while the bases remain in solution; the alcohol is distilled off, and the residue treated with acidulated water, from which, on the addition of ammonia, the strychnia and brucia are precipitated. The two alkalies are separated by converting them into nitrates, and crystallizing; strychnia nitrate, being the least soluble of the two, is first deposited. Both strychnia and brucia exert a left-handed rotatory effect upon a ray of polarized light; but the rotatory power of strychnia is twice as great as that of brucia.

(1403) STRYCHNIA ($C_{21}H_{22}N_2O_2=334$) is contained in the St. Ignatius's bean, to the extent of nearly $1\frac{1}{2}$ per cent.; and it is one of the active constituents of the upas poison. Strychnia is one of the most powerful of the vegetable bases; it precipitates many metallic oxides from their salts, either completely or partially: in the latter case, it forms double salts,—such as strychnia cupric sulphate, which crystallizes in long green needles. Strychnia crystallizes from dilute alcohol, in white anhydrous octahedra, or in square prisms, which do not fuse on the application of heat. It is insoluble in absolute alcohol, ether, and the caustic alkalies; but it is soluble in the essential oils, and in chloroform. Cold water does not dissolve more of it than $\frac{1}{7000}$ of its weight; but this solution, even when diluted with

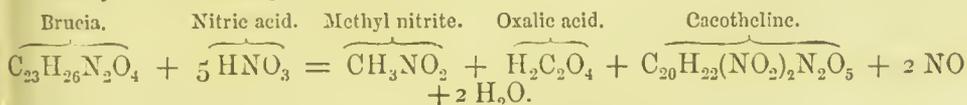
100 parts of water, still possesses a distinctly bitter taste. If distilled with caustic potash, strychnia, like cinchonia and quinia, yields the oily base quinoline. A portion of the hydrogen in strychnia may be displaced by chlorine or by bromine, and the body thus obtained still retains basic properties. Strychnia, when triturated with iodine, forms a peculiar crystalline compound, which is soluble in alcohol, and yields orange-coloured scales $[(C_{21}H_{22}N_2O_2)_2I_3]$, from which the acids separate strychnia unaltered. This compound is analogous to those which iodine yields with the opium bases (1395). Strychnia, when pure, is turned yellow by concentrated nitric acid, and yields a nitrate of a new substitution base, *nitro-strychnia*. If brucia be present with the strychnia, as is usual in most commercial specimens, the colour produced by nitric acid is deep orange, or red. With ethyl iodide, strychnia yields *ethylstrychnium* iodide $(C_{21}H_{22}, C_2H_5, N_2O_2, I)$, from which argentic oxide separates a crystallizable hydrated oxide of an ammonium base $(C_{21}H_{22}, C_2H_5, N_2O_2, HO)$; strychnia is therefore a nitrile base.

Salts of Strychnia.—Sulphuric acid forms a neutral and an acid salt with strychnia; the crystals of the neutral sulphate $[(C_{21}H_{22}N_2O_2)_2H_2SO_4, 7H_2O]$ are square prisms. The presence of strychnia may be detected in very minute quantities in complicated organic liquids, by rendering them alkaline with potash, and agitating thoroughly with a few draehms of chloroform; the chloroform dissolves the strychnia, and leaves it in the solid form on evaporation: from this residue it may be extracted by dilute hydrochloric acid; and it may afterwards be submitted to the usual tests. Strychnia yields, with a solution of carbazotic acid, characteristic hook-like crystals, easily distinguished by a moderate magnifying power even when the quantity of the base does not exceed $\frac{1}{1000}$ of a grain (Dr. Guy). A solution which does not contain less than $\frac{1}{375}$ its weight of the base gives, on the addition of a strong solution of potassic sulphocyanide, tufts of crystals, after the lapse of a few minutes. A minute quantity of strychnia with concentrated sulphuric acid, to which is added a fragment of lead dioxide, or what is still better, of potassic dichromate, gives a beautiful violet tint, which gradually fades into a pale rose colour; other oxidizing agents produce a similar effect. With solution of auric chloride, salts of strychnia give a bright blue colour.

(1404) *Brucia* $(C_{23}H_{26}N_2O_4, 4H_2O = 394 + 72; \text{Regnault})$ is more soluble in water, and in strong alcohol, than strychnia. This alkali is contained in *nux vomica* in larger quantity than

strychnia. It may also be readily obtained from the false angustura bark (*Brucea antidysenterica*), which does not appear to contain any strychnia, but furnishes brucia more abundantly than the beans of the *nux vomica*. Brucea crystallizes in colourless, transparent, oblique rhombic prisms, which are insoluble in ether. This base melts readily on the application of heat, and loses its water of crystallization. It is less active as a poison than strychnia. Its salts have a bitter taste, and may be distinguished from those of strychnia, after they have been mixed with tartaric acid, by not yielding any precipitate on the addition of hydric sodic carbonate. This base is further distinguished from strychnia by the bright scarlet colour gradually passing into yellow, which brucia or any of its salts gives with nitric acid; if a little stannous chloride be added, a beautiful violet colour is produced.

The action of nitric acid upon brucia is attended with the production of definite results, from which it appears to be probable that methyl enters into the composition of this base. When the concentrated acid is poured upon brucia, the mixture assumes a deep red colour, becomes hot, and emits a colourless gas with the peculiar smell of apples, and a portion of which is soluble in water and in alcohol. This gas consists of a mixture of methyl nitrite with nitric oxide and carbonic anhydride, the anhydride being the secondary result of the decomposition of oxalic acid, which is found in the liquid, accompanied by a new substance termed *cacotheline*; this last-named body is a nitro-substitution-compound, of feebly basic properties. Strecker represents the action of nitric acid upon brucia by the following equation:—



A further proof of the presence of methyl in brucia is found in the fact, that when this base is distilled with dilute sulphuric acid and black manganese oxide, or with potassic dichromate and sulphuric acid, formic and carbonic acids are produced, and an inflammable liquid passes over, burning with a blue flame, and presenting the properties of wood spirit.

Igasuria.—This name has been given to a third alkali discovered in *nux vomica*. It is more soluble in water than either strychnia or brucia. The *Urari* or *woorara* poison of South America appears to be obtained from a plant of the strychnos tribe; it acts as a fatal poison if introduced into the blood by a wound, but it may be swallowed with impunity.

Schutzenberger (*Ann. de Chimie*, III. liv. 65) states that he found in the base reputed to be igasuria, no fewer than nine closely related bases, which could be separated by fractional crystallization from boiling water. They are all intensely bitter, and are poisonous, resembling strychnia in their effects. They all are reddened by nitric acid; he assigns to them the following formulæ:—

- (a) $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_4, 3 \text{H}_2\text{O}$ very sparingly soluble;
- (b) $\text{C}_{18}\text{H}_{24}\text{N}_2\text{O}_7, 3 \text{H}_2\text{O}$ sparingly soluble;
- (c) $\text{C}_{18}\text{H}_{24}\text{N}_2\text{O}_4, 3 \text{H}_2\text{O}$ moderately soluble;
- (d) $\text{C}_{17}\text{H}_{32}\text{N}_2\text{O}_8, 3 \text{H}_2\text{O}$ moderately soluble;
- (e) $\text{C}_{18}\text{H}_{26}\text{N}_2\text{O}_4, 3 \text{H}_2\text{O}$ soluble;
- (f) $\text{C}_{21}\text{H}_{30}\text{N}_2\text{O}_4, 3 \text{H}_2\text{O}$ or $4 \text{H}_2\text{O}?$ soluble;

- (g) $C_{21}H_{29}N_2O_6$, 3 H_2O sparingly soluble;
 (h) $C_{21}H_{26}N_2O_6$, 2 H_2O moderately soluble;
 (i) $C_{20}H_{26}N_2O_7$, 4 H_2O soluble.

These results afford an illustration of the vast number of bases which may be produced by the actions of a single plant; they show the difficulty of investigations of this kind, and may serve to explain the discordant analytical results sometimes arrived at by chemists of tried ability.

(1404 a) *Effect of additive combination on Physiological Action of Bases.*—A series of interesting experiments has been recently made by Drs. Crum-Brown and Fraser, on the changes produced in the physiological action of certain of the organic bases by the addition of methyl or ethyl to their constituents. These inquiries have been at present limited to the salts of the ammonium bases derived from strychnia, brucia, thebaia, codeia, morphia, and nicotylia. (*Trans. Roy. Soc. Edin.* xxv. 1.) These observers found that the poisonous action of the original bases is much more energetic than that of the ammonium bases formed from them; whilst it also differs from them in character in a striking manner.

For example, in the case of methyl-strychnium salts, if the compound sulphate be injected under the skin, a fatal dose in the rabbit is about four-fifths of a grain, and 5 grains of methyl-thebium sulphate; whilst one-twentieth of a grain of pure strychnia, and one-fifth of a grain of thebaia hydrochlorate, produced a fatal result in less than three quarters of an hour in two other rabbits of similar size.

These observers summarize their results by stating that "the change in the *character* of the physiological action is remarkably illustrated by strychnia, brucia, and thebaia, whose purely spinal stimulant action is converted into a paralysing action on the periphery (end organs) of motor nerves. It is apparent in codeia and morphia, whose convulsant action is also converted into a paralysing action on the motor nerve end organs, and whose hypnotic action is apparently altogether destroyed in the case of codeia, and certainly greatly diminished in that of morphia; and it is obviously, though less so than with the others, in the case of nicotia, whose convulsant action is diminished, if not altogether removed. We may conclude from these facts that when a nitrile base possesses a strychnia-like action, the salts of the corresponding ammonium bases have an action identical with that of curare."

The recent experiments of Matthiessen and Wright upon morphia (p. 535) show the importance of further researches of this nature.

(e) *Other less known Bases.*

(1405) The bulbs of the *Colchicum autumnale* and the roots and seeds of different species of *Veratrum* contain several alkaloids, the most important of which, *veratria*, has been employed medicinally. *Veratria* ($C_{32}H_{52}N_2O_8$; Merck, *Lieb. Ann.*, xev. 200) occurs principally in combination with gallic acid; it is an extremely acrid and violent poison, producing dangerous fits of sneezing if it come in contact, even in minute quantity, with the mucous membrane of the nose. It acts as a valuable sedative in some cases of neuralgia, if applied in the form of ointment to the surface of the body. *Veratria* is almost insoluble in water and in alkaline solutions; alcohol dissolves it freely, and deposits it by spontaneous evaporation, in long delicate needles, fusible at 260° . Ether dissolves it with difficulty; fuming sulphuric acid colours it yellow, then blood-red, and lastly, violet. Nitric acid strikes with it a red which after a time becomes yellow. Three other poisonous bases, *sabadilla*, *colchinea*, and *jervia*, are found, along with *veratria*, in the *Veratrum album*, or white hellebore. *Jervia* ($C_{30}H_{46}N_2O_3 \cdot 2H_2O$? Gerhardt, from Will's analysis) is white, crystalline, and fusible.

Aconitina ($C_{30}H_{47}NO_7$? *Planta*, *Lieb. Ann.*, lxxiv. 257) is another intensely poisonous alkaloid, which is employed medicinally, but the composition of which is uncertain; it is obtained from various species of monkshood or aconite. It crystallizes with difficulty, and is more soluble in water than most of these bases; it is dissolved easily by alcohol and ether. These solutions have a powerfully alkaline reaction; and the base forms perfectly neutral salts, which when moistened with concentrated sulphuric acid acquire a colour which at first is yellowish, and then becomes of a dirty violet red. It fuses at about 200° .

Many of the *Solanaceæ* and *Umbelliferae* contain alkaloids. The henbane (*Hyoscyamus niger*) and both the common and the deadly nightshade (*Solanum dulcamara*, and *Atropa belladonna*) owe their poisonous qualities to compounds of this kind. To *Solanum* Zwenger assigns the formula $C_{43}H_{70}NO_{16}$.

Atropia [$C_{17}H_{23}NO_3$; *Planta*, *Lieb. Ann.*, lxxiv. 255; *Fusing pt.* 194° (90° C.)] crystallizes in colourless silky needles, which are freely soluble in alcohol and in chloroform, but less so in ether. The crystals fuse at 194° , and undergo sublimation and partial decomposition at 284° (140° C.). Solutions of atropia are speedily altered by evaporation when exposed to the atmosphere. Atropia is present in all parts of the belladonna, but is commonly ex-

tracted from the root. It appears to be identical with *daturia*, the active principle contained in the seeds of the *Datura stramonium*. The salts of atropia are bitter, acrid, and highly poisonous, producing a remarkable dilatation of the pupil of the eye.

In addition to these bases two others may be mentioned, viz., *harmaline* and *harmine*, which are found, probably combined with phosphoric acid, in the husk of the seeds of the *Peganum harmala*, or Syrian rue, a plant extensively grown in the steppes of Southern Russia. The seeds of this plant are used in dyeing silk, to which they impart various shades of pink, rose, or red. The seeds also possess narcotic properties, but the active principle to which this effect is due has not been investigated. *Harmaline* ($C_{13}H_{14}N_2O$) when pure crystallizes in colourless prisms, but they generally retain a brownish yellow tint, and tinge the saliva yellow. It has a bitter, astringent, acrid taste; it is freely soluble in alcohol, but sparingly so in water and in ether. It is fusible and volatile; with acids it forms yellow, very soluble, crystallizable salts. Oxidizing agents transform it into a red colouring matter which combines with acids, forming salts which constitute the basis of the *harmala red* of commerce. Harmaline contains two atoms more of hydrogen than *harmine* ($C_{13}H_{12}N_2O$; Fritzsche, *Lieb. Ann.*, lxiv. 365; lxxxviii. 327), into which it may be converted by oxidation; harmine crystallizes in long delicate prisms; it forms colourless salts which are quite neutral.

Emetia, the active principle of ipecacuanha, also possesses the properties of a feeble base: it is nearly insoluble in water and ether, but is readily soluble in alcohol and in dilute acids; chloroform also dissolves it with facility. It is powerful poison, and acts as a violent emetic in doses of one-sixteenth of a grain or less. It fuses readily, and is accompanied in the ipecacuanha root by a large proportion of oily matter, which emits a feeble odour of tobacco when heated. The base is easily obtained by treating the alcoholic extract of the root with dilute sulphuric acid, filtering from the oily matter, and after slightly supersaturating the solution with ammonia, agitating the turbid liquid with chloroform. On evaporating the chloroform, the emetia is left as a yellowish resinous-looking mass. It may be purified by conversion into a salt, and digesting its solution with a small quantity of animal charcoal; on adding an alkali to the filtered liquid the emetia is precipitated. The salts of emetia do not readily crystallize.

(f) *Alkaloids of Coffee, Tea, and Chocolate.*

(1406) CAFFEINE, OR THEINE: $C_8H_{10}N_4O_2 \cdot H_2O = 194 + 18$; *Fusing pt.* $453^{\circ} \cdot 2$ (234° C.); Strecker.—This substance occurs in tea, coffee, and in *maté*, a shrub used by the natives of Paraguay and a large number of the inhabitants of South America, for making an infusion which they substitute for tea, as well as in the *kola-nut* used by the natives of Central Africa. It is also contained to the extent of 5 per cent. (Stenhouse) in *guarana*, an astringent species of chocolate prepared from the fruit of the *Paullinia sorbilis*. Tea appears to contain from 2 to 4 per cent. of caffeine (Péligot), but the quantity of it in coffee, according to Stenhouse, seldom exceeds 1 per cent.

Caffeine is easily obtained from tea by making a strong infusion of the leaf, mixing it with tribasic acetate of lead and a little free

ammonia, to separate tannic acid, and transmitting sulphuretted hydrogen to remove the excess of lead; on then evaporating the solution and allowing it to cool, the caffeine crystallizes out in long flexible silky needles.

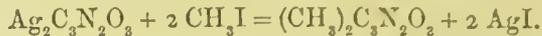
It has a slightly bitter taste, and is sparingly soluble in cold water and in alcohol; both boiling water and ether dissolve it in considerable quantity. The crystals deposited from alcohol and from ether are anhydrous. Caffeine fuses when heated, and at a higher temperature it may be sublimed without decomposition. The basic properties of caffeine are only slightly marked, but it forms crystallizable salts with hydrochloric and sulphuric acids; both these compounds are, however, decomposed by solution in water. Caffeine absorbs about a third of its weight of dry hydrochloric acid gas; the compound must be crystallized from a concentrated solution of hydrochloric acid, and the crystals washed with ether. With auric and with platinic chloride the hydrochlorate forms double salts, which crystallize easily. Caffeine also forms with argentic nitrate a crystalline compound ($C_8H_{10}N_4O_2, AgNO_3$) which may be recrystallized from boiling water or from alcohol; it is sparingly soluble in cold water.

Wurtz found that when caffeine is boiled with potash, methylica is liberated. Concentrated nitric acid decomposes caffeine with evolution of nitrous fumes, and the formation of a yellow liquid, in which at a particular stage, the addition of ammonia develops a beautiful purple colour, resembling that of murexid; by longer boiling the decomposition proceeds further, salts of methylica are found in solution, and cholestrophan is formed. Similar results are furnished by the action of chlorine. The purple reaction is most easily obtained by treating the caffeine with a mixture of hydrochloric acid and potassic chlorate, evaporating to dryness, and then adding a little ammonia.

When chlorine is transmitted through a magma of caffeine suspended in water, the crystals gradually disappear, and a mixture of several products is obtained; of these the most remarkable are *amalic acid* ($C_{12}H_{14}N_4O_8$), so called from ἀμαλός, 'weak,' in allusion to its feeble acidity, and *nitro-theine* or *cholestrophan* ($C_5H_6N_2O_3$), whilst a salt of methylica is formed. By evaporating the solution, amalic acid may be obtained in colourless crystals, which are insoluble in alcohol; they assume a violet colour if moistened with baryta water. On evaporating the solution, cholestrophan may be obtained in pearly scales, resembling those of cholesterin in appearance, and hence its name (from cholesterin, φαίνω, to appear); it may be sublimed unaltered. According to the researches of Rochleder (*Liebig's Annal.*, lxxiii. 123), the products of the oxidation of caffeine resemble those obtained from uric acid by similar treatment, and the two classes of compounds are homologous, or rather substitution-products from the same organic group; for amalic acid corresponds to alloxantin, in which 4 atoms of hydrogen have been displaced by 4 of methyl; and cholestrophan is dimethylated parabanic acid, or methylparabanic ether:—

| | |
|---|---------------------------------|
| Alloxantin | $C_8H_6N_4O_8, 2 H_2O$ |
| Amalic acid (tetramethyl-alloxantin) | $C_8H_2(CH_3)_4N_4O_8$ |
| Parabanic acid | $C_3H_2N_2O_3 = H_2, C_3N_2O_3$ |
| Cholestrophan (dimethyl-parabanic acid) | $(CH_3)_2C_3N_2O_3$ |

Strecker, by heating dry argentic parabanate with anhydrous methyl iodide in a scaled tube, has, indeed, effected its conversion into cholestrophan and argentic iodide:—



Amalic acid also possesses the property, like alloxantin, of staining the fingers pink; and if exposed to the vapour of ammonia, it produces a compound homologous with murexid, which, like the latter compound, is distinguished by its magnificent purple colour:—



(1407) *Chemical and Dietetic characters of Coffee and Tea.*—

Caffeine is a compound which presents a high degree of interest, both from the metamorphoses of which it is susceptible, and from the circumstance that it affords an ingredient in three substances, namely, tea, coffee, and a third substance of less importance, *maté* (or Paraguay tea, obtained from the *Ilex Paraguayensis*), one or other of which constitutes a portion of the daily diet of three-fourths of the human race. The circumstance that these different shrubs should have been selected by different nations, for the purpose of yielding a beverage, when infused with boiling water, shows that the ingredient which they furnish is one which is adapted in a special manner to some craving of the human frame. Although these bodies differ so widely in flavour, they all contain the same azotised principle, the physiological effects of which have not been submitted to the detailed examination which they well deserve. A series of experiments upon this point is due to Julius Lehmann, who watched for some weeks the effects of roasted coffee, as well as of its essential oil, and of caffeine, upon two individuals in good health (*Liebig's Annal.*, lxxxvii. 205). The use of coffee as an article of diet appears to exercise an important influence in retarding the waste of the tissues of the body; since it was observed that during its use the proportion of phosphoric acid and of urica excreted by the kidneys was much smaller than when the coffee was omitted, the diet being in all other respects the same in both cases. Thus, it was found that when an infusion of three-quarters of an ounce of roasted coffee-berries was taken daily for a fortnight, the average proportion of urea and of phosphoric acid which passed off by the kidneys in 24 hours, was less by one-third than it was during a similar period in which the coffee was omitted. The empyreumatic oil of the coffee was found to exert a stimulating effect upon the nervous system. When too large a quantity of this essential oil was taken, it produced loss of sleep, nervous excitement, and symptoms of congestion of the brain. In smaller quantities it produced a gentle perspira-

tion, removed the sensation of hunger, and acted upon the bowels as a laxative. It likewise reduced the amount of urea and of phosphoric acid in the urine. It was also concluded from the production of similar alterations in the quality of the urine, when a solution of pure caffeine was substituted for the ordinary infusion of coffee, that caffeine likewise exerted a power of retarding the disintegration of the constituents of the animal frame.

Tea, coffee, and the Paraguay tea-plant, in the form in which they are used dietetically, all contain the following principles:—
1. Caffeine. 2. One of the forms of tannic acid. 3. An aromatic essential oil, which is different in each plant, and is the main cause of their different and peculiar flavours.

Constituents of Coffee.—When the coffee berry is first gathered and dried in the air, it has but little fragrance, and only a slightly bitter and astringent taste. The raw coffee berry is hard and horny, and it swells up with difficulty even when treated with boiling water; it contains in its green state about the same quantity of soluble matter as after it has been roasted, but the amount varies greatly in different specimens.

Coffee swells considerably during roasting, the increase in volume amounting to one-third or even to one-half of its original bulk; at the same time it loses in weight to an extent varying from 15 to 25 per cent. upon the weight of the berries before roasting, the amount of this loss depending upon the extent to which the roasting is carried. The roasting should be stopped as soon as the berry has become friable. The agreeable bitter aromatic taste of coffee is developed during this operation. It is worthy of remark that inferior coffee becomes improved in quality by keeping, and if roasted after it has been kept for some years, it yields an infusion of a finer flavour than if roasted immediately after it has been gathered. Both the essential oil and the bitter flavour are developed from one of the soluble constituents of the berry, since the aqueous extract of the raw berry when roasted acquires the full odour and taste of coffee. The proportion of this aromatic oil in roasted coffee is very minute; not exceeding, according to Payen, one five-thousandth of the weight of the coffee. Coffee also contains 14 or 15 per cent. of fixed oil. The astringent acid, *caffeic acid*, as it has been termed, is allied to the quinic; it constitutes about 5 per cent. of the dry berry: it does not blacken a solution of ferrous sulphate, but turns it green, and it does not precipitate solutions of gelatin; it is dissolved by strong sulphuric acid, and produces a red liquid. When exposed to the air in contact with alkalis, caffeic acid

absorbs oxygen, and forms a yellow insoluble resin. Vlaanderen and Mulder have made a minute investigation of the *caffeic acid*, which gives a yellow precipitate with salts of lead, and to which they assign the formula, when anhydrous, of $C_{14}H_{16}O_7$? A second acid termed *caffelic acid*, $C_7H_8O_6$, gives a white precipitate with salts of lead. A peculiar reaction occurs with caffeic acid when 1 part of its concentrated solution is heated with 4 parts of finely-powdered black manganese oxide, and 1 part of oil of vitriol diluted with an equal bulk of water. Yellow crystals of quinone (1337) are deposited upon the neck and sides of the retort, and the acid liquid which distils over is saturated with quinone, and contains formic acid. (See a Report on the adulteration of coffee, by Graham, Stenhouse, and Campbell, *Q. J. Chem. Soc.*, ix. 52.) The acid of Paraguay tea, and that of the leaves of the holly tribe, also furnish quinone by similar treatment. The following is the average composition of the coffee-berry, according to Payen:—

| | |
|--|--------------|
| Ligneous tissue | 34·0 |
| Hygroscopic water | 12·0 |
| Fixed fatty matters | 10 to 13·0 |
| Gum, sugar, and a vegetable acid | 15·5 |
| Azotised matter, analogous to legumin | 13·0 |
| Free caffeine | 0·8 |
| Compound of caffeine with potash and chlorogenic (caffic) acid* | } 3·5 to 5·0 |
| Aromatic essential oil | |
| Solid fatty essence | 0·001 |
| Saline matters | 6·697 |

The saline matters found in coffee contain more than half their weight of potash (as K_2O , 51·5 to 55·8 per cent.), chiefly in the form of carbonate and phosphate; they are almost entirely free from silica and soda. The sugar in raw coffee is in the form of cane sugar (Graham, Stenhouse, and Campbell), and its quantity varies from 6·2 to 7·7 per cent. The process of roasting not only expels the greater part of the hygroscopic moisture, but it considerably modifies the properties of the caffeic acid, and converts nearly the whole of the sugar into caramel. The solid portion left after infusing the ground berry in water contains a large amount of nutritious substance, in the form of an azotised prin-

* Containing 39 per cent. of caffeine; 3·5 parts, therefore, indicate 1·36 of caffeine. This salt has not been found by other chemists.

ciple resembling casein or legumin. This may account for the practice among the Arabs and other oriental nations, of swallowing the undissolved portions of the grain with the decoction: in the countries of Central Asia the use of animal food is rare, and hence the inhabitants have been led to vary the mode of preparing their coffee in such a manner as to enable them to use the substance, in some measure, as a substitute for the nitrogenous constituents supplied by a flesh diet.

The dried leaves of the coffee-plant also contain as much as $1\frac{1}{2}$ per cent. of caffeine (Stenhouse), as well as an astringent vegetable acid, and a large proportion (13 per cent.) of an azotised principle allied to gluten. The dried coffee-leaf has an agreeable aroma; it is used largely in the form of infusion by the natives of Sumatra.

Constituents of the Tea-plant.—The dried leaves of the *Thea Sinensis*, which constitute our ordinary 'tea,' contain about 45 per cent. of soluble matter; but, according to Péligot, tea does not usually give up more than about one-third of its weight of soluble matter to boiling water. The most important constituents of the leaf, in the form in which it is consumed in Europe, are:—

1. *The essential oil*, to which it owes its peculiar aroma, and the proportion of which, according to Mulder, is about 0.79 in green, and 0.60 per cent. in black tea. This oil exerts a most powerfully stimulating and intoxicating effect. In China, tea is seldom used till it is a year old, on account of the well-known intoxicating effects of new tea, due probably to the larger proportion of essential oil contained in the freshly-dried leaf.
2. *Caffeine*, or theine, the quantity of which varies considerably in different varieties of tea: in different kinds of green tea furnished to Péligot, the amounts ranged from 2.2 to 4.1 per cent.
3. A *nitrogenized compound* analogous to casein, amounting to 14 or 15 per cent. of the weight of the leaf. Almost the whole of this material is thrown away in the spent leaves, which when dry contain not less than 28 per cent. of their weight of this substance. The Mongol Tartars economise a large portion of this nutritive matter by boiling the powdered tea with the alkaline water of their steppes, to which a quantity of salt is added; by this means a notable proportion of the gluten is dissolved or suspended in the liquid, which they commonly eat thickened with butter, milk, and baked flour (Lehmann).
4. *The astringent principle*, which is a modification of tannin; it occasions a precipitate in solutions of gelatin, and produces a black with ferrous sulphate: it constitutes from 13 to 18 per cent. of the dried leaf.

The ash of tea varies from 5·3 to 5·6 per cent. of the dried leaf; a portion of this ash is probably due to the colouring matter which the Chinese are in the habit of adding to their green teas, for the foreign market; this colouring matter is in some cases indigo, in others a mixture of Prussian blue and pipe-clay.

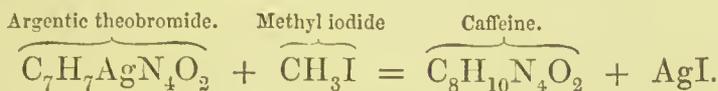
It appears from the observations of Mr. Fortune, that either green or black tea can be obtained at pleasure from the same plant. *Green tea* is prepared from the young leaves, which, within an hour or two after they have been gathered, are roasted in pans over a brisk wood fire. After four or five minutes' roasting the leaves become flaccid, and are rolled by the hands upon a wooden table; they are then again thrown into the drying pans, where they are kept in rapid motion, and in about an hour, or an hour and a half, are completely dried.

Black tea is allowed to lie in heaps for ten or twelve hours after the leaves have been gathered: they are then tossed about for some time till the leaves become flaccid. At this stage they begin to emit a fragrant smell; they are next rolled in balls, with the hand, upon a wooden table, and a large quantity of liquid is expressed from them; after which they are shaken out, roasted for a few minutes, again rolled, and, whilst still flaccid, are exposed to the air for some hours upon shallow bamboo trays: this alternate heating and rolling is repeated three or four times; and finally, the leaves are dried slowly over charcoal fires. A species of fermentation appears to occur during the drying of the leaf, in consequence of which a development of essential oil takes place, by which the agreeable aroma is occasioned: this aroma is wanting in the fresh leaf. The change of the leaf from green to black is mainly due to chemical alterations produced by the oxygen of the air upon the constituents of the leaf, and especially upon the astringent principle; this change is prevented in green tea by the rapid process of drying to which it is subjected.

(1408) *Theobromine* ($C_7H_8N_4O_2$; Glasson).—This body is present in chocolate. It is extracted from the cacao-nut (*Theobroma cacao*) by a process similar to that employed in obtaining caffeine from tea or coffee. Theobromine is sparingly soluble in boiling water, and still less so in alcohol and in ether; it has a slightly bitter taste. At a high temperature it may be sublimed, a part of it undergoing decomposition during the process. It resembles caffeine in its property of forming crystallizable salts with some of the acids; but these compounds are decomposed by water, and its basic powers are very feeble.

Theobromine when dissolved in ammonia, and mixed with

argentic nitrate, yields a gelatinous precipitate, which, by boiling with a solution of ammonia, becomes converted into a crystalline mass; if this be dried and heated in a sealed tube with anhydrous methyl iodide, argentic iodide is formed, and caffeine is produced (Strecker) :—



Caffeine is, therefore, a methyl-compound of theobromine, and not a true homologue of it, as its formula might seem to indicate.

The cacao-nut is remarkable for the large proportion of fatty matter which it furnishes. This fat is not liable to become rancid, a circumstance which adds greatly to the value of the nut as an article of food. The nut, when deprived of its husk, is said to contain nearly 56 per cent. of this fat, 17 per cent. of a substance resembling gluten, from 1.2 to 1.5 of theobromine, and 22 of starch, gum, sugar, and ligneous tissue. The aromatic flavour of cocoa is due to the roasting to which the nut is subjected before grinding it. If the roasted nut be simply crushed after it has been freed from its husk, it forms the *cocoa nibs* of the grocer. *Chocolate* (a Mexican dish, *chocolatl*) is prepared by grinding the roasted nut into a paste between hot rollers, and mixing it with sugar, vanilla, cinnamon, and other spices.

Many of the alkaloids, when heated carefully, between two plates of glass, furnish characteristic sublimates, as was first pointed out by Helwig. A careful examination of the mode of applying this process as a test for many of the vegetable bases has been made by Dr. Guy. (*Pharm. Journ.* 1867 and 1868, and *Trans. Microsc. Soc.* 1867.)

§ III. GENERAL REVIEW OF THE MONATOMIC ALCOHOLS, ($\text{C}_n\text{H}_{2n+2}\text{O}$).

(1409) Having now completed the description of the more important bodies connected with the alcohols of the form ($\text{C}_n\text{H}_{2n+2}\text{O}$), it may be serviceable to take a general review of the connexion of these different compounds with each other. For this purpose the table on the following page has been constructed; it furnishes a synoptic view of the more important classes of heterologous derivatives from these alcohols.

If space allowed us to map out the whole of the various derivatives of each alcohol in a table similar in principle to that given at pages 38 and 39, each of the general formulæ given in the second column of the following table would stand at the head of one of the columns of such a table. Each substance enumerated in this table is, therefore, to be regarded as the representative of

Heterologous Series derived from the Alcohols.

| Name of the Series | and | General Formula. | Examples. | |
|--|-----|----------------------------------|---|-----------------------------|
| 1. Electro-positive radicle | | $(C_n H_{2n+1})_2$ | Diethyl | $(C_2 H_5)_2$ |
| 2. Mixed radicle | | $(C_n H_{2n+1}, C_m H_{2m+1})$ | Ethyl-butyl . . . | $C_2 H_5, C_4 H_9$ |
| 3. Alcohol | | $(C_n H_{2n+1}, H)O$ | Alcohol | $C_2 H_5, H, O$ |
| 4. Simple ether | | $(C_n H_{2n+1})_2 O$ | Ethylic ether . . . | $C_2 H_5, C_2 H_5, O$ |
| 5. Mixed ether | | $(C_n H_{2n+1}, C_m H_{2m+1})O$ | Ethyl-amylc ether | $C_2 H_5, C_5 H_{11}, O$ |
| 6. Hydracid ether | | $(C_n H_{2n+1})\bar{W}$ | Hydrochloric ether | $C_2 H_5, Cl$ |
| 7. Sulphuretted ether . . . | | $(C_n H_{2n+1})_2 S$ | Hydrosulphuric } ether } | $C_2 H_5, C_2 H_5, S$ |
| 8. Disulphuretted ether . . | | $(C_n H_{2n+1})_2 S_2$ | Ethyl disulphide . | $C_2 H_5, C_2 H_5, S_2$ |
| 9. Mercaptan | | $(C_n H_{2n+1}, H)S$ | Ethyl-mercaptan . | $C_2 H_5, H, S$ |
| 10. Compound ether (mono- basic) | } | $(C_n H_{2n+1})\bar{X}$ | Acetic ether . . . | $C_2 H_5, C_2 H_5, O_2$ |
| 11. Compound ether (di- basic) | | $(C_n H_{2n+1})_2 \bar{Y}$ | Oxalic ether . . . | $(C_2 H_5)_2, C_2 O_4$ |
| 12. Vinic acid | | $H(C_n H_{2n+1})\bar{Y}$ | Ethyl-sulphuric acid | $H C_2 H_5, S O_4$ |
| 13. Salt of vinic acid | | $M(C_n H_{2n+1})\bar{Y}$ | Potassic ethylsulphate | $K C_2 H_5, S O_4$ |
| 14. Compound ether (tri- basic) | } | $(C_n H_{2n+1})_3 \bar{Z}$ | Citric ether | $(C_2 H_5)_3, C_6 H_5, O_2$ |
| 15. Cyanide, or Nitrile . . . | | $(C_n H_{2n+1})CN$ | Hydrocyanic ether } (propio-nitrile) } | $C_2 H_5, Cy$ or $C_3 H_7$ |
| 16. Amide base | } | $H_2(C_n H_{2n+1})N$ | Ethylia | $H_2, C_2 H_5, N$ |
| 17. Imide base | | $H_3(C_n H_{2n+1})_2 N$ | Diethylia | $H, (C_2 H_5)_2, N$ |
| 18. Nitrile base | | $(C_n H_{2n+1})_3 N$ | Triethylia | $(C_2 H_5)_3, N$ |
| 19. Oxide of ammonium } base (hydrated) } | | $(C_n H_{2n+1})_4 NHO$ | Oxide of tetrethy- } lium (hydrated) } | $(C_2 H_5)_4, NHO$ |
| 20. Homologues of urea | | $H_3(C_n H_{2n+1})N_2 CO$ | Ethyl-urea | $H_3(C_2 H_5)_2, N_2, CO$ |
| 21. Zinc radicle | | $Zn(C_n H_{2n+1})_2$ | Zinc-ethyl | $Zn(C_2 H_5)_2$ |
| 22. Diarsenio-radicle | | $[As(C_n H_{2n+1})_2]_2$ | Dikakodyl | $[As(CH_2)_2]_2$ |
| 23. Hydrated oxide of di- arsenio-radicle | } | $As(C_n H_{2n+1})_2 HO$ | Hydrated kakodyl } oxide } | $As(CH_3)_2 HO$ |
| 24. Acid of diarsenio- radicle | | $HAs(C_n H_{2n+1})_2 O_2$ | Kakodylic acid . . | $HAs(CH_3)_2 O_2$ |
| 25. Triarsenio-radicle | | $As(C_n H_{2n+1})_3$ | Triarsenethyl . . . | $As(C_2 H_5)_3$ |
| 26. Oxide of triarsenio- radicle | } | $As(C_n H_{2n+1})_3 O$ | Triarsenethyl oxide | $As(C_2 H_5)_3 O$ |
| 27. Hydrated oxide of tetrarsenio-radicle } | | $As(C_n H_{2n+1})_4 HO$ | Hydrated tetrar- } senethylum oxide } | $As(C_2 H_5)_4 HO$ |
| 28. Stanno-radicle | } | $Sn(C_n H_{2n+1})_2$ | Stanno-diethyl . . | $Sn(C_2 H_5)_2$ |
| 29. Stanno stannic-radicle . . | | $Sn(C_n H_{2n+1})_3$ | Stanno-trimethyl . | $Sn(C_2 H_5)_3$ |
| 30. Stannic-radicle | | $Sn(C_n H_{2n+1})_4$ | Stannic tetrethyl . | $Sn(C_2 H_5)_4$ |
| 31. Alcohol-radicle hydride | | $(C_n H_{2n+1})H$ | Ethyl hydride . . . | $C_2 H_5, H$ |
| 32. Olefine | | $C_n H_{2n}$ | Olefiant gas . . . | $C_2 H_4$ |
| 33. Homologues of acety- lene. | } | $C_n H_{2n-2}$ | Acetylene | $C_2 H_2$ |
| 34. Aldehyd | | $(C_n H_{2n-1}O)H$ | Acetic aldehyd . . | $C_2 H_5, O, H$ |
| 35. Volatile acid | | $H(C_n H_{2n-1}O)O$ | Acetic acid | $H C_2 H_5, O_2$ |
| 36. Ketone | | $C_n H_{2n-1}O, C_m H_{2m+1}$ | Acetone | $C_2 H_5, O, CH_3$ |
| 37. Dibasic acid | | $H_2(C_n H_{2n-4})O_4$ | Succinic acid . . . | $H_2 C_4 H_4 O_4$ |
| 38. Monobasic anhydride . . . | | $C_n H_{2n-1}O, C_n H_{2n-1}O_2$ | Acetic anhydride . | $C_2 H_5, O, C_2 H_5, O_2$ |
| 39. Mixed anhydride | | $C_n H_{2n-1}O, C_m H_{2p-1}O_2$ | Benzo-acetic do. . | $C_2 H_5, O, C_7 H_5, O_2$ |
| 40. Dibasic anhydride | | $C_n H_{2n-4}O_3$ | Succinic anhydride | $C_4 H_4 O_3$ |
| 41. Monobasic oxychloro- ride | } | $C_n H_{2n-1}OCl$ | Acetyl chloride . . | $C_2 H_5 OCl$ |
| 42. Dibasic oxychloride | | $C_n H_{2n-1}O_2 Cl_2$ | Succinyl chloride . | $C_4 H_4 O_2 Cl_2$ |

a homologous series of compounds like that of the fatty acids, or of the alcohols, in which each of the members differs by (CH_2) from those which immediately precede and follow it.

It will be observed that the letters \overline{W} , \overline{X} , \overline{Y} , and \overline{Z} , are occasionally employed in the column headed "General Formula:—"

\overline{W} indicates chlorine, or one of the halogens.

\overline{X} indicates all the constituents of a monobasic acid, except the basic hydrogen.

\overline{Y} indicates the corresponding portion of a dibasic acid.

\overline{Z} indicates the corresponding constituents of a tribasic acid.

It must be remembered that this table, extensive as it is, does not specify all the known heterologous derivatives of any single alcohol. The different forms of the phosphorus bases are not mentioned, because they are represented by the formulæ of those of ammonium, from which they differ in containing an atom of phosphorus in the place of one of nitrogen. Of the homologues of urea two distinct series are known, the first of which corresponds to ethyl-urea $[\text{H}_3(\text{C}_2\text{H}_5)\text{N}_2\text{CO}]$, and the second to diethyl-urea $[\text{H}_2(\text{C}_2\text{H}_5)_2\text{N}_2\text{CO}]$, though the former series only is indicated in the table. With the exception of the ureas, neither amides nor polyatomic bases appear in the table. The zinc-radiée again represents other metallic compounds, such as those containing cadmium, which are formed upon the same type. The various arsenio-compounds are also representatives of the antimony series, which are not mentioned in the table; the arsenical compounds likewise are representatives of the compounds which contain bismuth in the place of arsenicum. Again, the tin-radiées, themselves a numerous group, are indicated by their three principal formulæ; whilst the compounds of lead and of mercury correspond to one or other of the different forms of the tin-radiée.

CHAPTER VII.

ESSENTIAL OILS AND RESINS.

§ I. ESSENTIAL OILS.

(1410) THE ODORIFEROUS principle of most plants resides in certain compounds consisting chiefly of carbon and hydrogen; and although the boiling point of these bodies lies considerably above

212°, they emit at ordinary temperatures minute quantities of an intensely odorous vapour. They have a certain resemblance to the fixed oils in their inflammability, sparing solubility in water, and ready solubility in alcohol and in ether; as well as in the production of a greasy stain when dropped upon paper, though this mark is only transient; and they feel harsh instead of unctuous when rubbed upon the skin: from the points of their similarity to the oils, and from the fact of their constituting in many cases the distinctive compound of the plant which yields them, they are termed *essential* or *volatile oils*.

The production of the essential oils is not limited to any particular portion of the vegetable organism. In some natural families—as, for instance, in the *Umbelliferae*—the oil is most abundantly contained in the seeds. The *Aurantiaceae* yield two different kinds of essential oil, one of which is obtained from the flower, and the other from the rind of the fruit. The *Myrtaceae* and the *Labiatae* supply it from the leaves, whilst the *Rosaceae* contain it only in the petals of the flower.

Generally speaking, the oils appear to exist ready formed in the plant, being enclosed in little saeculi, which are often visible to the naked eye, as in the leaves of the *Myrtaceae* and the peel of the *Aurantiaceae*. In a few cases, such as those of the oil of bitter almonds and of mustard, they are produced by a species of fermentation operating on a principle contained in the cells of the seed; this change does not commence until the seed has been crushed and mixed with water. A peculiar azotised body present in the seed is thus brought into contact, under favourable circumstances, with the compound which yields the oil, and the characteristic aroma of the essence is speedily developed.

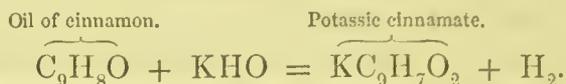
The oils of lemon and orange are extracted by simple pressure, from the rind of the fruit; but the general process of extraction consists in placing the appropriate portions of the plant in a still, with water, and applying heat: in order to prevent the vegetable materials from being over-heated by resting against the sides of the still, which would give to the distillate a disagreeable odour, it is customary to suspend them in a net or perforated metallic vessel in the upper part of the still. A better method of obtaining the essence is to allow steam to pass over the plant, and to condense the vapour afterwards in the usual way. The presence of steam favours the volatilization of the oils at a comparatively low temperature, for it mechanically carries over the vapour: the distillate is at first milky, but the greater portion of the essence separates from the milky liquid on standing. The water which

is condensed in the receiver with the oil acquires the odour and taste of the essence ; such waters constitute the fragrant *distilled waters* of the apothecary : by a second distillation, these waters are freed from some impurities which are mechanically carried over, and which would cause the liquid to become mouldy, and destroy its fragrance. A small quantity only of the essential oil is retained in solution in the distilled water, and the greater portion of the oil which is thus dissolved may be separated by saturating the liquid with sodic chloride ; the essence on standing rises to the surface. It may also be removed by agitating the distilled water with ether, which dissolves the oil ; and on expelling the ether from the layer which separates on standing, the pure oil is procured. In some cases, where the essence becomes altered during the act of distillation, the fragrance of the plant is obtained and concentrated by dissolving it in a fixed oil which is itself destitute of odour, such as oil of poppy-seeds. The leaves of the flower are in such instances spread in thin layers upon woollen cloths saturated with the fixed oil ; the cloths thus charged are then piled one upon another, and submitted to the action of a press.

The essential oils vary in specific gravity, but in general they are lighter than water. These oils are usually liquid at ordinary temperatures, but oil of aniseed is solid at all temperatures below 59° (15° C.). If cooled slowly, many of them separate into a solid and a fluid portion, sometimes respectively termed *stearopten* and *elæopten*. This fact is readily explained by the circumstance that most of the essential oils are mixtures of two or more distinct chemical compounds which differ in volatility and fusibility ; one of these compounds generally contains no oxygen, while the others are often substances formed from it by oxidation. Of these the pure hydrocarbon is generally the more volatile ; it acts as a solvent to the oxidized compounds, which, by a depression of temperature, may frequently be separated from it in a crystallized form.

Most of the essential oils have a yellowish colour, which deepens when exposed to the air ; during such exposure they absorb oxygen more or less rapidly, and are thus gradually converted into a solid, resinous, or camphreous mass. Those oils which absorb oxygen the most rapidly have in general the most powerful odour. This absorption of oxygen is sometimes attended with a simultaneous extrication of carbonic anhydride and water : this occurs in the case of the oil of anise, and of lavender ; and in such instances the resulting resinous mass is not a simple oxide of the hydrocarbon.

The essential oils are insoluble in potash, and are not capable of saponification by treatment with alkalies: but if the oils be transmitted in the form of vapour over heated caustic potash, hydrogen is frequently disengaged, and the oil becomes oxidized, forming an organic salt with the potassium. Oil of cinnamon may thus be converted into potassic cinnamate:—



Chlorine, iodine, and bromine act upon most of the essential oils, and form compounds in which a certain number of atoms of one of these elements displaces a corresponding number of atoms of hydrogen. Nitric acid oxidizes most of the essential oils with great violence.

The essences may be arranged under three principal divisions, viz.:—*A.* Pure hydrocarbons; *B.* Oxidized essences; *C.* Sulphuretted essences.

The pure hydrocarbons are generally lighter than water; the other two varieties often have a specific gravity greater than that of water.

The essences which belong to the first class always occur in a state of admixture with a larger or smaller proportion of an oxidized compound.

(A.) *Pure Hydrocarbons.*

(1411) The group of chemical compounds formed by the essential oils which contain no oxygen presents many interesting features; sixteen or twenty of these substances are isomeric. These isomeric bodies may be subdivided into two metameric classes; in one of these, *the terebenes*, the molecule is represented by $\text{C}_{10}\text{H}_{16}$, and to this class oil of turpentine belongs; in the other, the molecule of the oil, like that of essence of eubeds, is represented by $\text{C}_{15}\text{H}_{24}$. The members of each of these groups, notwithstanding the diversity of their odour and taste, are strictly metameric; equal weights of all the members of the same group yielding exactly equal volumes of vapour.

The group of *terebenes*, or *camphogens*, is the more numerous and important. Many characters, both chemical and physical, are common to all the members of the group: for example, they have a specific gravity in the liquid form closely approaching to 0.860; and the boiling point, though subject to greater variations, in most instances is very near 320° (160° C.). Although the general formula of the group contains 4 atoms of hydrogen less than that of the olefine with an equal number of atoms of carbon,

no transformation of the olefines into terebenes, or of terebene into olefine derivatives, has yet been accomplished.

Many of the terebenes cannot be distinguished from each other except by their action upon polarized light: some varieties of oil of turpentine, for example, cause left-handed rotation of a ray of polarized light; oil of lemons produces rotation to the right hand; whilst other oils are destitute of rotatory action upon the plane of polarization. A slight change in the molecular arrangement of the constituent particles of these bodies modifies their action upon polarized light, for it has been found that oil of turpentine by peculiar treatment at a high temperature may be deprived of its rotatory power, although it retains its usual chemical properties (1414).

The terebenes rapidly absorb dry hydrochloric acid gas, and yield compounds termed *artificial camphors*; some of these bodies crystallize, and much resemble natural camphor in appearance and properties; while others of the oils form combinations with the acid equally definite, but which preserve the liquid form, and often retain their optical rotatory power. Oil of turpentine and oil of lemons both form solid compounds with hydrochloric acid as well as liquid ones; but the oils of black pepper and of bergamotte form only liquid compounds:—

Artificial camphors.

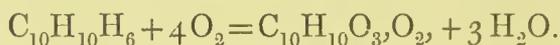
| | | | |
|------------------------------|------------|-----------------------|-----------------|
| From oil of turpentine . . . | } solid { | $C_{10}H_{16}$, | HCl |
| From oil of lemons . . . | | $C_{10}H_{16}$, | 2 HCl |
| From oil of black pepper | } liquid { | 5 ($C_{10}H_{16}$), | 8 HCl? |
| From oil of bergamotte | | 6 ($C_{10}H_{16}$), | 2 HCl, H_2O ? |

Analogous compounds with the other hydracids, such as the hydrobromic and the hydriodic, may also be obtained.

Another remarkable feature of the terebenes is their power of combining with water, and thus forming solid volatile crystalline substances which have a still closer analogy to camphor, both in composition and properties, than the hydrochloric compounds. Mere contact of the oil with water, or with alcohol slightly acidulated with nitric acid, in most instances gives rise to these compounds. Oil of turpentine furnishes not fewer than three such hydrates, viz.: *terpine hydrate* ($C_{10}H_{16}, 3 H_2O$); *terpine* ($C_{10}H_{16}, 2 H_2O$); and *terpinol* [$(C_{10}H_{16})_2H_2O$]: the first two are solid, the last is liquid. Oil of lemons gives two such compounds, viz.: ($C_{10}H_{16}, 3 H_2O$) and ($C_{10}H_{16}, 2 H_2O$); and oil of juniper one such hydrate ($C_{10}H_{16}, 2 H_2O$): the camphor of the *Dryobalanops camphora*, or Borneo camphor, may be represented as $C_{10}H_{16}, H_2O$. All these varieties of camphor, when distilled with phosphoric

anhydride, lose their water, and yield hydrocarbons, having the composition $C_{10}H_{16}$; ordinary camphor $C_{10}H_{16}O$, when similarly treated, also gives a hydrocarbon termed cymol ($C_{10}H_{14}$). Indeed, the simple act of sublimation deprives the solid hydrate ($C_{10}H_{16}, 3H_2O$) of the oil of turpentine, and of lemon, of an atom of water; the sublimate in each case being represented by the formula, $C_{10}H_{16}, 2H_2O$.

The terebenes when exposed to the air absorb oxygen; they become brown and viscid; and are ultimately converted into resins. In many instances this oxidation may be regarded as a simple substitution of oxygen for hydrogen, the number of atoms of oxygen absorbed corresponding exactly to the amount of hydrogen removed in the form of water; but in other cases this constitutes only the first stage of the process, and an additional quantity of oxygen combines with the newly formed oxide: a good example of the latter mode of oxidation is seen in the conversion of the liquid oil of lemons into the solid:—



(1412) OIL OF TURPENTINE ($C_{10}H_{16}$); *Sp. gr. of liq.* 0.864; *of vap.* 4.76; *Rel. wt.* 68; *Boil. pt.* 320° ($160^\circ C.$).—Various species of pine, when wounded, pour out a semi-solid resin, of which there are different varieties: that obtained from the *Pinus abies* constitutes *common turpentine*; that from the larch, *Larix Europæa*, is known as *Venice turpentine*; and that from the *Pistacia lentiscus* forms *Chian turpentine*.

If the turpentine of the *Pinus abies*, or of the *Pinus sylvestris*, be distilled with water, it yields nearly one-fourth of its weight of an essential oil: this oil passes over with the vapour of water as a volatile, limpid, very inflammable liquid, of a penetrating well-known balsamic odour. The residue in the retort constitutes common *rosin*, or *colophony*. Oil of turpentine may be distilled unchanged. It mixes in all proportions with absolute alcohol, with carbon disulphide, with benzol, and with ether, but not with water; it dissolves the fixed and essential oils, and is largely used in the preparation of many kinds of varnish, since it readily dissolves the resins, and on volatilizing leaves them behind in the form of a transparent coating upon the surface of the objects to which it had been applied. Oil of turpentine dissolves sulphur, and phosphorus with facility; it is also one of the best solvents for caoutchouc. Most of the oil of turpentine sold as *camphine* in England produces a right-handed rotation ($= 18^\circ.6$), and is said to be furnished by the *Pinus australis* of the Southern States of North America.

Commercial oil of turpentine frequently consists of a mixture of several isomeric hydrocarbons, which act differently on polarized light. The rotation occasioned by Bordeaux turpentine, which is produced chiefly from the *Pinus maritima*, is left-handed, but the amount of the rotation in different samples varies with the proportions in which the oils are mingled. According to Berthelot, if the ordinary Bordeaux turpentine be distilled *in vacuo*, after saturating the acids which it contains, a homogeneous hydrocarbon, *terebenthene* (*Sp. gr.* 0·864, at 59°), is obtained. It boils at 321°·8 (161° C.). It is endowed with left-handed rotatory action upon a polarized ray = $-42^{\circ}\cdot3$. With hydrochloric acid it gives a solid and a liquid hydrochlorate of similar composition, ($C_{10}H_{16}, HCl$). When the solid compound is heated with dry soap at a temperature of about 401° (205° C.), a white solid, resembling camphor, is obtained; it fuses at 113° (45° C.), and boils at about 320° (160° C.): it has a left-handed rotation = -63° . To this substance ($C_{10}H_{16}$) the name of *terecamphen* has been given. If English camphine be distilled *in vacuo* from potassic carbonate, it gives a corresponding liquid, *australene*, of *sp. gr.* 0·864, boiling at 321°·8, with a right-handed rotation = $+21^{\circ}\cdot5$. It yields with hydrochloric acid compounds corresponding to those of terebenthene, and when distilled with soap furnishes a similar solid, *austracamphen* (rotation $+22^{\circ}$). If either of the solid hydrochlorates of the terebenthenes be heated with baric stearate, or sodic benzoate, instead of with a potash soap, a solid *inactive camphen*, with no rotatory power on polarized light, is obtained.

(1413) *Modifications of Oil of Turpentine*.—Deville (*Ann. de Chimie*, II. lxxv. 37, and III. xxvii. 80) and Berthelot (*Ib.*, III. xxxix. 5) have carefully studied the modifications of which oil of turpentine is susceptible without undergoing any change in the proportion of its components. Some of these modifications retain their rotatory power upon polarized light, whilst others are inactive in this respect:—

a. Active Modifications.—When English essence of turpentine is simply heated in a closed vessel to 464° or 482° (240° or 250° C.), it becomes converted into a mixture of several compounds, which boil at different temperatures; two of these, *isoterebenthene* and *metaterebenthene*, may be separated from each other by fractionated distillation. These modifications may be produced at a lower temperature if the essence be heated with water, or with the chloride of calcium, of strontium, of zinc, or of ammonium. Boric fluoride, as well as many organic acids, such as the acetic, oxalic, and tartaric, also produces similar effects.

1. *Isoterebenthene* ($C_{10}H_{16}$); *Sp. gr.* 0.843, at 71° ; *Boil. pt.* about $350^{\circ}6$ (177° C.).—This is a colourless liquid, having an odour of stale lemons. It exerts a left-handed rotation upon polarized light, but the intensity of this power appears to vary with the duration and intensity of the heat to which it has been exposed. It may be made to yield a crystalline hydrate and a solid hydrochlorate.

2. *Melaterebenthene*, $C_{20}H_{32}$; *Sp. gr.* 0.913, at 68° (20° C.).—This body forms at least one-third of the entire quantity of the essence submitted to heat; it constitutes the residue left in the retort after all the matters volatile below 662° (350° C.) have been expelled. It may be volatilized without decomposition, at a temperature somewhat beyond this. It is a viscous yellowish body, possessed of a strong disagreeable odour, and a tendency to rapid oxidation. It exerts a left-handed rotatory power upon polarized light.

Intermediate between these two bodies are other isomeric compounds, of intermediate boiling points; but they have not been specially examined.

b. Inactive Modifications.—Besides these modifications which retain their rotatory power, four other forms of the essence have been procured, which exert no action upon polarized light. These substances are:—

- | | |
|--------------|---------------------------|
| 1. Terebene | 3. Camphylene, or dadyl |
| 2. Colophene | 4. Terebiline, or peucyl. |

The first two have been obtained by acting upon oil of turpentine with sulphuric acid; the last two by decomposing artificial camphor by means of quicklime (1414).

In order to procure terebene and colophene, Deville mixes any variety of oil of turpentine with about a twentieth of its weight of oil of vitriol, in a flask which is artificially cooled. After brisk agitation, the mixture becomes viscous and of a dark-red colour. It must be left at rest for twenty-four hours, during which time it separates into two layers, the lower one being nearly black and strongly acid. The clear liquid is then to be decanted and gently heated: bubbles of sulphurous anhydride escape, and the colour gradually disappears, whilst the liquid becomes converted into a mixture of terebene and colophene. Upon subjecting it to distillation, terebene passes over in the first portion, and when rectified from a fresh portion of oil of vitriol, is obtained in a state of purity. The last portions of the distillate consist of colophene. Boric fluoride produces a similar effect upon oil of turpentine: it acts still more energetically and rapidly.

Terebene has a characteristic odour, resembling that of oil of thyme. It boils at the same temperature as the unmodified essence of turpentine, yielding a vapour of the same density, but it is less prone to oxidation. It combines with hydrochloric acid, and forms a liquid compound, $(C_{10}H_{16})_2HCl$.

Colophene [$C_{20}H_{32}$; *Sp. gr. of liq.* 0.940; *Boil. pt.* from 590° to 599° (310° to 315° C.)] yields a vapour, the density of which is twice as great as that of terebene, with which it is polymeric. It absorbs hydrochloric acid, and forms with it a compound of the colour of indigo. In order to obtain colophene in a state of purity, it must be rectified from an alloy of potassium and antimony (849). Colophene may also be produced by the distillation of colophony, from which it derives its name. When viewed by direct light it is colourless, but it exhibits the fluorescent character in so marked a degree, that in particular directions it appears to be of a deep indigo-blue. It is slightly viscous.

(1414) *Artificial Camphors, and Oils obtained from them.*—It has already been stated that essence of turpentine combines with hydrochloric acid, with which it may be made to form two compounds, $C_{10}H_{16}, 2HCl$; and $C_{10}H_{16}, HCl$.

The first of these bodies may be obtained by allowing the essence of turpentine to remain for some weeks in contact with an excess of a concentrated solution of hydrochloric acid. It forms flattened rectangular prisms, which have an aromatic odour resembling that of oil of thyme. It is fusible at $111^{\circ}\cdot 2$ (44° C.), and is decomposed by distillation. This dichlorhydrate is optically inactive, and according to Kekulé, whenever produced from any sample of oil of turpentine, is perfectly identical in all its properties.

The second compound [$C_{10}H_{16}, HCl$; *Fusing pt.* 239° (115° C.)] is obtained by transmitting dry hydrochloric acid gas into the artificially cooled essence of turpentine so long as it is absorbed. As soon as this absorption ceases, the compound must be submitted to the action of a freezing mixture of snow and salt, by which it is separated into two portions, one of which crystallizes, whilst the other remains liquid, even at 0° F. The production of the liquid compound is favoured by elevation of temperature; if the temperature of the essence be raised to 212° during the absorption of the hydrochloric acid, the liquid compound only is formed. Both the solid and the liquid portion are found, on analysis, to possess the same composition ($C_{10}H_{16}, HCl$). The solid body has been termed *hydrochlorate of camphene* or of *dadyl*. It crystallizes in white prisms, which have an aromatic smell and taste, resembling that of ordinary camphor. It is insoluble in water; alcohol dissolves one-third of its weight of it. This artificial camphor melts at 239° (115°), and boils at 329° (165° C.), at the same time undergoing partial decomposition.

Camphene, Camphilene, or Dadyl: *Boil. pt.* $273^{\circ}\cdot 2$ (134° C.).—If the vapour of the solid compound ($C_{10}H_{16}, HCl$) with hydrochloric acid be transmitted over heated quicklime, it is decomposed, calcic chloride and water are formed, and a body termed *camphilene* (Deville), having the composition of oil of turpentine, is liberated; this body may again be combined with hydrochloric acid, in which case the solid artificial camphor is reproduced. Camphilene is entirely devoid of the power of rotation upon a ray of polarized light.

The liquid hydrochlorate ($C_{10}H_{16}, HCl$) has been termed *hydrochlorate of peucyl*: it is somewhat viscous, and has a sp. gr. of 1.017. If it be distilled with quicklime, *terebilene* (Deville), another hydrocarbon isomeric with essence of turpentine, comes over; it possesses no rotatory power upon polarized light. When again combined with hydrochloric acid, it furnishes a liquid uncrystallizable compound.

Oil of turpentine is not the only one of these essential oils or hydrocarbons which exhibits this remarkable facility of assuming

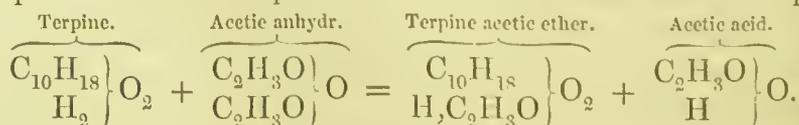
different isomeric states under the influence of heat and of acids. Oil of lemons produces an analogous, though different series of modified products, and most probably the greater number of the essential oils metameric with oil of turpentine would be found to furnish like results when subjected to similar treatment.

Hydrates of Oil of Turpentine.—Mention has been already made (1411) of the power which oil of turpentine possesses of combining slowly with water, and forming crystalline compounds. One of these, *terpine hydrate* ($C_{10}H_{16}, 3H_2O$) may be obtained in the form of rhombic prisms, by agitating together frequently, for two or three days, a mixture of 4 measures of oil of turpentine, 1 of nitric acid (sp. gr. 1.36), and 3 of alcohol (sp. gr. 0.840). In the course of a month or six weeks, especially if it be exposed to the sun's rays, voluminous crystals are formed. This hydrate is soluble in 22 parts of boiling water, from which it crystallizes on cooling. It is also freely soluble in alcohol, ether, oil of turpentine, and acetic acid. When sublimed it loses H_2O , and is converted into terpine.

Terpine [$C_{10}H_{16}, 2H_2O$; Sp. gr. of vap. 6.257; Fusing pt. 302° (150° C.); Boil. pt. 482° (250° C.)] may also be procured when oil of turpentine and water are brought into contact, especially if the temperature be maintained at about 122° (50° C.): when heated it melts, and may be sublimed without being decomposed. When exposed to the air it absorbs water, and becomes reconverted into the hydrate with $3H_2O$.

A third hydrate, termed *terpinol* [$(C_{10}H_{16})_2H_2O$; Sp. gr. 0.852; Boil. pt. $334^\circ.4$ (168° C.)], which is liquid at ordinary temperatures, may be obtained by dissolving either of the preceding hydrates in boiling water, adding a little hydrochloric or sulphuric acid, and distilling. Terpinol passes over as an oily liquid, with an odour like that of hyacinths. None of these hydrates possess any optical rotatory power.

The hydrates of oil of turpentine have been specially studied by Oppenheim (*Liebig's Ann.*, exxix. 149), who represents terpine ($C_{10}H_{20}O_2$) as a diatomic alcohol, and the dihydrochlorate of turpentine as the corresponding hydrochloric ether ($C_{10}H_{18}Cl_2$). By heating terpine to 284° (140° C.) with acetic anhydride, he obtained a compound which he represents as the monoacetic ether of terpine:



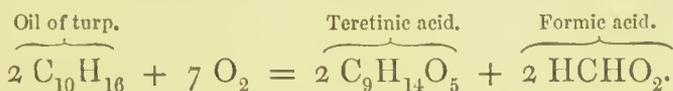
The vapour density of this body is unknown, as it is decomposed when heated beyond 284° .

Kekulé regards these compounds not as bodies corresponding to glycols, but as simply produced by additive combination, and he represents the monaetic compound as $C_{10}H_{16}, C_2H_4O_2, H_2O$. They require, however, further study.

(1415) *Products of the Oxidation of Oil of Turpentine.*—Oil of turpentine gradually absorbs oxygen from the air, with the formation of a certain proportion of ozone. Besides the resins which are formed by the spontaneous oxidation of essence of turpentine, various compounds may be obtained from it by artificial processes of oxidation.

When the essence is distilled with potassic dichromate and sulphuric acid, formic acid is produced abundantly. If it be distilled with water and chloride of lime, a copious extrication of carbonic anhydride takes place with tumultuous violence, and chloroform is found among the products of the distillation. Chlorine acts violently upon oil of turpentine, the reaction being often attended with sufficient heat to inflame the mixture. Bromine and iodine also act similarly but much less energetically.

If oil of turpentine be heated gently with plumbic oxide, it absorbs oxygen rapidly, and becomes converted into formic and *teretic* acids, which enter into combination with the plumbic oxide:



Teretic acid is soluble in alcohol, from which it may be obtained crystallized in tufts of delicate colourless needles: it is insoluble in water. Most of the compounds of this acid with the metallic oxides are insoluble in water, but soluble in alcohol.

If a few teaspoonfuls of essence of turpentine be introduced into a jar nearly filled with oxygen gas, standing over water, and exposed to the rays of the sun, the interior of the jar speedily becomes coated with brilliant crystals of *hydrated oxide of turpentine* ($C_{10}H_{16}O, H_2O$). This substance may be dissolved in alcohol, from which it may be obtained in crystals. It is also soluble in ether and in boiling water.

Nitric acid acts violently upon oil of turpentine, often causing it to inflame: the two liquids must, therefore, be mixed very cautiously. As the result of the action, a yellow resin is formed, and a quantity of oxalic and terebic acid (1481), besides three other acids, one of which is fusible, and may be sublimed; it is termed *terebenzic acid* ($HC_7H_6O_2?$). The second is isomeric with phthalic acid, and is hence termed *terephthalic acid* ($C_8H_6O_4$); it is insoluble in water, alcohol, and ether. The third is termed

terechrysic acid ($C_6H_8O_5$?) in allusion to its yellow colour; it is very soluble in water, and is not susceptible of crystallization.

(1416) *Other Essences which yield Oils isomeric with Oil of Turpentine.*—The following are some of the principal essences which are metameric or isomeric with oil of turpentine:—

Oil of Bergamotte (*Sp. gr.* 0·869), which is obtained from the rind of the ripe fruit of the bergamotte or lime, consists of two portions, viz., a hydrocarbon ($C_{10}H_{16}$), and a solid substance ($C_{15}H_{10}O_5$), which may be supposed to be formed from the liquid essence by oxidation; $3 C_{10}H_{16} + 12 O_2 = 2 C_{15}H_{10}O_5 + 14 H_2O$.

2. *Oil of Lemons* also contains a solid oxidized essence in small quantity ($C_{10}H_{10}O_5$), but the bulk of the oil consists of a hydrocarbon, *citrene* ($C_{10}H_{16}$), which may be obtained in a state of purity by distilling the crude essence. This hydrocarbon is susceptible of a variety of modifications, analogous to those which may be produced in oil of turpentine. The essential oil from the rind of the *orange* appears to be identical with the essence of lemons.

3. *Oil of Neroli* is the fragrant oil obtained from the blossoms of the orange tree. It is colourless when recently distilled, but becomes red by exposure to light, or by admixture with sulphuric acid. This oil also consists of a hydrocarbon $C_{10}H_{16}$, and of an oxidized portion which is solid and destitute of odour, the fragrance of the oil being due to the hydrocarbon.

4. The oil of the *common birch*, which is used in the preparation of Russian leather, to which it imparts its agreeable odour, is obtained from the tar furnished by the imperfect combustion of the bark of the tree. It consists of a mixture of several oils, amongst which the principal is the hydrocarbon $C_{10}H_{16}$, which may be isolated by repeated fractionated distillation.

5. *Essence of Camomile*: of this there are two varieties, one obtained from the *Anthemis nobilis*, is of a greenish colour, and consists of a hydrocarbon ($C_{10}H_{16}$), and an oxidized portion ($C_5H_8O^?$), which when heated with caustic potash is converted into potassic angelate ($KC_5H_7O_2$), with evolution of hydrogen (1296). The second variety is obtained from the *Matricaria chamomilla*. It is remarkable for its deep blue colour: it contains an oxidized oil ($C_{10}H_{16}O$), which has the composition of laurel camphor. It may be distilled without change, and remains liquid below 32° (0° C.).

The oil of the *Achillea millefolium* is also distinguished by its beautiful blue colour, but it has not been minutely examined.

6. *Essence of Juniper* boils at 320° (160° C.). It produces left-handed rotation on a ray of polarized light, and if left in contact with water gradually deposits a white crystalline hydrate ($C_{10}H_{16} \cdot H_2O$).

(1417) 7. *Oil of Caraway* (*Sp. gr.* 0·938) is obtained from the seeds of the *Carum carvi*. It consists of two portions: the hydrocarbon ($C_{10}H_{16}$) has been termed *carvene*; the oxidized portion is known as *carvol*. Carvene is a very fluid, colourless oil, lighter than water, with a slight agreeable odour, and an aromatic taste; it absorbs hydrochloric acid gas, and forms with it a crystallizable solid which melts at 123° ($50^\circ \cdot 5$ C.). Carvol, $C_{10}H_{14}O$, is a liquid of sp. gr. 0·953; it boils at about 437° (225° C.; Voelckel): it is isomeric with thymol and with cuminic alcohol. Carvol yields a liquid camphor ($C_{10}H_{14}O \cdot HCl$) with hydrochloric acid. With sulphuretted hydrogen carvol yields a compound termed *carvol hydrosulphate* [$(C_{10}H_{14}O)_2 \cdot H_2S$]: this substance is obtained by agitating the less volatile portion of oil of caraway with an equal bulk of alcohol recently saturated with ammonia and sulphuretted hydrogen; it is deposited in yellowish crystals, which may be recrystallized from boiling alcohol; they may be volatilized without decomposition. If this compound be agitated with an alcoholic solution of potash, it is decomposed; pure carvol is liberated and dis-

solved by the alcohol, and on the addition of water it rises to the surface in the form of an oily layer.

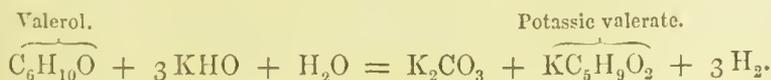
(1418) 8. *Oil of Cloves* (*Sp. gr.* 1.055 – 1.060).—The berries of the pimento and the unexpanded flower-buds of the *Caryophyllus aromaticus*, or 'cloves,' yield an essential oil which is not solidified by a cold of 0° F. It consists chiefly of a hydrocarbon isomeric with oil of turpentine, holding in solution an acid body termed *eugenic acid* (C₁₀H₁₂O₂); *sp. gr. of liq.* 1.079; *of vap.* 6.5; *boil. pt.* 469°.4 (243° C.; Ettling). This acid forms a colourless liquid, which emits the odour of oil of cloves: it forms crystallizable salts with the alkali-metals. Two crystallizable substances are also obtained from oil of cloves; one of them is named *eugenin*, and is said to be isomeric with eugenic acid. The other, termed *caryophyllin*, (C₁₀H₁₆O), is isomeric with ordinary camphor; it is gradually deposited from the oil in crystalline needles.

9. *Oil of Ginger* (*Sp. gr.* 0.893) is yellow, and intensely burning and aromatic. It boils at about 474°.8 (246° C.). It appears to have the composition of a hydrate of a hydrocarbon isomeric with oil of turpentine, [8 (C₁₀H₁₆) 5 H₂O].

(1419) 10. *Oil of Cubebs* (*Sp. gr.* 0.929).—When cubebs (*Piper cubeba*) are distilled with water, they furnish an essence which is colourless and somewhat viscous; it has a camphreous, aromatic taste. It boils at a little below 500 (260° C.), and when distilled yields a hydrocarbon which furnishes a crystalline compound with hydrochloric acid, consisting of (C₁₅H₂₄, 2 HCl). This substance fuses at 267°.8 (131° C.). When essence of cubebs is redistilled with water, it deposits a species of camphor (C₁₅H₂₄, H₂O), which melts at 154°.4, (68° C.), and may be distilled at 302° (150° C.) without decomposition. The essence of cubebs, therefore, though isomeric with oil of turpentine, contains the hydrocarbon in a more condensed form, viz., as (C₁₅H₂₄).

11. *Essence of Capivi* (*Sp. gr.* 0.878), which is obtained by distilling balsam of capivi with water, appears to belong to the same class as that of cubebs. It boils at 500° (260° C.), undergoing partial decomposition. It yields a crystalline compound with hydrochloric acid (C₁₅H₂₄, 2 HCl).

(1420) 12. *Essence of Hops*.—This essence is procured by distilling dried hop-cones with water. The oil when first obtained is of a beautiful green colour, but it is rendered colourless by rectification. It remains liquid at 1°.4 (– 17° C.), and begins to boil at about 284° (140° C.), but the boiling point rises rapidly till it exceeds 599° (315° C.). Its odour somewhat resembles that of the hop. When exposed to the air it becomes converted into an acid resinous mass. Oil of hops is a mixture of the hydrocarbon C₁₀H₁₆, with *valerol* (C₈H₁₀O). The hydrocarbon may be freed from valerol by allowing the oil to fall drop by drop upon caustic potash, when potassic carbonate and valerate are formed from the valerol, and the hydrocarbon distils unaltered:—



13. *Essence of Valerian* also consists of valerol and of a hydrocarbon C₁₀H₁₆, which is identical with borneène, the hydrocarbon which accompanies Borneo camphor (1427). By distilling off the essence at a temperature of 392° (200° C.) the borneène may be expelled. Valerol when exposed to a temperature of 32° (0° C.) crystallizes in transparent prisms, which do not melt until heated to 68° (20° C.). It gradually becomes oxidized by exposure to the air, and the disagreeable odour of valeric acid is developed. In its pure form its odour is but slight, resembling that of hay. Sulphuric acid dissolves it, and forms a blood-red solution, which contains a colligated sulpho-acid.

(1421) 14. *Oil of Thyme*.—This consists of an oxidized portion, *thymol*, and of a hydrocarbon, *thymene*. The latter constitutes the more volatile portion

of the oil; it has an agreeable odour of the plant: it boils at 329° (165° C.), and exerts no action on polarized light. *Thymol* [($C_{10}H_{14}O$); *Fusing pt.* 111° ·2 (44° C.); *Boil. pt.* 446° (230 C.); *Sp. gr. of vap.* 5·51; *Rel. wt.* 75] is isomeric with carvol and with cuninic alcohol (1446); it has the agreeable odour of thyme, and constitutes about one-half the essence of thyme. It is a fusible solid which crystallizes in oblique rhombic prisms, and is very soluble in alcohol and in ether. This substance is also contained in the oil of horse-mint (*Monarda punctata*), and in that of an Indian plant, the *Ptychotis ajowan*. Thymol combines with sulphuric acid, and forms a crystallizable colligated acid, the *thymyl-sulphuric* ($HC_{10}H_{13}SO_4$), which is analogous to the ethylsulphuric.

According to Lallemand, when thymol is treated with oxidizing agents such as chromic acid, or a mixture of black oxide of manganese and sulphuric acid, it yields a substance termed *thymoil* ($C_{12}H_{16}O_2$)* which sublimes in brilliant orange-coloured quadrangular plates, of an aromatic odour and an appearance resembling that of quinone (1337), with which it is homologous. If treated with sulphurous anhydride or other reducing agents, it combines with hydrogen and yields *thymoilol* ($C_{12}H_{18}O_2$), the homologue of hydroquinone; and by mixing a solution of equal weights of thymoil and thymoilol in boiling alcohol, the liquid immediately becomes of a deep red colour, and deposits beautiful violet-coloured prismatic crystals, which have a bronze lustre. These correspond to what has been termed green hydroquinone.

(1422) Table of Essential Oils not containing Oxygen.

| Oil. | Formula. | Specific Gravity. | | Boiling Point. | | Direction of rotation. | Compound with HCl. | Remarks. | | |
|-------------------------|------------------------|---|---------|----------------|-----------|------------------------|--------------------|-------------------------------------|--|------------------------------------|
| | | Liquid. | Vapour. | ° F. | ° C. | | | | | |
| From Oil of Turpentine. | Terebenthene | $C_{10}H_{16}$ | 0·864 | 4·812 | 321·8 | 161 | left. | { solid & liquid. | Many of the oils enumerated in this table contain oxidized compounds in addition to the hydrocarbon, — as may be seen by the formulæ given in this column. | |
| | Isoterebenthene | " | 0·843 | | 350·6 | 177 | left. | solid. | | |
| | Metaterebenthene | " | 0·913 | | above 680 | 360 | | | | |
| | Terebene | " | 0·86 | | 320 | 160 | none. | liquid. | | |
| | Terebilene | " | 0·843 | 4·767 | 273·2 | 134 | uoue. | liquid. | | |
| | Camphylene | " | 0·87 | | 273·2 | 134 | uone. | solid. | | |
| | Bergamotte | " | 0·869 | | 361·4 | 183 | right. | | | $C_{20}H_{16}$ & $C_{15}H_{10}O_5$ |
| | Borneène | " | | 4·60 | 320 | 160 | left. | solid. | | |
| | Birch, (tar from bark) | " | 0·847 | 5·28 | 312·8 | 156 | | | | { Consists of several oils. |
| | Camomile | " | | | 347 | 175 | | | | $C_{20}H_{16}$ & C_8H_8O |
| | Caraway | " | 0·938 | 5·17 | 343·4 | 173 | right. | solid. | | $C_{20}H_{16}$ & $C_{10}H_{14}O$ |
| | Cloves | " | 1·060 | | 289·4 | 143 | | liquid. | | $C_{16}H_{16}$ & $C_{10}H_{12}O_2$ |
| | Elemi | " | 0·849 | | 345·2 | 174 | left. | { solid & liquid. | | |
| | Hop | " | | | | | right. | | | $C_{10}H_{16}$ & $C_6H_{10}O$ |
| | Juniper | " | 0·86 | | 320 | 160 | left. | liquid. | | |
| | Lemons | " | 0·851 | 4·87 | 343·4 | 173 | right. | { solid & liquid. | | { Contain also |
| | Orange | " | 0·83 | 4·64 | 356 | 180 | right. | | | $C_{10}H_{10}O_5$ |
| | Parsley | " | | | 320 | 160 | | | | Contains an oxide. |
| | Pepper | " | 0·864 | 4·73 | 332·6 | 167 | | liquid. | | |
| | Savine | " | | | 320 | 160 | | | | |
| Tolu | " | 0·837 | | 320 | 160 | | | | | |
| Thyme | " | | 4·76 | 329 | 165 | none. | liquid. | $C_{10}H_{16}$ & $C_{10}H_{14}O$ | | |
| Valerian | " | This hydrocarbon is identical with Borneène | | | | | | $C_{10}H_{16}$ & $C_6H_{10}O$ | | |
| Capivi | $C_{15}H_{24}$ | 0·878 | | 500 | 200 | left. | solid. | | | |
| Cubebs | $C_{15}H_{24}$ | 0·929 | | 489·2 | 254 | left. | solid. | $C_{15}H_{24}$ & $C_{15}H_{24}H_2O$ | | |
| Cedrene | $C_{16}H_{26}$ | 0·984 | 7·9 | 458·6 | 237 | right. | | $C_{16}H_{26}$ & $C_{16}H_{28}O$ | | |
| Menthene | $C_{10}H_{18}$ | 0·851 | 4·94 | 325·4 | 163 | | | From oil of peppermint | | |
| Colophene | $C_{20}H_{32}$ | 0·940 | | 595·4 | 313 | uone. | | | | |
| Attar of roses | $(CH_2)_x$ | | | 590 | 310 | | | | | |

* It is possible that the formula of thymoil should be indicated as one-half of that given by Gerhardt and Lallemand; so that thymoil should be represented

(1423) *Essences which contain other Hydrocarbons.*—1. *Oil of Peppermint.*—This essence, when distilled with phosphoric anhydride, yields a hydrocarbon termed *menthene*, $C_{10}H_{18}$. The essence also appears to contain a solid hydrate of this compound ($C_{10}H_{13}, H_2O$), which is analogous to camphor; this substance may be obtained in crystals; it fuses at $93^{\circ}.2$ (34° C.), and boils at $416^{\circ}.3$ ($213^{\circ}.5$ C.), emitting a vapour of sp. gr. 5.62.

2. Essence of *Cedar wood* is somewhat analogous in its nature to the foregoing oil. It consists of a crystallizable solid ($C_{16}H_{28}O$)—dissolved in a hydrocarbon ($C_{16}H_{26}$), which has been termed *cedrene*.

3. *Attar of Roses* consists also of two compounds, one of which has but little odour; it remains solid at temperatures below 203° (95° C.), and boils at about 590° (310° C.). It is polymeric with olefiant gas. The fragrant portion is liquid; it contains oxygen, but its composition is not accurately known.

The table on the preceding page includes a list of the more important essences which contain unoxidized hydrocarbons.

(B.) *Oxidized Essences.*

(1424) Several varieties of oxidized essential oils are known; viz.:—(a) Solid crystallized essences which have the composition of hydrates of a hydrocarbon; these constitute the *camphors*, of which laurel camphor ($C_{10}H_{14}, H_2O$) affords the best illustration. (b) *Indifferent* oils, such as spear-mint oil ($C_{10}H_{20}O$). (c) *Aldehyds* of aromatic acids, such as oil of bitter almonds (C_7H_5O, H), and of cinnamon (C_9H_7O, H). (d) *Compound ethers*, such as oil of winter-green (methyl salicylate, $CH_3, C_7H_5O_3$).

(1425) (a) CAMPHORS.—From the statements already given, it is clear that the camphors are closely related to the different varieties of turpentine. Two species of camphor are known in the east, *Borneo camphor* and *laurel camphor*; the one called Borneo camphor ($C_{10}H_{18}O$) is obtained from the *Dryobalanops camphora*, and is so highly prized by the natives of the east that but little of it finds its way into the European market.

Laurel Camphor ($C_{10}H_{16}O$); *Sp. gr. of solid* 0.996; *of vap.* 5.3147; *Kel. wt.* 76; *Fusing pt.* 347° (175° C.); *Boil. pt.* $399^{\circ}.2$ (204° C.).—This constitutes the common camphor of the shops. The commercial supply is furnished by the *Laurus camphora*, but

as C_6H_8O , since it is not easy to see how a body which, like thymol, contains in its molecule only 10 atoms of carbon, should by oxidation yield a compound containing 12 atoms of carbon.

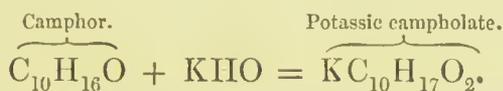
it is also produced in small quantity by many other plants, apparently from the oxidation of their essential oils. This is easily understood, since the formula of this substance is the same as that of oil of turpentine to which 1 atom of oxygen has been added. The oil of lavender, of rosemary, and of marjoram, and that of several of the *Labiatae*, such as the oil of pennyroyal and of spear-mint, contains camphor in solution. Amber, and the oils of valerian, tansy, and sage also yield it when treated with nitric acid.

Three isomeric modifications of camphor are known; they cannot be distinguished from each other, except by their action upon a ray of polarized light: one of the varieties produces rotation of the ray to the right; the second variety produces left-handed rotation; whilst the third variety has no sensible effect upon a polarized ray. The common camphor of the shops, and that obtained by the action of nitric acid upon borneone, is the right-handed modification. The camphor contained in the oil of *Matricaria parthenium* exerts a left-handed rotatory action upon a ray of polarized light (Chautard); whilst, according to Biot, the camphor deposited by oil of lavender is destitute of any rotatory power.

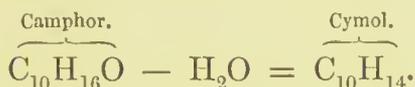
In the ordinary process of extracting camphor, the wood and branches of the camphor laurel are chopped up, and placed with water in a rude kind of still, the head of which is filled with rice straw. On the application of heat the camphor rises in vapour with the water, and becomes condensed in the straw. It is then submitted to a second sublimation, by which means it is obtained in the form of the crude, granular camphor of commerce. This article is subsequently refined in this country, by placing charges of 10 lb. or 12 lb. of the crude camphor in large globular glass flasks, furnished with a short wide neck: heat is applied to the bottom of these flasks by means of a sand bath; and as soon as the camphor is melted, a portion of lime is added to each flask, after which the heat is steadily maintained for forty-eight hours: during this period the camphor is slowly sublimed into the upper part of the flasks. When the operation is finished the flasks are cooled, and at the same time broken, by sprinkling them with cold water: the pure camphor can then be removed with facility. The produce of this operation assumes the form of white, tough, translucent masses. Camphor has a peculiar odour and an aromatic taste, at first hot, and afterwards cooling. It floats in water, and is sparingly soluble in this liquid; but is dissolved freely by alcohol, ether, acetic acid, and the essential oils. Although pure camphor is tough and difficult to pulverize, yet if moistened with a few drops of alcohol, it may be reduced to powder with facility. When particles of powdered camphor are thrown on the surface of water, free from grease, each fragment begins to be dissolved with a remarkable and rapid gyratory

motion, which is instantly checked by allowing a drop of any essential oil to fall upon the surface of the water. Camphor is very inflammable, and burns with a white smoky flame. It volatilizes slowly at common temperatures; if kept in glass bottles it becomes gradually sublimed, and condenses in octahedral crystals on the side of the vessel which is coolest. If a coil of red-hot platinum wire be suspended just over a lump of camphor, the metal continues to glow, and produces a slow combustion of the camphor, which may be maintained so long as any portion remains unconsumed.

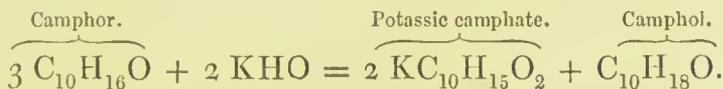
If camphor be heated under pressure with caustic potash, it combines with the alkali, a salt termed *potassic campholate* being formed:—



When camphor is distilled with phosphoric anhydride, or with dry zinc chloride, it undergoes decomposition, and is deprived of the elements of water, whilst *cymol* is formed:—



If 2 parts of camphor be heated under pressure to about 356° or 392° (180° or 200° C.), with 1 of caustic potash, in 5 or 6 of alcohol, the camphor is converted into Borneo camphor and *potassic camphate*. Camphic acid ($\text{HC}_{10}\text{H}_{15}\text{O}_2$) bears to Borneo camphor the same relation that acetic acid does to ethyl alcohol:—



(1426) *Camphoric Acid* ($\text{H}_2\text{C}_{10}\text{H}_{14}\text{O}_4$); *Fusing pt.* 158° (70° C.).

—Camphor, when heated with ten times its weight of concentrated nitric acid, is slowly oxidized, and becomes converted into *camphoric acid*. This substance is sparingly soluble in water, but is freely dissolved by alcohol, as well as by ether and the essential oils. It is deposited from its solutions in the form of prismatic needles, which have a very sour taste: they are destitute of odour. Camphoric acid is dibasic; it may be deprived of its basic water, and obtained in the form of anhydride by sublimation. A solution of camphoric acid produces a precipitate in a solution of normal plumbic acetate.

It appears that three isomeric modifications of camphoric acid exist: the compound just described is characterized by its power of producing right-handed rotation of a ray of polarized light;

but, according to Chautard, the camphoric acid obtained by treating the camphor of the *Matricaria parthenium* with nitric acid, exerts a left-handed rotatory action; and if concentrated alcoholic solutions of the right-handed and left-handed camphoric acids be mixed in equivalent proportions, the temperature rises several degrees, and a copious white crystalline deposit of *paracamphoric* acid is obtained, which like racemic acid, is destitute of any rotatory action upon the plane of polarization: paracamphoric acid differs somewhat in chemical properties from either of its two components, being less soluble in alcohol, ether, and water. A similar acid may be obtained by the oxidation of lavender camphor.

(1427) *Borneo Camphor*, *Borneol*, or *Camphol* ($C_{10}H_{15}O$); *Fusing pt.* $388^{\circ}.4$ ($198^{\circ} C.$); *Boil. pt.* $413^{\circ}.6$ ($212^{\circ} C.$).—This substance differs from the preceding variety of camphor in containing 2 atoms more of hydrogen. It is less fusible and volatile than common camphor, but is denser and harder. It exerts a right-handed rotatory action* upon polarized light = $33^{\circ}.4$, but its power in this respect is weaker than that of ordinary camphor, from which it can scarcely be distinguished in taste, smell, solubility, and general appearance. It crystallizes in small, transparent, regular, colourless, six-sided prisms. If gently warmed with nitric acid of moderate strength, it loses 2 atoms of hydrogen, and is converted into ordinary camphor. Indeed, this camphor has been regarded as an alcohol of which ordinary camphor would be the aldehyd. When heated with benzoic acid a compound termed *camphyl benzoate*, or camphobenzoic ether ($C_{10}H_{17}, C_7H_5O_2$), is obtained, while water is separated.

Camphol occurs in the *Dryobalanops*, in combination with an oil ($C_{10}H_{16}$) termed *borneène*, which has the composition of ordinary oil of turpentine: the same hydrocarbon also occurs in the essential oil of valerian. In order to procure the camphor, punctures are made into the wood of the growing tree, and the oil which exudes is submitted to distillation: the borneène is volatilized, and an imperfect separation of the camphor and oil is thus effected. If borneène be repeatedly distilled with a solution of potash, it combines with the elements of an atom of water, and is converted into camphol. A similar conversion into the same camphor also occurs if the oil be dissolved in an equal

* A lævo-rotatory and a nearly inactive variety of this camphor are also known. The former is obtained among the products of fermentation of madder root.

bulk of an alcoholic solution of potash, and be left at rest in imperfectly closed vessels for a few days; on dilution with water, the camphor is separated. Camphol, if mixed with phosphoric anhydride and distilled, loses an atom of water, and is reconverted into borneène, which corresponds to the olefine of ordinary alcohol.

Allusion has already been made to other camphors, such as—

| | | |
|---------------------------|-----------|--|
| Cubeb's camphor (1419) | | (C ₁₅ H ₂₄ H ₂ O) |
| Turpentine camphor (1414) | | (C ₁₀ H ₁₆ , 2 H ₂ O) |
| Peppermint camphor (1423) | | (C ₁₀ H ₁₈ , H ₂ O), |

and so on. These compounds, however, are of little importance.

(1428) (b) *Indifferent essential Oils containing Oxygen.*—The properties of many of these have been already mentioned when speaking of the hydrocarbons with which they are associated (1416—1423).

1. *Oil of Lavender (Sp. gr. 0.898).*—The exact composition of this fragrant and well-known oil has not been accurately ascertained. It is soluble in concentrated acetic acid: when long kept it deposits a large proportion of laurel camphor.

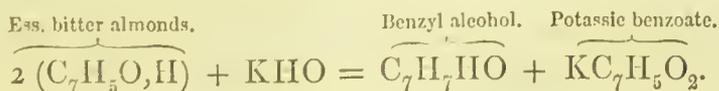
2. *Oil of Wormwood* is isomeric with laurel camphor.

Besides these, there are a great variety of essences which contain oxygen, but which have been only imperfectly examined; such, for instance, as the oils of cajeput, dill, marjoram, pennyroyal, sage, sassafras, and many other plants.

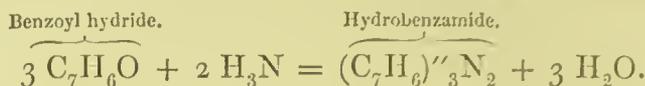
(1429) (c) *Aromatic Aldehyds.*—The oils of bitter almonds, spiræa, cinnamon, and cumin are characterized by forming crystallized compounds with hydric-sodic sulphite, and, like the aldehyds of the series homologous with ordinary alcohol, they exhibit a strong tendency to form acids by the absorption of one atom of oxygen. The oils of this class, however, differ from the ordinary aldehyds in the facility with which they allow the displacement of one atom of the hydrogen which they contain, by an atom of chlorine, of bromine, of cyanogen, and of various electro-negative elements. They have been regarded as hydrides of peculiar oxidized radicles; for example:—

| | | |
|-------------------------|--|---------------------|
| Oil of bitter almonds . | C ₇ H ₅ O, H = Bz, H | (Benzoyl hydride) |
| Oil of cumin | C ₁₀ H ₁₁ O, H = Cu, H | (Cumyl hydride) |
| Oil of cinnamon . . . | C ₉ H ₇ O, H = Ci, H | (Cinnamyl hydride). |

When these aldehyds are heated with an alcoholic solution of potash they are not resinified like the aldehyds of the fatty acids, but yield the alcohol and a potassium salt of the acid of the series (Cannizzaro). Bitter almond oil, for example, furnishes the alcohol of the benzoic series and potassic benzoate:—



Ammonia does not combine directly with these aldehyds, but causes a separation of water: three atoms of the oil react upon two of ammonia, furnishing a hydramide; as for example:—



In describing these oils it will be convenient to consider their most important derivatives, which are very numerous, and embrace compounds many of which present several points of interest.

In this section the following compounds will be examined:—

1. Essence of bitter almonds.—Benzoic series.—Hippuric acid.
2. Essence of cumin.—Cuminic series.
3. Essence of cinnamon.—Cinnamic series.
4. Essence of spiræa.—Salicylic series.—Salicin.—Populin.—Coumarin.
5. Essence of aniseed.—Anisic series.

1. *Essence of Bitter Almonds.—Benzoic Series.*

(1430) The essence of bitter almonds is the most important member of the group of oxidized essential oils. It formed the subject of a remarkable memoir by Liebig and Wöhler (*Ann. de Chimie*, II. li. 273), in which they first systematically applied the theory of compound radicles to substances of organic origin. The publication of this paper exercised an immediate and extraordinary influence upon the study of organic chemistry, in which, indeed, it inaugurated a new era, and thus led to a series of brilliant discoveries, which followed in rapid succession.

The following compounds of the benzoic series will be briefly described, or the mode of their formation will be indicated:—

| | | |
|-------------------------------|--|---------------------------|
| Amygdalin | $\text{C}_{20}\text{H}_{27}\text{NO}_{11}, 3 \text{ H}_2\text{O}$ | |
| Amygdalic acid | $\text{H}_2\text{C}_{40}\text{H}_{52}\text{O}_{25}$ | |
| <hr/> | | |
| Benzoyl hydride | $\text{C}_7\text{H}_5\text{O}, \text{H}$ | = BzH |
| Nitro-benzoyl | $\text{C}_7\text{H}_5\text{O}, \text{NO}_2$ | = BzNO ₂ |
| Chlorobenzol | $\text{C}_7\text{H}_6\text{Cl}_2$ | |
| Benzoyl chloride | $\text{C}_7\text{H}_5\text{O}, \text{Cl}$ | = BzCl |
| Benzoyl chlorohydride | $\text{C}_7\text{H}_5\text{O}, \text{H} . \text{C}_7\text{H}_5\text{O}, \text{Cl}$ | = BzH, BzCl |
| Benzoyl sulphide | $(\text{C}_7\text{H}_5\text{O})_2\text{S}$ | = Bz ₂ S |
| Benzoyl bromide | $\text{C}_7\text{H}_5\text{O}, \text{Br}$ | = BzBr |
| Benzoyl iodide | $\text{C}_7\text{H}_5\text{O}, \text{I}$ | = BzI |
| Benzoyl cyanide | $\text{C}_7\text{H}_5\text{O}, \text{CN}$ | = BzCy |
| Formobenzoylic acid | $\text{HC}_7\text{H}_6\text{O}, \text{C}\text{H}\text{O}_2$ | = H BzH, CHO ₂ |
| Benzoyl-hydride benzoate | $2 \text{ C}_7\text{H}_6\text{O}, \text{C}_7\text{H}_6\text{O}_2$ | = 2 BzH, H BzO |

| | | |
|--|-------------------------|-------------------------|
| Benzoyl-hydride hydro- cyanate | C_7H_6O, HCN | = BzH, HCy |
| Benzimide (cyano-benzoyl hydride) | $C_{23}H_{18}N_2O_2$ | |
| Benzoic acid | $HC_7H_5O_2$ | = HBzO |
| Benzoic anhydride | $(C_7H_5O)_2O$ | = BzBzO |
| Aceto-benzoic anhydride | $C_7H_5O, C_2H_3O_2$ | = AcBzO |
| Sulphobenzoic acid | $H_2C_7H_4SO_5$ | |
| Nitrobenzoic acid | HC_7H_4, NO_2, O_2 | |
| Amidobenzoic acid | HC_7H_4, H_2N, O_2 | |
| Benzamide | H_2, C_7H_5O, N | = H_2, Bz, N |
| Benzanilide | C_6H_5, H, C_7H_5O, N | = C_6H_5, H, Bz, N |
| Hydrobenzamide | $C_{21}H_{18}N_2$ | |
| Dibenzoylimide | $C_{14}H_{13}NO$ | |
| Benzhydramide | $C_{22}H_{18}N_2O$ | |
| Benzoylic azotide | $C_{15}H_{12}N_2$ | |
| Azobenzoyl | $C_{21}H_{15}N_2$ | |
| Benzyl alcohol | C_7H_7, HO | |
| Benzyl-ether | $(C_7H_7)_2O$ | |
| Toluylia (toluidine) | C_7H_7, H_2N | |
| <hr/> | | |
| Benzoine | $C_{14}H_{12}O_2$ | = $C_{14}H_{11}O_2, H$ |
| Benzile | $C_{14}H_{10}O_2$ | |
| Benzilic acid | $HC_{14}H_{11}O_3$ | = $HC_{14}H_{11}O_2, O$ |
| Benzile chloride | $C_{14}H_{11}O_2Cl$ | = $C_{14}H_{11}O_2, Cl$ |
| Benzoinamide | $C_{42}H_{36}N_4$ | |
| Benzoinam | $C_{28}H_{24}N_2O$ | |

(1431) *Amygdalin* ($C_{20}H_{27}NO_{11}, 3H_2O$).—The pulp of the bitter almond (*Amygdalus communis*) contains a large portion of a bland, nearly tasteless, colourless fixed oil, which can be separated from it by pressure, and which is identical in properties with that furnished by the sweet almond; but the kernel does not contain any essential oil ready formed. As soon, however, as the pulp is bruised and moistened with water, the fragrant odour of the essence is perceived. This development of the essential oil is due to the decomposition of *amygdalin*, a crystallizable azotised principle which is contained in the kernel, in addition to the oily, starchy, saccharine, albuminous, and ligneous constituents of the seed.

In order to extract the amygdalin, the cake which remains after the fixed oil has been separated by expression is broken into fragments, and digested with hot alcohol of sp. gr. 0.825. The solution must be filtered, and the alcohol distilled off; the syrupy

residue must then be diluted with water, mixed with yeast, and set aside to ferment, in order to decompose the sugar; and on filtering the liquid and evaporating, the amygdalin crystallizes in acicular tufts. It is very soluble in water, from which it is deposited in prisms with $3\text{H}_2\text{O}$. The whole of this water is expelled by a temperature below 248° (120°C).

Amygdalin has a sweetish, somewhat bitter taste, and is not poisonous. Its solution exerts a left-handed rotation upon a ray of polarized light. When it is treated with alkaline solutions, ammonia is expelled, and the salt of a new acid, the *amygdalic* ($\text{H}_2\text{C}_{40}\text{H}_{52}\text{O}_{25}$), is found in the liquid; this decomposition is analogous to that produced in asparagin under similar circumstances:—



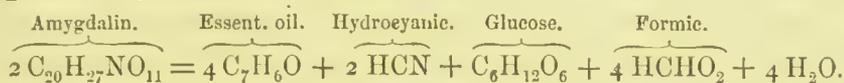
The most remarkable change, however, to which amygdalin is subject, is that which it undergoes when the bruised kernel in which it is contained is brought into contact with water. As soon as this is done, the peculiar and agreeable odour of bitter almonds is perceived; in twenty-four hours all traces of amygdalin will have disappeared, and in its place an essential oil, hydrocyanic acid, sugar, and formic acid will be found. This singular transformation is the result of a species of fermentation produced by the action of a peculiar azotised matter allied to casein, and which resembles the diastase of malt; to this substance the name *synaptase*, or *emulsin*, has been given. This ferment is contained both in the bitter and the sweet almond. If boiling water be poured upon the pulp, the synaptase is coagulated, and no formation of the essence ensues. In preparing the essence, cold water should therefore be employed, and the mixture should be allowed to stand for some hours before proceeding to distillation.

Synaptase (so called from $\sigma\upsilon\nu$, together, $\acute{\alpha}\pi\tau\omega$, to unite) is a ferment which may be advantageously applied to many organic compounds in order to effect their transformation into new products. It may be procured from the cake left after the expression of the oil of the sweet almond. This mass must be diffused through a quantity of pure water equal to about thrice its weight; the liquid must be strained through a cloth, and the undissolved portions submitted to pressure. The emulsion thus procured must be left for three or four days at a temperature of from 68° to 86° (20° to 30°C .), during which time it becomes separated into two layers; the upper one consisting of a curd-like coagulum, and the lower one forming a clear liquid, like whey. In the course of two or three days this lower stratum ceases to yield any precipitate on the addition of acetic acid; when this point has been reached, alcohol must be added so long as it occasions a precipitate. This precipitate consists of synaptase in admixture with phosphates of

calcium and magnesium: it must be washed with absolute alcohol, and dried *in vacuo* over sulphuric acid.

The synaptase thus obtained cannot be freed from the salts which accompany it, but it is sufficiently pure to enable its action as a ferment to be studied. When dried as directed, it may be preserved unaltered: but if left in a moist condition, it speedily becomes putrid. It is completely soluble in cold water; the liquid has an acid reaction, which enables it to hold the earthy phosphates in solution. In this state it speedily transforms amygdalin into the essence of bitter almonds and other products. The aqueous solution of synaptase becomes turbid when heated, owing to the separation of a portion of the earthy phosphates; the liquid, however, again becomes clear as it cools, but no longer possesses the power of effecting the transformation of amygdalin into benzoyl hydride. A solution of synaptase is entirely precipitated by one of plumbic acetate, and the precipitate so obtained acts upon amygdalin in the same way as synaptase itself.

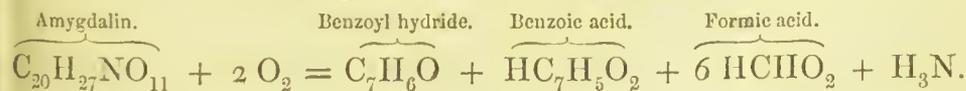
The change which occurs in amygdalin under the influence of synaptase may be thus represented:—



100 parts of amygdalin yield about 41 of the essential oil, and 6 of hydrocyanic acid. The latter contains all the nitrogen of the amygdalin.

The proportion of hydrocyanic acid liberated by the reaction is perfectly definite, and it has been proposed by Liebig and Wöhler to take advantage of this fact in prescribing hydrocyanic acid medicinally. Amygdalin may be dissolved in water, and it may be kept unchanged; but if it be mixed with an emulsion of sweet almonds, decomposition commences immediately, and the characteristic odour of the essence is developed. Seventeen grains of amygdalin, when dissolved in one ounce of emulsion of sweet almonds, would furnish exactly one grain of pure hydrocyanic acid; or it would contain an amount of the acid equivalent to 50 minims of the dilute hydrocyanic acid of the Pharmacopœia.

Oxidizing agents, such as nitric acid, or a mixture of black manganese oxide and sulphuric acid, decompose amygdalin with formation of benzoyl hydride, benzoic acid, formic acid, ammonia, and sometimes carbonic anhydride from the oxidation of the formic acid:



(1432) ESSENCE OF BITTER ALMONDS, or *Benzoyl Hydride* ($\text{C}_7\text{H}_5\text{O}$, $\text{H} = 106$); *Sp. gr.* 1.0499, Kopp; *Boil. pt.* 356° (180°C).

—In order to extract this essence, the bitter almond cake, which is left after the expression of the fixed oil, is crushed and made into a thin cream with water. It is then introduced into a still, where it is allowed to remain for twenty-four hours, with occasional agitation, in order that the amygdalin may be completely

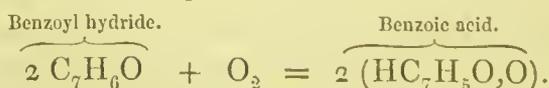
decomposed. At the end of that time the distillation is proceeded with. This operation is best effected by the injection of steam; the liquid is thus speedily raised to the boiling point, and all risk of charring the vegetable matter is averted: the oil passes over as usual with the vapour, and may be condensed in suitable receivers. The distillation must be continued so long as the distillate comes over with a milky appearance.

A considerable quantity of the essence is dissolved in the distilled water, but most of this can be recovered by subjecting the water to a second distillation, the essence coming over with the first portions. The kernels of the peach, the plum, the cherry, and other stone fruit, as well as the leaves of the laurel (*Prunus laurocerasus*), also yield this essence in notable quantities.

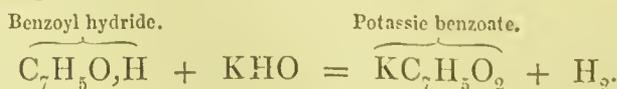
Small quantities of this oil are likewise formed during the oxidation of albuminous and gelatinous bodies by means of dilute sulphuric acid and black manganese oxide (1646).

The crude essence from bitter almonds, in addition to benzoyl hydride, contains hydrocyanic and benzoic acids, and a crystalline body termed benzoine (1439): the essence is extremely poisonous, owing to the presence of hydrocyanic acid; but it may be purified from the latter compound by agitating the oil briskly with a mixture of milk of lime and ferrous chloride, and then submitting it to distillation.

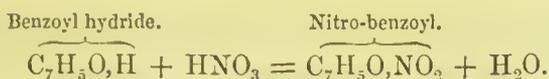
The purified oil is not poisonous. It is inflammable, and burns with a smoky flame. Benzoyl hydride is soluble in 30 parts of water, but it is dissolved by alcohol and by ether in all proportions. This oil exerts no rotatory action upon polarized light. It behaves like an aldehyd; for instance, when essential oil of bitter almonds, either in its pure or its rectified condition, is left in contact with the atmosphere and with water, it gradually absorbs oxygen, and is at length wholly converted into a crystalline mass, consisting of benzoic acid:—



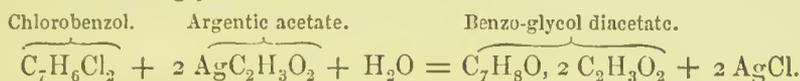
When oil of bitter almonds is heated with caustic potash, it yields hydrogen and potassic benzoate:—



Concentrated nitric acid converts the essence into nitrobenzoic acid ($\text{HC}_7\text{H}_4\text{NO}_2\text{O}_2$) with brisk evolution of heat; but if the reaction be moderated by the addition of water, a yellowish oil termed *nitro-benzoyl* is formed, which gradually solidifies; it is a compound in which the hydrogen of the hydride has been displaced by nitroxyl (NO_2):—



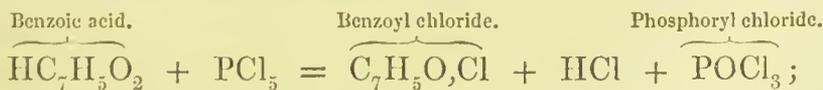
When oil of bitter almonds is treated with phosphoric chloride it yields a compound termed *chlorobenzol* [$\text{C}_7\text{H}_6\text{Cl}_2$; *Sp. gr. of liq.* 1.245; *of vap.* 5.625; *Rel. wt.* 80.5; *Boil. pt.* 402.8 (206° C.)], in which the oxygen of the essence appears to have been displaced by chlorine, whilst phosphoryl chloride (POCl_3) is formed, and can be expelled by heat. Chlorobenzol is a limpid, colourless liquid, which has but little odour at ordinary temperatures, but when heated it gives off an irritating vapour. It is insoluble in water, but readily soluble in alcohol and in ether. Linpricht regards this body as the chloride of *benzo-glycol*, the diatomic alcohol of the benzoic series: when treated with salts of silver it yields compounds of benzo-glycol; thus:—



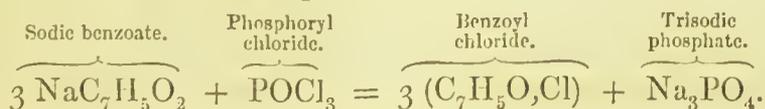
On attempting to isolate the benzo-glycol it becomes decomposed into oil of bitter almonds and water; $\text{C}_7\text{H}_8\text{O}_2 = \text{C}_7\text{H}_6\text{O} + \text{H}_2\text{O}$.

(1433) *Benzoyl Chloride*, or *Benzoic Oxychloride* ($\text{C}_7\text{H}_5\text{O,Cl} = 140.5$); *Sp. gr. of liq.* 1.25, Cahours; *of vap.* 4.987; *Rel. wt.* 70.2; *Boil. pt.* 383° (195° C.).—When a current of dry chlorine is transmitted through the essential oil of bitter almonds gently warmed, much hydrochloric acid is evolved, and benzoyl chloride is obtained in the form of a colourless liquid, the vapour of which produces lachrymation; it has a peculiar irritating odour resembling that of horse-radish. Benzoyl chloride burns with a green smoky flame. This substance sinks in water without mixing with it; but if boiled with water, it is gradually dissolved, and decomposed into hydrochloric and benzoic acids; $\text{C}_7\text{H}_5\text{O,Cl} + \text{H}_2\text{O} = \text{HC}_7\text{H}_5\text{O}_2 + \text{HCl}$.

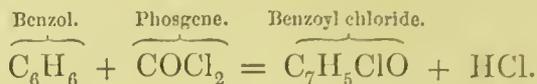
The best method of preparing benzoyl chloride, when required in considerable quantity, consists in heating gently in a retort a mixture of 122 parts of crystallized benzoic acid, and 211 of phosphoric chloride (1 atom of each substance): a violent reaction occurs, attended with a copious extrication of hydrochloric acid:—



when this has terminated, the mixture is submitted to distillation. As soon as the boiling point rises to 383° (195° C.), pure benzoyl chloride passes over, the portions which distil at a lower point consisting of a mixture of phosphoryl chloride and benzoyl chloride. This mixture may be purified by distilling it from anhydrous sodic benzoate, the phosphoryl chloride becoming decomposed in the following manner:—



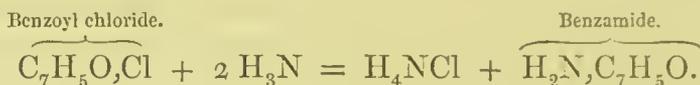
Benzoyl chloride may also be obtained synthetically by acting upon vapour of benzol with phosgene (Harnitzky, *Lieb. Annal.*, cxxxii. 72):—



Probably by acting upon the homologues of benzol the corresponding chlorides would be obtained.

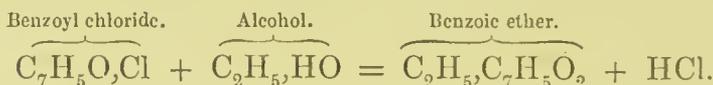
Benzoyl chloride has been extensively employed by Gerhardt in the preparation of the anhydrides of the organic acids (1268).

Gaseous ammonia decomposes it, and yields benzamide (1350), and ammonia hydrochlorate:—



Aniline attacks it in a similar manner, and produces *benzanilide* ($\text{C}_6\text{H}_5, \text{HN}, \text{C}_7\text{H}_5\text{O}$).

When mixed with alcohol it yields benzoic ether:—



Sometimes in the reaction of chlorine upon the hydride of benzoyl, brilliant colourless plates of a substance sparingly soluble in cold alcohol are deposited. They are formed by a combination of chloride with hydride of benzoyl ($\text{C}_7\text{H}_5\text{OH}$, $\text{C}_7\text{H}_5\text{OCl}$), which is termed *benzoyl chlorohydride*.

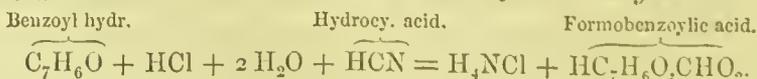
When benzoyl chloride is treated with phosphoric chloride, *benzotrichloride*, $\text{C}(\text{C}_6\text{H}_5)\text{Cl}_3$, the analogue of chloroform, CHCl_3 , is produced. It is a liquid which boils at about 419° (215° C.), and is gradually decomposed by water into benzoic and hydrochloric acids.

Benzoyl sulphide, $(\text{C}_7\text{H}_5\text{O})_2\text{S}$, is formed by distilling benzoyl chloride with plumbic sulphide, when it passes over as a yellowish oil, which gradually solidifies into a yellow crystalline mass, of a disagreeable sulphurous odour.

A *bromide of benzoyl* ($\text{C}_7\text{H}_5\text{O}, \text{Br}$), and an *iodide* ($\text{C}_7\text{H}_5\text{O}, \text{I}$) may be obtained by analogous methods, in the form of very fusible crystallizable solids.

Benzoyl cyanide ($\text{C}_7\text{H}_5\text{O}, \text{Cy}$) may be obtained as a yellow oil, by distilling benzoyl chloride with mercuric cyanide.

(1434) *Formobenzoylic* or *Mandelic Acid* ($\text{HC}_7\text{H}_6\text{O}, \text{CHO}_2$).—When the distilled water of bitter almonds (containing hydrocyanic acid and the essential oil) is boiled with hydrochloric acid, a curious reaction occurs; the hydrocyanic acid is decomposed—into ammonia which unites with the hydrochloric acid, and formic acid which enters into combination with the oil of almonds,—producing a new body possessed of acid properties, and termed *formobenzoylic acid*:—



On evaporating the solution, the acid may be obtained in mixture with ammonia hydrochlorate, from which it may be separated by ether; the ethereal solution deposits it in rhomboidal tables. It has a sour taste, and is easily soluble in alcohol. When heated, it fuses at a low temperature, emitting an agreeable odour of hawthorn blossoms. Formobenzoylic acid is also obtained by dissolving amygdalin in concentrated hydrochloric acid. Formobenzoylic acid fur-

nishes one of the best instances of the class of colligated acids in which the saturating power of the original acid, the formic, remains unimpaired by its union with the colligate. It forms soluble crystallizable salts with barium and silver, and with other basyls.

A compound of *benzoic acid with benzoyl hydride* [$2(C_7H_5O, H), C_7H_6O_2$] ? is obtained by acting upon the moist essence of bitter almonds with undried chlorine gas; 3 molecules of the essence concur to its formation, but 1 molecule only undergoes oxidation during its production; $3 C_7H_6O + H_2O + Cl_2 = 2 HCl + (2 C_7H_5O, C_7H_6O_2)$. This reaction presents a certain analogy with that by which acetal (1251) is formed. Benzoyl-hydride benzoate is insoluble in water, but it crystallizes from its alcoholic solution in square prisms, which may be fused at a gentle heat and volatilized without decomposition: it presents none of the characters of an acid. An alcoholic solution of potash gradually decomposes it, and crystals of potassic benzoate are deposited. It appears that under certain circumstances 3 molecules of the essence combine with 1 of benzoic acid (Laurent and Gerhardt), but the conditions required to ensure its production are not clearly known.

Benzoyl-hydride Hydrocyanate.—If the mixture of hydrochloric acid and the distilled water of bitter almonds be evaporated at a gentle heat, without boiling, a yellow oily liquid of sp. gr. 1.124 is formed: this substance is sparingly soluble in water, but freely so in alcohol and in ether. Voelckel states it to be a compound of hydrocyanic acid with benzoyl hydride (C_7H_5O, HCN): it is decomposed into its two components by a temperature of 338° (170° C.).

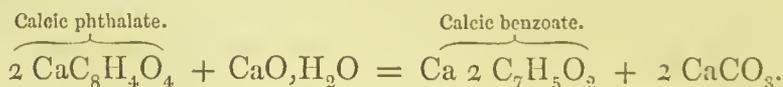
The substance to which the name of *benzimide* ($C_{23}H_{18}N_2O_2$) was given by Laurent, is the result of the action of hydrocyanic acid upon the essence. If benzoyl hydride be mixed with a fourth of its bulk of anhydrous hydrocyanic acid, and gently warmed after agitation with an alcoholic solution of potash, white curdy flocculi of *benzoyl cyano-hydride* (benzimide) [$C_7H_5(CN)_2, 2 C_7H_6O$] are deposited. The same substance is also sometimes met with in the resinous residue of the distillation of the crude essence; and on treating this with boiling alcohol, benzimide is deposited in white flocculi as the liquid cools. Benzimide is sparingly soluble in alcohol and in ether. It fuses on the application of heat, and at a high temperature is decomposed, leaving a carbonaceous residue; fuming sulphuric acid dissolves it with a blue colour, which fades on dilution.

(1435) BENZOIC ACID ($HC_7H_5O_2 = 122$); *Sp. gr. of vap.* 4.27; *Rel. wt.* 51; *Fusing pt.* 248° (120° C.); *Boil. pt.* $462^\circ.2$ (239° C.).—Benzoic acid occurs abundantly in the balsamiferous plants, independently of its artificial origin from bitter almond oil already mentioned.

Gum Benzoin, the produce of the *Styrax benzoin* of the Asiatic archipelago, is the principal source of the supply of benzoic acid. Common benzoin occurs in reddish lumps, which sometimes have a lamellated fracture, and contain whitish opaque masses. When recent it emits an odour of bitter almonds. Gum benzoin appears to be composed of a mixture of three varieties of resin, with benzoic acid and a small quantity of a fragrant essential oil. Only one of the resins is soluble in ether, a second is soluble in alcohol only. The white opaque masses appear to consist of the resin which is soluble in ether: they yield less benzoic acid than the brown portions.

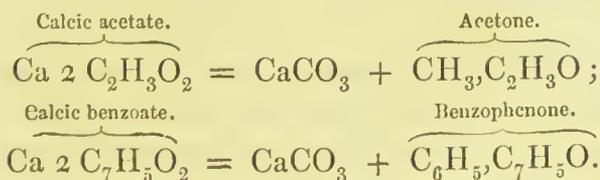
Preparation.—Benzoic acid may be extracted from powdered benzoin by boiling it for some hours with milk of lime, filtering the solution of calcic benzoate from the insoluble compound of resin and lime, and, after concentrating the filtrate, adding hydrochloric acid; benzoic acid is thus precipitated, and may be purified by sublimation. The acid is, however, generally extracted by the less economical but simpler process of direct sublimation from gum benzoin, which contains 14 or 15 per cent. of the acid: if the resin be coarsely powdered and exposed to a temperature of about 302° (150° C.), the acid which exists ready formed in it is expelled, and may be condensed in suitable receivers. Mohr's plan of conducting the sublimation, which has been already described when speaking of the preparation of pyrogallin (1334), is the simplest and best method. The resins of tolu and benzoin when treated with boiling nitric acid yield an amorphous form of benzoic acid, coloured yellow with a resinous matter which accompanies it into its salts, and hinders them from crystallizing: balsam of tolu often yields nearly half its weight of this acid. This resinous acid is completely soluble in boiling water. When this form of the acid is exposed to the sun's rays it becomes covered with white crystals of pure benzoic acid; and when sublimed, the ordinary crystalline acid is obtained.

Benzoic acid is now prepared artificially from naphthalin on a large scale; the naphthalin is converted by means of nitric into phthalic acid (1562), and by heating a mixture of normal calcic phthalate with dry slaked lime for some hours to a temperature of from 626° to 662° (330° to 350° C.), taking care to exclude free access of air, the salt is entirely converted into a mixture of calcic carbonate and benzoate:—



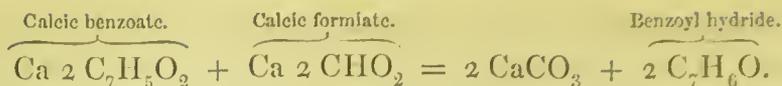
Properties.—Benzoic acid assumes the form of white, glistening, extremely light, flexible needles, which usually have an agreeable aromatic odour, and a hot bitterish taste. The odour, however, is not due to the acid, but to the presence of a trace of essential oil which accompanies the acid during the sublimation. Benzoic acid melts at 248° (120° C.); it sublimes at 293° (145° C.), and boils at $462^{\circ}.2$ (239° C.). Its vapours are acrid and irritating; when kindled in the open air, they burn with a smoky flame. The acid requires about 200 parts of cold water, and 25 of boiling water, for its solution; but it is readily dissolved by alcohol and by ether.

Benzoates.—Most of the benzoates are soluble in water, and in alcohol. If a strong acid, such as the sulphuric or hydrochloric, be added to their aqueous solutions, a crystalline precipitate of benzoic acid is deposited. Potash and ammonia form both normal and acid salts with benzoic acid. *Normal potassic benzoate*, $(\text{KC}_7\text{H}_5\text{O}_2)_2\text{H}_2\text{O}$, crystallizes with difficulty in prismatic crystals, which creep up the sides of the vessel during their formation. *Hydric-potassic benzoate* ($\text{KH}_2\text{C}_7\text{H}_5\text{O}_2$) may be procured from its solution in alcohol, in colourless pearly tables, which are sparingly soluble in water. It is obtained as a secondary product in the preparation of acetic anhydride by decomposing potassic acetate with benzoyl chloride. Normal *ammonic benzoate* is very soluble in water. It is sometimes used as a means of separating iron from nickel and cobalt. If a solution of the normal ammoniac benzoate be allowed to evaporate spontaneously, plates of an acid salt are deposited. *Ferric benzoate* falls as a bulky, brownish-white gelatinous mass when a neutral solution of a ferric salt is mixed with one of ammoniac benzoate; it is soluble in alcohol. The benzoates of *yttrium*, *zirconium*, *tin*, and *lead* are insoluble in water; that of *silver* is sparingly soluble in boiling water. A neutral solution of a ferric salt may be used for detecting the presence of benzoic acid in solution. When any of the benzoates are heated with phosphoric acid, benzoic acid is sublimed, and may be recognized by its characteristic odour. The benzoates of the metals of the alkalies and of the earths when submitted to destructive distillation yield a particular hydrocarbon termed *benzol*, or *benzine* (C_6H_6), and a compound termed *benzophenone*, or phenyl-benzoyl ($\text{C}_6\text{H}_5\text{C}_7\text{H}_5\text{O}$); these substances are intimately related to the *phenic* group of compounds, which will be described in the chapter upon the products of destructive distillation. *Benzophenone* stands in the same relation to benzoic acid that acetone does to acetic acid; for example:—



When a mixture of calcic benzoate and formiate is distilled in the proportion of one equivalent of each, benzoyl hydride is the result (Piria):—*

* Piria finds that cinnamic, cuminic, and other aldehyds may be obtained by distilling the salts of their corresponding acids with calcic formiate. Thus a mixture of calcic cinnamate and formiate yields oil of cinnamon.

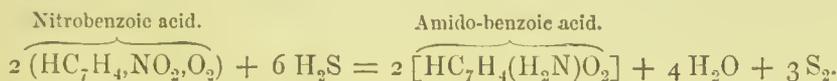


Benzoic acid is dissolved by oil of vitriol, and is precipitated unchanged on dilution with water; but fuming sulphuric acid converts it into a dibasic compound acid, the *benzosulphuric* ($\text{H}_2\text{C}_7\text{H}_4\text{SO}_5$). Fuming nitric acid converts the benzoic into *nitrobenzoic acid* ($\text{HC}_7\text{H}_4\text{NO}_2\text{O}_2$); and a mixture of oil of vitriol and nitric acid produces *dinitrobenzoic acid* [$\text{HC}_7\text{H}_3(\text{NO}_2)_2\text{O}_2$]. Chlorine gives rise to not less than three chlorinated acids: viz., *chlorinated*, *dichlorinated*, and *trichlorinated* benzoic acid, in which 1, 2, and 3 atoms of hydrogen in the benzoyl are respectively displaced by a corresponding number of atoms of chlorine. When benzoic acid is treated with phosphoric chloride, it yields benzoyl chloride in abundance (1433).

Benzoic Anhydride (C_7H_5)₂O; *Fusing pt.* about $107^{\circ}.6$ (42° C.); *Boil. pt.* 590° (310° C.).—This compound is obtained by decomposing anhydrous sodic benzoate with benzoyl chloride, or with phosphoryl chloride (1268). The result of the reaction is washed with water weakly alkalized with sodic carbonate: benzoic anhydride is left in the form of a white, pasty mass insoluble in water, but soluble in ether and in hot anhydrous alcohol, from which it crystallizes in oblique prisms. After undergoing fusion it long remains liquid, emitting a peculiar odour, recalling that of benzoic acid with a slight smell of oil of bitter almonds. It may be distilled unaltered. Boiling water converts it slowly into the normal acid; the change is hastened by the addition of an alkali. It enters into the formation of many double anhydrides (1269): such, for example, as *benzoacetic anhydride* ($\text{C}_7\text{H}_5\text{O}, \text{C}_2\text{H}_3\text{O}$)O, which is obtained by heating acetyl chloride ($\text{C}_2\text{H}_3\text{O}, \text{Cl}$) with dried sodic benzoate. A brisk reaction occurs at ordinary temperatures; when this is over, the residue must be washed with water, and with a weak solution of sodic carbonate: benzoacetic anhydride is left in the form of a neutral oil, which is heavier than water, and emits an agreeable odour of sherry wine. Boiling water decomposes it slowly into a mixture of acetic and benzoic acids; but the solutions of the alkalis or of their carbonates quickly convert it into acetate and benzoate of the basyl. It cannot be distilled without experiencing decomposition: acetic anhydride passes over first, and if the distillation be stopped as soon as the temperature of the boiling liquid reaches 536° (280° C.), the residue in the retort solidifies on cooling into a mass of crystallized benzoic anhydride.

(1436) *Amido-benzoic acid*, *Benzamic acid*, or *Oxybenzamic acid* ($\text{C}_7\text{H}_7\text{NO}_2$)

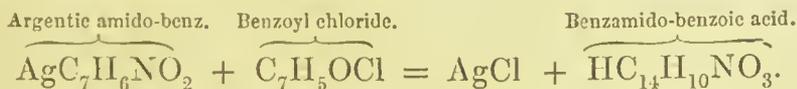
or $\text{H}_7\text{C}_7\text{H}_4\text{H}_2\text{N}_2\text{O}_2$), is not a true amidated acid (1341), but benzoic acid in which an atom of hydrogen has been displaced by an equivalent of amidogen. It is isomeric with anthranilic acid (1517) and with salicylamide, and is obtained by the action of reducing agents upon nitrobenzoic acid. If an alcoholic solution of nitrobenzoic acid be saturated with ammonia and with sulphuretted hydrogen, and then boiled, it becomes green, and a copious deposit of sulphur occurs: this operation must be repeated two or three times, in order to complete the decomposition of the nitrobenzoic acid:—



The liquid must be evaporated to the consistence of syrup, supersaturated with acetic acid, and the precipitate drained upon a porous tile. It must then be redissolved in boiling water; the solution digested with animal charcoal, filtered, and allowed to crystallize. Amido-benzoic acid crystallizes in radiated tufts of delicate needles, which are readily soluble in alcohol and in ether. It has a sweet, sourish taste, but no odour. It forms an insoluble green precipitate when mixed with a solution of a cupric salt; with salts of silver it gives a white curdy precipitate, which if left in the liquid becomes crystalline.

This acid likewise possesses the property of combining with other acids. Oil of vitriol dissolves amido-benzoic acid by the aid of heat, and on cooling, it deposits brilliant crystals ($2 \text{C}_7\text{H}_7\text{NO}_2, \text{H}_2\text{SO}_4, 2 \text{H}_2\text{O}$), which may be recrystallized from boiling water or from alcohol: their aqueous solution has an extremely sweet taste. A similar compound ($\text{C}_7\text{H}_7\text{NO}_2, \text{HNO}_3$) may be formed with nitric acid. Phosphoric, oxalic, hydrochloric, and other acids form similar combinations with amido-benzoic acid. The compound with hydrochloric acid forms a crystalline double salt with platinic chloride.

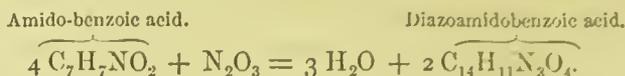
Amido-benzoic acid is the representative of a class of compounds which the aromatic acids furnish when their nitro-derivatives are submitted to reduction. In this manner *amido-toluic* ($\text{HC}_8\text{H}_6\text{H}_2\text{N}_2\text{O}_2$), *amido-cuminic* ($\text{HC}_{10}\text{H}_{10}\text{H}_2\text{N}_2\text{O}_2$), and *amido-anisic* acids ($\text{HC}_8\text{H}_6\text{H}_2\text{N}_2\text{O}_3$) may be procured. They all exhibit a similar tendency to combine with acids, as well as with bases; and if the silver salt of one of these acids, such as argentic amido-benzoate, be treated with benzoyl chloride, a compound crystallizable acid is obtained, analogous to the hippuric and cuminuric (1442) which are procured by similar treatment of zinc glycoic acid ($\text{Zn } 2 \text{C}_2\text{H}_4\text{NO}_2$):—



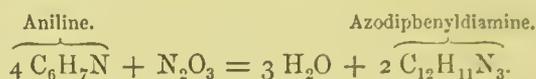
These so-called amido-acids are isologous with glycoic acid (1614) and its homologues, and resemble them considerably in properties.

Griess (*Proceed. Roy. Soc.*, ix. 594, x. 309 and 591) has described a series of azotised bodies in some measure connected with the amidic bases. These new bodies are generated by the action of nitrous anhydride upon alcoholic solutions of amido-acids of the benzoic group, the change consisting in the substitution of one atom of nitrogen for three atoms of hydrogen in two molecules of the amido-acid. When, for example, amido-benzoic acid is dissolved in alcohol, an orange-yellow crystalline precipitate is obtained, constituting a dibasic acid insoluble in

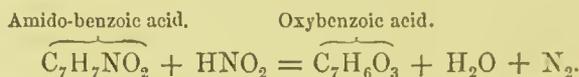
water, in alcohol, and in ether, but soluble in the alkalies, forming with them crystallizable salts which yield precipitates with plumbic acetate and with argentic nitrate. The reaction by which it is formed may thus be represented:—



A similar substitution of one atom of nitrogen for three atoms of hydrogen was effected by Griess upon aniline and nitraniline, two molecules of each compound being linked into one molecule of the new body (1362); for example:—



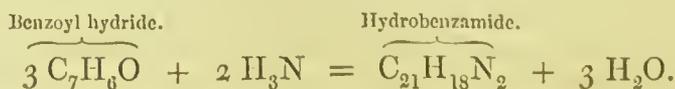
If an *aqueous* solution of the amido-benzoic acid be decomposed by nitrous acid, nitrogen is liberated abundantly, and a new compound, the *oxybenzoic acid* ($\text{HC}_7\text{H}_5\text{O}_3$) of Gerland is obtained. It is metameric with salicylic acid, but does not crystallize easily. It furnishes very soluble salts with the alkalies, and sparingly soluble crystalline compounds with the alkaline earths. Oxybenzoic acid is sparingly soluble in cold water and alcohol. It fuses when heated, and may be sublimed without alteration. The reaction by which it is obtained may be thus represented:—



By the action of reducing agents upon dinitro-benzoic acid (1435), a compound analogous to the amido-benzoic acid, having the composition of *diamidobenzoic acid* [$\text{C}_7\text{H}_4(\text{H}_2\text{N})_2\text{O}_2$] has been obtained (Voit), but it possesses none of the characters of an acid; it combines readily with acids, the introduction of the second atom of amidogen having given it a decided basic energy.

(1437) *Action of Ammonia on the Oil of Bitter Almonds.*—Several compounds are produced by the action of ammonia upon this essence, which are different according as the essence employed is pure, or contains hydrocyanic acid. If it be pure, hydrobenzamide and dibenzoylimide are the result of the reaction; if it be in the crude state, the hydrocyanic acid takes part in the reaction, and benzhydramide and benzoylic azotide are formed.

1. *Hydrobenzamide* [$\text{C}_{21}\text{H}_{18}\text{N}_2$; *Fusing pt.* 230° (110°C.)] is the most interesting of these compounds; it may be formed by simply agitating the oil with a solution of ammonia, and afterwards leaving it at rest for some days at the ordinary temperature; but the reaction is completed in a few hours if the mixture be heated to the boiling point. In either case the mixed liquids become gradually converted into a crystalline mass of hydrobenzamide, which must be washed with ether, and crystallized from boiling alcohol:—

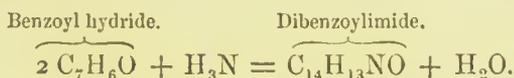


Hydrobenzamide forms colourless octahedra with a rhombic base. It is destitute of odour, and insoluble in water, but readily soluble in ether. It melts at 230° (110° C.); and if heated for some time to about 257° (125° C.), or if boiled with a solution of potash, it is converted into the isomeric base termed amarinc or benzoline (1387).

When hydrobenzamide is fused with caustic potash, several new compounds are formed, such as *benzostilbine* ($C_{31}H_{22}O_2$?), and *benzolute* ($C_{11}H_8O$?), whilst the nitrogen is expelled in the form of ammonia.

Hydrobenzamide, when boiled with hydrochloric acid, is decomposed; sal ammoniac is formed, and benzoyl hydride is set at liberty. A similar change is also produced by the mere boiling of its alcoholic solution, but the ammonia in that case is liberated in the uncombined form.

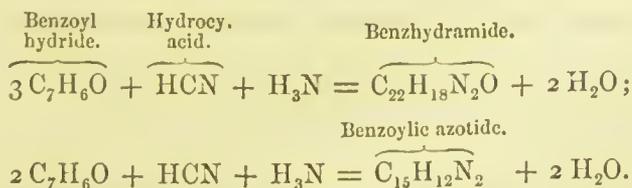
2. *Dibenzoylimide* ($C_{14}H_{13}NO$) is obtained by passing ammoniacal gas into an alcoholic solution of essential oil of bitter almonds. It is gradually separated in the form of a resinous mass which is soluble in boiling alcohol, and from which it is deposited as a yellowish powder composed of brilliant feathery crystals (Robson):—



3. *Benzhydrylamide*, or a *Cyanazobenzoyl Hydride* ($C_{22}H_{18}N_2O$).—This body was originally stated by Laurent to be isomeric with hydrobenzamide, but when he re-examined it conjointly with Gerhardt, this statement was ascertained to be an error. If the crude essence of bitter almonds be heated to 212° , and saturated with ammonia, then dissolved in a mixture of alcohol and ether, and left to itself for three or four days, a deposit is formed which consists of two portions, viz., *benzhydrylamide* and *benzoylic azotide*: they may be separated by the action of boiling alcohol. Benzhydrylamide is soluble in boiling alcohol, from which on cooling and spontaneous evaporation it is deposited in small brilliant needles, which are freely soluble in ether: and which, when boiled with hydrochloric acid, are decomposed into hydrocyanic acid, ammonia hydrochlorate, and benzoyl hydride.

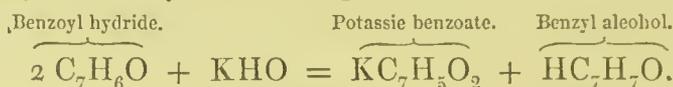
4. The portion which is left undissolved by alcohol is the *benzoylic azotide* of Laurent. It is in the form of a white crystalline powder, nearly insoluble in alcohol and in ether: it fuses on the application of heat, and crystallizes on cooling.

The formation of these two compounds is explained by the following equations:—



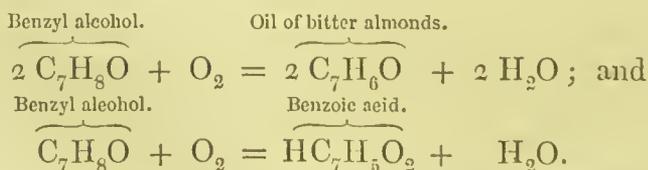
5. *Azobenzoyl* ($C_{21}H_{15}N_2$) is a third substance which was obtained by Laurent by the action of ammonia on the crude essence. It is nearly insoluble in alcohol, but soluble in ether: on the application of heat it fuses into a transparent mass, resembling gum in appearance.

(1438) *Benzoic* or *Benzyl Alcohol* (C_7H_7HO , Cannizzaro); *Sp. gr. of liq.* 1.059; *of vap.* 3.84; *Rel. wt.* 54; *Boil. pt.* 401° (205° C.).—In order to obtain this compound the following process is adopted:—Oil of bitter almonds is dissolved in its own volume of alcohol, and this liquid is mixed with three or four times its bulk of an alcoholic solution of caustic potash (of sp. gr. 1.020): a considerable evolution of heat occurs, followed by a copious deposition of crystals of potassic benzoate: when this reaction has terminated, boiling water is added to the liquid in quantity sufficient to dissolve the benzoate. The greater part of the alcohol must then be distilled off, and more water added to dissolve the benzoate if necessary; the turbid liquid thus obtained must be agitated with ether, and the ethereal layer which separates on standing, must be drawn off and subjected to distillation. The first portions consist of ether, but subsequently pure benzyl alcohol passes over. The reaction of caustic potash upon the benzyl hydride may be thus represented:—



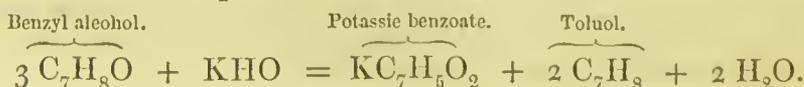
Hermann finds that benzyl alcohol may also be obtained by reducing a hot aqueous solution of benzoic acid by means of an amalgam of sodium, but the alcohol is mixed with some secondary products. Another process by which benzyl alcohol may be obtained is the decomposition of toluyl chloride by potassic hydrate; $C_7H_7Cl + KHO = C_7H_8O + KCl$.

Benzyl alcohol is a colourless oily liquid, which is readily converted by nitric acid at a gentle heat into oil of bitter almonds: and is transformed by chromic acid into benzoic acid: both of these products are the results of oxidation, which may be thus represented:—



It is obvious that oil of bitter almonds and benzoic acid stand in the same relation to benzyl alcohol that aldehyd and acetic acid do to ordinary alcohol (*vide* Table, p. 168).

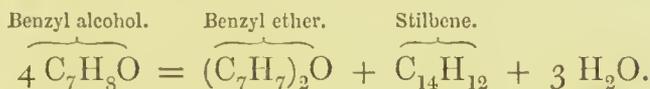
If benzyl alcohol be distilled from caustic potash, it is decomposed into potassic benzoate and the hydrocarbon known as toluol, which corresponds to olefant gas in the alcohol series:—



Benzyl alcohol may be made to yield a series of ethers, the radiée of which is the hydrocarbon *benzyl* (C_7H_7), analogous to ethyl (C_2H_5): among these ethers are the following:—

| | | Boiling Point. | |
|-------------------------|---------------------|----------------|-------|
| | | ° F. | ° C. |
| Benzyl-ether | $(C_7H_7)_2O$ | about 590 | 310 |
| Benzyl-ehloride | C_7H_7Cl | about 360 | 182.2 |
| Benzyl-acetate | $C_7H_7, C_2H_3O_2$ | 410 | 210 |
| Benzyl-benzoate | $C_7H_7, C_7H_5O_2$ | 653 | 345 |

Benzyl-ether is obtained by heating benzyl alcohol with boracic anhydride in a closed vessel to about 248° (120° C.) for several hours. The boracic acid must then be extracted with boiling water and a weak solution of sodie carbonate, and the residue must be distilled at a temperature of about 590° (310° C.); benzyl-ether passes over, and stilbene ($C_{14}H_{12}$) remains in the retort:—



Benzyl chloride when heated in a sealed tube with ammonia furnishes the volatile base *benzylia*, C_7H_9N , which corresponds to ethylia in the ethylic series and is isomeric with toluidine. When benzyl alcohol is mixed with oil of vitriol, it yields a compound acid ($HC_7H_7SO_4$), the *benzylsulphuric* corresponding to the ethylsulphuric. It may be obtained in crystalline plates.

The hydrocarbon of this series, *dibenzyl* [$(C_7H_7)_2$; *Fusing pt.* $125^\circ.6$ (52° C.); *Boil. pt.* $543^\circ.2$ (284° C.); Cannizzaro and Rossi, *Lieb. Annal.*, exxi. 250] may be obtained by heating benzyl ehloride with sodium. It is a crystalline solid, insoluble in water, but soluble in alcohol and in ether. It combines directly with bromine, $C_{14}H_{14}Br_2$ being formed.

(1439) BENZOINE ($C_{14}H_{12}O_2$); *Fusing pt.* 248° (120° C.).—It has been already mentioned that when the vapour of benzoyl hydride is transmitted over heated caustic potash, potassic benzoate and hydrogen are produced: but if the crude essence be agitated with its own bulk of a saturated alcoholic solution of potash, the oil is slowly changed into a mass of crystals, which are isomeric with benzoyl hydride: the same change occurs if the pure hydride be digested with an alcoholic solution of potassic cyanide: to the substance thus formed the name of *benzoiné* has been given. The presence of hydrocyanic acid is necessary to the production of this metamorphosis; but the mode in which it acts is entirely unknown, since it remains in the liquid, unaltered in amount, after the change has been effected.

Benzoine may be obtained in a state of purity by crystallizing it from boiling alcohol, in which it is readily soluble. Ether also dissolves it freely. It is nearly insoluble in cold water, but is somewhat soluble in boiling water. Benzoine is destitute of odour and of taste: at 248° it fuses, and at a higher temperature it may be distilled unaltered. If its vapour be transmitted through

red-hot tubes, it is reconverted into the essential oil of bitter almonds. Cold sulphuric acid dissolves it with the production of a violet colour. Benzoine has been regarded as $(C_{14}H_{11}O_2, H)$, or as the hydride of a new radicle *stilbyl** $(C_{14}H_{11}O_2)$, but the series to which it gives rise has been hitherto but incompletely investigated. When benzoine is fused with caustic potash, it becomes converted into potassic benzoate with evolution of hydrogen: but if it be boiled with an alcoholic solution of potash, a beautiful violet-coloured solution is formed which is gradually bleached by boiling, whilst hydrogen is disengaged, and *potassic benzilate* is formed; $C_{14}H_{12}O_2 + KHO = KC_{14}H_{11}O_2 + H_2$.

Benzilic or *Stilbylic Acid* $[(HC_{14}H_{11}O_3)]$; *Fusing pt.* 248° (120° C.) is obtained by decomposing a hot solution of the potassic benzilate, by means of hydrochloric acid: it crystallizes from the solution on cooling, in brilliant needles. Benzilic acid is sparingly soluble in cold water, but is freely dissolved by alcohol and by ether; at 248° it melts to a colourless liquid, which becomes red at a higher temperature; when heated still more strongly it is decomposed, emitting fumes of benzoic acid, and violet vapours; the latter may be condensed into a reddish, aerid, oily liquid. Benzilic acid is soluble in oil of vitriol with a beautiful crimson colour, which disappears on diluting the solution. The benzilates are monobasic; those of silver and lead are white and nearly insoluble.

(1440) *Benzile* $(C_{14}H_{10}O_2)$.—When a current of chlorine is transmitted through melted benzoine so long as hydrochloric acid is evolved, hydrogen is removed and benzile is formed. It may also be obtained more readily by heating benzoine gently with twice its weight of concentrated nitric acid; benzile rises to the surface in the form of a liquid oil which solidifies on cooling; it may be purified by crystallization from ether or from alcohol, and is deposited in beautiful regular six-sided prisms, which are of a yellowish colour. Benzile is tasteless, and insoluble in water. It may be fused, and it solidifies again between 194° and 197.6° (90° and 92° C.) into a fibrous mass. At a higher temperature it may be distilled unaltered. Benzile is isomeric with dibenzoyl.† It contains one atom less of water than normal benzilic acid. When dissolved in a hot solution of potash it forms a violet-coloured liquid, which by boiling becomes colourless; the benzile becoming converted into potassic benzilate; $C_{14}H_{10}O_2 + KHO = KC_{14}H_{11}O_3$.

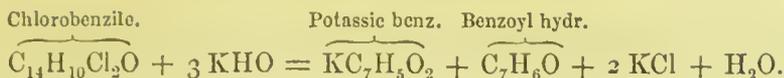
Benzile is soluble in about 6 parts of acetic acid, and if this solution be digested with iron it is reconverted into benzoine, as the hydrogen liberated by the iron at the moment of its solution combines with the benzile (Zinin).

Zinin states that if benzile be treated with an equivalent amount of phosphoric chloride, *chlorobenzile*, $C_{14}H_{10}Cl_2O$, a white crystalline compound, is obtained, in which 2 atoms of chlorine have displaced 1 of oxygen, according to the equation; $C_{14}H_{10}O_2 + PCl_5 = C_{14}H_{10}Cl_2O + POCl_3$.

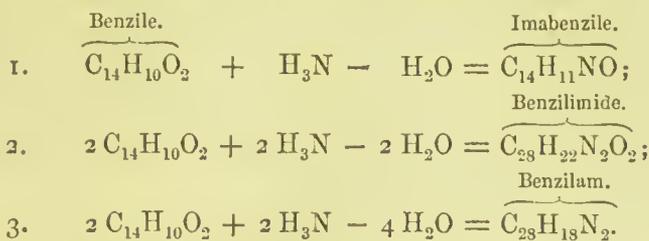
If alcoholic solutions of chlorobenzile and caustic potash be heated together, equivalent quantities of benzoyl hydride and potassic benzoate are formed, the resulting changes being the following:—

* When disulphotoluol $(C_{14}H_{12}S_2)$; sulphide of benzoine) is distilled, it yields, among other products, a hydrocarbon termed by Laurent *stillbene* $(C_{14}H_{12})$, owing to its tendency to crystallize in silky groups (from $\sigma\tau\lambda\beta\omega$, to shine). It fuses above the boiling point of water, and boils at 557.6° (292° C.). The derivatives of this body constitute the stilbylic series, of which little is at present known.

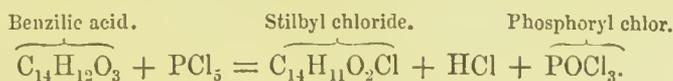
† If eupric benzoate be cautiously distilled, an oily distillate passes over having the odour of geranium. It crystallizes in oblique rhomboidal prisms, which fuse at 158° (70° C.). It may be regarded as *dibenzoyl* $(C_7H_5O)_2$, the radicle of the benzoic series. When heated with caustic potash it is readily converted into potassic benzoate while hydrogen escapes; $(C_7H_5O)_2 + 2 HKO = 2 KC_7H_5O_2 + H_2$.



When benzile is treated with ammonia it gives rise to a series of compounds which contain nitrogen, viz. *imabenzile*, *benzilimide*, and *benzilam* :—

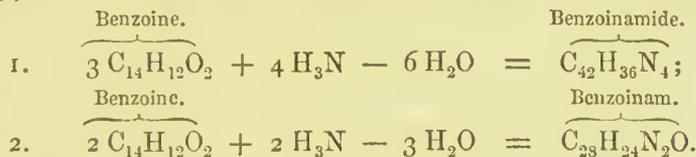


Stilbyl- or Benzile-Chloride ($\text{C}_{14}\text{H}_{11}\text{O}_2\text{Cl}$); *Boil. pt. about 518° (270° C.)*.—When phosphoric chloride is heated with benzilic acid, a violent reaction occurs, stilbyl chloride, phosphoryl chloride, and hydrochloric acid being formed :—



By collecting those portions which distil at a temperature above 482° (250° C.), stilbyl chloride is obtained in the form of a colourless oil which is denser than water. It has a powerful and peculiar odour; on exposure to the air it absorbs moisture, and is converted into benzilic and hydrochloric acids; $\text{C}_{14}\text{H}_{11}\text{O}_2\text{Cl} + \text{H}_2\text{O} = \text{HC}_{14}\text{H}_{11}\text{O}_3 + \text{HCl}$.

(1441) Two crystallizable products are obtained by digesting benzoine for several weeks in an aqueous solution of ammonia, viz. *benzoinamide*, and *benzoinam* :—

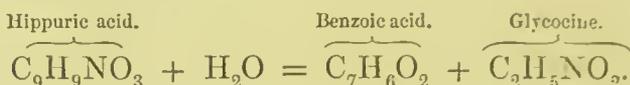


Benzoinamide is polymeric with hydrobenzamide; when heated, it melts, and may be distilled unchanged. It is very sparingly soluble both in alcohol and in ether, even at a boiling temperature.

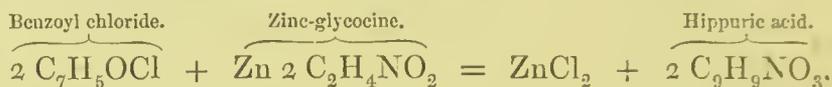
Besides the compounds already described, there are numerous others derived from the essence of bitter almonds, which contain sulphur; but for a description of them the reader is referred to Gerhardt's *Traité de Chimie Organique*, tom. iii., and to various memoirs there cited; particularly to one by Laurent (*Ann. de Chimie*, III. i. 291).

(1442) **HIPPURIC ACID** ($\text{HC}_9\text{H}_8\text{NO}_3 = 179$).—This acid is a constituent of the urine of the herbivora, and hence the name, from *ἵππος*, a horse, though it is most readily obtained from the urine of the cow, which, according to Boussingault, contains about 1.3 per cent. of it. The urine of the horse also yields hippuric acid if the animal be kept at rest, but if he be kept actively at work, the greater part of the hippuric acid disappears, and benzoic acid is found in its stead. Hippuric acid, in minute quantity, is also a normal constituent of human urine, but its amount may be voluntarily increased by taking benzoic acid in any form into the system, since benzoic acid during its passage

through the human body becomes converted into the hippuric, and is excreted in this form by the kidneys. If the urine be allowed to become putrid, the hippuric acid is decomposed, and benzoic acid is formed in its place. The facility with which these changes occur is explained by the fact that hippuric acid is truly a colligated benzoic compound. When hippuric acid is boiled for some hours with concentrated hydrochloric acid, it assimilates the elements of water, and is resolved into benzoic acid and glycocine, in the following manner:—



Dessaignes has also shown that hippuric acid may be reproduced from benzoyl chloride and zinc-glycocine:—



Preparation.—Hippuric acid may be obtained by adding milk of lime to the fresh urine of cows, boiling for a few minutes, straining from the precipitated phosphates, then adding hydrochloric acid to exact neutralization, and boiling the liquid down to one-eighth of its original bulk; on adding hydrochloric acid in considerable excess to this concentrated liquid, brown crystals of hippuric acid are deposited; they may be dissolved in hot water, and decolorized by transmitting a current of chlorine: the solution on cooling deposits long, colourless, transparent needles of hippuric acid. These crystals often become milk-white when kept.

Properties.—Hippuric acid crystallizes in forms derived from the rhombic prism. It requires about 600 times its weight of cold water for solution, and is still less soluble if this liquid be strongly acidulated with hydrochloric acid; boiling water dissolves it readily, so does hot alcohol, but it is nearly insoluble in ether. Hippuric acid has a bitterish taste; its solutions redden litmus powerfully. The acid melts at a gentle heat, and appears to enter into ebullition at about 464° (240° C.), but it is in reality becoming decomposed; the distillate contains a crystalline sublimate of benzoic acid, and a reddish oil (benzotrile) which has the agreeable odour of the Tonka bean; hydrocyanic acid is also formed at the same time, and a considerable residue of carbon is left in the retort.

Hippurates.—Hippuric acid is monobasic. Its compounds with the metals of the alkalis and with magnesium are very soluble, and are crystallized with difficulty. Acid hippurates of potassium and ammonium may be obtained. *Calcic hippurate* ($\text{Ca}_2\text{C}_9\text{H}_5\text{NO}_3$,

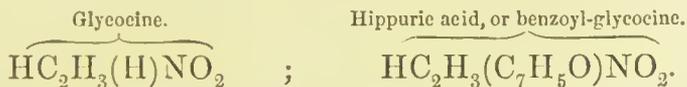
$3 \text{H}_2\text{O}$) crystallizes in beautiful rhombic prisms. *Plumbic hippurate* is deposited from concentrated solutions in the form of a dense curdy precipitate, but it may be obtained from very dilute boiling solutions in tufts of silky needles with $2 \text{H}_2\text{O}$, which gradually become changed into broad brilliant quadrangular plates ($\text{Pb}_2\text{C}_9\text{H}_8\text{NO}_3, 3 \text{H}_2\text{O}$).

Solutions of the hippurates give white insoluble precipitates with mercurous and with argentic salts: with the ferric salts they yield a characteristic brown precipitate. The hippurates when in the solid form are readily distinguished by distilling them with caustic potash, when they furnish ammonia and benzol.

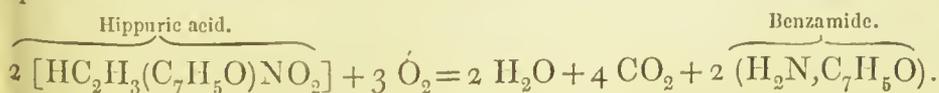
Hippuric acid is soluble in concentrated nitric acid, and if this solution be mixed with an equal bulk of sulphuric acid, carefully avoiding any elevation of temperature, it produces a *nitro-hippuric acid* ($\text{HC}_9\text{H}_7, \text{NO}_2, \text{NO}_3$), which, when the solution is diluted with three times its bulk of water, is gradually deposited in crystals. If the solution of this acid be boiled with sulphuric or hydrochloric acid, it is converted into nitrobenzoic acid and glycocine.

By boiling hippuric acid with a strong solution of potash, it is resolved into potassic benzoate and glycocine. It is also resolved into benzoic acid and glycocine when boiled with concentrated hydrochloric acid; and a similar change occurs if dilute sulphuric, nitric, or oxalic acid be employed instead of the hydrochloric.

Considerable difference of opinion has prevailed respecting the nature of hippuric acid, but the reaction of benzoyl chloride upon the substitution-product of zinc with glycocine seems to favour the view that this acid is *benzoyl-glycocine*, or glycocine in which an atom of hydrogen has been displaced by its equivalent of benzoyl, the nearly neutral character of glycocine being changed to that of an acid by the addition of the electro-negative radicle benzoyl:—



This view is strengthened by the fact that when hippuric acid is boiled with lead dioxide (PbO_2), carbonic anhydride is evolved, and benzamide is formed; the oxygen in the dioxide producing the change in the manner illustrated by the following equation:—

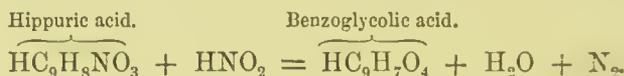


Dessaignes has also succeeded in procuring hippuric acid synthetically by exposing a mixture of equivalent quantities

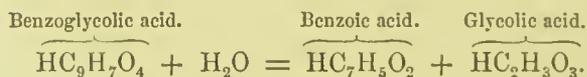
of glycoic and benzoic acid in a sealed glass tube for some hours to a temperature of 320° (160° C.) or upwards.

Cahours finds that by treating zinc glycoic with cumyl chloride and with anisyl chloride, he obtains crystalline acids corresponding to hippuric in composition—*cuminuric* acid, consisting of $(\text{HC}_{12}\text{H}_{14}\text{NO}_3)$, and *anisuric* acid of $(\text{HC}_{10}\text{H}_{10}\text{NO}_4)$.

(1443) *Benzoglycolic Acid* $(\text{HC}_9\text{H}_7\text{O}_4)$ —Strecker was disposed to regard hippuric acid as an amidated acid; and in order to test this theory he subjected it to the action of nitrous acid, which would liberate the dibasic acid of which it was supposed to be the amidic compound if this view were true. Instead of this he obtained a new monobasic acid, which he termed the *benzoglycolic*, since it is evidently a compound of the benzoic and glycolic acids. Benzoglycolic acid may be obtained by exposing a solution of hippuric acid in nitric acid to the action of a current of nitric oxide, in which case nitrogen gas is evolved, and benzoglycolic acid is formed. This compound is produced by the reaction of nitrous acid upon hippuric acid, and the action of the nitric oxide on the nitric acid merely presents nitrous acid in the nascent condition to the hippuric acid; $4\text{NO} + 2\text{HNO}_3 + 2\text{H}_2\text{O} = 6\text{HNO}_2$. The reaction of nitrous acid upon hippuric acid may be thus represented:—



Benzoglycolic acid crystallizes in rhomboidal prisms, or in thin plates. It is sparingly soluble in cold water, but is freely dissolved by alcohol and by ether. Boiling water also dissolves, but gradually decomposes it; if the acid be heated with a quantity of water insufficient for its solution, it melts to an oily-looking liquid; when heated with dilute acids, it is resolved into benzoic and glycolic acids:—



Strecker and Socoloff also obtained a compound of benzoic with lactic acid termed *benzo-lactic acid* $(\text{HC}_{10}\text{H}_9\text{O}_4)$, by heating the two acids together to about $359^{\circ}6$ (182° C.). It is analogous in properties to its homologue benzoglycolic acid.

2. *Essence of Cumin—Cuminic Series.*

(1444) *Cumyl Hydride; Essence of Cumin; Cuminic Aldehyde* $(\text{C}_{10}\text{H}_{11}\text{O}, \text{H} = 148)$; *Sp. gr. of vap.* 5.24; *Rel. wt.* 74; *Boil. pt.* 428° (220° C.).—The essential oil obtained by distilling the seeds of the *Cuminum cyminum* with water consists of a mixture of cumyl hydride and of a hydrocarbon $(\text{C}_{10}\text{H}_{14})$ termed *cymol*. The hydrocarbon is homologous with benzol (the hydrocarbon obtained by the distillation of dry calcic benzoate), and the oxidized portion is homologous with benzoyl hydride. Cumyl hydride is isomeric with essence of aniseed and of fennel.

The two components of the oil of cumin may be readily separated by agitating this oil with a moderately concentrated solution of hydric-sodic sulphite: a crystalline compound is thus

formed which yields the pure cumyl hydride when heated with a solution of potash and submitted to distillation.

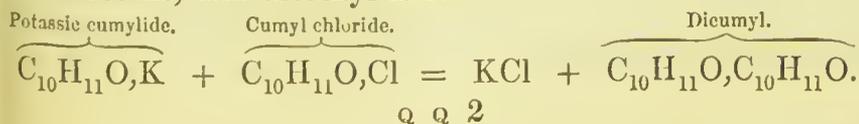
Cumyl hydride may be distilled unaltered in vessels from which air is excluded, but if exposed to the air it quickly absorbs oxygen and becomes brown, producing cuminic acid and a resinous compound. Oxidizing agents, such as nitric and chloric acids, also convert cumyl hydride into cuminic acid: if it be treated with caustic potash, potassic cuminate is produced, whilst hydrogen is liberated.

(1445) *Cuminic acid* ($\text{HC}_{10}\text{H}_{11}\text{O}_2 = 164$) may be prepared by decomposing potassic cuminate with hydrochloric acid. It crystallizes in colourless plates, which emit an odour resembling that of the common bug (*cimex lectularius*). Cuminic acid is fusible, and may be distilled unaltered at about 500° (260°C.). It is sparingly soluble in water, but freely so in alcohol and in ether. Fuming nitric acid converts it into nitro-cuminic acid. If distilled with an excess of caustic baryta it yields a hydrocarbon (C_9H_{12}) termed *cumol*, which is homologous with benzol. *Cuminic anhydride* may be obtained by decomposing dry sodic cuminate with phosphoryl chloride.

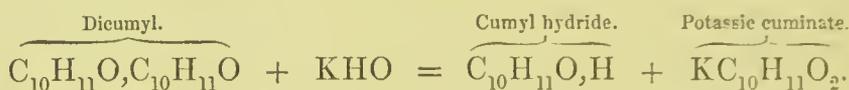
The cumينات are monobasic; *baric cuminate* ($\text{Ba}_2\text{C}_{10}\text{H}_{11}\text{O}_2$) forms beautiful iridescent plates: *argentic cuminate* is white, insoluble, and anhydrous; it speedily blackens by exposure to light.

(1446) *Cuminic alcohol* [$\text{C}_{10}\text{H}_{14}\text{O}$; *Boil. pt.* about $469^\circ.4$ (243°C.); *Kraut*] may be obtained by treating the essence with an alcoholic solution of potash in the manner directed for preparing benzyl alcohol (1438). It is a colourless oily liquid of an aromatic odour and burning taste: it may be distilled unchanged. It does not absorb oxygen when exposed to the air. When heated with caustic potash it yields cymol and cuminic acid. It does not form a colligated acid with sulphuric acid. Cuminic alcohol is isomeric with the oxidized component of oil of thyme.

(1447) *Cumyl Cumylide*, or *Dicumyl* ($\text{C}_{10}\text{H}_{11}\text{O}$)₂.—When cumyl hydride is treated with potassium, hydrogen is evolved, and *potassic cumylide* ($\text{C}_{10}\text{H}_{11}\text{O}, \text{K}$) is formed, constituting a gelatinous mass, 1 molecule of which rapidly absorbs 1 atom of oxygen from the air, and is thereby converted into potassic cuminate. Water decomposes it into caustic potash and cumyl hydride. When potassic cumylide is heated with cumyl chloride, mutual decomposition occurs, and dicumyl is formed:—



Dicumyl may be obtained from the result of this reaction by treating the mass first with a weak solution of potash, in order to convert any undecomposed essence of eumin into potassic euminate, and then agitating it with ether; the supernatant ethereal layer which contains dicumyl in solution is dried over calcic chloride, and heated gently to expel the ether, when pure dicumyl is left. Dicumyl presents the appearance of a viscous oil which is heavier than water; when gently heated it emits an agreeable odour like that of the geranium. It is freely soluble in boiling alcohol, and cannot be distilled without undergoing decomposition; caustic potash converts it into potassic euminate, whilst a portion of oil of eumin is simultaneously produced:—



(1448) *Cumyl Chloride*, or *Cuminic Oxychloride* ($C_{10}H_{11}O, Cl = 182.5$); *Sp. gr.* 1.070; *Boil. pt.* about 494.6 ($257^{\circ}C.$)—This is a colourless mobile liquid which is obtained by distilling cuminic acid with phosphoric chloride.

Many other compounds of the cuminic series may be formed, analogous to those of the benzoic series which have been already described.

Toluic aldehyd, C_8H_7O, H , may be formed from one of the compounds of toluic (or tolylic) acid ($HC_8H_7O_2$), which is obtained by oxidizing cymol by long-continued boiling with nitric acid diluted with about six times its bulk of water: by Piria's process of heating the calcic toluate with calcic formiate (*note*, p. 583), the aldehyd may be procured. On exposure to air it absorbs oxygen and is gradually reconverted into toluic acid.

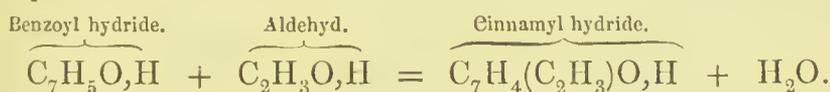
Xylyl alcohol, C_8H_9O , may be obtained by decomposing toluic aldehyd with caustic potash by a reaction analogous to that which yields benzyl alcohol, potassic toluate being formed; $2 C_8H_8O + KHO = C_8H_9O + KC_8H_7O_2$.

3. *Essence of Cinnamon—Cinnamic Series.*

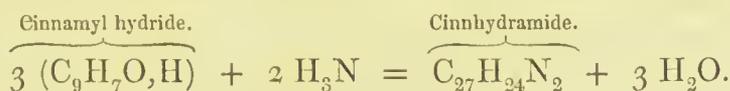
(1449) *Oil of Cinnamon: Cinnamyl Hydride* ($C_9H_7O, H = 132$).—Essence of cinnamon and essence of cassia consist chiefly of cinnamyl hydride, with a small proportion of a hydrocarbon isomeric with oil of turpentine. The commercial essence has a *sp. gr.* varying between 1.025 and 1.05. It boils at from 428° to 446° (220° to $230^{\circ}C.$) Cinnamyl hydride is readily obtained in a state of purity by agitating the crude essence with a solution of hydric-potassic sulphite. The crystalline product thus obtained must be pressed, washed with cold alcohol, and dried; after which it must be dissolved at a gentle heat in dilute sulphuric acid: the cinnamyl hydride then collects upon the surface of the liquid in the form of a colourless fragrant oil. This oil is slightly heavier than water; it absorbs oxygen rapidly from the air and becomes yellow, owing to the formation of a solid resin, mixed with cinnamic

acid. Nitric acid combines with the hydride, and converts it into a solid mass of crystals. This compound is immediately decomposed by water into nitric acid and free cinnamyl hydride. Dumas made use of this fact in separating the hydride from its associated hydrocarbon.

If cinnamyl hydride be boiled with nitric acid, abundance of benzoyl hydride is evolved, and benzoic acid is found in the solution. If the essence be boiled with chloride of lime, calcic benzoate is produced. Chiozza has also made the interesting observation that benzoyl hydride may be converted into oil of cinnamon by dissolving the pure benzoyl hydride in aldehyd, and saturating the mixture with hydrochloric acid gas: on the application of a gentle heat the liquid becomes brown; and on afterwards proceeding to distillation, oil of bitter almonds first passes over, and then oil of cinnamon. Oil of cinnamon may, in fact, be regarded as benzoyl hydride, in which an atom of hydrogen has been displaced by an equivalent of the hydrocarbon (C_2H_3), in which case the reaction in the foregoing experiment might be thus represented; water being eliminated under the influence of the hydrochloric acid, which is not indicated in the equation:—

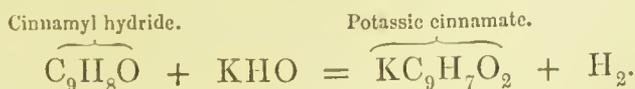


With ammonia the oil of cinnamon forms a crystalline solid termed *cinnhydramide*, analogous to hydrobenzamide:—



Several chlorinated substitution-compounds may be obtained from oil of cinnamon: one of these, *chlorocinnose* ($C_9H_3Cl_4O,H$), crystallizes in white needles, which are fusible, and may be volatilized without decomposition.

(1450) *Cinnamic Acid* ($HC_9H_7O_2=148$); *Fusing pt.* $264^{\circ}.2$ ($129^{\circ} C.$); *Boiling pt.* $559^{\circ}.4$ ($293^{\circ} C.$).—When cinnamyl hydride is heated with caustic potash, hydrogen is evolved, and potassic cinnamate is formed:—

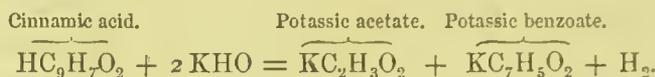


This acid is contained in many balsams, such as those of storax, of tolu, and of Peru; and it is sometimes deposited in old specimens of essence of cinnamon. It may be extracted from storax and from balsam of tolu after distilling off the portion

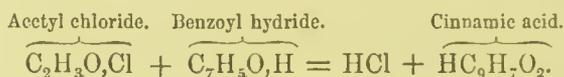
which can be volatilized by distillation with water, by treating the residue with a weak solution of sodic carbonate; the acid may be precipitated from the impure sodic cinnamate by the addition of hydrochloric acid.

Pure cinnamic acid resembles benzoic acid in appearance, but is not so soluble in boiling water, from which it crystallizes in brilliant plates. Alcohol dissolves it with facility. It fuses when heated, and may be distilled unaltered.

Nitric acid converts it into *nitro-cinnamic* acid ($\text{HC}_9\text{H}_6\text{NO}_2\text{O}_2$) if care be taken to avoid heating the mass; otherwise it is decomposed, and benzoyl hydride is formed, which is converted, by continuing the action, into benzoic and nitro-benzoic acids. If cinnamic acid be distilled with potassic dichromate and sulphuric acid it yields benzoyl hydride. When fused with an excess of caustic potash it is resolved into potassic acetate and benzoate, whilst hydrogen is liberated:—

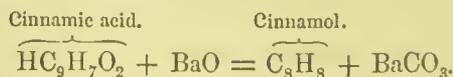


These reactions clearly indicate a close relation between cinnamic and benzoic acids: cinnamic acid may, in fact, be regarded as benzoic acid, in which one atom of hydrogen has been displaced by (C_2H_3); thus $\text{HC}_9\text{H}_7\text{O}_2 = \text{HC}_7\text{H}_4(\text{C}_2\text{H}_3)\text{O}_2$; and Bertagnini has succeeded in converting oil of bitter almonds into cinnamic acid by heating the essence for some hours to 260° or 270° with an equivalent quantity of acetyl chloride in a sealed tube. The reaction which occurs may be thus represented:—



The cinnamates are monobasic salts; those of the alkali-metals are readily soluble and are crystallizable. A solution of these salts gives a yellow precipitate with ferric salts.

If cinnamic acid be intimately mixed with four times its weight of caustic baryta and distilled, it loses carbonic anhydride, and becomes converted into cinnamol or styrolene, a hydrocarbon which bears the same relation to the cinnamic series that benzol does to the benzoic:—



When cinnamic acid is distilled with phosphoric chloride it yields a compound corresponding to benzoyl chloride. It may be termed *cinnamyl chloride* ($\text{C}_9\text{H}_7\text{O.Cl}$).

(1451) *Styrone; Peruvine; Cinnyl Alcohol?* ($\text{HC}_9\text{H}_9\text{O}$); *Fusing pt.* $91^\circ.4$ (33° C.).—This substance is procured by the distillation of styracin ($\text{C}_{18}\text{H}_{16}\text{O}_2$; 1453) with a concentrated solution of potash or of soda: a milky liquid passes over, from which on saturating it with common salt a whitish cream rises to the surface, and gradually solidifies. According to Toel, cinnyl alcohol may be obtained in beautiful silky needles, which have an agreeable odour of hyacinths; it may be distilled unaltered; it is freely soluble in alcohol and in ether, less soluble in water. Nitric acid liberates benzoyl hydride from it.

No ethers corresponding to this supposed alcohol have as yet been obtained. When exposed to the action of atmospheric air under the influence of platinum black, it yields oil of cinnamon, the aldehyd of this alcohol (Strecker).

(1452) The *Storax* from which the preceding compound is obtained is a gum-resin of the consistence of honey, and of a brownish-grey colour; it has a powerful oppressive odour, and an aromatic taste; it consists of a mixture of styraein, of einnamic acid, of a peculiar resin, and of styrolene, which is an essential oil isomeric if not identical with einnamol.

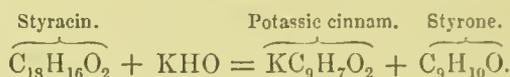
Styrolene, styrol, or cinnamol [C_8H_8 ; *Sp. gr. of liq.* 0.924; *Boil. pt.* 293° (145° C.)], is distinguished by the remarkable change which it experiences on the application of a temperature of about 401° (205° C.), when it becomes converted into a polymeric solid termed *metastyrol*, or *draconyl*. In order to obtain styrolene, three parts of storax, and one of sodie carbonate, should be subjected to distillation with water: the alkali retains the einnamic acid, and the styrolene passes over. It may also be procured by distilling a einnamate with caustic baryta (1450). Styrolene may be distilled at 293° (145° C.); but during this operation the residue in the retort is apt suddenly to rise in temperature, and to be converted into metastyrol. Styrolene also comes over mixed with toluol, when the resin termed dragon's-blood (from the *Dracæna draco*) is submitted to distillation. Styrolene is a very mobile, colourless oil, endowed with an aromatic persistent odour, recalling both that of benzol and of naphthalin. It does not solidify when cooled to -4° (-20° C.). When treated with potassic dichromate and dilute sulphuric acid, styrolene is converted into benzoic acid. Styrolene may be formed synthetically by transmitting the vapour of benzol, mixed with acetylene, through a red-hot tube, $C_6H_6 + C_2H_2$ becoming C_8H_8 . It may also be obtained more readily by treating a mixture of benzol vapour and olefiant gas in a similar manner, hydrogen being liberated; $C_6H_6 + C_2H_4$ yielding $C_8H_8 + H_2$ (Berthelot). Moreover, a mixture of styrolene and benzol vapour similarly treated yields anthracene; $C_8H_8 + C_6H_6 = C_{14}H_{10} + 2H_2$, and a mixture of styrolene with ethylene under like circumstances furnishes naphthalin in considerable quantity; $C_8H_8 + C_2H_4 = C_{10}H_8 + 2H_2$.

Metastyrol is polymeric with styrolene; it is a colourless solid of high refracting power, and is destitute both of smell and taste. It softens on the application of heat, and may be drawn out into threads. It is insoluble in water and in alcohol, and is but very sparingly soluble in ether. When subjected to a high temperature it may be distilled, and is reconverted into styrolene; and this liquid may be again reduced to the solid form of metastyrol by heating it to 401° (205° C.) in a sealed tube.

(1453) Two other balsams, closely resembling storax, are also met with as articles of commerce, viz., the balsams of Peru and of tolu.

Balsam of Peru is a fragrant resin produced by several species of leguminous plants of the genus *Myrospermum*. It is sold in the form either of a hard resin, or of a black, semi-solid body, which contains a peculiar resin and two other closely related substances, viz., cinnamic acid and styracin.

Styracin [$(C_{18}H_{16}O_2)$; *Fusing pt.* 111°·2 (44° C.)], is a crystallizable solid, which is freely soluble in alcohol and in ether; it is polymeric with cinnamyl hydride. When treated with potash it undergoes a change analogous to saponification, and furnishes potassic cinnamate and styrene:—



Balsam of tolu is stated to be the produce of the *Myrospermum toluiferum*. It is met with in commerce in the form either of a rusty brown, semi-transparent resin, or in that of a soft, dark-coloured, transparent balsam, of the consistence of turpentine, with a remarkably fragrant and agreeable odour. It is composed of the same substances as the balsam of Peru, but the proportion of styracin is much smaller. The solid resinous portion, according to E. Kopp, consists of two resins which have the composition of hydrated oxides of styracin: styracin being $C_{18}H_{16}O_2$; resin α being $H_2O, C_{18}H_{16}O_2$; and resin β , $2 H_2O, C_{18}H_{16}O_3$. When balsam of tolu is distilled, it yields benzoic ether, and a hydrocarbon (C_7H_8) termed *toluol*.

4. Oil of Spiræa—Salicylic Series.

(1454) *Salicyl Hydride*; *Salicylous Acid* ($H, C_7H_5O_2 = 122$); *Sp. gr. of liq.* 1·173; *of vap.* 4·276; *Rel. wt.* 61; *Freezing pt.* -4° (-20° C.); *Boil. pt.* 359°·6 (182° C.).—When the flowers of the meadow-sweet (*Spiræa ulmaria*) are distilled with water, they yield an essential oil which consists chiefly of a fragrant compound termed *salicyl hydride*, but which also contains a small quantity of a hydrocarbon isomeric with oil of turpentine, and a crystalline substance analogous to camphor. If the essence be agitated with a solution of potash, the salicyl hydride is dissolved, and can afterwards be separated by the addition of an acid. It is, however, generally prepared artificially by decomposing salicin (1461) by means of potassic dichromate: 2 parts of salicin and 2 of the dichromate are to be mixed with 16 parts of water in a retort, and 3 parts of oil of vitriol diluted with 8 of water are to be added; a slight reaction commences, attended with extrication of heat, and a sparing disengagement of gas: as soon as this has ceased a gentle heat may be applied, and oil of spiræa passes over and collects in the receiver in the form of an oil, heavier than water, and may be purified by digestion with calcie chloride and redistillation. Carbonic and formic acids are produced at the same time, whilst potassic-chromic sulphate (chrome alum)

remains in the retort: 25 parts of salicin yield about 6 of the essence.*

Salicyl hydride is a colourless oil, which by exposure to the air speedily assumes a more or less intense red tint. It is probably the aldehyd of salicylic acid, but it decomposes the carbonates with effervescence, and yields crystallizable compounds with the metals. It forms with potassium and sodium combinations which contain one and two atoms of the metal; they are permanent when dry, but when moist they undergo spontaneous decomposition, and become black. The potassic salicylide ($K, C_7H_5O_2, H_2O$) is soluble in alcohol. The hydric-potassic compound, ($KH_2C_7H_5O_2$) is sparingly soluble in water, but crystallizes from boiling alcohol in groups of delicate needles. A solution of potassic salicylide gives yellow insoluble precipitates with the salts of barium, manganese, lead, and silver, and with both mercurous and mercuric salts; eupric salicylide is of a green colour; but the most characteristic reaction of salicyl hydride is the production with the ferric salts of an intense violet colour, which gradually disappears on exposure to the air.

It is, however, probable that these metallic salicylides are not true salts, but that the hydrogen displaced corresponds with that of alcohol, inasmuch as it has been found by Perkin that the sodium compound when treated with an iodide of one of the alcohol radicles, yields sodic iodide and a corresponding form of salicyl. With methyl iodide for instance, it yields methyl-salicyl, $Na, C_7H_5O_2 + CH_3I = CH_3, C_7H_5O_2 + NaI$. Similar compounds with ethyl and other radicles have been formed, which are acted on by chlorine and bromine as salicyl hydride is.

Ammonia transforms salicyl hydride into *salhydramide*, $C_{21}H_{18}N_2O_3$ (1343).

(1455) *Chlorosalicyl Hydride*, or *Chlorosalicylous Acid* ($HC_7H_4ClO_2$).—This substance was formerly termed chloride of salicyl,† but its reactions show that it must be regarded as salicylous acid in which an atom of the hydrogen in the radicle has been displaced by chlorine. It is procured by transmitting a current of dry chlorine gas through oil of spiræa, gently heated: copious evolution of hydrochloric acid ensues, and as soon as this ceases to be evolved the transformation is complete; on allowing the mass to cool, the compound crystallizes. It may be dissolved in boiling alcohol, which deposits it on cooling in

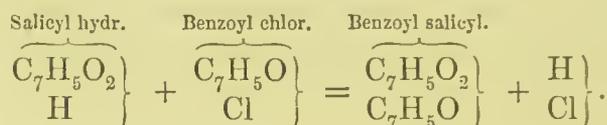
* Büchner states that the unexpanded flower-buds of the meadow-sweet contain salicin, and that this substance, during flowering, by exposure to the air, absorbs oxygen, and thus furnishes salicyl hydride.

† Gerhardt has obtained a compound which appears to be true *salicyl chloride* ($C_7H_5O_2, Cl$) by the action of phosphoric chloride on oil of winter-green. It is a fuming, slightly coloured liquid, which evolves heat when mixed with water, whilst the chloride is converted into salicylic and hydrochloric acids; $C_7H_5O_2Cl + H_2O = HC_7H_5O_3 + HCl$.

colourless, rectangular, glistening plates. It melts at a gentle heat, and may be sublimed without decomposition. This substance is insoluble in water, but soluble in ether and in oil of vitriol. The alkalis dissolve it and furnish crystallizable salts. Baric chlorosalicylide ($\text{Ba } 2 \text{ C}_7\text{H}_4\text{ClO}_2, \text{H}_2\text{O}$) forms a yellow, crystalline, sparingly soluble powder. Dry ammonia is absorbed rapidly by chlorosalicylic acid, and forms a yellow resinous-looking compound termed *chlorosamide*: it is soluble in hot ether, and crystallizes on cooling.

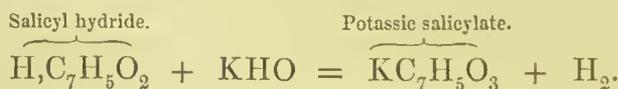
Corresponding compounds may be obtained, which contain respectively an atom of bromine and one of nitroxyl, in the place of the atom of chlorine. These bodies likewise, when acted upon by the alkalis, form crystallizable salts.

(1456) It will be observed that salicyl hydride is metameric with benzoic acid. It is, however, supposed to be formed by the union of hydrogen with a peculiar radiée, termed *salicyl* ($\text{C}_7\text{H}_5\text{O}_2$), which contains 1 atom more of oxygen than benzoyl. Although salicyl has not been isolated, yet a compound of salicyl with benzoyl, *benzoyl salicyl* ($\text{C}_7\text{H}_5\text{O}, \text{C}_7\text{H}_5\text{O}_2$) is known; this substance may be procured by the action of benzoyl chloride on salicyl hydride (Cahours):—



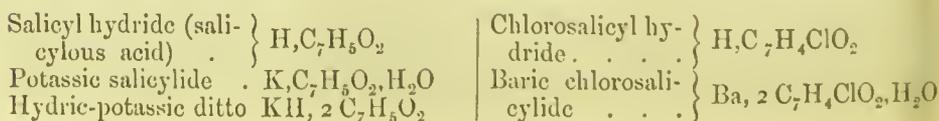
It is a yellow crystalline solid which fuses at $260^{\circ}.6$ (127°C.), and may be sublimed at about 356° (180°C.) It is identical with the *parasalicyl* of Ettling obtained by the distillation of cupric salicylide.

If salicyl hydride be fused with caustic potash, hydrogen is liberated, and salicylic acid is formed, which stands in the same relation to salicyl hydride that benzoic acid does to benzoyl hydride, so that salicyl hydride would be the aldehyd of salicylic acid; thus:—



The hydride is also oxidized to a salicylate by boiling it in an alkaline liquid with cupric or argentic oxide. Like the aldehyds generally, it forms a crystalline compound with hydric sodic sulphite.

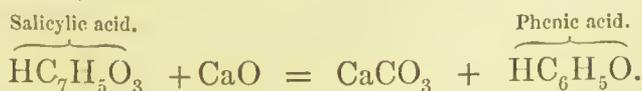
The following table gives a synoptic view of the principal compounds related to the oil of spiræa, embracing the compounds of the salicyl series:—



| | | | |
|--|---|-------------------------------------|--|
| Bromosalicyl hy- dride | H, C_7H_4, BrO_2 | Potassic gaultherate | $KC_7H_4(CH_3)O_3$ |
| Nitrosalicyl hy- dride | H, C_7H_4, NO_2, O_2 | Methyl gaultherate | $CH_3C_7H_4(CH_3)O_3$ |
| Salicyl chloride . | $Cl, C_7H_5O_2$ | Salhydramide . . . | $C_{21}H_{18}N_2O_3$ |
| Benzoyl-salicyl (parasalicyl) . . . | $C_7H_5O, C_7H_5O_2$ | Thiosalicol | C_7H_6OS |
| Salicylic anhydride | $C_{14}H_{10}O_5$ | Salicin | $C_{13}H_{18}O_7$ |
| Salicylide | $C_{14}H_8O_4$ | Chlorosalicin . . . | $C_{13}H_{17}ClO_7, 2 H_2O$ |
| Salicylic acid . . | $HC_7H_5O_3$ | Dichlorosalicin . . | $C_{13}H_{16}Cl_2O_7, H_2O$ |
| Potassic salicylate | $2 (KC_7H_5O_3), H_2O$ | Trichlorosalicin . . | $C_{13}H_{15}Cl_3O_7, H_2O$ |
| Salicylate of cop- per & potassium | $K_2C_{14}H_8CuO_6, 4 H_2O$ | Helicin | $4 C_{13}H_{16}O_7, 3 H_2O$ |
| Nitrosalicylic (anilic) acid . . . | $HC_7H_4NO_2, O_3$ | Helicoidin | $2 (C_{13}H_{18}O_7, C_{13}H_{16}O_7) 3 H_2O$ |
| Dinitrosalicylic do. | $HC_7H_3(NO_2)_2O_3$ | Saligenin | $C_7H_8O_2$ |
| Chlorosalicylic do. | $HC_7H_4ClO_3$ | Chlorosaligenin . . | $C_7H_7ClO_2$ |
| Dichlorosalicylic ditto | $HC_7H_3Cl_2O_3$ | Dichlorosaligenin . | $C_7H_6Cl_2O_2$ |
| Oil of winter-green (methyl salicylate or gaultheric acid) | $CH_3C_7H_5O_3$ or $HC_7H_4(CH_3)O_3$ | Trichlorosaligenin . | $C_7H_5Cl_3O_2$ |
| | | Saliretin | C_7H_6O |
| | | Populin or Benzoyl-salicin . . . | $C_{20}H_{22}O_8, 2 H_2O$; or $C_{13}H_{17}(C_7H_5O)O_7, 2 H_2O$ |
| | | Benzoyl-helicin . . . | $C_{13}H_{15}(C_7H_5O)O_7$ |
| | | Coumarin | $C_9H_6O_2$ |

(1457) *Salicylic Acid* ($HC_7H_5O_3 = 138$); *Fusing pt.* $316^{\circ}.4$ ($158^{\circ} C.$).—This compound may be obtained also by mixing 1 part of salicin with a concentrated solution of 3 parts of caustic potash in a silver capsule, and fusing the materials, continuing the heat until the mixture becomes white, taking care not to allow the temperature to rise beyond 752° ($400^{\circ} C.$). On adding hydrochloric acid to the mass after it has been dissolved in water, salicylic acid is precipitated. The acid is also readily prepared from the oil of winter-green, by boiling it for a few minutes with a solution of caustic potash; in this operation wood spirit is liberated, and on the addition of an acid, salicylic acid is precipitated. Coumarin (1463) also yields this acid when exposed to similar treatment. It is likewise obtained by decomposing anthranilic acid (1517) with nitrous anhydride.

Salicylic acid is sparingly soluble in cold water, but is readily dissolved by boiling water, from which it crystallizes on cooling in long slender needles. It fuses at 316° , and if pure, may at a higher temperature be sublimed unaltered. When salicylic acid is distilled with an excess of lime, it yields calcic carbonate and phenic (carbolic) acid:—



A similar result is obtained by mixing the acid itself with pounded glass and distilling, gaseous carbonic anhydride escaping. The monobasic salicylates of the alkalis yield pure phenic acid on distillation; and Kolbe states that on transmitting a stream

of carbonic anhydride into carbonic acid whilst it is dissolving sodium, sodic salicylate is reproduced, and hydrogen escapes.

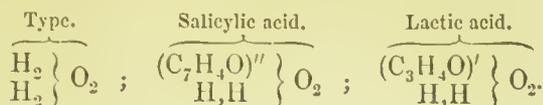
Salicylates.—Salicylic acid forms compounds which are in many respects anomalous. It is generally considered to be a monobasic acid, but it forms two distinct classes of salts, one of which contains one atom, the other two atoms of a metallic monad; the acid, therefore, has been represented by the formula $\text{HC}_7\text{H}_5\text{O}_3$, as well as by that of $\text{H}_2\text{C}_7\text{H}_4\text{O}_3$. The monobasic salts may be preserved unaltered in a dry state, but they become brown if exposed to the air in a moist condition.

The soluble salicylates are characterized by the property which they possess of forming an inky blue precipitate when mixed with solutions of the ferric salts. This colour disappears on the addition of free hydrochloric acid. The anomalous character of the salicylates renders their constitution an object of interest, and we shall therefore describe a few of these compounds.

The *normal potassic salicylate* ($\text{K}_2\text{C}_{14}\text{H}_{10}\text{O}_6, \text{H}_2\text{O}$) crystallizes from its alcoholic solution in silky needles. Piria (*Liebig's Annal.*, xiii. 262), has obtained a *cupric potassic salicylate* ($\text{K}_2\text{C}_{14}\text{H}_5\text{CuO}_6, 4\text{H}_2\text{O}$), which crystallizes in large emerald green plates. The ordinary *calcium salt* ($\text{CaC}_{14}\text{H}_{10}\text{O}_6, 2\text{H}_2\text{O}$) is very soluble, and crystallizes in octahedra of great beauty. If a solution of this salt be mixed with a solution of lime in syrup, a *dibasic calcic salicylate* ($\text{CaC}_{14}\text{H}_8\text{CaO}_6, 2\text{H}_2\text{O}$), which is sparingly soluble in water, is deposited in hard crystalline grains. The aqueous solution of this salt has an alkaline reaction, and is decomposed by the action of carbonic acid, calcic carbonate being formed, and the monobasic calcium salt being set free. A similar salt may be obtained with *barium* ($\text{BaC}_{14}\text{H}_8\text{BaO}_6, 4\text{H}_2\text{O}$); if heated to 212° it loses 4 atoms of water. With lead, salicylic acid forms three distinct compounds: the *monobasic plumbic salicylate* ($\text{PbC}_{14}\text{H}_{10}\text{O}_6, \text{H}_2\text{O}$) is a sparingly soluble salt, which is crystalline and has a silky lustre. If tribasic plumbic acetate be added to a boiling solution of this salt, a *dibasic plumbic salicylate* is deposited as a heavy, white, crystalline, anhydrous powder ($\text{PbC}_{14}\text{H}_8\text{PbO}_6$); but if the solution of the monobasic salt be decomposed by adding an excess of ammonia, instead of the tribasic acetate of lead, the liquid when boiled deposits a *pentabasic lead salt* ($\text{PbC}_{14}\text{H}_8\text{PbO}_6, 3\text{PbO}$).

These anomalies may be explained by supposing that the normal salts of salicylic acid are monobasic, but that the second atom of hydrogen, like that in alcohol, admits in certain cases of being displaced by a metal, thus giving rise to a series of salts which present the characters of basic salts.

Salicylic is probably, like lactic acid, a monobasic acid on the diatomic type (1261, 1307):—



Gerhardt has found (*Ann. de Chimie*, III. xlv. 90) that this second or alcoholic atom of hydrogen is displaceable by benzoyl, and other electro-negative groups. The mode of forming these compounds will be best understood after the properties of methyl salicylate, or oil of winter-green, have been described.

When salicylic acid in solution is treated with amalgam of sodium, a new acid, the *salylic*, $\text{HC}_7\text{H}_5\text{O}_2$, is formed: it is metameric with the benzoic, and stands in the same relation to salicylic acid that propionic does to lactic acid, containing 1 atom of oxygen less.

(1458) *Methyl Salicylate; Oil of Winter-green, or Gaultheric Acid* [$\text{HC}_7\text{H}_4(\text{CH}_3)\text{O}_3$]; *Sp. gr. of liq.* 1.18; *of vap.* 5.42; *Rel. wt.* 76; *Boil. pt.* $431^{\circ}6$ (222° C.).—The flowers of the *Gaultheria procumbens* furnish an essence consisting chiefly of methyl salicylate, mixed with a small proportion of a hydrocarbon, termed *gaultherilene*, which is isomeric with oil of turpentine. This hydrocarbon boils at 320° (160° C.), and constitutes the more volatile portion of the essence; the methyl salicylate is procured by collecting separately those portions which come over after the boiling point has risen to 432° , at which point it continues stationary. It may also be obtained artificially by distilling a mixture of 2 parts of crystallized salicylic acid, 2 of anhydrous wood spirit, and 1 part of oil of vitriol.

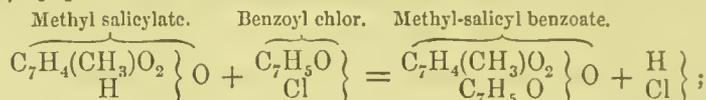
In whichever mode it is obtained it presents the appearance of a colourless or yellowish oil, with a powerful, agreeable, and persistent odour. It is sparingly soluble in water, and its aqueous solution acquires a violet tint when mixed with a ferric salt. Several substitution-products, containing chlorine, bromine, and nitroxyl, may be obtained from the essence.

Methyl salicylate is metameric with anisic acid; it possesses feebly acid properties, and if mingled with a cold concentrated solution of potash, it becomes converted into a crystalline mass, termed *potassic gaultherate* [$\text{KC}_7\text{H}_4(\text{CH}_3)\text{O}_3$], which may be obtained in a state of purity by recrystallization from alcohol. This salt is completely soluble in water; on the addition of an acid to the aqueous solution, the methyl salicylate is separated unaltered, but if the solution be heated with an excess of alkali, wood spirit is liberated, and potassic salicylate is formed. The essence of gaultheria may be regarded as existing in this compound in the form of salicylic acid, in which an atom of hydrogen has been displaced by an equivalent of methyl. If the solution of potassic

gaultherate be mixed with salts of barium, lead, or mercury, insoluble gaultherates of these metals are precipitated.

(1459) *Other Ethers of Salicylic Acid.*—The other ethers of salicylic acid also present the properties of acids, and Cahours has made the singular discovery that they may be again etherified; thus, a methyl gaultherate $[\text{CH}_2\text{C}_7\text{H}_4(\text{CH}_2)_2\text{O}_3]$ may be procured, which it will be observed corresponds exactly with the dibasic salts of salicylic acid; the dibasic lead salt, for instance, being $[\text{PbC}_{14}\text{H}_8(\text{Pb})\text{O}_6]$. The salicylic ethers may be acted upon by chlorine, so as to yield substitution-compounds, but the action of chlorine upon these ethers is anomalous. In the case of the compound ethers generally, the ethylic or methylic portion is that which is first attacked, but in the salicylic ethers, it is the acid constituent which first experiences the displacement of its hydrogen, so that the first step in the reaction is the formation of a chlorosalicylic ether.

Induced by considerations arising partially out of these facts, Gerhardt was led to attempt the formation of ethers in which the salicylates of methyl and of ethyl should act the part of an alcohol; and he succeeded in obtaining compounds corresponding to the ethers:—thus, if benzoyl chloride be made to act upon oil of gaultheria, a compound is obtained, termed *methyl-salicyl benzoate* ($\text{C}_7\text{H}_4, \text{CH}_3, \text{O}_2, \text{C}_7\text{H}_5, \text{O}_2$), which crystallizes in rhombic prisms:—



and by employing an oxychloride of a dibasic acid, such as the succinic, a dibasic ether, *methyl-salicyl succinate* $[2(\text{C}_7\text{H}_4, \text{CH}_3, \text{O}_2), \text{C}_4\text{H}_4\text{O}_4]$ may be formed, and obtained crystallized from its alcoholic solution in fibrous rectangular plates.

(1460) The body formerly known as *Salicylic anhydride* ($\text{C}_{14}\text{H}_{10}\text{O}_5$) is probably disalicylic acid; it may be procured by the action of phosphoryl chloride on dry sodic salicylate; at the same time a quantity of the *salicylic anhydride*, formerly termed *salicylide* ($\text{C}_{14}\text{H}_8\text{O}_4$) is produced. These bodies are analogous to dilactic acid and lactic anhydride (p. 413). Both are rapidly converted into ordinary salicylic acid, when heated with a solution of potash.

When salicylic acid is swallowed, a portion of it finds its way into the urine, but it becomes converted into a crystallizable colligated combination of glycoic acid, termed *salicyluric acid* ($\text{HC}_9\text{H}_8\text{NO}_4$) by a process analogous to that which converts benzoic acid, under similar circumstances, into hippuric acid. The solutions of salicyluric acid give a violet colour with ferric salts. When boiled with concentrated hydrochloric acid, salicyluric acid is split up into salicylic acid and glycoic acid, whilst the elements of water are assimilated.

Portions of the hydrogen in salicylic acid may be displaced by chlorine and by bromine, forming *chlorosalicylic* and *dichlorosalicylic*, *bromosalicylic* and *dibromosalicylic* acids. A mixture of hydrochloric acid and potassic chlorate converts salicylic acid into chloranile (perchloroquinone) $\text{C}_6\text{Cl}_4\text{O}_2$.

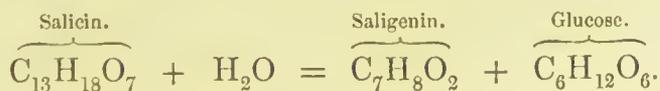
Fuming nitric acid converts the salicylic into *nitrosalicylic* (indigotic or anilic) acid ($\text{HC}_7\text{H}_4\text{NO}_2\text{O}_3$), and by prolonged digestion with it furnishes carbazotic acid $[\text{HC}_6\text{H}_2(\text{NO}_2)_3\text{O}]$. Nitrosalicylic acid may also be obtained by adding indigo in small quantities at a time to boiling nitric acid, which has been previously diluted with ten or twelve parts of water: as the liquid cools the acid crystallizes. It is sparingly soluble in cold water, but freely so in boiling water and in alcohol: it fuses easily, and may be sublimed unaltered at a gentle heat. Its solutions when mixed with ferric salts give a red colour. With salts of lead it gives a pale yellow voluminous precipitate, $\text{Pb} 2(\text{C}_7\text{H}_4\text{NO}_2\text{O}_3), \text{H}_2\text{O}$. The salt of potassium and of ammonium may be obtained in orange-coloured silky needles. A *dinitrosalicylic acid* $[\text{HC}_7\text{H}_3(\text{NO}_2)_2\text{O}_3]$ may also be formed.

Paroxybenzoic Acid ($\text{HC}_7\text{H}_5\text{O}_3 \cdot \text{H}_2\text{O}$; Saytzeff) is the name given to an acid metameric with the salicylic, which crystallizes in delicate long needles, and furnishes a sparingly soluble salt with copper. The cadmium salt crystallizes readily in rhombohedra, and its salts with lead and silver are also characteristic.

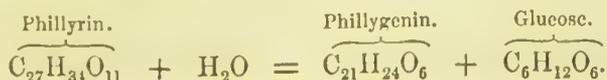
Paroxybenzoic acid is produced by various reactions, such as that of fused potash upon tyrosin (1618) and upon carthamin, and of hydriodic upon anisic acid. Indeed, anisic acid may be viewed as methyl-paroxybenzoic acid [$\text{H}, \text{C}_7\text{H}_4, (\text{CH}_3)\text{O}_3$].

(1461) SALICIN ($\text{C}_{13}\text{H}_{18}\text{O}_7 = 286$); *Fusing pt.* 248° (120°C.).—This substance was made the subject of a series of interesting researches by Piria (*Ann. de Chimie*, II. lxxix. 281, and III. xiv. 257). Salicin is contained in the bark of most of the willows, and confers upon them their peculiar bitterness. It is procured by adding to an aqueous infusion of the bark, hydrated plumbic oxide, and boiling, by which the tannin and colouring matters are removed, and then on filtering and evaporating the liquid, the salicin is obtained in crystals. It is soluble in five or six parts of cold water, and is still more readily dissolved by alcohol. These solutions exert a left-handed rotatory action upon a ray of polarized light. A solution of salicin is not precipitated by infusion of gelatin, nor by one of tannin, but with an ammoniacal solution of plumbic acetate it yields a precipitate consisting of $\text{C}_{13}\text{H}_{14}\text{Pb}_2\text{O}_7$. When salicin is moistened with strong sulphuric acid it acquires a deep red colour, and a compound acid is formed which has been termed *sulpho-rufic acid*.

If salicin is boiled for a few minutes with dilute sulphuric or hydrochloric acid a remarkable change occurs; grape sugar is found in the solution, and on neutralizing the acid, the liquid strikes a very intense blue with the ferric salts, owing to the presence of *saligenin* ($\text{C}_7\text{H}_8\text{O}_2$)*. On agitating the solution with ether, the saligenin is separated, and may be obtained on evaporation crystallized in pearly tables, which fuse at $179^\circ.6$ (82°C.). A similar transformation is effected when salicin is allowed to stand for some time after mixture with a solution of synaptase (p. 576). The change which occurs may be thus represented:—

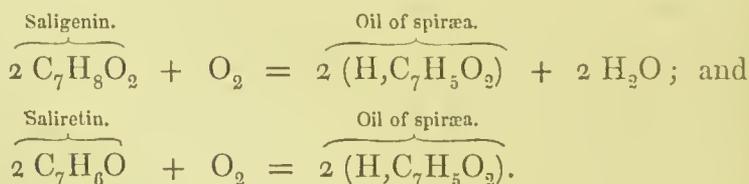


* *Phillyrin* ($2 \text{C}_{27}\text{H}_{34}\text{O}_{11}, 3 \text{H}_2\text{O}$) is the name given to a crystallizable substance contained in the bark of the *Phillyrea*, which splits, when boiled with acids, into grape sugar and a resinous substance; when submitted to lactic fermentation, it yields *phillygenin* and sugar, phillygenin containing the elements of 3 atoms of saligenin (Bertagnini).



By heating saligenin carefully in closed vessels, an atom of water is expelled, and a resinous body named *saliretin* (C_7H_6O) remains. The same effect is produced by boiling salicin or saligenin for some time with a dilute acid; the solution becomes turbid and deposits the resin, which is insoluble in water, but soluble in alcohol, ether, and concentrated acetic acid. It acquires a red colour if moistened with oil of vitriol.

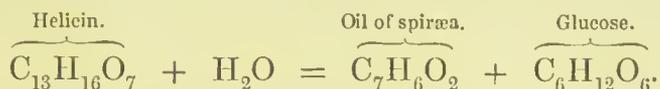
When salicin is heated to 248° (120° C.) it fuses, and at a higher temperature is completely decomposed. If heated with caustic potash it is also decomposed, and potassic oxalate and salicylate are formed. Concentrated nitric acid converts salicin into oxalic and carbazotic acids. If salicin be boiled with sulphuric acid and peroxide of manganese, formic acid is the principal product. But the most interesting transformation of which it is susceptible is that produced by chromic acid:—if 1 part of salicin be mixed with 1 part of potassic dichromate, $1\frac{1}{2}$ of sulphuric acid, and 20 parts of water, on the application of a gentle heat formic and carbonic acids are produced, whilst a fragrant oily liquid distils over with the vapour of water, and condenses in the receiver; it has exactly the odour of the meadow-sweet or the heliotrope, and analysis has proved it to have the same composition ($C_7H_6O_2$) as the essential oil of these plants. Both saligenin and saliretin also yield oil of spiræa when treated with the dichromate and sulphuric acid, the change effected being simply one of oxidation:—



Chlorine produces three different substitution-products with salicin; viz., $C_{13}H_{17}ClO_7$; $C_{13}H_{16}Cl_2O_7$; and $C_{13}H_{15}Cl_3O_7$. When digested with synaptase they each furnish a corresponding chlorinated form of saligenin (see table, p. 603), and if boiled with dilute acids each yields a corresponding chlorinated form of saliretin.

Helicin ($4C_{13}H_{16}O_7, 3H_2O$).—When one part of salicin is digested without the application of heat in ten parts of nitric acid of sp. gr. 1.160 for twenty-four hours, it becomes gradually dissolved, and loses 2 atoms of hydrogen; the solution acquires a yellow colour, and crystals of helicin are deposited: the mother liquor must be removed by sublimating the crystals to pressure in linen, after which they must be washed with cold water and with

ether, which leaves them in a state of purity. Helicin crystallizes in small delicate colourless needles, which are very soluble in boiling water and in alcohol, but not in ether. It has a bitterish taste; when heated to 212° it loses its water of crystallization; it fuses at 347° (175° C.), and is gradually decomposed, becoming converted into an insoluble resinoid mass. Under the influence of alkalies, or of synaptase, helicin assimilates the elements of water and is converted into oil of spiræa, and glucose:—



Dilute nitric acid also decomposes helicin, and liberates oil of spiræa. When boiled with dilute nitric acid, nitrosalicic and oxalic acids are formed.

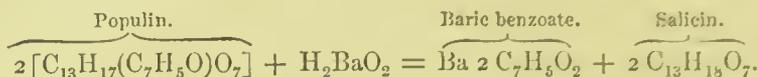
Helicoidin [$(\text{C}_{26}\text{H}_{34}\text{O}_{14})_2 \cdot 3 \text{H}_2\text{O} = (\text{C}_{13}\text{H}_{18}\text{O}_7, \text{C}_{13}\text{H}_{16}\text{O}_7)_2 \cdot 3 \text{H}_2\text{O}$] is a crystalline compound which is the result of the imperfect oxidation of salicin. It is prepared in the same manner as helicin, but the specific gravity of the nitric acid employed must not exceed 1.09. The circumstances necessary to insure its production are, however, not accurately known.

Both chlorine and bromine form compounds with helicin, in which 1 atom of hydrogen is displaced by an atom of chlorine or of bromine, the formula of *chlorohelicin* being $\text{C}_{13}\text{H}_{15}\text{ClO}_7$: it is decomposed by synaptase into glucose and salicyl chloride.

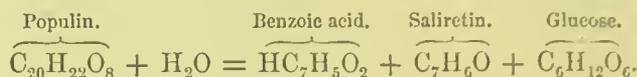
Nature of Salicin.—The foregoing observations and experiments appear to lead definitely to the conclusion that salicin must be regarded as a colligated body derived from saligenin and grape sugar. Saligenin is a substance which readily undergoes transformations by chemical agents, being converted by sulphuric acid into a peculiar red compound, by nitric acid into carbazotic acid, and by other oxidizing agents into oil of spiræa. When salicin is submitted to the action of chemical agents, the saligenin is the constituent which is first affected if these agents act with moderate intensity; whilst the sugar either remains in combination with the modified saligenin, as in the various forms of chlorosalicin, or it is set at liberty. If the reaction be more violent, the elements of the sugar also take part in the changes which are effected: for example, when salicin is oxidized by chromic acid, the saligenin yields the oil of spiræa, and the sugar produces formic acid.

(1462) *Populin* [$\text{C}_{20}\text{H}_{22}\text{O}_8, 2 \text{H}_2\text{O}$; Piria].—This compound may be regarded as salicin, in which one atom of hydrogen has been displaced by benzoyl. It is found in the bark and the leaves of the aspen (*Populus tremula*), and probably also in other varieties of the poplar. It is extracted by a process similar to that employed for salicin. Populin requires about 70 parts of boiling water for its solution, and 2000 parts of cold water: it is freely soluble in boiling alcohol. When crystallized from a hot aqueous solution it forms colourless, silky, extremely delicate needles, which have a sweetish taste resembling that of liquorice;

these crystals, if heated to 212° , lose $2\text{H}_2\text{O}$; at a higher temperature they are decomposed, benzoic acid being amongst the products. When boiled with baryta water for a few minutes, a clear solution is obtained, and on separating the excess of baryta by means of a current of carbonic acid, the solution is found to contain salicin and baric benzoate:—



When boiled with dilute acids, populin assimilates the elements of water, and is decomposed into a mixture of benzoic acid, saliretin, and glucose:—



Synaptase is without action upon populin; concentrated nitric acid converts it into a mixture of nitrobenzoic, carbazotic, and oxalic acids; dilute nitric acid converts it into *benzoyl-helicin*, $\text{C}_{13}\text{H}_{15}(\text{C}_7\text{H}_5\text{O})\text{O}_7$. A mixture of potassic dichromate and sulphuric acid liberates oil of spiræa from populin in abundance.

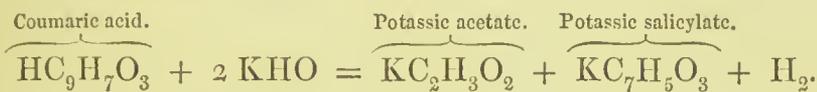
(1463) *Coumarin* ($\text{C}_9\text{H}_6\text{O}_2$); *Fusing pt.* $153^{\circ}\cdot 5$ ($67^{\circ}\cdot 5\text{ C.}$); *Boil. pt.* 555° ($290^{\circ}\cdot 6\text{ C.}$).—This substance is found in the Tonka bean (*Coumaroma odorata*), in the common melilot, in the sweet-scented vernal grass, to which much of the fragrance of hay is owing, and in several other sweet-scented plants. Coumarin is most easily extracted from the Tonka bean by digesting the powdered seeds in alcohol; on evaporating the alcoholic solution, crystals of coumarin are obtained, and may be purified by digestion with animal charcoal, and by recrystallization. Coumarin assumes the form of colourless rectangular plates, or of rhombic prisms with slightly rounded faces. It may be distilled unaltered. Its vapour has an agreeable aromatic odour. It has a burning taste, and is but slightly soluble in cold water, though it is freely dissolved by boiling water; the solution on cooling deposits coumarin in silky needles. Dilute acids dissolve it without alteration. Concentrated nitric acid converts it at first into *nitrocoumarin* [$\text{C}_9\text{H}_5(\text{NO}_2)\text{O}_2$], but by prolonged boiling it transforms it into carbazotic acid. Substitution-compounds containing chlorine and bromine may also be formed from it. One of its most singular compounds is obtained by heating coumarin with a solution of antimonie chloride in hydrochloric acid: gas is evolved, and as the liquid cools, a canary-yellow precipitate ($\text{C}_9\text{H}_6\text{O}_2, \text{SbCl}_3?$) is deposited in crystals.

When coumarin is boiled with a concentrated solution of caustic potash it assimilates the elements of water, and is converted into potassic *coumarate*; $\text{C}_9\text{H}_6\text{O}_2 + \text{KHO} = \text{KC}_9\text{H}_7\text{O}_3$.

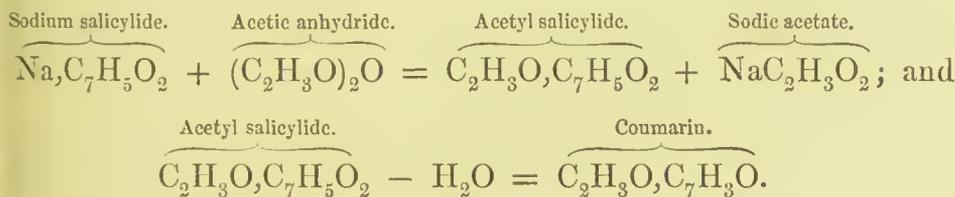
Coumaric acid may be obtained from this salt crystallized in brilliant transparent plates, by decomposing a hot solution of the coumarate by hydrochloric acid. Coumaric acid fuses at about

374° (190° C.); at a higher temperature it is decomposed, yielding a crystalline sublimate, and an oil which combines with potash, and reddens the ferric salts.

When coumaric acid is fused with caustic potash, it is decomposed into potassic acetate and salicylate (Chiozza), whilst hydrogen escapes:—



Perkin, following up this observation (*Journ. Chem. Soc.*, 1868, 60, 181, 472) has shown that coumarin may be prepared artificially by treating sodium salicylide with acetic anhydride; the yellow colour of the salicyl compound quickly disappears, and the mixture becomes very hot and liquefies. If the product, after boiling for a few minutes, is poured into water, an oily liquid subsides, which, when decanted from the solution of sodic acetate, and heated, gives off a little unaltered acetic anhydride and salicyl hydride: the temperature at which the liquid boils then rises rapidly till it reaches 555° (290°·6 C.) and the distillate crystallizes in needles of coumarin, which may be recrystallized from alcohol. In this process acetylsalicylide is formed in the first instance, and this by the loss of an atom of water furnishes coumarin:—



Other similar compounds, *butyryl-coumarin* (C₁₁H₁₀O₂), and *valeryl-coumarin* (C₁₂H₁₂O₂), have been obtained by substituting butyric and valeric for acetic anhydride in the preparation, and other homologues may no doubt be obtained without difficulty. Each of these coumarins when decomposed by potash yields a corresponding coumaric acid; these acids are represented by Perkin as follows:—



5. *Oil of Aniseed.*—*Anisic Series.*

(1464) The essential oils furnished by the seeds of *Pimpinella anisum*, or common anise, of the *Anethum feniculum*, or fennel, of the *Illicium anisatum*, or star anise, and of the *Artemisia dracunculus*, or tarragon, are closely allied to each other; they vary in odour, but all consist of two portions, one of which is a hydrocarbon isomeric with oil of turpentine, and the other is a solid crystalline oxidized compound ($C_{10}H_{12}O$), sometimes called *anise camphor*, which is convertible by oxidation into anisyl hydride ($C_8H_7O_2H$).

Solid Essence of Aniseed ($C_{10}H_{12}O$); *Sp. gr. of solid* 1.014; *of vap.* 5.19; *Rel. wt.* 74; *Fusing pt.* $64^{\circ}.4$ (18° C.); *Boil. pt.* $431^{\circ}.6$ (222° C.).—The crude essence of aniseed contains nearly four-fifths of its weight of this oxidized compound; which may be separated by exposing the oil to a low temperature, submitting the magma to pressure between folds of filtering paper, and crystallizing the residue from hot alcohol (sp. gr. 0.850). This substance when treated with chlorine or with bromine yields substitution-compounds.

When essence of aniseed is mixed with concentrated oil of vitriol it is dissolved, and a red solution is formed; on the addition of water, this solution is decomposed, and a substance termed *anisoine*, isomeric with the solid essence, is precipitated in white resinoid masses. A similar change is produced by treating the essence with stannic chloride or with antimonious chloride. This modification is insoluble in alcohol, but is soluble in ether and the essential oils: it is rather heavier than water, and is fusible above 212° . The oils of tarragon and bitter fennel appear each to contain a distinct compound which is isomeric with anisoine and with the solid portion of oil of anise; the principal portion of essence of tarragon consists of a modification which boils at $402^{\circ}.8$ (206° C.), and requires a low temperature for its solidification. These bodies, when oxidized, yield aniseic acid, and other products which are identical with those furnished by oil of aniseed. Oil of eumin is also isomeric with the solid essence of anise, but the products of its oxidation are different (1444).

If oil of aniseed be heated in a sealed tube to 428° (220° C.), in contact with a mixture of caustic soda and lime, a small quantity of an acid is formed, which is isomeric with euminic acid, but not identical with this compound.

The action of nitric acid upon oil of aniseed gives rise to a series of compounds which have been particularly examined by

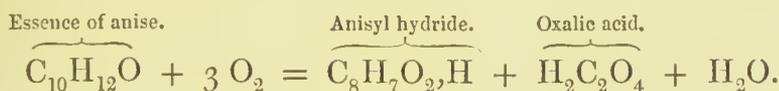
Cahours. They present a close analogy with the compounds of the salicylic series. They may be regarded as containing a radicle termed *anisyl* ($C_8H_7O_2$), which may be viewed either as a homologue of salicyl, or as a body in which one atom of the hydrogen in salicyl has been displaced by an equivalent of methyl; thus—



The principal members of the anisic group are—

| | | |
|------------------|-----------|-----------------------|
| Anisyl hydride | | $C_8H_7O_2, H$ |
| Anisylic alcohol | | C_8H_9O, HO |
| Anisic acid | | $HC_8H_7O_2, O$ |
| Anisyl chloride | | $C_8H_7O_2, Cl$ |
| Anisine | | $C_{24}H_{24}N_2O_3.$ |

(1465) *Anisyl Hydride* ($C_8H_7O_2, H$); *Sp. gr.* 1.09; *Boil. pt.* about $489^{\circ}.2$ ($254^{\circ} C.$).—When oil of aniseed is acted upon by dilute nitric acid, a reddish oil is obtained, consisting of a mixture of anisic acid and anisyl hydride. A quantity of oxalic acid is always formed during its preparation, which may be explained by the following equation:—



If the oil thus obtained be washed with a weak solution of potash, in order to remove anisic acid, and be then cautiously distilled, the hydride passes over in the form of an amber-coloured liquid, which has an aromatic odour resembling that of new hay. Anisyl hydride is homologous with oil of spiræa. It is freely soluble in alcohol and in ether, but insoluble in water. Sulphuric acid dissolves it and forms a dark red liquid, from which on dilution with water the oil is separated unaltered. Anisyl hydride forms crystalline compounds with the hydric sulphites of the alkali metals. Indeed, it constitutes the aldehyd of the anisic series.

Anisylic Alcohol (C_8H_9O, HO); *Boil. pt.* about 482° ($250^{\circ} C.$).—If anisyl hydride be dissolved in an equal volume of alcohol and mixed with three times its volume of a solution of potash (sp. gr. 1.05) it is decomposed into anisylic alcohol and potassic anisate. The salt crystallizes out, while the new alcohol remains in solution; it is decanted and distilled to get rid of the ordinary alcohol; and is then mixed with ether, which dissolves the anisylic alcohol, and leaves it on evaporation as a yellowish oil. This product may be distilled and freed from a

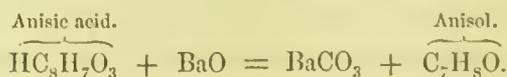
trace of anisyl hydride by digestion with hydrie-sodic sulphite. On redistillation it is obtained as an oil which solidifies when anhydrous at $73^{\circ}4$ (23° C.), but if it contains water it crystallizes at a lower temperature in hard shining needles; it is heavier than water, and has a feebly spirituous odour and a burning taste. Oxidizing agents, such as dilute nitric acid, gradually convert it into anisyl hydride, and then into anisic acid. Platinum black easily changes it into anisic acid in the presence of air.

Ammonia converts anisyl hydride into *anishydramide*; $3C_8H_8O_2 + 2H_3N = C_{24}H_{24}N_2O_3 + 3H_2O$. If anishydramide be maintained for two hours at a temperature of 329° or 338° (165° or 170° C.), it fuses and becomes converted into an isomeric base, termed *anisine*. This body is soluble in alcohol, but scarcely soluble in water or in ether. Its alcoholic solution has a strongly alkaline reaction and a bitter taste; it deposits the alkali in colourless prisms. The salts of this base may be obtained in crystals.

(1466) *Anisic Acid* ($HC_8H_7O_3 = 152$); *Fusing pt.* 347° (175° C.).—This substance is isomeric with methyl salicylate, and has the composition of methyl-paroxybenzoic acid; it may be prepared synthetically by heating potassic methyl-oxybenzoate with methyl iodide, and decomposing the anisic methyl ether by boiling it with potash; $K, C_7H_8(CH_3)O_3 + CH_3I = CH_3, C_7H_8(CH_3)O_3 + KI$, and $CH_3, C_7H_8(CH_3)O_3 + KHO = CH_4O + KC_7H_8(CH_3)O_3$ (p. 607). It may be obtained by boiling oil of anise with nitric acid of sp. gr. 1.20; a yellow resinous mass termed *dinitraniside* [$C_{10}H_{10}(NO_2)_2O$] is thus formed, and the liquid on cooling deposits long, colourless brilliant prisms of anisic acid. Anisic acid is scarcely soluble in cold water, but is freely soluble in boiling water, in alcohol, and in ether. It may be sublimed unaltered, condensing in white needles; boiling concentrated nitric acid converts it into *nitranisic acid* ($HC_8H_6NO_2O_3$). The anisates are monobasic; those of the metals of the alkalis and of the earths are soluble and crystallizable: but those of lead, silver, and mercury are insoluble in cold water.

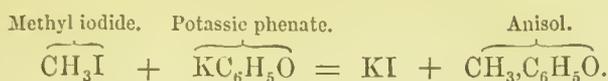
Anisyl Chloride [$C_8H_7O_2, Cl = 170.5$; *Sp. gr.* 1.261; *Boil. pt.* $503^{\circ}6$ (262° C.)] is a colourless oil, of a penetrating, powerful odour; it is procured by distilling anisic acid with phosphoric chloride.

(1467) *Anisol* (C_7H_8O); *Sp. gr.* 0.991; *Boil. pt.* $305^{\circ}6$ (152° C.).—If anisic acid be distilled with an excess of caustic baryta, it yields a compound termed *anisol*, or *phenomethol*, whilst baric carbonate remains in the retort:—

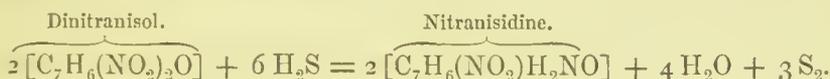


Anisol has the composition of methyl phenate (CH_3, C_6H_5O). Cahours has

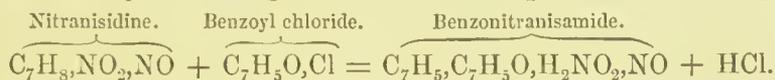
obtained it synthetically by decomposing methyl iodide with potassic phenate (1555):—



Anisol is a colourless liquid of an aromatic odour; it is soluble in water as well as in alcohol and ether. With sulphuric acid it combines readily, forming the *sulphanisolic acid* ($\text{HC}_7\text{H}_7\text{SO}_4$). When anisol is treated with fuming nitric acid, substitution-compounds are obtained, which may contain 1, 2, or 3 atoms of nitroxyl (NO_2). *Nitranisol* ($\text{C}_7\text{H}_7\text{NO}_2\text{O}$), when treated with an alcoholic solution of ammoniac sulphhydride, yields a base termed *anisidine* ($\text{C}_7\text{H}_9\text{NO}$), whilst sulphur is deposited; and if *dinitranisol* be similarly treated, a nitro-base, *nitranisidine* is obtained:—



Nitranisidine crystallizes in long brilliant needles, which are of a reddish-brown colour: it forms well-defined crystallizable salts with sulphuric, nitric, and hydrochloric acids. If *trinitranisol* [$\text{C}_7\text{H}_5(\text{NO}_2)_3\text{O}$] be treated with ammoniac sulphhydride, it yields a third base, *dinitranisidine* [$\text{C}_7\text{H}_5(\text{NO}_2)_2\text{H}_2\text{NO}$], the salts of which, however, are very unstable, and are decomposed by contact with water. Nitranisidine when treated with the chloride of benzoyl, of cinnamyl, or of cumyl yields a new compound, in which benzoyl, cinnamyl, or cumyl is substituted for hydrogen, and a compound analogous to benzamide is produced; for example:—



Experiments of this nature present an interest in connexion with the question of the artificial formation of the natural organic bases; the empirical formula of *benzonitranisamide* ($\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_4$), presenting considerable resemblance to that of some of the natural alkaloids.

(C.) Essential Oils which contain Sulphur.

(1468) THE ALLYL SERIES.—The basis of all the oils of the sulphuretted essences which have been accurately examined is the hydrocarbon termed allyl (C_3H_5). Common garlic (*Allium sativum*) yields a volatile oil which is a mixture of allyl oxide with allyl sulphide; and the essences of onions and assafœtida, and many of the *Asphodeleæ* and *Cruciferae*, yield similar oils: the essential oils of mustard, of horse-radish, and of scurvy-grass consist chiefly of allyl sulphoeyanide.

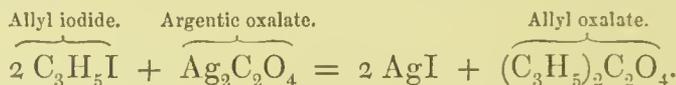
The allyl series has been invested with new interest by the labours of Berthelot and De Luea, who have succeeded in preparing the *allyl iodide*, or iodized propylene, as they term it, by decomposing glycerin with phosphorus diiodide (1238); a discovery which in the hands of these chemists (*Comptes Rendus*, Feb. 4, 1856), and in those of Hofmann and Cahours (*Ann. de Chimie*, III. l. 432) has led to the formation of numerous derivatives of allyl, and has demonstrated the intimate connexion of

these compounds with acrolein and the products of its oxidation.

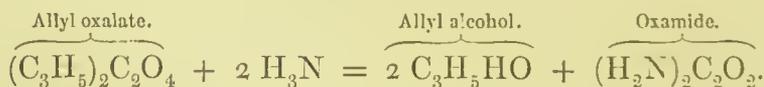
(1469) *Diallyl* (C_3H_5)₂; *Sp. gr. of liq.* 0.684; *of vap.* 2.92; *Rel. wt.* 41; *Boil. pt.* 138°·2 (59° C.).—When allyl iodide is treated with sodium it is decomposed, sodie iodide is formed, and diallyl is liberated in the form of a very volatile liquid, possessed of a peculiar penetrating odour, resembling that of radishes. Its vapour burns with a very luminous flame. It is miscible with sulphuric acid, the mixture being attended with great elevation of temperature, and on standing for a few hours it gradually separates in a modified condition.

Diallyl is immediately attacked by chlorine, bromine, and iodine, with which it forms compounds to which the formulæ (C_3H_5)₂Cl₄; (C_3H_5)₂Br₄; and (C_3H_5)₂I₄, have been assigned. It is probable that these bodies are compounds of diallyl with 4 atoms of the halogen.

(1470) *Allyl Alcohol* (C_3H_5HO); *Boil. pt.* 217°·4 (103° C.).—When allyl iodide is digested with argentic oxalate, violent action takes place, double decomposition occurs, in consequence of which allyl oxalate and argentic iodide are produced:—



Allyl oxalate, or allyl-oxalic ether, is an aromatic liquid which boils at 404°·6 (207° C.): when treated with ammonia it yields oxamide, and allyl alcohol:—

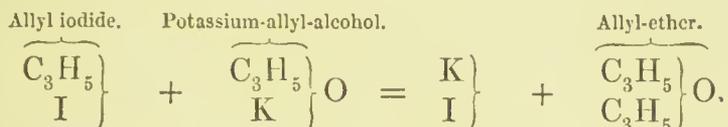


Allyl alcohol is metameric with acetone, and with propionic aldehyd, but it differs from them in properties. It is lighter than water, in which it is soluble in all proportions: its vapour is inflammable, and burns with a luminous flame. By gradual oxidation with platinum black, or by the action of sulphuric acid and potassic dichromate, acrolein or allyl aldehyd is formed, and passes rapidly into acrylic acid. Allyl alcohol when treated with potassium gives off hydrogen, whilst *potassium-allyl-alcohol* (C_3H_5KO) is obtained in the form of a gelatinous mass.

Allyl alcohol when mixed with sulphuric acid unites with it, and forms *allyl-sulphuric acid* ($HC_3H_5SO_4$), which corresponds with the ethyl-sulphuric. It is the vinic acid of the series.

If the alcohol is distilled with phosphoric anhydride, allylene (C_3H_4) is obtained (1208.)

(1471) *Allyl Oxide; Allyl Ether* $[(C_3H_5)_2O]$; Boils between 185° and $190^\circ.4$ (85° and $88^\circ C.$)—When the compound of potassium with allyl alcohol is mixed with allyl iodide, violent action occurs; potassie iodide is formed, and allyl ether is produced, by a decomposition analogous to that which attends the formation of ordinary ether when sodium-alcohol is treated with ethyl iodide (p. 201).



Berthelot and De Luea state that allyl oxide may also be formed by distilling allyl iodide with mercuric oxide. It is lighter than water, and has an ethereal odour resembling that of radishes.

Allyl oxide appears to exist ready formed in small quantity in oil of garlic, and in some other oils which resemble it. Wurtheim also states that it may be obtained by decomposing oil of mustard by distillation in a closed tube with caustic soda and lime, but the decomposition of the allyl sulphocyanide thus effected is slow and imperfect. It enters into direct combination with argentic nitrate, and forms a compound $[(C_3H_5)_2O, 2AgNO_3]$, which may be obtained by mixing rectified essence of garlic with an excess of a concentrated alcoholic solution of argentic nitrate: in the course of twenty-four hours a black deposit of argentic sulphide is formed; the liquid must be boiled, and filtered; on cooling, the compound of allyl oxide with argentic nitrate crystallizes in brilliant colourless radiated prisms, which are freely soluble in water, but sparingly so in cold alcohol. If this body be dissolved in ammonia, allyl oxide is set at liberty.

A double allyl ether has also been formed by decomposing allyl iodide by an alcoholic solution of potash; in which case *allyl-ethyl ether* (C_3H_5, C_2H_5, O) , a liquid which boils at $144^\circ.5$ ($62^\circ.5 C.$), is produced. *Allyl-amyl ether* $[C_3H_5, C_5H_{11}, O]$; Boil. pt. 248° ($120^\circ C.$), may be obtained by substituting a solution of potash in fousel oil for the alcoholic solution of potash used in the previous experiment.

Hofmann and Cahours have obtained the same compounds by decomposing potassium-allyl-alcohol by ethyl iodide, and by amyl iodide.

(1472) *Allyl chloride* (C_3H_5Cl) is readily obtained by distilling allyl alcohol with phosphoric chloride, and the *bromide* (C_3H_5Br) may be obtained with equal facility by distilling the alcohol with phosphoric bromide.

Allyl Iodide; Iodized Propylene $(C_3H_5I=168)$; Sp. gr. of liq. 1.789; Boil. pt. $213^\circ.8$ ($101^\circ C.$).—This interesting compound is obtained by the action of equal parts of phosphorus diiodide and glycerin upon each other (1238). It is a colourless liquid, insoluble in water, but soluble in alcohol and in ether; it

has an ethereal, somewhat alliaceous odour; when exposed to air and light it rapidly becomes brown, and emits an irritating odour allied to that of mustard; it may be distilled unaltered. Allyl iodide is decomposed by digestion with an aqueous solution of ammonia, and on distillation with potash a volatile base of a fishy ammoniacal odour is formed, probably *allylia* ($C_3H_7N = C_3H_5, H_2N$).

The following compounds investigated by Wurtz (*Ann. de Chimie*, III. li. 87) are connected with these bodies:—

(1473) *Tritylene Dibromide* ($C_3H_6Br_2$); *Boil. pt.* between 284° and 293° (140° and 145° C.).—This is a colourless liquid, having the odour of Dutch liquid. It is most readily prepared by transmitting through bromine the gaseous products procured by passing the vapours of fousel oil through a red-hot tube, and submitting the liquid thus obtained to fractionated distillation. This substance may be regarded as the hydrobromic ether of trityl glycol.

Bromotritylene Dibromide (C_3H_5Br, Br_2); *Sp. gr. of liq.* 2.392; *Boil. pt.* about 383° (195° C.).—When the vapour of the foregoing compound is submitted at its boiling point to the action of the vapour of bromine, the two bodies react upon each other, hydrobromic acid gas is formed, and a new brominated substance having the above formula is obtained. After purification by distillation it is procured in the form of a colourless liquid of a powerfully irritating and very persistent odour. It acts rapidly upon the salts of silver.

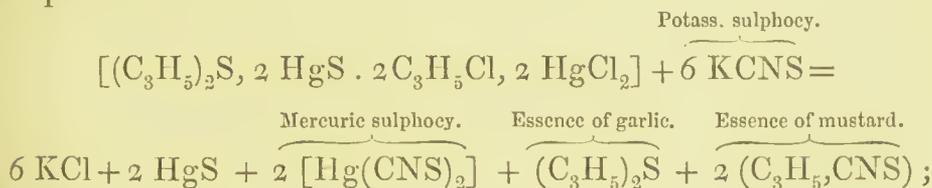
A compound metameric with the foregoing one, which has been termed *allyl tribromide* ($C_3H_5Br_3$), is obtained by decomposing 1 part of allyl iodide with $2\frac{1}{2}$ parts of bromine. It has a sp. gr. of 2.436, and boils at $422^\circ.6$ (217° C.), but unlike its isomeric it becomes converted into a solid mass at temperatures below 50° (10° C.). When cooled slowly it deposits magnificent brilliant prisms fusible at $62^\circ.6$ (17° C.). An alcoholic solution of potash decomposes it, liberating an ethereal compound which boils at 275° (135° C.).

Allyl tribromide is readily attacked by argentic acetate, 1 atom of the bromide requiring 3 atoms of the acetate for its decomposition. It is thus converted into triacetin ($C_9H_{14}O_6$); and this substance, when decomposed by baryta water, yields a product which, when purified by distillation in vacuo at 392° (200° C.), was found to be pure glycerin.

(1474) *Allyl Sulphide* ($C_3H_5)_2S$; *Boil. pt.* 284° (140° C.).—This compound is contained in various essential oils, particularly in those of garlic, onions, leeks, cress, radishes, and assafœtida. It may be prepared artificially by allowing allyl iodide to fall drop by drop into an alcoholic solution of dipotassic sulphide. A slight excess of the alkaline sulphide must be maintained, and, on diluting the mixture with water, the allyl sulphide is separated in the form of a yellowish limpid oil. When rectified, allyl sulphide is a colourless oil which is lighter than water; it has a high refracting power; its odour is less repulsive than that of crude oil of garlic. It may be distilled without undergoing decomposition; concentrated nitric acid converts it into formic and oxalic acids, whilst the sulphur is oxidized. Cold sulphuric acid dissolves it with a purple tint, but the oil is separated unaltered on dilution. It is dissolved rapidly by hydrochloric acid, and the

mixture acquires a deep blue colour, which disappears on the addition of water. Solutions of the alkalies do not decompose allyl sulphide.

Allyl sulphide causes a precipitate in many metallic solutions, such as those of silver, mercury, gold, platinum, and palladium, but it does not precipitate the salts of lead or of copper. Argentic nitrate gradually decomposes it, argentic sulphide being formed, and the compound of allyl oxide and argentic nitrate (1471) is produced. A peculiar sulphuretted compound of allyl with mercuric chloride is obtained by mixing alcoholic solutions of allyl sulphide and corrosive sublimate, when an abundant white precipitate is formed $[(C_3H_5)_2S, 2 HgS, 2 C_3H_5Cl, 2 HgCl_2]$. If this compound be distilled with potassic sulphocyanide it is decomposed, and oil of mustard, mixed with allyl sulphide, is amongst the products:—



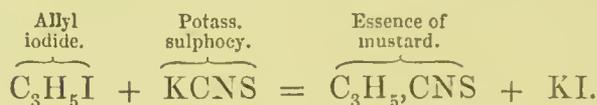
in this reaction the double chloride of mercury and allyl is alone acted upon by the sulphocyanide, potassic chloride and mercuric sulphocyanide being formed, whilst the allyl sulphide passes over unaltered, accompanied by the oil of mustard, leaving mercuric sulphide in the retort.

Essence of Garlic.—When the cloves of garlic are distilled with water, a brown heavy fœtid oil passes over, constituting little more than 0.2 per cent. of the fresh root. It is partially decomposed by redistillation over an open fire, but if rectified from a bath of salt water, about two-thirds of the oil may be obtained in the form of a yellowish liquid which is lighter than water, and which, when treated with calcic chloride, and subsequently distilled from fragments of potassium, furnishes pure allyl sulphide. The crude oil appears to contain portions of allyl oxide, and of a higher sulphuretted compound of allyl, which becomes decomposed during the distillation.

The *essence of assafœtida* contains a larger proportion of sulphur than that of garlic; it evolves sulphuretted hydrogen spontaneously, and cannot be redistilled without undergoing decomposition.

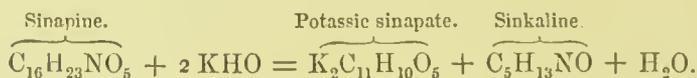
(1475) *Allyl Sulphocyanide* (C_3H_5, CNS); *Sp. gr. of liq.* 1.010; *of vap.* 3.54; *Boil. pt.* 298°.4 (148° C.).—This compound constitutes the principal portion of the essential oil of mustard, from

which it may be obtained in a state of purity by simple redistillation; this operation frees the essence from a brown resinous matter with which it is usually contaminated. The pungency of the horse-radish, of the scurvy-grass, and of one or two other allied plants is also due to allyl sulphocyanide. Berthelot and De Luca made the interesting observation that when allyl iodide is distilled with potassic sulphocyanide, an oil is formed identical with the chief constituent of essence of mustard—an observation which afforded the first indication of the intimate relation subsisting between the allylic series and that of glycerin:—



The seeds both of the black and of the white mustard (*Sinapis nigra* and *alba*) yield by expression a large quantity of a bland fixed oil, but they do not contain any essential oil ready formed; white mustard does not yield allyl sulphocyanide.

According to Von Babo and Hirschbrunn, white mustard contains the hydro-sulphocyanide of a peculiar alkali, termed *sinapine*, $\text{C}_{16}\text{H}_{23}\text{NO}_5$. This base, when acted upon by caustic potash or soda, is decomposed into a salt of *sinapic* acid, and a new alkali, termed *sinkaline*, in the manner represented in the following equation, adopting the altered formula $\text{C}_{16}\text{H}_{23}\text{NO}_5$ proposed by Gerhardt:—



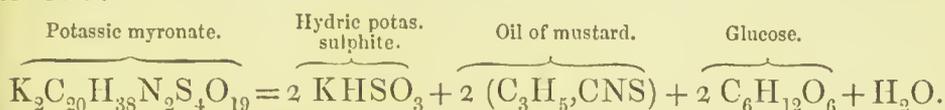
An aqueous solution of sinapine has an intensely yellow colour. Sinapine cannot be isolated in a pure condition, owing to the facility with which it is decomposed: it forms crystallizable salts. The hydro-sulphocyanide is extracted from white mustard, after treating the dried flour successively with ether and absolute alcohol to remove the fixed oil and colouring matter, and then boiling the residue in alcohol of sp. gr. 0.825. After the solution has been sufficiently concentrated by evaporation, the salt is deposited in crystals as the liquid cools. If the solution of this salt be mixed with an alkali, it assumes an intensely yellow colour, and on boiling the solution, and subsequently adding hydrochloric acid in slight excess, sinapic acid is deposited. If baryta water be used to decompose the salt of sinapine, the sinapic acid is precipitated as an insoluble baryc sinapate, and sinkaline may be obtained from the solution. Sinapic acid crystallizes in prisms; it is sparingly soluble in cold water, very soluble in boiling alcohol, and insoluble in ether; it fuses at a temperature above 302° (150° C.): nitric acid dissolves it, and produces an intense red colour.

Sinkaline may be obtained in deliquescent crystals, which absorb carbonic acid from the air; it is a powerful base, but readily undergoes decomposition. With platinic chloride it forms a magnificent double salt, which crystallizes in orange-coloured six-sided prisms [$2(\text{C}_5\text{H}_{13}\text{NO}, \text{HCl}), \text{PtCl}_4, 2 \text{H}_2\text{O}$].

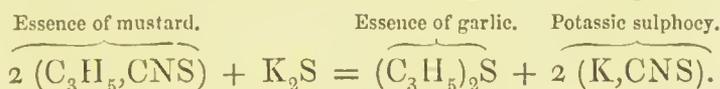
Black mustard contains the potassium salt of a compound termed *myronic acid*, which is susceptible of a decomposition analogous to that experienced by amygdalin. This decomposition

is not effected until the crushed seed is moistened with water; a peculiar azotised ferment contained in the seed, and analogous to the synaptase of the almond, is thus brought into action, and the essential oil is developed.

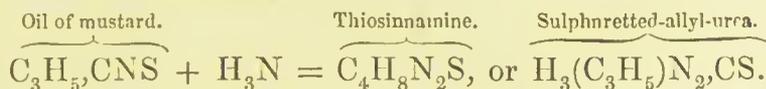
Ludwig and Lange (*Knop's Centralblatt*, 1861, p. 149) obtained 1 part of potassic myronate from 500 of black mustard, crystallized in colourless brilliant needles; and according to their analysis this salt consists of $K_2C_{20}H_{38}N_2S_4O_{19}$: it splits into oil of mustard, sugar, and probably also into hydric potassic sulphite, as follows:—



The essence of mustard is a colourless oil of a burning and painfully penetrating odour, which produces a copious flow of tears. If the essence be applied to the surface of the body, it speedily raises a blister upon the part. Essence of mustard is soluble in all proportions in alcohol, and in ether, but very sparingly so in water: if exposed to the air it absorbs oxygen and becomes brown. When hot it dissolves both sulphur and phosphorus in considerable quantities, but, as the solutions cool, these bodies are again deposited in crystals. Oil of mustard can be converted into essence of garlic by heating it to a temperature of 250° for some hours in a sealed tube, with dipotassic sulphide:—

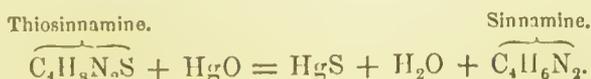


(1476) Oil of mustard combines at once with ammonia, and forms a compound which enters into direct combination with acids like a true organic base; from its origin this compound has been termed *thiosinamine*:—



Thiosinamine corresponds to the urea of the allyl series, in which 1 atom of sulphur is present instead of 1 of oxygen. Allyl sulphocyanide also unites with other bases, such as ethylia, aniline, and naphthalidine, and forms with them compounds analogous to thiosinamine.

If thiosinamine be triturated with mercuric oxide, water and mercuric sulphide are formed, and a new basic substance free from sulphur, termed *sinnamine*, is obtained:—



Plumbic oxide produces a similar decomposition.

Sinamine has been regarded as a compound of ammonia, in which one atom of hydrogen has been displaced by allyl, and a second atom by cyanogen; as for example:—



Sinamine is soluble in water, and may be obtained in prismatic crystals. It is a powerful base, and expels ammonia from its salts. It occasions precipitates in solutions of lead, of iron, and of copper. The oxalate is the only salt of sinamine which crystallizes readily; solutions of the salts of sinamine which contain an excess of acid impart a yellow colour to a slip of deal.

(1477) *Sinapoline* ($C_7H_{12}N_2O$).—This base is usually formed by digesting essence of mustard upon hydrated plumbic oxide:—



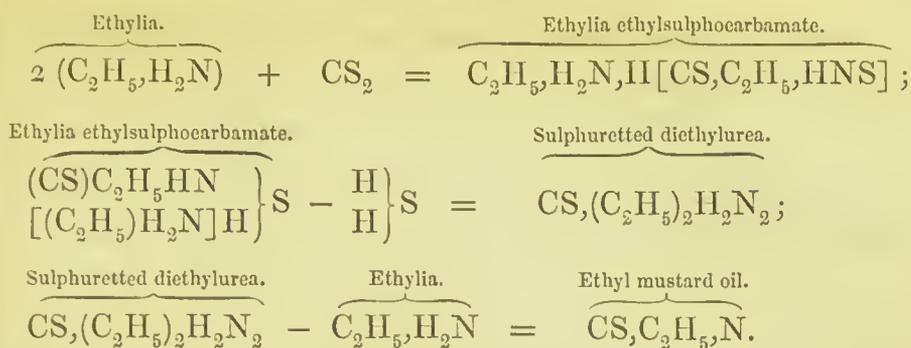
but it may also be produced by the action of water upon allyl-cyanic ether, which will be immediately described. Sinapoline is a feeble base which crystallizes from its solution in water in brilliant greasy flakes: it fuses below 212° . Its aqueous solution occasions a precipitate in solutions of corrosive sublimate and of platinic chloride.

(1477a) *Homologues and Analogues of Mustard Oil*.—Hofmann has recently described a method by which a series of bodies analogous to mustard oil has been obtained (*Proceed. Roy. Soc.* xvi. 254, and xvii. 67).

Among these are the following:—

| Name of Compound. | Formula. | Fusing Point. | | Boiling Point. | | Vapour density. |
|-----------------------------------|---|---------------|-------------|----------------|-------------|-----------------|
| | | $^\circ F.$ | $^\circ C.$ | $^\circ F.$ | $^\circ C.$ | |
| Methyl mustard oil . . | $C \begin{array}{l} H \\ CN \end{array} \left. \begin{array}{l} H \\ H \\ H \end{array} \right\} S$ | 93.2 | 34 | 246.2 | 119 | 2.61 |
| Ethyl ditto . . | $C_2H_5 \begin{array}{l} H \\ CN \end{array} \left. \begin{array}{l} H \\ H \\ H \end{array} \right\} S$ | | | 273.2 | 134 | 3.03 |
| Amyl ditto . . | $C_5H_{11} \begin{array}{l} H \\ CN \end{array} \left. \begin{array}{l} H \\ H \\ H \end{array} \right\} S$ | | | 362 | 183.3 | 4.40 |
| Tolyl ditto . . | $C_7H_7 \begin{array}{l} H \\ CN \end{array} \left. \begin{array}{l} H \\ H \\ H \end{array} \right\} S$ | 78.8 | 26 | 458.6 | 237 | |
| Benzyl ditto . . | $C_7H_7 \begin{array}{l} H \\ CN \end{array} \left. \begin{array}{l} H \\ H \\ H \end{array} \right\} S$ | | | 469.4 | 243 | |
| Allyl ditto (true mustard oil) | $C_3H_5 \begin{array}{l} H \\ CN \end{array} \left. \begin{array}{l} H \\ H \\ H \end{array} \right\} S$ | | | 298.4 | 148 | 3.54 |

In order to prepare these compounds, the monammonia of the alcohol is treated with carbon disulphide in alcoholic solution. The alcohol sulpho-carbonates of the bases so produced are then heated, and converted with loss of one atom of sulphuretted hydrogen into sulphuretted ureas; and these finally are deprived of the alcohol base by means of phosphoric anhydride; for example, the reactions attending the formation of ethyl mustard oil may be thus represented:—

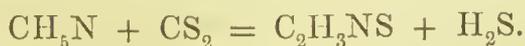


Individual compounds may be obtained by simpler methods, for which the reader is referred to the original paper. All these compounds are distinguished by a peculiar irritating pungency analogous to that of true mustard oil, but each has an odour which is also characteristic of the compound. The odour of the benzyl compound is like that of watereresses, the tolyl oil greatly resembles anise oil in odour, and the methyl compound smells powerfully of horse-radish.

The most characteristic feature of the mustard oils is the facility with which they act upon ammonia and its derivatives. If dissolved in alcoholic ammonia and digested with it for a few hours under pressure at 212° , the sulphuretted urea of the series is obtained; and analogous bodies are obtained by substituting methylia, ethylia, or aniline for ammonia. These ureas are crystalline bodies possessed of feeble basic power, and their chlorides furnish with platinic chloride yellow crystalline precipitates.

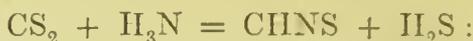
The mustard oils are isomeric with the true sulphoeyanic ethers, though they entirely differ from them in properties: there is a similar double series of hydrocyanic ethers (1149a). These ethers have no power of uniting with the ammonias; and though their odour is sufficiently repulsive, it exerts no marked irritating effect upon the nose and eyes.

Hofmann states that, conceived in its simplest form, the generation of methyl mustard oil consists in the action of ammonia on methyl alcohol, methylia being formed with separation of water; $\text{CH}_4\text{O} + \text{H}_3\text{N} = \text{CH}_5\text{N} + \text{H}_2\text{O}$. In the second phase of the process, methylia is acted upon by carbon disulphide, methyl mustard oil being formed, while sulphuretted hydrogen is liberated:—



Methyl sulphocyanide must be regarded as formed from the same compounds in inverse order. Ammonia, by action on carbon

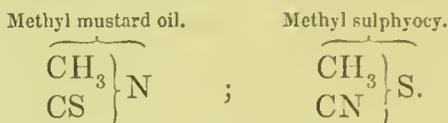
disulphide, yields hydrosulphoeyanic acid, with separation of sulphuretted hydrogen:—



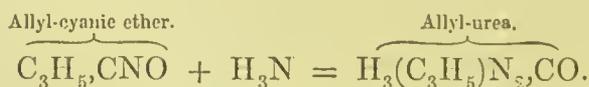
and hydrosulphoeyanic acid acting on methyl alcohol furnishes methyl sulphoeyanide and water:—



If this view be true the two bodies may be represented by the annexed formulæ which are typical of the two classes:—



(1478) Hofmann and Cahours have also obtained a variety of compound allylic ethers. These bodies have an ethereal odour which recalls that of mustard. The most interesting of them are the oxalate and the cyanate. *Allyl-cyanic ether* or *cyanate of allyl* [$\text{C}_3\text{H}_5\text{CNO}$; *Sp. gr. of vap.* 3.045; *Boil. pt.* 179°·6 (82° C.)], is prepared by acting upon argentic cyanate with allyl iodide; the heat generated by the reaction is sufficient to cause the distillation of the ether, whilst argentic iodide remains in the retort. A colourless liquid is thus obtained, the vapour of which possesses an intensely penetrating odour, and produces a copious flow of tears. When this ether is gently warmed with a solution of ammonia it is dissolved, and the solution on evaporation deposits magnificent crystals of allyl-urea:—

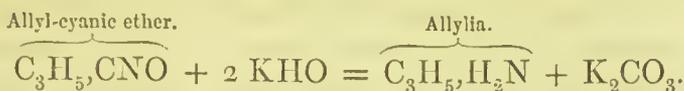


Corresponding crystalline compounds may be obtained if methyllia, ethyllia, amyliia, or aniline be substituted for ammonia. When allyl-cyanic ether is treated with water, carbonic anhydride is eliminated, and the ether is slowly converted into *sinapoline* ($\text{C}_7\text{H}_{12}\text{N}_2\text{O}$), which by its production in this manner, is shown (1164) to be *diallyl-urea*:—



(1479) *Allylia* ($\text{C}_3\text{H}_7\text{N}$).—A concentrated solution of potash decomposes allyl-cyanic ether; sinapoline is formed, and if the liquid be distilled, *allylia*, a basic substance which boils between 356° and 374° (180° and 190° C.), passes over, mixed with

methylia and tritylia. Allylia is the volatile alkali of the allyl series; it corresponds to ethylia in the ethyl series:—



The following table gives a synoptic view of the principal compounds in the allylic series:—

| | | | |
|--------------------------------|--|--|---|
| Diallyl | $\text{C}_3\text{H}_5, \text{C}_3\text{H}_5$ | Allyl-acetic ether . . . | $\text{C}_3\text{H}_5, \text{C}_2\text{H}_3\text{O}_2$ |
| Allyl alcohol | $\text{C}_3\text{H}_5, \text{HO}$ | Allyl-benzoic ether . . . | $\text{C}_3\text{H}_5, \text{C}_7\text{H}_5\text{O}_2$ |
| Allyl ether | $\text{C}_3\text{H}_5, \text{C}_3\text{H}_5\text{O}$ | Allyl-cyanic ether . . . | $\text{C}_3\text{H}_5, \text{CNO}$ |
| Allyl-ethyl ether | $\text{C}_3\text{H}_5, \text{C}_2\text{H}_5\text{O}$ | Allylia | $\text{C}_3\text{H}_5, \text{H}_2\text{N}$ |
| Allyl sulphide | $\text{C}_3\text{H}_5, \text{C}_3\text{H}_5\text{S}$ | Cyanallylia (sinnamine) | $\text{C}_3\text{H}_5, \text{CN}, \text{H}, \text{N}$ |
| „ chloride | $\text{C}_3\text{H}_5\text{Cl}$ | Allyl-urea | $\text{H}_3(\text{C}_3\text{H}_5)_2\text{N}_2, \text{CO}$ |
| „ bromide | $\text{C}_3\text{H}_5\text{Br}$ | Diallyl-urea (sinapo- line) | $\text{H}_2(\text{C}_3\text{H}_5)_2\text{N}_2, \text{CO}$ |
| „ iodide | $\text{C}_3\text{H}_5\text{I}$ | Sulphallyl-urea (thio- sinnamine) | $\text{H}_3(\text{C}_3\text{H}_5)_2\text{N}_2\text{CS}$ |
| „ sulphocyanide | $\text{C}_3\text{H}_5, \text{CNS}$ | Acrolein (acrylic al- dehyd) | $\text{C}_3\text{H}_3\text{O}, \text{H}$ |
| Allyl-sulphuric acid | $\text{HC}_3\text{H}_5, \text{SO}_4$ | Acrylic acid | $\text{HC}_3\text{H}_3\text{O}_2.$ |
| Allyl-oxalic ether | $(\text{C}_3\text{H}_5)_2\text{C}_2\text{O}_4$ | | |
| Allyl-oxamic ether | $\text{C}_3\text{H}_5, \text{H}_2\text{N}, \text{C}_2\text{O}_3$ | | |
| Allyl-carbonic ether | $(\text{C}_3\text{H}_5)_2\text{CO}_3$ | | |

§ II. RESINS.

(1480) These substances are produced by certain families of plants in considerable abundance, and they are also very numerous. They have a considerable commercial value, and are extensively employed in the preparation of the different kinds of varnish. They are generally obtained by making incisions into the wood of trees which produce them, when they exude in the form of a viscid liquid, consisting of the resin in solution in the essential oil of the plant. In the majority of cases the resins are formed by the oxidation of the essential oils contained in the trees that yield them; hence it is not surprising that in many instances they have the composition of oxides of the hydrocarbon $\text{C}_{20}\text{H}_{32}$, or of a hydrocarbon derived from this, which has lost a certain number of atoms of hydrogen in exchange for half that number of atoms of oxygen.

As a class, the resins are insoluble in water, but they are soluble in alcohol, especially when heated with it; many of them may be obtained from this solution in crystals by evaporation. A considerable number of them possess acid characters, in which case their alcoholic solutions redden litmus. The acid resins combine with the alkalis, and remain soluble in alkaline leys; these solutions, when agitated, produce a lather like that furnished by soap, but they are not precipitated like ordinary soap on the addition of sodic chloride. Like the essential oils, the natural

resins are usually mixtures of two or more resins, which often admit of separation by their unequal solubility in different menstrua. Mr. Hunt has contrived a method of distilling common resin in a current of superheated steam, by which means he has been enabled to separate and purify these different resinous acids on a very large scale for the manufacture of soap.

The resins are transparent or translucent brittle solids; they are insulators of electricity, and become negatively electric by friction; they fuse at a moderate temperature, are very inflammable, and burn with a white smoky flame. If heated in closed vessels they undergo decomposition, and yield various forms of hydrocarbon.

Common rosin is thus found to furnish the following products among others which have been less perfectly investigated:—

| Hydrocarbon. | Formula. | Boiling Point. | | Specific Gravity. | |
|-------------------------|-----------------|----------------|------|-------------------|---------|
| | | ° F. | ° C. | Liquid. | Vapour. |
| Terebene | $C_{10}H_{16}$ | 320 | 160 | 0·86 | 4·81 |
| Colophene | $C_{20}H_{32}$ | 599 | 315 | 0·94 | |
| Resinein | $C_{20}H_{28}O$ | 482 | 250 | | |
| Retinaphtha or Toluol . | C_7H_8 | 226·4 | 108 | 0·86 | 3·23 |
| Retinyl or Cumol . . . | C_9H_{12} | 302 | 150 | 0·87 | 4·24 |
| Retinol | $C_{16}H_{16}$ | 460·4 | 238 | 0·90 | 7·11 |
| Naphthalin | $C_{10}H_8$ | 428 | 220 | | 4·528 |
| Metanaphthalin | $C_{20}H_{16}?$ | 617 | 325 | | |

(1481) *Common Rosin, or Colophony.*—When ordinary turpentine is distilled with water, it leaves a residue of rosin amounting to from 75 to 90 per cent. of the turpentine employed. There are two principal kinds of rosin in the market, a brown and a white resin. The brown variety is furnished by the *Pinus abies*; it is an amber-coloured brittle solid, which consists of two distinct but isomeric resinous acids, the *sylvic* and the *pinic* ($HC_{20}H_{29}O_2$; Laurent). Cold alcohol (sp. gr. 0·87) dissolves pinic acid, which forms the larger proportion of the resin, and leaves it on evaporation as an amorphous mass. It may be purified from adhering traces of a neutral resin by precipitating its solution in cold alcohol by the addition of an alcoholic solution of cupric acetate: the cupric pinate thus precipitated may then be decomposed by any acid. When pinic acid is heated to partial decomposition, the residue in the retort is found to consist of another isomeric resinous acid, the *colopholic*; it neutralizes bases more perfectly than pinic acid, and is much less soluble in alcohol (Unverdorben).

The other constituent of brown rosin, *sylvic* acid, may be ob-

tained from its solution in hot alcohol, in colourless rhombic prisms or plates, fusible at $260^{\circ}\cdot6$ (127° C.). Its ethereal solution expels carbonic acid from the alkaline carbonates. It furnishes with plumbic oxide a salt which crystallizes in slender four-sided needles.

White resin or *galipot* is obtained from Bordeaux turpentine, furnished by the *Pinus maritima*, and consists almost entirely of an acid resin, the *pimaric*, isomeric with the preceding compound. This acid may be extracted by removing from the powdered resin the substances which are soluble in a mixture of six parts of cold alcohol and one of ether: the residue, if treated with boiling alcohol, deposits pimaric acid as it cools. When the alcoholic solution of pimaric acid is evaporated, the acid is deposited in masses indistinctly crystallized. If this acid be melted and allowed to cool, it yields a colourless glass as clear as crystal: this melted resin when powdered is dissolved by an equal weight of alcohol, but the solution thus obtained, if left for a few minutes, suddenly begins to deposit elliptical crystals, which require for solution ten times their weight of alcohol, and possess all the properties of pimaric acid before fusion. Pimaric acid is freely soluble in ether. If it be distilled in vessels from which air is excluded, the distillate is found to consist principally of another isomeric resin, termed *pyromaric acid*, distinguished by forming with lead a salt which crystallizes in delicate needles. Pyromaric acid, according to Gerhardt, is identical with sylvic acid.

Ordinary rosin is dissolved completely by alkaline leys: it enters largely into the formation of yellow soap.

If nitric acid be boiled upon ordinary rosin, the compound is oxidized and dissolved, and on evaporating the solution to the consistence of a syrup, it deposits, when left to itself for some weeks, small four-sided prisms with an oblique terminal face. This substance is named *terebic acid* ($\text{HC}_7\text{H}_9\text{O}_4$). It is sparingly soluble in cold water, but much more soluble in boiling water, as well as in alcohol and in ether; it requires a high temperature for its fusion, and is decomposed at about 401° (205° C.).

(1482) *Varnishes*.—The resins most extensively employed in the preparation of the different kinds of varnish are those of copal (from the *Hymenæa verrucosa*?), mastic (from the *Pistachia lentiscus*), sandarach (from the *Juniperus communis*), lac, and occasionally those of elemi and anime. Copal is a hard, nearly colourless, transparent resin, which is dissolved with difficulty in the state in which it is imported; but if powdered and exposed to the

air for some weeks, or if fused so as to enable it to absorb oxygen, it is more readily attacked by solvents.

The solvents employed in preparing varnishes are oil of turpentine, wood naphtha, and spirit of wine; the resin before being added to the solvent must be pulverized, and afterwards mixed with sand or broken glass in order to prevent the powder from agglutinating into lumps. When the varnish is spread over the surface of any object which it is intended to protect, the solvent evaporates and leaves a thin transparent coating of resin. The spirituous varnishes dry the most rapidly, but they are apt to crack and seal off. This defect is partially remedied in the turpentine varnishes, which dry more slowly; and it is still more effectually obviated in what are termed oil varnishes, in which a small quantity of some drying oil, such as that of linseed or of poppy, is added to the solution in rectified turpentine: these varnishes require a considerable time for complete hardening, but they are very durable. The common varnish used for oil paintings and maps consists of 24 parts of mastie, 3 of Venice turpentine, and 1 of camphor; these are mixed with 10 parts of pounded glass, and dissolved in 72 of rectified oil of turpentine.

(1483) GUAIAECUM resin is the exudation of the *Guaiacum officinale*. It is of a dark greenish-brown colour, and is readily pulverized. It has a taste which is at first slight, but afterwards becomes acrid and hot; its odour is feeble, but resembles that of benzoin. Alcohol dissolves the greater part of this resin; ether does not dissolve it so completely, and it is insoluble in the fixed oils. It is also freely soluble in a solution of potash and in oil of vitriol. The alcoholic tincture yields a blue precipitate when acted on by chlorine: with sulphuric acid it gives a green precipitate. White paper when stained with tincture of guaiacum acquires a pale yellow tint; and if this be exposed to the more refrangible rays of the solar spectrum, it becomes of a fine blue or greenish-blue colour. The pale yellow tint is restored when the altered paper is exposed in the less refrangible portion of the spectrum, or when a gentle heat is applied to it. This restoration of the colour depends upon the absorption of oxygen: powdered guaiacum when exposed to the air absorbs oxygen and becomes green. Fuming nitric acid dissolves the resin and acquires a green colour; if a certain quantity of water be added, a green precipitate is formed, and the solution becomes blue, but the addition of a larger quantity of water renders the precipitate blue and the solution brown.

Resin of guaiacum appears to consist of two distinct resinous acids, one of which, *guaiacic acid* ($\text{HC}_6\text{H}_7\text{O}_3$; Deville), may be obtained from its alcoholic solution, crystallized in beautiful needles, which are freely soluble in water.

Guaiacum resin melts at a moderate heat, and begins to undergo decomposition at about 599° (315° C.). Amongst the products of its destructive distillation Deville enumerates three definite compounds:—1. A light volatile oil, *guaiacene* ($\text{C}_5\text{H}_8\text{O}$), of sp. gr. 0.874: it boils at $244^\circ.4$ (118° C.), giving off a vapour of sp. gr. 2.92, and it absorbs oxygen from the air, forming a beautiful crystalline compound. 2. A volatile compound, *pyro-guaiacin* ($\text{C}_{19}\text{H}_{22}\text{O}_3$), which crystallizes in pearly scales. And, 3. An oil heavier than water, *guaiacyl hydride* or *guaiacol* ($\text{C}_7\text{H}_8\text{O}_2$); sp. gr. of liq. 1.119; of vap. 4.49; boil. pt. 410° (210° C.); this liquid is probably a homologue of kreasote, containing CH_2 less than this body. It is soluble in alcohol, ether, and acetic acid, but not in water. By oxidation with nitric acid it yields oxalic acid and a brown resin.

(1484) LAC.—One of the most valuable of the resins is lac, which occurs in commerce under three distinct forms; viz., as *stick-lac*, *seed-lac*, and *shell-lac*. This resin exudes from the branches of several trees in tropical climates, and in particular from the *Ficus Indica*, *Ficus religiosa*, and *Rhamnus jujuba*, in consequence of the punctures of the female of a small insect of the cochineal tribe, the *Coccus ficus*; the resinous juice which exudes hardens over the insects. The young shoots when cut off, covered with the resin, and enclosing the cocci, constitute *stick-lac*. The crude stick-lac is then bruised, and the fragments of the branches are removed; after which the resinous mass is digested in a weak solution of sodic carbonate, by which means a red colouring matter contained in the insects is extracted. This red material is now extensively used as a dye, and has largely displaced the more expensive cochineal. The residue, which is insoluble in the alkaline ley, forms the commercial *seed-lac*. When this is melted, strained through a long cotton bag, and the viscous resin while soft compressed into flat sheets, between leaves or stones, it forms the sealy purified mass which is sold under the name of *shell-lac*. This resin appears to consist of a mixture of four or five distinct compounds, one of which is acid and may be obtained in crystals, and according to Unverdorben, it also contains both oleic and margaric (palmitic) acids. Lac is soluble in an aqueous solution of borax, by which it may be distinguished from most common resins with which it is sometimes adulterated.

Lac is extensively used as a stiffening for hats, and it forms the principal constituent of the better kinds of sealing-wax. Red sealing-wax owes its brilliant colour to vermilion; 48 parts of shell-lac, 12 of Venetian turpentine, 1 part of balsam of Peru, melted at a gentle heat, and incorporated with 36 parts of vermilion, furnish red sealing-wax of the best quality (Löwig). When lac is mixed with half its weight of sandarach and a small quantity of Venice turpentine, it forms, with 10 or 12 parts of alcohol, a varnish, technically termed *lacquer*, which is much employed for heightening the colour of brass and bronzed articles.

(1485) BALSAMS.—The soft viscous resins which consist of a large mixture of essential oil with the resin, are termed balsams; such, for example, as balsam of copaiba, and balsam of Canada. Some of them contain in addition benzoic or cinnamic acid, as in the case of the balsams of benzoin, tolu, storax, and Peru.

Balsam of Copaiba is obtained from several species of *Copai-fera*. It consists of a volatile essential oil isomeric with oil of turpentine; a resinous acid, *copivic acid* $C_{20}H_{30}O_2$, isomeric with pinic acid; and a viscous neutral resin. *Balsam of Canada* is the nearly colourless liquid resin of the *Pinus balsamea*.

(1486) GUM RESINS are the milky juices of many plants, solidified by exposure to air. They consist chiefly of the peculiar resins and essential oils of the plants, mixed with a large proportion of gum; consequently they produce, when rubbed up with water, a milky-looking liquid, or emulsion, the gum becoming dissolved, and retaining the resin and oil in suspension. Dilute alcohol dissolves the gum resins in great measure, as do also weak alkaline solutions. The gum resins form a numerous and important class of medicinal remedies. Ammoniacum, assafœtida, aloes, euphorbium, galbannum, gamboge, myrrh, olibanum, and scammony, all belong to this class of bodies.

(1487) AMBER.—Some fossil substances approach more closely to the resins than to any other class of compounds; of these, one of the most important is *amber*. It is a light-yellow, transparent substance, with a density generally a little greater than that of water. Its property of becoming electric by friction is familiarly known. It occurs often in beds of wood coal, but is chiefly found after storms, on the coasts of the Baltic, between Königsberg and Memel. Amber consists of a mixture of several resinous bodies, which have not been accurately examined; about one-eighth of its weight is soluble in alcohol, and about one-tenth of it is soluble in ether. If heated in closed vessels it melts, gives off succinic acid, water, and a peculiar empyreumatic oil, which consists of a

mixture of several hydrocarbons having nearly the same composition as oil of turpentine. The succinic acid appears to be furnished solely by that portion of the resin which is soluble in ether (Schrötter). A small quantity of succinic acid exists ready formed in the resin, and can be extracted by digesting powdered amber in an alkaline solution. The empyreumatic oil is furnished principally by the bituminous portion, which is insoluble in ether and in alcohol. Amber, when treated with nitric acid, is gradually dissolved; succinic acid crystallizes from the solution when concentrated, and ordinary camphor is found in the distillate.

(1488) CAOUTCHOUC, or *Indian rubber* ($x\text{C}_5\text{H}_8$); *Sp. gr.* from 0.92 to 0.96.—This substance occurs in small quantities in the juices of many plants, particularly of the *Urticaceæ*, *Euphorbiaceæ*, and *Apocynaceæ*. Its available supply, however, is the spontaneously solidified milky juice of the *Hevæa elastica*, *Jatropha elastica*, and some other tropical plants. As first procured by incisions into the stem of the plant, it appears as a yellowish milky fluid, which, in addition to caoutchouc, contains albumin; the albumin occasions the juice on being boiled to coagulate. When the fresh juice is exposed to the air in thin films, it speedily dries, and hardens into elastic layers of brownish-yellow caoutchouc. The caoutchouc is not dissolved in the juice, but is merely suspended in it, and when the liquid is diluted with water it rises to the surface like cream; when once become coherent it cannot again be diffused through water. Commercial caoutchouc, from the mode of its preparation, retains the albumin and other constituents of the juice, but pure caoutchouc is a peculiar form of hydrocarbon (Faraday). In its solid condition it is extremely elastic, especially when warm. Although insoluble in water, it softens considerably in this liquid at the boiling temperature, and is thereby rendered more easily acted upon by its peculiar solvents. Caoutchouc may be preserved unaltered for an indefinite time if excluded from the light, but if exposed in the air for a few months to diffused daylight it gradually absorbs oxygen and becomes converted into a viscid mass which has lost its elasticity, and is soluble in alcohol (W. A. Miller on Electric Cables, *Journ. Chem. Soc.*, 1865, 273). Alkaline solutions are without effect upon caoutchouc. Even chlorine attacks it very slowly; concentrated nitric and sulphuric acids decompose it, but when dilute they are entirely inert.

The proper solvents of caoutchouc are washed ether, chloroform, carbon disulphide, coal naphtha, and rectified oil of turpen-

tine. In these liquids it first swells up very considerably, and eventually forms a ropy liquid, which on evaporation furnishes the caoutchouc with its original elasticity. This property is turned to account in the manufacture of various waterproof or 'Macintosh' articles. According to Payen, caoutchouc consists of two portions, one of which is soluble in the liquids above mentioned, whilst the other portion merely softens and swells up, but does not undergo true solution. Caoutchouc is also dissolved by the fixed oils, but its elasticity is thereby destroyed. Waterproof cloth is prepared by varnishing one surface of a fabric constructed for the purpose, with a solution of caoutchouc, then bringing it into contact with a second sheet similarly prepared, and passing the two together between rollers. The freshly-cut edges or surfaces of a piece of caoutchouc cohere readily; this property, with its pliancy and elasticity, together with its power of resisting most chemical agents, renders it invaluable in the laboratory for forming the flexible tubes and joints, used in connecting apparatus in a secure and air-tight manner. Caoutchouc melts at a heat of about 257° or $260^{\circ}\cdot6$ (125° or 127° C.); after it has been melted it does not solidify on cooling, but forms a sticky mass which does not become solid even when exposed to the air for months. Owing to this property it furnishes a valuable material for the lubrication of stop-cocks, and joints intended to remain moveable yet air-tight. If caoutchouc be heated strongly in the open air it takes fire, and burns with a bright luminous flame.

If distilled in closed vessels, caoutchouc furnishes a mixture of several different hydrocarbons of the general formula $n(C_5H_8)$.

To the most volatile of these G. Williams has given the name of *Isoprene* (C_5H_8); *Sp. gr. of liq.* $0\cdot6823$; *of vap.* $2\cdot43$; *Boil. pt.* $98\cdot6^{\circ}$ (37° C.). It remains liquid at very low temperatures. This hydrocarbon absorbs oxygen slowly when exposed to the air, becoming viscid, and acquiring the power of bleaching a solution of sulphate of indigo. If in this state it be submitted to careful distillation, unchanged isoprene passes over, and at a particular stage, the contents of the retort suddenly thicken, and become converted into a pure white spongy elastic mass, consisting of $C_{10}H_{16}O$.

To another of these hydrocarbons which has exactly double the vapour density of isoprene, Himly has given the name of *caoutchine* ($C_{10}H_{16}$); *Sp. gr. of liq.* $0\cdot842$; *of vap.* $4\cdot65$; *Boil. pt.* $339^{\circ}\cdot8$ (171° C.); it is isomeric with oil of turpentine, which it resembles in being miscible in all proportions with alcohol, ether, and the fixed and volatile oils. It may be exposed to a cold of -22° (-30° C.) without becoming solid; it dissolves caoutchouc freely. Greville Williams, by acting on this compound with bromine, has obtained the body

$C_{10}H_{14}Br_2$; and on treating this with an amalgam of sodium, has converted it into cumol, $C_{10}H_{14}$.

Boucharlat found, among the less volatile portions of the oil, a yellow hydrocarbon, *heveène*, which he considered to be polymeric with olefiant gas, though this is doubtful. It had a sp. gr. of 0.921, and boiled at 599° (315° C.).

(1489) A highly valuable modification of caoutchouc, discovered by Goodyear, has lately been introduced into the arts under the name of *vulcanized* Indian rubber, which from its almost perfect elasticity at all temperatures below that of 239° (115° C.), admits of a variety of useful applications. The cut edges of this form of caoutchouc do not cohere by pressure, and it does not become adhesive to other bodies at a temperature below 212° . Caoutchouc when immersed in the form of sheet into melted sulphur at 257° (125° C.), gradually imbibes from 12 to 15 per cent. of its weight of sulphur, but it does not at this temperature experience any change in its physical or chemical properties. If, however, such sulphurized rubber be heated for a few minutes to about 302° (150° C.), the peculiar elastic modification is produced, and if the temperature be allowed to rise much higher than this, the mass becomes black, hard, and horny, and is changed into a substance which has been introduced into the arts under the name of *vulcanite*, or *ebonite*, and applied to many of the purposes for which horn is fitted. At a temperature a few degrees beyond that necessary to the production of vulcanite the mass is converted into a hard brittle substance, which at a higher temperature undergoes carbonization and decomposition. Ebonite is largely prepared for the manufacture of combs, and articles such as were formerly made of papier-mâché, the proportions used being two parts of caoutchouc to one of sulphur. Exposure for some hours to a heat of from 302° to 356° (150° to 180° C.), effects the conversion. Ebonite, or vulcanite, is one of the best insulators of electricity that is known, and becomes powerfully negatively electric when excited by friction. Elastic vulcanized caoutchouc appears to consist of a combination of the elastic gum with 2 or 3 per cent. of its weight of sulphur. The excess of sulphur which is usually present is only mechanically distributed through the mass, and may be removed by the use of solvents, such as benzol or sodic sulphite. This excess of sulphur is injurious to the elasticity of the material, and gradually renders it brittle and rotten. Several modes of effecting the combination of sulphur with caoutchouc are employed. One of the most usual consists in grinding the caoutchouc between heated rollers with the proper proportion of sulphur; the mixture of caoutchouc and sulphur is left endued with the properties of common caoutchouc,

and may be easily moulded into the form of the various articles required: it is only on the application of a temperature ranging from 266° to 302° (130° to 150° C.), that the peculiar properties of the sulphurized compound are developed. The heat is most advantageously applied by exposing the articles to the direct action of high pressure steam at 270° or 280° ($132^{\circ}\cdot 2$ or $137^{\circ}\cdot 8$ C.). A still easier method adapted for thin articles consists in immersing the caoutchouc for a few moments in a solution of 1 part of sulphur chloride (S_2Cl_2) in 60 of carbon disulphide: by simple exposure of the object thus treated to the air, it assumes the character of vulcanized caoutchouc without the aid of heat. The addition of a certain proportion of plumbic carbonate to the compound is found to produce an article better adapted for some purposes, such as the manufacture of overshoes or goloshes, than one in which sulphur only is used; due proportions of sulphur and of the salt of lead are incorporated with the caoutchouc by causing the caoutchouc mixed with the other ingredients to pass repeatedly between polished hollow iron rollers maintained at a temperature of about 167° (75° C.), by the injection of steam into their interior. Vulcanized Indian rubber withstands prolonged digestion in naphtha or turpentine without undergoing solution.

(1490) GUTTA PERCHA.—This substance, which is similar in chemical properties to caoutchouc, was introduced into this country as an article of commerce about the year 1844. Gutta percha is the concrete juice of the *Isonandra percha*, a tree belonging to the family of the *Sapotaceæ*, which grows abundantly in Singapore, Borneo, and other islands of the Eastern archipelago. The name *percha* is that given by the Malays to the tree which produces it; it grows to a diameter of five or six feet, and though as timber it is valueless, the fruit yields an oil fit for food. On cutting notches through the bark into the wood, a milky juice exudes, which speedily solidifies. Gutta percha is a tough inelastic substance, which at ordinary temperatures retains any shape which may have been impressed upon it, but below 212° it becomes so soft that it may be moulded like wax, and indeed may be employed for taking casts and impressions, since it will copy the finest lines with fidelity; beautiful mouldings, and a variety of useful and ornamental articles are thus made with great facility. It also possesses the valuable property of welding together when in this soft condition, provided that the surfaces are quite free from any film of moisture. Below 113° (45° C.), it again becomes hard, and is possessed of extraordinary tenacity.

It is, when pure, of a pale brown colour, possessing a peculiar odour somewhat resembling that of caoutchouc. When rubbed it becomes negatively electric, and if dry it is an insulator of electricity; this property has led to its extensive employment in the covering of wires for telegraphic purposes (309). It is also largely used as a waterproofing material, and is employed as a substitute for leather in soling boots and shoes. It furnishes a valuable material for the preparation of tubes for conveying liquids; it is likewise used as a substitute for leather in the construction of bands for driving machinery, and is daily receiving new and useful applications.

Gutta percha is quite insoluble in water; it is not attacked by Stockholm tar, or by linsced oil; but it is dissolved readily by benzol, chloroform, carbon disulphide, oil of turpentine, and the essential oils in general. If heated moderately it melts; and beyond this point is decomposed, yielding hydrocarbons identical with those from caoutchouc (G. Williams). Solutions of the alkalis are without action upon gutta percha. Hydrochloric and dilute hydrofluoric acids, as well as the dilute acids in general, have no action upon it; hence it is employed in the preparation of bottles and vessels used for containing these liquids. The principal drawback to this use is the difficulty of preventing it from retaining a certain degree of porosity, which allows the slow transudation of liquids through its mass. Concentrated nitric acid attacks and disintegrates it rapidly, and oil of vitriol produces the same effect more gradually.

Purified commercial gutta percha consists of three distinct portions; the most abundant of these, the *pure gutta*, constitutes from 75 to 82 per cent. of the mass: it is milk-white and fusible at about 302° (150° C.); it is insoluble in alcohol, but is soluble in ether. This substance is a hydrocarbon of the form $C_{20}H_{32}$. The other two constituents are a white and a yellow resin, both of which are soluble in boiling alcohol; but the white resin ($C_{20}H_{32}O_2$) is nearly insoluble in this liquor when cold; by deposition from a hot alcoholic solution it may be obtained crystallized in pearly plates, disposed in radiated tufts. The yellow resin ($C_{20}H_{32}O$) is amorphous. Pure gutta percha, indeed, absorbs oxygen slowly when exposed to the combined influence of light and atmospheric air, and is gradually converted into a brittle resin freely soluble in hot alcohol. It then entirely loses its plastic character, and this is one of its principal defects; but it may be preserved in the dark or under water for an indefinite period without change.

(1491) RESIN OF JALAP.—This substance has been made the subject of numerous careful experiments. It may be obtained in a colourless form by treating the chopped roots of jalap with boiling water repeatedly, submitting them to pressure between each operation, and when the expressed liquid is no longer coloured, extracting the resin from the undissolved portion by means of boiling alcohol (sp. gr. 0·880). This resin amounts to from 10 to 15 per cent. of the weight of the root operated on. It is a mixture of two definite resins. One of these (*pararhodeoretin*) is soluble in ether, and is powerfully acid; it has the peculiar odour and acrid taste of jalap. It does not crystallize from its alcoholic or ethereal solutions, but if these be mixed with water, the semi-solid mass which is formed becomes gradually filled with needle-shaped crystals; it may be sublimed. According to the analysis of Johnston it may be represented as $(C_{20}H_{34}O_9)$.

The resin which is insoluble in ether (*jalapin* or *rhodeoretin*), is remarkable for being susceptible of decomposition into glucose and a resinous acid. Jalapin, according to Spirgatis, is identical with the active principle of scammony. Jalapin is white, and destitute of odour and taste. It is fusible at $300^{\circ} \cdot 2$ ($149^{\circ} C.$). Alcohol and acetic acid dissolve it readily. It is also easily soluble in alkaline solutions, especially if boiled with them. Mayer terms it *convolvulin*, and assigns to it the formula $(C_{81}H_{50}O_{16})$. This resin appears to constitute the purgative principle of the jalap. Oil of vitriol dissolves it slowly, and assumes a beautiful red colour, which gradually passes into brown. On dilution an oily-looking acid body $(HC_{16}H_{29}O_3)$ is precipitated, and glucose remains in solution. According to Mayer, the fusiform variety of jalap (*Convolvulus Orizabensis*) contains a resin homologous with rhodeoretin $(C_{34}H_{56}O_{11})$, which when treated with sulphuric acid is similarly decomposed, glucose remaining in the solution.

§ III. GLUCOSIDES, OR COMPOUNDS WHICH FURNISH GLUCOSE.

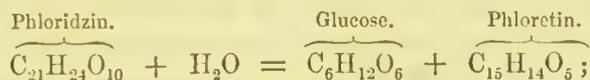
(1492) In the course of the present chapter some crystalline compounds have been described which, like amygdalin, salicin, and populin, under certain circumstances, break up into glucose, and into some compound or compounds characteristic of the substance from which it is derived. The simplest condition under which this transformation is effected consists in exposing the compound to the action of water at a high temperature under pressure: salicin and phloridzin may thus be made to furnish glucose. The compounds which yield sugar when broken up by any of these processes are termed *glucosides*. They may be subdivided into two classes: one of these consists of neutral substances, like amygdalin and salicin; the other consists of acid bodies, such as gallotannic acid. We shall now proceed to notice a few more of these compounds; viz., phloridzin, quercitrin, datiscin, arbutin, esculin, and saponin, with one or two others.

(1493) PHLORIDZIN $(C_{21}H_{24}O_{10}, 2H_2O; \text{Strecker})$.—This is a substance which occurs in the bark of the apple, pear, cherry, and plum, and probably in that of other fruit trees, and especially as its name implies, in the root-bark of those trees (from $\phi\lambda\omicron\iota\delta\varsigma$, bark, $\rho\iota\zeta\alpha$, root). In order to extract it, it is sufficient to boil

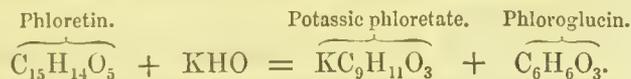
the bark for some time with water, and to allow the liquid to cool. Phloridzin is deposited in silky crystals, which may be purified by redissolving them in water, digesting with animal charcoal, and recrystallizing. It has a slightly bitter flavour, followed by a sweetish taste. It requires upwards of 1000 parts of cold water for solution, but it is largely soluble in boiling water. Alcohol and wood spirit dissolve it freely, but it is nearly insoluble in ether. Its alcoholic solution causes left-handed rotation in a ray of polarized light. When heated to 212° it loses $2\text{H}_2\text{O}$, and at a temperature between $222^{\circ}\cdot 8$ and $228^{\circ}\cdot 2$ (106° and 109° C.) undergoes fusion, after which, by an additional elevation of temperature, without experiencing any further loss of water, it becomes solid, and does not melt again until the temperature has been raised to 320° (160° C.) At 392° (200° C.) it again begins to give off water, and assumes a red colour, forming a resinoid body ($\text{C}_{21}\text{H}_{20}\text{O}_8$), termed *rufin*; this substance is soluble in alcohol; boiling water also dissolves it, but the solution is entirely colourless.

An aqueous solution of phloridzin yields a white precipitate with one of basic plumbic acetate ($3\text{PbO}, \text{C}_{21}\text{H}_{24}\text{O}_{10}$?). It also forms compounds with baryta and lime, but these substances become brown by exposure to air.

Phloridzin, when boiled with weak acids, is decomposed into grape sugar, and a resinous matter termed *phloretin* :—



and phloretin, when boiled with potash ley, yields potassic *phlorctate*, and a very sweet crystallizable compound termed *phloroglucin* by Hlasiwetz :—



Phlorctic Acid ($\text{HC}_9\text{H}_{11}\text{O}_3$) is a crystallizable solid.

Phloroglucin ($\text{C}_6\text{H}_6\text{O}_3, 2\text{H}_2\text{O}$) is sweeter than common sugar. It crystallizes in efflorescent prisms, which contain $2\text{H}_2\text{O}$. It is very soluble in ether, and crystallizes in anhydrous crystals, which are fusible at 428° (220° C.), and are susceptible of partial sublimation. It reduces an alkaline solution of cupric tartrate, but does not undergo fermentation.

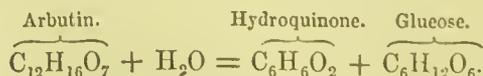
Phloridzin, under the combined influence of air and ammonia, yields a red, bitter, uncrystallizable compound termed *phlorizein*, ($\text{C}_{21}\text{H}_{30}\text{N}_2\text{O}_{13}$), which is readily soluble in boiling water. When phloridzin is exposed to the vapour of ammonia, it produces a beautiful blue compound with a coppery lustre, which appears to be a compound of phlorizein with ammonia; this substance is very soluble in water, and cannot be obtained in crystals; sulphuretted hydrogen and other deoxidizing agents destroy this blue colour, but it is restored by exposure to the air.

Phloridzin does not yield any essential oil when treated with chromic acid or

other oxidizing agents; in this respect it presents an important difference from salicin, which in other points it greatly resembles.

(1494) QUERCITRIN ($C_{33}H_{20}O_{17}, H_2O$; at 212° , Hlasiwetz).—This substance is the yellow, crystallizable colouring matter contained in the bark of the quercitron, or *Quercus tinctoria*, and it appears to occur in some other plants. It may be extracted from the bark by means of alcohol, of sp. gr. 0.84; the tannic acid is removed by the addition of gelatin, and the liquid on evaporation yields quercitrin, which may be purified by recrystallization from alcohol. It is sparingly soluble in boiling water and in ether, but is readily dissolved by hot acetic acid, as well as by weak solutions of the alkalis, with which it forms a liquid of a greenish-yellow colour, which gradually passes into dark brown. A solution of alum slowly develops a beautiful yellow colour in its solutions. Solutions of plumbic or of cupric acetate, and of stannous chloride, precipitate it in yellow flocculi. With ferric sulphate it produces an olive-green colour. When quercitrin is boiled with dilute sulphuric or hydrochloric acid, it is decomposed into glucose (Rigaud) and *quercetin* ($C_{27}H_{18}O_{12}$; Hlasiwetz), a substance sparingly soluble in water, but readily soluble in alcohol: it may be obtained in minute lemon-yellow crystals. Quercetin is also soluble in solutions of potash and of soda, to which it communicates a golden-yellow colour: by boiling, these solutions yield phloroglucin (1493) and a *quercetate* of the form ($K_2C_{27}H_{15}O_{13}$). The decomposition of quercitrin by acids, however, according to Hlasiwetz and Pfaundler, yields not glucose, but a sweet unfermentable body ($C_6H_{12}O_5, H_2O$) *isodulcite*, metameric with dulcite, yet not identical with it: so that it is not improbable that two analogous compounds exist, which have hitherto both been called quercitrin.

(1495) ARBUTIN ($C_{12}H_{16}O_7 = 272$; Strecker) is a crystallizable principle contained in the leaves of the *Arctostaphylos uva ursi*, which when treated with synaptase is decomposed into glucose, and a crystalline body originally termed *arctuin*, but which Strecker finds to be identical with hydroquinone. Arbutin according to this chemist is not a homologue of salicin, though it differs from it in containing CH_2 less. The following equation represents the decomposition of arbutin under the influence of synaptase:—

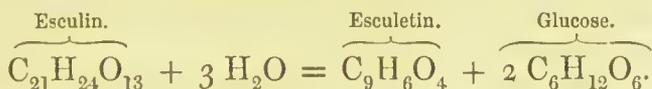


(1496) DATISCIN ($C_{21}H_{22}O_{12}$; Stenhouse) is the name given to a crystalline colourless substance extracted from the *Datisca cannabina*, the leaves of which furnish a yellow colouring matter extensively used in India for dyeing silk. It is largely soluble in alcohol and in boiling water, sparingly so in cold water and in ether. It gives yellow lakes with oxides of lead and tin, and forms intensely yellow solutions with the alkalis. Dilute acids, when boiled with datiscin, cause it to split into glucose and *datiscetin* ($C_{15}H_{10}O_6$), a substance which crys-

tallizes in colourless needles, soluble in ether and in alcohol, but nearly insoluble in water.

(1497) **ESCULIN**, or *Polychrome* ($C_{21}H_{24}O_{13}$; at 212° ; Rochleder and Schwarz).—This substance is contained in the bark of the horse-chestnut (*Esculus hippocastanum*). It contains H_2O more than daticin, but does not present any of the properties of a hydrate of this body. It has 3 atoms more of oxygen than phloridzin. In order to obtain esculin, the aqueous infusion of the bark is treated with plumbic acetate, and filtered, the excess of lead is removed by means of sulphuretted hydrogen, and the liquid is evaporated to the consistence of a syrup; in the course of a few days the esculin crystallizes: it may be washed with cold water, and recrystallized, first from weak alcohol (of sp. gr. 0.940), and afterwards from boiling water. Esculin forms small colourless needles, which have a bitter taste and a slightly acid reaction. It is coloured red by chlorine. It is sparingly soluble in cold water and in ether, but is dissolved abundantly by boiling water, and less freely by hot alcohol. Solutions of esculin are particularly remarkable for their fluorescent power, in consequence of which they appear in certain positions to be of a deep blue, although colourless if viewed by transmitted light. Acids destroy this property, but the addition of an alkali to the liquid heightens the fluorescent character. Esculin fuses and loses water when heated to 320° (160° C.); at a higher temperature it is decomposed, emitting an odour of burnt sugar, whilst a small quantity of esculetin is sublimed in crystals.

Esculin when boiled with dilute acids, or when digested with synaptase, undergoes decomposition into esculetin and glucose:—



Esculetin is a substance which has a slightly acid reaction upon litmus; it is sparingly soluble in cold water, in cold alcohol, and in ether; but it is freely soluble in boiling alcohol, which deposits it in crystalline needles or plates resembling those of benzoic acid. Esculetin is soluble in solutions of the alkalies, forming a golden-yellow liquid; and a hot concentrated solution of it in ammonia, as it cools, deposits a yellow crystalline compound. The presence of a trace of a ferric salt gives to esculetin a dark-green tinge, but the colour is destroyed on the addition of an acid. A solution of plumbic acetate, when mixed with one of esculetin, produces a lemon-yellow precipitate ($C_9H_4PbO_4$).

Fraxin [$2(C_{32}H_{38}O_{20}), H_2O$; Rochleder] is a crystalline body similar to esculin, obtained from the bark of the ash, and from that of the horse-chestnut.

Cyclamin ($C_{20}H_{24}O_{10}$; Martius), from the *Cyclamen Europaeum*, is another crystalline body, which splits into glucose and a resinous compound on boiling it with dilute acids.

(1498) **SAPONIN** ($C_{32}H_{54}O_{18}$; Rochleder).—This substance is contained in a considerable number of plants, including the *Saponaria*

officinalis, the *Polygala senega*, and the root of the common pink: it is also found in the pimpernel, in the fruit of the horse-chestnut, and in several varieties of *Lychnis*. Saponin is easily extracted, by means of boiling alcohol (of sp. gr. 0.840), from the root of the *Saponaria*, or *soap-wort*; as the liquid cools the saponin is deposited as an amorphous sediment, which if coloured must be digested in ether, in order to remove the colouring matter.

When dry, saponin forms a colourless friable mass, which is destitute of odour, and of a sweetish, styptic, persistent taste. If applied to the mucous membrane of the nose it produces violent sneezing. Saponin is soluble in water in all proportions, yielding a somewhat opalescent liquid, which froths strongly on agitation, like a solution of soap, even though it may not contain more than a thousandth of its weight of saponin: the liquid when evaporated leaves the saponin in the form of a transparent, brittle varnish. Its solution, or an infusion of soap-wort, is sometimes employed instead of a solution of an alkaline soap, for cleansing the finer varieties of wool from grease. Saponin is also soluble in dilute alcohol, but insoluble in ether. Its solutions yield a white precipitate with basic plumbic acetate.

When boiled with dilute acids saponin yields a peculiar acid, the *saponic* or *esculic*, and at the same time a substance resembling gum ($C_{12}H_{22}O_{11}$) is separated (Roehleder and Schwarz). Saponic acid may also be obtained by digesting saponin in weak alkaline solutions. The composition of saponic acid is doubtful, but it presents well-marked characters. It is nearly insoluble in water and in ether, but is readily dissolved by alcohol, which deposits it in granular crystals. Its salts with potassium, sodium, and ammonium, are soluble in hot water, and the liquid on cooling sets into a jelly. A solution of these salts in dilute alcohol, of sp. gr. 0.960, deposits them in pearly crystals. Saponic acid forms compounds with calcium, barium, copper, and lead, which are insoluble in water, but soluble in dilute alcohol.

(1499) A variety of other neutral crystallizable and often poisonous principles have been obtained from plants, many of which are used medicinally; but few of them have been minutely examined. It is probable that many of these bodies will prove to be identical with substances already known, and many others will most likely be found to belong to the class of glucosides.

The following are some of these bodies:—

1. *Antiarin* ($C_{14}H_{20}O_5 \cdot 2 H_2O$; Mulder), the poisonous principle of the *Upar antiar*, which when introduced into a wound causes vomiting, convulsions, and death. It crystallizes in pearly scales, soluble in alcohol, sparingly so in ether; 27 parts of boiling ether dissolve 1 part of antiarin.

2. *Daphnin*, from the bark of *Daphne mesereum*, forms colourless radiated needles, soluble in hot water, alcohol, and ether.

3. *Elaterin* ($C_{20}H_{28}O_5$; Zwenger) is the active principle of *Momordica elaterium*. It is a white silky crystalline powder, insoluble in water and dilute acids, but soluble in alcohol, ether, and the oils: when heated it melts and sublimes.

4. *Gentianin* ($C_{14}H_{10}O_5$; Baumert), the bitter principle of *Gentiana lutea*, crystallizes in yellow needles freely soluble in alcohol and in ether, sparingly soluble in cold water, more abundantly soluble in boiling water. It possesses the properties of a weak acid.

5. *Hesperidin* is a white, tasteless, crystallizable body, extracted from the white spongy part of the rind of oranges and lemons.

6. *Picrotoxin* ($C_5H_6O_2$; Oppermann) is an intensely bitter substance to which *Cocculus Indicus* owes its activity: the name is derived from $\piικρ\acute{o}\varsigma$, bitter, $\tau\omicron\xi\kappa\acute{o}\nu$, poison. It forms small colourless stellate needles soluble in 25 parts of boiling alcohol.

7. *Santonin* ($C_{15}H_{13}O_3$; Heldt).—This substance possesses feebly acid properties; it is obtained from the seeds of *Artemisia santonica*, and several others of the wormwood tribe. It is soluble in water and in alcohol. In order to obtain it, the seeds should be digested in alcohol with lime; a combination of lime and santonin is dissolved, from which the alcohol is expelled by distillation, and on adding acetic acid the santonin crystallizes.

8. *Colocynthin* ($C_{56}H_{84}O_{23}$?) is a crystallizable bitter substance insoluble in ether, which is contained in the *Cucumis colocynthis*, and which by boiling with acids is separated into glucose and a resin.

9. *Physostigmia* ($C_{15}H_{21}N_3O_2$; Hesse) is a strong base to which the active properties of the Calabar bean (*Physostigma venenosum*) are owing. It precipitates ferric oxide from a solution of neutral ferric chloride, and is readily soluble in alcohol, ether, chloroform, and benzol; it is tolerably soluble in water, but it has no marked taste. It occasions a remarkable contraction of the pupil, and is a powerful poison, producing prostration and paralysis.

CHAPTER VIII.

COLOURING MATTERS.

(1500) THE substances which are about to be treated of in the present chapter under the head of *colouring matters*, are grouped together on account of the similarity in the modes of applying them in the arts, and not from any well-marked chemical relations which exist between them. The relations of several of these bodies to other groups are, however, remarkable, and present many points of considerable interest.

The colouring matters are found in all the organs of plants. In the madder, turmeric, and alkanet they are obtained from the roots; in logwood, Brazil-wood, and fustic they are found in the wood; in quercitron in the bark; in safflower they are furnished by the petals, and in saffron by the stigmata of the flowers; whilst in the Persian berry and in annatto they are obtained from the seed.

Many colouring matters in the form in which they exist in the growing plant give little or no indication of their tinctorial power.

This is the case with indigo, and with the blue colouring matters of the lichens; but by the action of fermentation and of atmospheric oxygen, or by the effect of ammonia, or by the action of other chemical agents, they may be made to furnish dye-stuffs of great brilliancy and beauty.

Most of the organic colouring matters fade or change their hue under the combined influence of oxygen and solar light; they undergo a species of slow combustion, and are in many cases rendered colourless. Many of them are also deprived of colour by reducing agents, such as sulphuretted hydrogen, the sulphides of the alkali-metals, and the ferrous and stannous salts; but in these cases of deoxidation, the colouring matter, when it is again exposed to the air, recovers its original hue. The roots of the plant appear to exert a reducing effect upon many colouring matters, whilst in the flower the opposite effect takes place; this is beautifully shown in an experiment by Persoz:—If the roots of a transparent plant, such as balsam (*impatiens*), be immersed in a coloured solution, such as one of logwood, the coloured liquid is absorbed by the radicles, it is deprived of a portion of oxygen, and loses its colour; in this form it continues to circulate through the plant until it reaches the petals of the flowers, where it again absorbs oxygen and resumes its original hue.

All organic colouring matters are destroyed by chlorine, which acts in some cases by displacing hydrogen, in others by decomposing water and setting oxygen at liberty, and thus producing new compounds destitute of colour. Sulphurous acid also in many instances combines with the colouring body, and produces new compounds not possessed of tinctorial power.

Almost all the colouring matters require a preparation more or less elaborate before they are fit for use; many of the processes employed in brightening and fixing their tints are of a complex nature, and still retain their original empirical character. In several of the colouring matters of organic origin, nitrogen is an essential constituent, though in a still greater number it is absent. The colouring matters in most frequent use exhibit the properties of very feeble acids. The concentrated alkalies, especially in the presence of free oxygen, however, for the most part decompose them rapidly; but they are more soluble in dilute alkaline liquids than in pure water, and they form definite insoluble compounds with the earths, and with some metallic oxides, such as those of lead and of tin. Such compounds with the metallic oxides, usually possess great tinctorial or colouring power, and are termed *lakes*. The formation of these insoluble compounds is a circumstance of fundamental importance to the dyer and calico-printer, since

upon it depends the general method of *mordanting* (1533), used in the arts of dyeing and calico-printing.

(1501) YELLOW DYES.—The most important yellow dye-stuffs are quercitron, fustic, saffron, turmeric, annatto, and weld. The colouring matters of the Persian berries, of purree, and of rhubarb, are less frequently employed.

1. *Quercitron* is the bark of the *Quercus tinctoria*. It yields a yellow crystallizable principle, *quercitrin* (1494), of feebly acid properties, soluble in alcohol, sparingly so in water, freely so in alkalies.

2. The *Morus tinctoria*, or *Old fustic*, is particularly employed for dyeing woollens yellow; it is also used to impart to them green and olive hues when mixed with indigo and salts of iron. Fustic furnishes a yellow colouring matter, which may be obtained in crystals by evaporating its aqueous infusion. To this body the name of *morin* ($C_{12}H_8O_5$; at 212° , Hlasiwetz) has been given. Besides this, fustic contains a tannic glucoside, termed *moritannic acid* (1330; $C_{18}H_{16}O_{10}$, Wagner); or *maclurin* ($C_{13}H_{10}O_6, H_2O$; Hlasiwetz). It has a bitter taste, is soluble in ether, and gives a green precipitate with salts of iron. Acids and alkalies deepen the tint of the aqueous solution without producing any precipitate. When mixed with alum it produces no precipitate, but on the addition of potassic carbonate to this solution, a yellow lake is formed.

3. The *Rhus cotinus*, or *Young fustic*, contains a different yellow dye, which is very soluble in water; potash renders it purple, passing into a reddish yellow; while the acetates of lead and of copper produce an orange-coloured lake with a decoction of this wood. Wool mordanted with alum acquires a bright yellow dye in a bath of this colouring principle.

4. The *Crocus sativus* yields *Saffron*, a colouring matter contained in the stigmata of the flower; it is very soluble in water and in alcohol. *Crocin* ($C_{18}H_{13}O_6$; Weiss), the pure colour, is a glucoside, and is decomposed by boiling with dilute acids.

5. *Curcumin*, or the colouring matter of *Turmeric* (*Curcuma longa*), is of a resinous nature: it is nearly insoluble in water, but is dissolved freely by alcohol and by ether. Alkaline solutions take it up abundantly, and change the colour to brown. This change of colour is often employed in the laboratory to indicate the presence of free alkali, since paper tinged yellow with tincture of turmeric becomes brown when immersed in a solution containing uncombined alkali. Curcumin is soluble without change of tint in the acetic, phosphoric, hydrochloric, and sulphuric acids. It is employed for dyeing wool and silk, as well as for colouring the *curry powder* of India.

6. *Annatto*.—This colouring matter is in the form of a paste, prepared from the seeds of the *Bixa orellana*, and is used for dyeing nankeen. It appears to contain an orange-red colouring substance called *bixin*, and a less important yellow one termed *orellin*. Bixin ($C_{16}H_{32}O_2$; Kerndt) is a resinous matter, sparingly soluble in water, but freely so in alcohol and in ether. The alkalies dissolve it, producing a deep red colour, and on neutralizing the solution with an acid it falls as an orange precipitate. The fixed oils also dissolve this colouring principle, which closely resembles that of the turmeric.

7. The root of the common *Rhubarb* yields a yellow colouring matter, termed *rhein* or *chrysophanic acid* (from $\chi\rho\acute{\upsilon}\sigma\epsilon\omicron\varsigma$, golden, $\phi\alpha\acute{\iota}\nu\omega$, to appear;

$C_{10}H_8O_3$; Rochleder and Heldt), which is also found in one of the lichens (*Parmelia parietina*). It is sparingly soluble in water, but freely soluble in the alkalies, producing a reddish-brown coloured liquid, from which on the addition of acetic acid it may be precipitated in flocculi; this change from yellow to red is effected by a minute trace of alkali, so that paper stained with rhubarb may be used as a test for the presence of a free alkali. Rhein is accompanied by a portion of resin, which may be precipitated by the addition of ether to the alcoholic solution. Chrysophanic acid is soluble in ether and in hot alcohol, from which it may be obtained in crystals of a golden yellow metallic lustre.

8. The *Weld*, or *Reseda luteola*, also furnishes a yellow colouring matter, which is highly prized for its solidity and durability. *Luteolin* ($C_{20}H_{14}O_6$; Moldenhauer), as this substance is termed, may be extracted from the dried plant by means of boiling water; it is freely soluble in alcohol, less so in ether, and but very sparingly soluble in water. It may be sublimed unaltered, and condenses in yellow needles. The alkalies, both caustic and carbonated, dissolve it abundantly, and form deep yellow solutions. Cold sulphuric acid also dissolves it, and deposits it unaltered on dilution. Its solutions yield yellow lakes with alum, stannous chloride, and plumbic acetate.

9. *Persian Berries*.—The fruit of various species of *Rhamnus* when gathered before it is fully ripe, contains a considerable amount of a yellow colouring matter, termed *chryso-rhamnin* ($C_{23}H_{22}O_{11}$?). This substance may be extracted by means of ether, which deposits it in brilliant stellate groups of golden yellow crystals; an alcoholic solution of this compound yields with an alcoholic solution of plumbic acetate, a yellow lake ($2 PbO, C_{23}H_{22}O_{11}$?). Chryso-rhamnin is nearly insoluble in cold water, but if boiled with water it is partially dissolved, and is converted into a compound termed *xantho-rhamnin* ($C_{23}H_{24}O_{14}$?), which is also one of the constituents of the ripe berries (Kaue). Gellatly found that xantho-rhamnin is a glucoside, and splits, when treated with a dilute acid, into a resin and glucose.

10. *Purree*, or *Indian Yellow*.—This substance has been particularly examined by Stenhouse and by Erdmann. It is a colouring matter highly esteemed by artists, and is supposed to be of animal origin; it is sold in masses of three or four ounces in weight, which have exteriorly a dark-brown colour, but when broken are of a bright orange yellow. Its odour is peculiar, and resembles that of castoreum. This substance consists chiefly of the magnesium salt of a peculiar acid, termed *purreic* or *euxanthic acid*. Purree is scarcely soluble in water or in alcohol, but it is entirely soluble in boiling dilute hydrochloric, or in acetic acid; as it cools pale yellow needles of euxanthic acid ($HC_{21}H_{17}O_{11}$; Laurent) are deposited in stellate groups. It is somewhat soluble in boiling water, and is readily dissolved by boiling alcohol and by ether. Cold water dissolves but very little of it; alkaline solutions dissolve it and form a yellow liquid. A solution of potassic euxanthate when mixed with the solutions of the salts of the earths gives brilliant yellow sparingly soluble precipitates; with plumbic acetate it forms a yellow insoluble lake.

When euxanthic acid is heated in a small tube to a temperature a little above 212° , it melts, and a yellow sublimate of *purrenone* or *euxanthone* ($C_{20}H_{12}O_6$) is formed, whilst water and carbonic acid are evolved: it is also obtained by transmitting chlorine through a hot solution of euxanthic acid in absolute alcohol; and the same compound is produced when euxanthic acid is dissolved in oil of vitriol, the solution gradually depositing crystals of euxanthone. The sulphuric solution contains a new colligated acid, termed *sulphohamathionic acid*, the composition of which is doubtful.

The yellow dyes are not often used alone. They are generally employed in combination with other colours, to modify

shades, or to produce compound colours, as when mixed with blues to produce green.

(1502) THE RED DYES are of greater importance; of these, madder, logwood, Brazil-wood, camwood, sandal-wood, safflower, cochineal, lac-dye, and the aniline dyes, are those in most extensive use.

(1503) 1. MADDER is the root of the *Rubia tinctorium*, a plant which is grown largely in the Levant, in the south of France, and in Alsace. It is consumed in enormous quantities for dyeing reds and purples; Turkey red cloth owes its brilliant hue to the colouring matter of this root. The composition of the madder root has been the subject of many chemical investigations, the most recent though still incomplete being those of Rochleder and Schunck.

According to the microscopic observations of Decaisne, the madder root, whilst growing, does not contain any red colouring matter; but its cells are filled with a yellow substance which increases in quantity with the age of the root; and this body by exposure to the air absorbs oxygen, after which the red colour is developed; an observation which agrees with the experiments of Higgin and of Schunck.

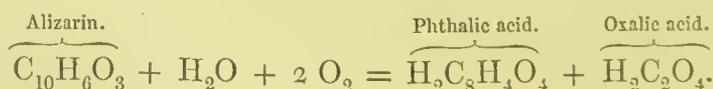
According to the last-named chemist, the madder root of commerce, in addition to ligneous fibre, contains several distinct substances; viz., a bitter principle, *rubian*,—which by its decomposition yields two colouring matters, *alizarin* and *rubiacin*,—two resins, pectic acid, and a brown substance which is probably a product of oxidation of some of the foregoing bodies. It also contains calcic oxalate and phosphate, besides other saline matters.

Some of these bodies are injurious to the brilliancy of the dye. Alizarin, according to Schunck, is the only true dyeing principle of the madder root. It has already been stated that alizarin does not exist ready formed in the growing root, but that it is produced by the decomposition of rubian; and it is well known to the dyer that the full colouring power of the root is not developed until after the dye-stuff has undergone partial fermentation.

In order to extract the whole of the colouring material, Schunck dissolves out the soluble matter from the root with water, and decomposes this solution by boiling it with dilute acid, when the whole of the colour-giving portion, including the alizarin, is precipitated. If this precipitate be boiled with water, the alizarin is dissolved, and the rubiacin and the resins are left. Another plan of obtaining alizarin consists in reducing the root to a coarse powder, treating it with hot sulphuric acid, and well washing it

till the last traces of acid are removed: the earthy matters are thus rendered soluble, and everything which water will take up is removed; but nearly the whole of the alizarin remains untouched, since it is insoluble in water containing free acid: the undissolved mass when dried is largely used in the print-works under the name of *garancin*. By boiling this *garancin* in a large quantity of water, the colouring matter is dissolved, and on adding sulphuric acid it is precipitated mixed with several impurities. If this precipitate be well washed, dried, and submitted to sublimation, beautiful orange-coloured needles of alizarin are obtained; these, if washed with cold alcohol and dried, are perfectly pure.

(1504) *Alizarin* ($C_{10}H_6O_3, 2H_2O$).—This, which has received its designation from *alizari*, the name by which madder is known in the Levant, is a red crystalline matter destitute of odour and of taste; it is neutral to test-papers, and is almost insoluble in cold water. It is but sparingly soluble in hot water; hot alcohol dissolves it more freely, and if this solution be evaporated, alizarin is deposited in plates resembling those of mosaic gold. It is also soluble in ether; acids brighten its tint, but do not dissolve it. Potash dissolves it freely, and strikes a beautiful purple; but it is precipitated unaltered on adding an acid; with lime, baryta, and ferric oxide, it forms insoluble purple lakes. With alumina it forms a beautiful red lake. Alizarin is not decomposed even by boiling sulphuric acid, which dissolves it, and on dilution deposits it unchanged. Boiling dilute nitric acid converts alizarin into phthalic (alizaric) acid, and probably into oxalic acid (Strecker and Wolff), whilst nitrous vapours are evolved:—



The crystals of alizarin deposited from its spirituous or aqueous solution lose about 18 per cent. of water at 212° . By a heat of about 419° (215° C.) alizarin is sublimed, but part of it undergoes decomposition. The sublimate forms beautiful transparent orange-coloured needles, which are anhydrous and of high lustre.*

(1505) *Rubian* ($C_{28}H_{34}O_{15}$? Sehunek); the *Ruberythric Acid* of Roehleder?—This is a bitter uncrystallizable principle, which

* Graebe and Liebermann propose a different formula for alizarin. They have succeeded in obtaining alizarin artificially, from anthracene, $C_{14}H_{10}$, by converting this hydrocarbon into a diatomic alcohol, $C_{14}H_{12}O_2$, which by subsequent oxidation furnishes alizarin $C_{14}H_8O_4$. Alizarin in turn may be reduced by heating it with zinc dust, the sole product being anthracene; $2C_{14}H_8O_4, H_2O$ yielding $2C_{14}H_{10}$ and $5O_2$.

under the influence of acids, of alkalies, and of a peculiar azotised ferment termed *erythrozym* (from ἔρυθρον, red, ζύμη, ferment), contained in the madder root, is broken up into a fermentable sugar, and into alizarin and other colouring matters. Synaptase produces a similar decomposition of rubian.

The preparation of rubian in a state of purity is not easy. Schunck takes advantage of its tendency to contract a superficial combination with charcoal, and recommends that ground madder be digested in hot water (1 lb. of madder to a gallon of water); that the undissolved portion be strained off, and that to each gallon of the hot liquid an ounce of bone charcoal be added. The mixture after brisk agitation is to be allowed to settle, and the charcoal collected on a filter and washed with cold water, until the washings no longer become green when heated with hydrochloric acid. The charcoal which has been thus treated has become saturated with rubian; it is next to be boiled with alcohol, and this treatment is to be repeated so long as fresh alcohol acquires a yellow colour when boiled with the charcoal. The alcoholic solutions on evaporation yield rubian, contaminated with a variable amount of lime, and with a green colouring matter; this colouring matter may, however, be got rid of by treating a solution of the rubian in water a second time with charcoal, and repeating the entire process. The alcoholic solution when evaporated leaves the rubian in the form of a brittle transparent mass of a dark yellow colour, resembling dried gum or varnish. It is not deliquescent, but is abundantly soluble in water, less freely so in alcohol, and insoluble in ether. When heated to about 266° (130° C.) it melts, swells up, disengages water, and gives off orange vapours of alizarin, leaving a bulky carbonaceous residue.

Rochleder's *ruberythric acid* was obtained in crystals from an infusion of madder by separating the alizarin and other colouring matters by means of neutral plumbic acetate, and then precipitating the rubian with basic plumbic acetate, decomposing this precipitate with sulphuretted hydrogen, and boiling the plumbic sulphide with alcohol (the rubian accompanies the plumbic sulphide). The rubian is dissolved by the alcohol, and is to be combined with baryta, dissolved in dilute acetic acid, reprecipitated by basic plumbic acetate, and again treated with sulphuretted hydrogen after the lead precipitate has been diffused through alcohol. On evaporation of the alcoholic solution, ruberythric acid is left in crystals ($C_{36}H_{40}O_{20}$?). Schunck considers this body to be the result of the decomposition of rubian, and not rubian itself.

Solutions of rubian are of a pale yellow colour; they are not precipitated by the metallic salts generally, but if mixed with basic plumbic acetate an insoluble compound is formed. Alkalies change the colour of a solution of rubian into blood red; but, if they be afterwards neutralized by the addition of an acid, the yellow tint is restored; if, however, the alkaline liquid be boiled, its colour changes to purple, and on the addition of an acid, red flocculi are precipitated. Oil of vitriol forms a blood-red solution with rubian. Cold nitric acid has little action upon rubian, but when heated with it, red nitrous fumes are evolved, and *alizaric* (phthalic) acid (1562) is found in the liquid.

If a solution of rubian be boiled with dilute sulphuric or hydrochloric acid, orange-coloured flocculi are precipitated, and an uncrystallizable sugar remains in the liquid. These coloured flocculi consist of alizarin, rubianin, and two resins.

For the mode of separating these bodies, the reader is referred to Schunck's paper (*Phil. Trans.*, 1851, p. 445).

Rubianin ($C_{22}H_{24}O_{10}$?) is deposited from its solution in boiling alcohol in silky lemon-yellow crystals, which are soluble in boiling water. Oil of vitriol dissolves it with a yellow colour; on the application of heat to this solution it becomes blackened, and evolves sulphurous acid. Nitric acid dissolves but does not decompose it.

Rubiacin ($C_{16}H_{11}O_6$? Schunck) is one of the components of commercial madder; it assumes the form of beautiful orange-coloured tables, or of brilliant yellow needles, resembling those of plumbic iodide. It is sparingly soluble in boiling water, but is readily dissolved by alcohol; it may with ease be sublimed unaltered. Rubiacin is a compound of considerable stability: its solution in oil of vitriol may be boiled without undergoing decomposition. Hydrated alumina acquires an orange tint when digested with an alcoholic solution of rubiacin.

When rubiacin is dissolved in a solution of ferric chloride or ferric nitrate it gives a brownish-red liquid, which on the addition of an acid deposits flocculi of *rubiacic acid* ($H_2C_{32}H_{16}O_{17}$?). This body is dissolved by the alkalies with a purple colour.

Some chemists consider that madder contains another colouring matter allied to alizarin, which they term *purpurin* [$(C_{10}H_6O_8)_2O$; Schutzenberger and Schiffert]; its solution was found by Stokes to give a spectrum quite distinct from that of alizarin; but the statements concerning the products from madder root are conflicting and unsatisfactory. See further, Stenhouse, *Proceed. Roy. Soc.*, xii. 633, and xiii. 145; Debus, *Liebig's Annal.*, lxxxvi. 117.

For additional details, the reader is referred to the papers of Schunck, *Liebig's Annal.*, lxvi. 175; *Phil. Trans.*, 1851, 1853, 1855; and of Rochleder, *Liebig's Annal.*, lxxx. 321, lxxxii. 205.

(1506) 2. LOGWOOD.—This valuable dye-stuff is extensively employed for dyeing black with alum, but acids change the colour to red. It is the produce of the *Hæmatoxylon Campechianum*. It contains a crystalline matter termed *hæmatoxylin* ($C_{16}H_{14}O_6, H_2O$, and $3 H_2O$; Gerhardt), which, however, in its pure state is not red, but straw-yellow or honey-yellow. Under the combined influence of the alkalies and oxygen it assumes an intensely red colour. In order to obtain hæmatoxylin, powdered commercial extract of logwood mixed with quartzose sand (to prevent it from agglomerating into masses) is digested for several days with five or six times its volume of ether. The liquid is distilled until it acquires the consistence of syrup; it is then mixed with water, and set aside in a vessel loosely covered. In the course of a few days the hæmatoxylin is deposited in crystals. Extract of logwood, when thus treated, yields from one-eighth to one-tenth of its weight of this substance.

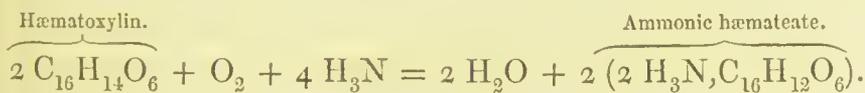
The crystals of hæmatoxylin are transparent, and consist of long, yellow, brilliant four-sided needles: these crystals contain $3 H_2O$, which they lose at 212° . If a solution of hæmatoxylin saturated at the boiling point be allowed to cool in a closed vessel, granular crystals with H_2O are deposited. Hæmatoxylin

has a sweet taste, free from astringency, like that of liquorice. It is sparingly soluble in cold water, but readily so in boiling water. Ether and alcohol dissolve it freely.

Solution of plumbic acetate gives in one of hæmatoxylin a white precipitate, which speedily becomes blue; salts of copper give a dirty green precipitate, which also quickly becomes blue; baric chloride occasions a red precipitate; stannous chloride gives a rose-coloured lake, and iron alum a scanty blackish violet precipitate; ordinary alum gives a red solution, but does not occasion any precipitate. A deep blue-black ink may be prepared by simply dissolving 120 grains of commercial extract of logwood in a pint of water, and adding 15 grains of potassic chromate, but it soon fades.

Sulphuric and hydrochloric acid exert little effect upon hæmatoxylin, but diluted nitric acid colours it red. Concentrated nitric acid converts it into oxalic acid.

Solution of potash communicates a violet tint to one of hæmatoxylin, and if the air have access to the solution, the latter becomes first blue and then brown, whilst oxygen is absorbed. A solution of hæmatoxylin is not altered by exposure to the air, but it furnishes an exceedingly delicate test of the presence of ammonia or its carbonate, in which case the liquid acquires a purple tint, whilst oxygen is absorbed, and ammoniac hæmateate is formed, and may be obtained abundantly by an addition of ammonia:—



The ammonia may be removed from this compound by means of acetic acid, when the hæmatein ($\text{C}_{16} \text{H}_{12} \text{O}_6$) is precipitated in voluminous red flocculi, resembling hydrated ferric oxide. Hæmatein is sparingly soluble in cold water, but is more readily soluble in boiling water, and the solution on evaporation yields a confused mass of green crystals with a metallic lustre. Sulphuretted hydrogen combines with hæmatein when transmitted through its solution, and deprives it of its colour; the solution by exposure to air loses the sulphuretted hydrogen, and deposits unaltered hæmatein.

Potash dissolves hæmatein with a blue colour, which becomes brown when exposed to the air. Its ammoniacal solution is of a fine purple, which also becomes brown on exposure. Ammoniac hæmateate yields coloured precipitates with many metallic salts; with plumbic acetate it gives a deep blue, with cupric sulphate a violet blue, with stannous chloride a violet, and with iron alum a black precipitate.

(1507) 3. BRAZIL-WOOD is the produce of the *Cesalpinia Braziliensis*. It yields by treatment with alcohol yellow or orange crystals of *brezilin* ($\text{C}_{22} \text{H}_{20} \text{O}_7$; Bolley and Greiff), which are likewise soluble in water and in ether. Acids, especially the citric

give it a bright yellow colour; with alkalis it yields a violet or purple colour: hence it is sometimes used as a test of the presence of alkali in a free state. It absorbs oxygen under the influence of ammonia, with which it forms a definite compound, analogous to that obtained by similar means from logwood. Brazilin forms, in combination with alumina, the basis of *red ink*. Like hæmatoxylin, it is bleached by nascent hydrogen and by sulphuretted hydrogen. Nitric acid converts it into carbazotic acid. *Sapan-wood* and *camwood* are stated to yield the same colouring principle as Brazil-wood. The colour of these red woods, though brilliant, is not very permanent.

Sandal-wood, *alkanet root*, and some other substances also afford red dyes, but in general the vegetable red colours are fugitive. The colouring matter of alkanet is soluble in oils.

(1508) 4. SAFFLOWER is obtained from the petals of the *Carthamus tinctorius*. These petals contain two colouring principles, one of which is yellow and soluble in water, but is of no value to the dyer: it is a weak acid of a bitter taste. If an infusion of safflower be mixed with an acetic solution of plumbic acetate, a soluble yellow salt of lead is formed, from which, on the addition of ammonia, a subsalt is precipitated in dark yellow flocculi.

The really valuable colouring principle of the safflower is red, and is employed in the preparation of *pink saucers* for artists, and for imparting a beautiful and brilliant rose-red to silk; but it fades quickly when exposed to the sun's light.

Carthamin ($C_{14}H_{16}O_7$; Schlicper), as this substance is termed, is insoluble in water and in acids, but is easily dissolved by the alkalis; on adding an acid to the solution it is again precipitated: it is also soluble in alcohol. Carthamin may be obtained by digesting safflower in weak acetic acid, in order to remove the yellow dye-stuff; the washed dye is next digested in a solution of sodic carbonate; a skein of cotton is then placed in the liquid, and lemon-juice, or a solution of citric acid, is added. The cotton yarn mechanically removes the flocculent precipitate of carthamin from the liquid; the yarn must be washed with cold water, the colouring matter again dissolved by sodic carbonate, and reprecipitated by the addition of citric acid. Carthamin when dry is a red pulverulent substance; it has a greyish metallic lustre when viewed in mass, but in thin layers it is of a beautiful purplish red. Its solutions in alkalis gradually absorb oxygen and become altered.

(1509) 5. CARMINE is contained in the *Coccus cacti*, being the colouring matter of the cochineal. After treating the powdered insects with ether to remove the fat, the insoluble portion is digested with water, and on adding plumbic acetate, a lead lake is precipitated of a purple colour. This must be well washed, decomposed by sulphuretted hydrogen, and the filtered solution evaporated to dryness *in vacuo* over sulphuric acid. De la Rue finds the colouring matter of the cochineal thus obtained to be an acid body, which he terms *carminic acid* ($C_{14}H_{14}O_8$). It is a purple-brown, friable mass, soluble in all proportions in alcohol and in water, but very slightly soluble in ether; it may

be dissolved unchanged in strong sulphuric and hydrochloric acids. Nitric acid even if dilute decomposes it; chlorine, iodine, and bromine also decompose it, and change its colour to yellow. The fixed alkalies change the colour of the aqueous solution to purple: the alkaline earths give purple precipitates; with alum no lake is produced till ammonia is added, when it falls as a beautiful crimson precipitate. The lakes, with plumbic acetate, and with salts of copper, zinc, and silver, are purple; with salts of tin a bright crimson solution is obtained.

When carminic acid is treated with dilute nitric acid it yields an acid of a yellow colour, which crystallizes in rhombic plates; it is very soluble in boiling water, in alcohol, and in ether. It is termed *nitro-coccusic acid* ($H_2C_8H_3(NO_2)_3O_3, H_2O$), and is isomeric with trinitranisic acid. It deflagrates strongly when heated. Its salts are soluble in water, and most of them are also dissolved by alcohol. Cochineal is extensively employed, in combination with oxide of tin, as a scarlet dye.

6. LAC DYE is very similar to cochineal in its nature, being also furnished by a species of coccus. Of late years this dye-stuff has been extensively substituted for the more costly cochineal, and it furnishes scarlets equally vivid, and even more permanent, but the pinks are not so good. In dyeing scarlets the liquid employed for dissolving the colouring matter is a solution of tin in concentrated hydrochloric acid, 20 lb. of acid being required for each pound of tin; the dye-stuff is digested in an equal weight of this liquid, and the cloth after being cleansed by boiling with fuller's earth, is introduced into a bath containing a *mordant* composed of a solution of stannous chloride, prepared by gradually dissolving 4 lb. of tin in a mixture of 27 lb. of hydrochloric acid, and $1\frac{1}{2}$ lb. of nitric acid (sp. gr. 1.19). In order to dye 100 lb. of cloth, the following process, according to Ure, is adopted:—300 gallons of water are raised to 149° (65° C.) in a tin boiler, and $1\frac{1}{2}$ lb. of solution of tin mordant and a handful of bran are added; when the liquor boils it is skimmed, and $10\frac{1}{2}$ lb. of lac dye previously dissolved in the acid, and $23\frac{1}{2}$ lb. of mordant, are introduced; immediately after which $10\frac{1}{2}$ lb. of cream of tartar, and 4 lb. of ground sumach are suspended in a bag in the bath for five minutes, and then withdrawn; the fire is now extinguished, and 20 gallons of cold water containing 10 lb. more of tin mordant are added, after which the cloth is introduced; the liquid is then boiled for an hour, and at the end of that time the cloth is withdrawn and well rinsed.

(1510) 7. EXTRACT OF ALOES.—This substance may, by the action of nitric acid, be made to yield various compounds, which admit of being fixed by means of mordants upon silken and

woollen fabrics, to which they impart dyes of great durability and beauty. Extract of aloes contains a compound termed *aloin*, which is soluble both in water and in alcohol; when exposed to the air it absorbs oxygen, and becomes of an intense red colour.

Aloin ($C_{17}H_{18}O_7$? Stenhouse).—In order to extract this substance, powdered Barbadoes aloes, mixed with sand to prevent the particles from agglomerating, is treated with cold water; the dark liquid thus obtained, if evaporated *in vacuo* to the consistence of syrup, and left for a few days in a cool place, deposits granular crystals, which are more or less deeply coloured: these must be pressed between folds of blotting paper, and recrystallized from water, the temperature of which is not to exceed 149° (65° C.). Aloin may likewise be obtained in hydrated crystals from a warm alcoholic solution, in groups of pale yellow needles. Cape aloes and Socotrine aloes also contain aloin, but it is accompanied by a large proportion of foreign matters, which interfere with its crystallization. Aloin is a neutral substance, with a sweetish, intensely bitter, persistent taste. It constitutes the purgative ingredient in aloes. At a temperature of 212° it is rapidly altered; at 302° (150° C.) it melts, and if heated strongly in the open air it burns with a smoky flame. The alkalis, both caustic and carbonated, dissolve it readily, forming orange-coloured solutions.

When extract of aloes is treated with nitric acid it yields *chrysammic acid* [$HC_7H(NO_2)_2O_2$; Mulder]. This compound is obtained by treating extract of aloes for some days with 8 times its weight of nitric acid (sp. gr. 1.37), distilling off the greater part of the acid, and then adding water; chrysammic acid is precipitated. It is nearly insoluble in water, but soluble in alcohol and in ether, from which it may be obtained in golden yellow plates, and hence its name, from *χρύσεος*, golden; on the application of heat it is decomposed with explosion. Its salts are soluble in hot water, and form deep red solutions; most of them may be crystallized, and the crystals exhibit a metallic lustre. Ammonia dissolves the acid with the formation of a beautiful purple-coloured solution, from which, on the addition of a neutral salt, such as potassic nitrate, an amidated compound is deposited in brilliant dark-green needles, which exert a polarizing action upon light when transmitted through them.

Schunck finds other acids in the mother liquor from which the chrysammic acid has been separated; one of these is carbazotic acid; two other resinoid acids, the *aloetic* [$(HC_8H_2(NO_2)_2O)_2 \cdot H_2O$], and *alocretinic*, are also formed at the same time: they have an intensely bitter taste, and form red salts.

(1511) BLUE DYES.—I. INDIGO.—The most important of the blue colouring matters, and the one which has been most accurately studied, is indigo. Crude indigo contains a definite colouring material, termed *indigotin*, or indigo blue, from which numerous derivatives belonging to the indigo series have been prepared. Such of them as contain nitrogen have hitherto been procured from natural indigo only, but by the metamorphosis of

these azotised compounds, bodies of a less complicated order have been obtained, many of which belong to the salicylic, the quinic, and the phenic groups. The following are the most important of the immediate derivatives of indigo: if indigo blue be described under the term *indyl*, their relation to it will then be represented by the formulæ of the fourth column:—

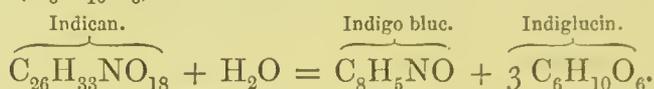
| | | | | |
|-----------------------|-------------------------|---|-----------------------|----------------------|
| Indigo blue | $C_8 H_5 N O$ | = | Indyl | In |
| White Indigo | $C_8 H_6 N O$ | = | Indyl hydride | In,H |
| Isatin | $C_8 H_5 N O_2$ | = | Indyl oxide | In,O |
| Isatic acid | $HC_8 H_6 N O_3$ | = | | HIn,H,O ₂ |
| Isathyd. | $C_8 H_6 N O_2$ | = | Indyl hydrate | InHO |
| Indin | $C_{16} H_{10} N_2 O_2$ | = | Polymeride of indyl . | In ₂ |
| Hydrindin | $C_{16} H_{11} N_2 O_2$ | = | Indin hydride | In ₂ ,H. |

(1512) *Condition of Indigo in the Plant.*—Indigo is extracted from the leaves of a variety of plants, principally the produce of India and America: it is especially obtained from the various kinds of *Indigofera*. The produce of the *Indigofera anil* was particularly examined by Chevreul: the *Isatis tinctoria*, or common woad, and several other plants, also yield indigo in small quantity, and it has been stated to occur occasionally in the milk of cows, and in human urine; so that indigo may be produced under circumstances apparently widely different.

The blue colouring matter of indigo is not soluble in water or in alkaline leys, but by treatment with deoxidizing agents in contact with water, it may be made to combine with an additional atom of hydrogen, and produce a white substance termed *reduced indigo*, which is also insoluble in water, but is soluble in alkaline leys. When an alkaline solution of this reduced indigo is exposed to the air it absorbs oxygen, and is converted into indigo blue, which is precipitated in the insoluble form.

In their growing state, the plants which yield indigo give no evidence of its presence, the juice being of a yellow colour. Chevreul supposed that the indigo exists in the plant in the reduced form; but, as Schunck has shown, this view is erroneous, since the juice of the plant is always acid, and reduced indigo requires an alkaline liquid for its solution. Moreover, as soon as a solution of reduced indigo is exposed to the air it becomes blue, and this is not the case with the juice of the *Indigofera*. Schunck has made the question of the condition in which indigo is contained in these plants the subject of a special inquiry; and although at present his experiments have only been conducted upon the woad, *Isatis tinctoria*, which may be readily cultivated in this country, the results which he has obtained possess con-

siderable value and interest [*Manchester Memoirs* (1855), vol. xii. p. 177]. From these experiments he concludes, that the woad does not contain indigo ready formed either in the blue or in the colourless state; that the indigo-producing substance is soluble in water; and that the formation of the blue colouring matter in watery extracts of the plant is neither caused nor promoted by the action of oxygen or of the alkalies, but that the plant contains a peculiar principle, which he terms *indican* ($C_{26}H_{33}NO_{18}$?). This body, by its decomposition, yields indigo. He found that, when heated with sulphuric or hydrochloric acid, it was decomposed: indigo blue, indigo red, and a particular species of sugar, *indiglucin* ($C_6H_{10}O_6$), were formed:—



Indican is a yellow, transparent, amorphous substance; it is very deliquescent, and is also soluble in alcohol and in ether. It has a slightly bitter, nauseous taste; when boiled with caustic alkalies it evolves ammonia. A solution of indican becomes of a bright yellow colour when mixed with alkalies, or with lime or baryta. Plumbic acetate occasions a sulphur-yellow precipitate in its alcoholic solution, but none in its aqueous solution till ammonia has been added. Solutions of indican must be evaporated without the application of heat, for if its aqueous solution be heated it undergoes a complete change; the elements of water are assimilated, and a substance is obtained which is not soluble in ether, and is dissolved but in small quantity by alcohol: the aqueous solution of this new body does not form indigo blue when boiled with acids, but it yields black flocculi consisting of two compounds; one of these is a resinous substance, fusible in boiling water, and the other a humus-like compound, which Schunck considers to be identical with the *indigo brown* of Berzelius. These observations show how important it is to avoid the use of boiling water in the preparation of indigo on a large scale. Solutions of indican which have been mixed with alkalies, and then boiled with acids, yield no indigo blue, but a mixture of this humus-like body and resin.

Extraction of Indigo.—If the dried leaves of the *Indigofera* be digested in cold water for some hours, a green solution is obtained, and this when exposed to the air undergoes fermentation, during which indigo is separated in the form of a blue sediment. The mode of preparing indigo, usually adopted in the East Indies, is stated to be the following:—The green plants, cut during the months of June and July, just before flowering time, are placed in wooden or brick troughs of about twenty feet square, and four or five feet deep (6 metres square, and about $1\frac{1}{2}$ metres in depth); the plants are then submitted to moderate pressure and covered with water; after the lapse of a few hours the mixture undergoes a sort of fermentation, which is allowed to continue for from twelve to fourteen hours; ammonia and carbonic acid are disengaged, the temperature rises to 100° or

110° (37°·8 or 43°·5 C.), and the liquid in the troughs becomes covered with a blue iridescent film. If the fermentation proceed too far the colouring matter is destroyed; when the process has reached a certain point, of which the manufacturer judges by experience, the liquid acquires a sherry wine colour; it is then drawn off into other troughs, where, on agitating briskly with oars, the pigment is separated as a deep blue granular powder. The supernatant liquor is run off; the sediment, with a portion of the liquid, is heated to the boiling point; the pasty mass is then drained on calico, pressed, cut into cakes, and dried.

The indigo of commerce is by no means a homogeneous body. Its most important constituent is *indigotin*, or indigo blue, but it contains several other substances, and in particular two bodies, known as *indigo brown* and *indigo red*. The brown colouring matter is soluble in caustic potash: the indigo red may be extracted by means of boiling alcohol.

(1513) *Indigo blue*, or *Indigotin* ($C_8H_5NO = 131$) may be separated from these impurities by the process of sublimation. If a small quantity of indigo be heated between two watch-glasses so as to protect it from the air, a considerable proportion of it is decomposed, but a portion is sublimed, and becomes condensed in light copper-coloured six-sided crystals upon the surface of the mass operated on. Pure indigo blue is, however, obtained more abundantly by the following plan contrived by Fritzsche:—4 ounces (about 113 grms.) of commercial indigo in fine powder, and 4 ounces of grape sugar, are placed in a flask capable of containing 10 pints (5·66 litres) of liquid; 6 ounces of a saturated solution of caustic soda are next added, and the flask is filled up with boiling alcohol; it is then closed so as to prevent the access of air, and the mixture after agitation is set aside. In a few hours it becomes clear; after which the yellowish-red solution is drawn off with a syphon, and if left exposed in open vessels it absorbs oxygen rapidly, becomes brown, and deposits crystals, which after being treated first with alcohol, and then with hot water, and dried, form perfectly pure indigo blue. Good indigo yields nearly half its weight of crystallized indigo blue.

Indigotin fuses at about 550°·4 (288° C.), and furnishes purple vapours. Amongst the products of its destructive distillation are ammoniac cyanide and carbonate, aniline, and a peculiar empyreumatic oil. Indigo blue is metameric with benzoyl cyanide. It is insoluble in water, alcohol, ether, and the fixed and volatile oils, as well as in dilute acids and alkalies.

(1514) *Compounds of Indigo with Sulphuric Acid*.—Sulphuric

acid appears to form several compounds with indigo; two of them have been analysed, viz., the *sulphindyllic*, or *sulphindigotic* acid, and the *sulphopurpuric*, or *sulphophenicic acid*; a third acid, the *hyposulphindigotic*, appears also to be produced along with the foregoing acids.

Sulphindyllic Acid ($\text{HC}_8\text{H}_4\text{NSO}_4$).—When commercial indigo is triturated with six times its weight of fuming sulphuric acid, considerable heat is developed, and a blue solution is formed, which is extensively used for dyeing cloth, under the name of *Saxony blue*. Ordinary oil of vitriol may also be employed to dissolve indigo, but more than double the quantity of such acid is required, and it must be heated to 131° or 140° (55° or 60° C.). If a sufficient amount of acid be employed, almost the whole of the indigo may be dissolved, and if the liquid be allowed to stand for a few hours, it will remain clear on being diluted. The filtered liquid contains a mixture of sulphindyllic and hyposulphindigotic acids. If the original acid liquid be diluted with from thirty to fifty times its bulk of water, and flannel which has been washed first with soap and sodic carbonate, and then with water, be immersed in the liquid, the indigo acids will attach themselves to the flannel, leaving the excess of sulphuric acid in the mother liquor. The colouring matter may be entirely removed from the flannel by digesting it in a dilute solution of ammoniac carbonate: a deep blue liquid is thus obtained, which when evaporated to dryness and treated with alcohol, is separated into ammoniac sulphindylate, which is insoluble, and ammoniac hyposulphindigotate, which is dissolved by the alcohol.

Potassic sulphindylate ($\text{KC}_8\text{H}_4\text{NSO}_4$) is sparingly soluble in cold water, and is precipitated in flocculi, when potassic acetate is added to a crude solution of indigo in sulphuric acid, after dilution with 10 parts of water. The sulphindylates form blue solutions, which appear to be red when held between the eye and the sun. These solutions are rendered colourless by the action of reducing agents, but regain their blue colour on exposure to the air.

Sulphopurpuric Acid ($\text{HC}_{16}\text{H}_9\text{N}_2\text{O}_2\text{SO}_4$).—This constitutes the greater part of the insoluble residue which is left upon the filter when indigo is treated with a proportion of sulphuric acid too small to dissolve it wholly. It is insoluble in liquids containing free acid; but it forms a blue solution in pure water. When potassic acetate is added to this liquid it gives a purple precipitate of potassic sulphopurpurate.

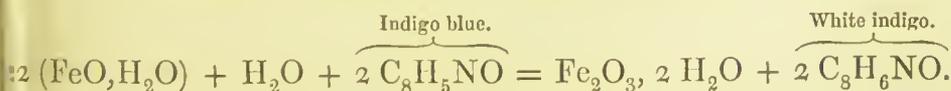
(1515) *White Indigo*, or *Indigogen* ($\text{C}_8\text{H}_6\text{NO}$).—When blue

indigo is treated with deoxidizing agents, such as a mixture of ferrous sulphate and caustic potash, a yellow solution is formed containing the so-called *reduced* indigo, a compound in which one atom more of hydrogen is present than in blue indigo. On neutralizing the alkaline liquid by acetic acid, the reduced indigo falls in dirty white flocculi, which are insoluble in water, but slightly soluble in alcohol and in ether; even when dry they absorb oxygen gradually from the air, but the absorption is much more rapid when moist, water and indigo blue being reproduced. The dilute acids are without effect upon white indigo; but fuming sulphuric acid dissolves it, forming a deep purple liquid, which if diluted with water becomes blue, and is converted into sulphindyllic acid. The alkaline solutions of white indigo are precipitated by many of the solutions of the metallic salts, and the compounds thus formed speedily become blue by exposure to the air.

The conversion of blue into white indigo may be effected by several processes:—

1. By means of sugar as already described (1513).

2. By the action of a mixture of ferrous sulphate and some alkali. Advantage is taken of this in the preparation of the indigo bath for dyeing purposes. The *copperas vat*, as it is termed, is employed in dyeing cottons and linen goods. The proportions to be used will vary with the quality of the indigo, but for laboratory purposes the following ingredients may be employed:— 1 part of powdered indigo, 2 of ferrous sulphate, 3 of slaked lime, and 150 or 200 of water. The reaction is somewhat complicated; the lime acting on the ferrous sulphate sets free hydrated ferrous oxide, and this oxide in the presence of water takes up an additional quantity of oxygen, becoming converted into the hydrated ferric oxide, whilst the liberated hydrogen unites with the indigo blue, and constitutes white indigo, which becomes dissolved by the excess of lime, and forms a yellow solution:—



If the alkaline liquid thus obtained be exposed to the air, it becomes covered with a blue film, and deposits nearly pure indigo; and if mixed with hydrochloric acid in vessels filled with gaseous carbonic anhydride, white indigo is precipitated. If yarn or woven goods be immersed in such a solution, and then exposed to the air, the white indigo absorbs oxygen rapidly, and becomes converted into blue indigo within the fibres of the tissue, with which it con-

tracts an intimate adhesion. The blue dye thus obtained is very intense and permanent, since it is insoluble in all ordinary solvents.

3. By means of orpiment and stannous chloride, which are sometimes substituted in calico-printing, as reducing agents, in the place of the ferrous sulphate; in this case potash is employed instead of lime water as the solvent of the white indigo.

4. By means of decaying vegetable matter, which answers the same purpose as the ferrous sulphate. This vat is chiefly used for dyeing yarns, and is prepared by some manufacturers in the following manner:—4 parts of finely powdered indigo, 50 of woad, 2 of madder, and 2 of potassic carbonate are mixed with 2000 of water, and the mixture is kept for some hours at a temperature of about 194° (90° C.); $1\frac{1}{3}$ part of recently slaked lime is then added in small quantities at a time, after which fermentation commences; formic, acetic, and carbonic acids are formed, as well as ammonia. The lime reduces the potassic carbonate to the caustic state, and enables it to dissolve the indigo which has been converted into the white hydride during fermentation by the decomposition of the vegetable matter. The addition of the lime is attended with the further advantage of precipitating a portion of brown colouring matter that would otherwise deaden the tint of the goods. The foam or *flower* of the vat has a beautiful blue iridescent appearance caused by oxidation of the indigo at the surface, but the liquid beneath is of a deep yellow colour; by exposure to air it becomes green, and finally deposits blue indigo. To prevent this oxidation the vats are kept covered when not in actual use; and fresh materials are added from time to time in order to maintain the liquor at a uniform strength.

Starch, sugar, bran, and other vegetable matters may be substituted for the madder and the woad in the indigo vat. These substances undergo fermentation, and act as deoxidizing agents: probably lactic and butyric acids are generated, and the indigo combines with the hydrogen, while the latter is in the act of being liberated.

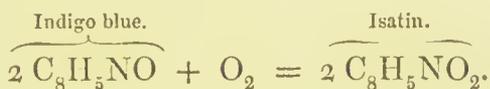
(1516) *Assay of Indigo*.—The quality of commercial indigo varies greatly: the purest specimens usually occur in small masses of an intense violet-blue colour, which by friction with a hard smooth body acquire a coppery lustre. The best kinds are sufficiently light to float upon water, and when broken they do not contain cavities which exhibit brown or whitish veins. Indigo is, however, frequently adulterated with sand, with starch, and sometimes, it is said, with powdered lead. Good indigo should not leave more than from 5 to 8 per cent. of ash, calculated upon the dried mass; during drying it loses from 5 to 8 per cent. of water. Starch may be detected by treating the indigo with boiling water very faintly alkalized, and, after neutralizing the filtrate, testing it with iodine.

A simple method of determining the relative value of any sample of indigo

has been proposed by Bolley, who estimates its tinctorial power by measuring the amount of a standard solution of potassic chlorate, which is required to destroy the blue colour of a given sample:—10 grains of the indigo for assay are reduced to a very fine powder, and triturated with 2 fluid drachms of fuming sulphuric acid; the mixture is allowed to digest for twelve hours in a closed vessel with occasional agitation. The indigo must be completely dissolved before the next part of the process is commenced. As soon as the solution is effected, the liquid is to be poured into a capsule with about a pint of water, containing an ounce of pure hydrochloric acid, and the mixture is brought to the boiling point. A solution of potassic chlorate containing 2·5 grains of the salt in 1000 grains of water, is then to be added to the boiling liquid from an ordinary alkalimeter, drop by drop; the blue colour first becomes green, then greenish brown, and when the last tinge of green disappears and has been replaced by a reddish brown, the operation is complete. The number of divisions of the liquid required does not indicate the percentage of indigo blue, but simply the relative value of the different samples compared together.

Penny substitutes potassic dichromate for the chlorate; 100 parts of pure indigo blue requiring exactly 75 of the dichromate for decoloration: by this means an exact determination of the amount of indigo blue may be effected.

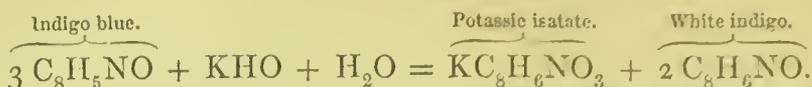
(1517) *Products of the Oxidation of Indigo.*—The action of oxidizing agents upon indigo gives rise to several interesting products. Concentrated chromic acid breaks up the constituent molecule of indigo, and occasions a copious disengagement of carbonic anhydride; but if a more dilute solution of chromic acid be employed, the indigo is converted into *isatin*: a similar change is effected by the action of dilute nitric acid:—



The oxidizing action proceeds further if the indigo be treated with nitric acid in a more concentrated form; thus, if indigo be boiled with fuming nitric acid diluted with 10 or 12 parts of water, indigotic, or nitro-salicylic acid is formed ($\text{HC}_7\text{H}_4\text{NO}_2\text{O}_3$; 1460); and by a prolonged action of the nitric acid, carbazotic acid [$\text{HC}_6\text{H}_2(\text{NO}_2)_3\text{O}$; 1557] is produced; both these compounds contain less carbon than the true indigo group, and this carbon is probably separated in the form of carbonic or of oxalic acid.

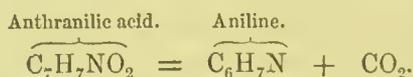
The oxidizing effect of caustic potash upon indigo is somewhat different from that of nitric acid. If indigo in fine powder be boiled with a solution of potash (of sp. gr. of 1·36), it is dissolved without the extrication of gas, and an orange-coloured liquid is formed, which on cooling deposits yellow crystals. If these crystals be dissolved in water, and treated with an excess of hydrochloric acid, a dirty bluish-red precipitate is formed; this substance constitutes Fritzsche's *chrysanilic acid*, but according to Gerhardt, the precipitate consists of a mixture of white indigo

with isatin, and the chemist last named represents the action of the solution of caustic potash on indigo thus:—



By exposure of the solution of the yellow crystals to the air, oxygen is absorbed, and indigo blue is deposited.

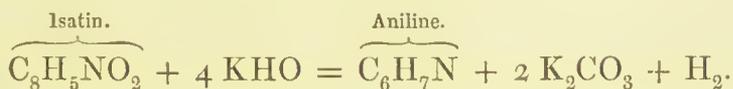
If indigo be fused with caustic potash, hydrogen is evolved, and potassic salicylate is amongst the products; but if to a concentrated boiling solution of potash indigo be added, care being taken to replace the water as it evaporates, and if to the boiling liquid powdered manganese dioxide be added until the solution ceases to deposit indigo when exposed to the air, a different compound is the result, and potassic anthranilate is obtained. *Anthranilic acid* ($\text{HC}_7\text{H}_6\text{NO}_2$) may be procured by just neutralizing the potash with sulphuric acid, evaporating to dryness, dissolving the potassic anthranilate by means of alcohol, which leaves the sulphate, and decomposing the anthranilate by the addition of acetic acid. On evaporating the alcoholic solution, anthranilic acid is obtained in brilliant plates, or in four or six-sided needles, metameric with amido-benzoic acid (1436). If heated gently it may be sublimed unchanged, but if the temperature be suddenly raised the acid becomes decomposed into aniline and carbonic anhydride:—



(1518) *Isatin* ($\text{C}_8\text{H}_5\text{NO}_2 = 147$).—This substance, the name of which is derived from *Isatis tinctoria*, the botanical appellation of the woad-plant, contains one atom more of oxygen than indigo blue: it may be obtained by heating indigo in a dilute solution of potassic dichromate and sulphuric acid, or by the following process:—Powdered commercial indigo, of good quality, is to be mixed with a sufficient quantity of water to reduce it to a thin cream, and the mixture is to be heated till it boils: undiluted nitric acid must then be added in small quantities at a time until the blue colour has disappeared; 10 parts of indigo require 6 or 7 parts of acid. The mass containing isatin mixed with a large quantity of a brown resinous matter must next be largely diluted with water, boiled, and filtered whilst boiling hot; the undissolved residue must be again boiled with water, and the filtered solution added to the first portions; crystals are deposited as the liquid cools; they must be washed with water containing a little ammonia, then dissolved in alcohol and recrystallized. When considerable quantities of isatin are required, Hofmann purifies the crude product of the action of nitric acid upon indigo by dissolving it in a dilute solution of potash: hydrochloric acid is next added to the deep brown liquid, until the precipitate, which is at first brown, assumes a clear red tint, the liquid is then filtered, and precipitated by an excess of hydrochloric acid; this precipitate consists of isatin, which, after washing with cold water, is chemically pure.

Isatin crystallizes in brilliant, transparent, orange-coloured, six-sided, or rhombic prisms; it is sparingly soluble in cold water, but is more readily dissolved by boiling water, and still more so by hot alcohol. Ether dissolves it less readily. On the application of heat to the crystals, they melt and are volatilized, emitting acrid vapours of a yellow colour. When isatin is distilled in closed vessels a considerable portion of it undergoes decomposition. Isatin is capable of exchanging an equivalent of hydrogen for one of a metal; thus, if an alcoholic solution of isatin be mixed with one of argentic nitrate, a wine-red amorphous precipitate of *argentisatin* ($C_8H_4AgNO_2$) is formed. Solution of potash dissolves isatin freely, and forms a purple liquid, which on boiling becomes yellow. When examined after this change of colour has occurred, the elements of the isatin are found to have combined with those of water, thus producing *isatic acid* ($HC_8H_6NO_3$), which remains in combination as potassic isatate.

If isatin be heated with solid caustic potash it is decomposed, hydrogen is liberated, potassic carbonate is formed, whilst aniline distils over:—



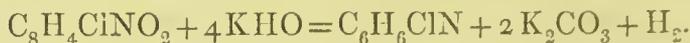
Concentrated nitric acid decomposes isatin; when heated with it copious ruddy fumes are evolved, a brown resinous body containing nitroxyl (NO_2) is formed, and if the action be carried further oxalic acid is found in the solution. No carbazotic acid is formed. Chlorine, if transmitted through water in which isatin is suspended, displaces one atom of hydrogen and forms chlorisatin.

(1519) The *action of chlorine upon indigo* is peculiar: gaseous chlorine has no action upon dry indigo, but if a current of chlorine gas be transmitted through water containing indigo in suspension, the blue colour is gradually destroyed, and a rusty brown compound is formed: this substance, in addition to formic acid, ammoniac hydrochlorate, and a brown resinous substance, contains four distinct chlorinated compounds. Two of these, viz., *chlorisatin* $C_8H_4ClNO_2$, and *dichlorisatin* $C_8H_3Cl_2NO_2$, are yellow, sparingly soluble, crystallizable substances formed upon the type of isatin. A third chlorinated compound is *trichloraniline* ($C_6H_4Cl_3N$), and it is usually accompanied by a certain quantity of *trichlorophenic acid* ($HC_6H_2Cl_3O$), and *chloranil* ($C_6Cl_4O_2$; 1337). Chlorisatin and dichlorisatin are soluble in alcohol; when heated with a solution of potash they yield a salt of a corresponding acid,—the

chlorisatic ($\text{HC}_8\text{H}_5\text{ClNO}_3$), and *dichlorisatic acid* ($\text{HC}_8\text{H}_4\text{Cl}_2\text{NO}_3$), derivatives of isatic acid; and if distilled with caustic potash, they give ehlorinated bases of a composition corresponding to that of aniline,—

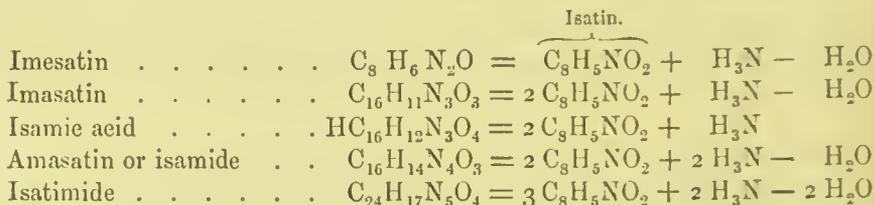
Chloraniline being composed of $\text{C}_6\text{H}_6\text{ClN}$, and
 Dichloraniline of $\text{C}_6\text{H}_5\text{Cl}_2\text{N}$.

The reaction is precisely analogous to that with pure isatin, *e.g.* :—



The action of bromine upon indigo is analogous to that of ehlorine, though it is less violent.

(1520) *Ammoniacal Derivatives of Isatin*.—When isatin is treated with ammonia it gives rise to a number of amidated products, the composition of which varies with the degree of concentration of the ammonia: they have been particularly studied by Laurent (*Ann. de Chimie*, III. iii. 483). The following table exhibits the reactions which attend their formation :—

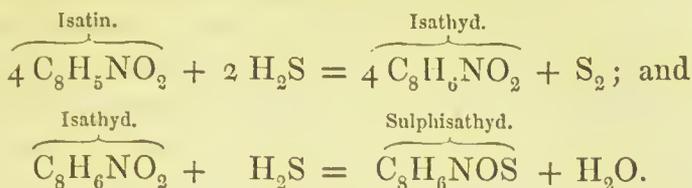


Chlorisatin and dichlorisatin when heated with ammonia yield corresponding compounds.

(1521) *Isathyd* ($\text{C}_8\text{H}_6\text{NO}_2$).—This substance, as its name implies (*isatin hydrogenized*), stands in the same relation to isatin that white indigo does to blue indigo; that is to say, its molecule contains one atom more of hydrogen than isatin. In order to procure isathyd, an alcoholic solution of isatin is mixed with one of ammonie sulphhydride (H_4NHS), and set aside for a week in a closed bottle; crystals of sulphur are gradually deposited, mixed with prismatic needles of isathyd. The sulphur must be removed by digestion with carbon disulphide. A better method, however, consists in placing powdered isatin in a flask with a considerable quantity of water acidulated with sulphuric acid, then introducing a plate of pure zine, and heating the whole to the boiling point. As the isatin becomes dissolved, it combines with the nascent hydrogen, and is converted into isathyd, which is deposited in the form of a crystalline powder. Isathyd is a greyish white, tasteless substance, which is insoluble in water, and but sparingly soluble in alcohol and in ether even at a boiling temperature: it is deposited from these solutions as they cool in minute oblique prisms. If heated, it softens and becomes decomposed, and acquires a violet-brown tint. Boiling nitric acid colours it violet, and dissolves it. Chlorisatin and dichlorisatin, when treated with ammonie sulphhydride, yield ehlorinated bodies corresponding with isathyd, termed *ehlorisathyd*, $\text{C}_8\text{H}_5\text{ClNO}_2$, and *dichlorisathyd*, $\text{C}_8\text{H}_4\text{Cl}_2\text{NO}_2$. By analogous methods corresponding compounds containing bromine may be obtained.

When a current of sulphuretted hydrogen is transmitted through a boiling concentrated alcoholic solution of isatin, the isatin is converted into isathyd, and this, at the moment of its formation, becomes decomposed, while *sulphisathyd*, a

sulphuretted compound corresponding in composition to isathyd, but containing an atom of sulphur in place of one of oxygen, is formed:—



When the liquid has become clear after the deposition of the sulphur, the sulphisathyd may be precipitated by the addition of water. It is a yellowish grey, tasteless powder, which softens at 212° ; alcohol and ether dissolve it, but do not yield it in a crystalline form on evaporation.

Various other sulphuretted derivatives may be obtained from isatin (Laurent, *loc. cit.*).

(1522) *Indin* ($\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2$).—This substance appears to be polymeric with indigo blue. It is of a beautiful rose-colour, is insoluble in water, and but sparingly soluble in alcohol and in ether, even at a boiling temperature. In order to prepare indin, sulphisathyd is triturated in a mortar for some minutes in a concentrated solution of potash, adding a few drops of the alkaline solution from time to time, until a rose-colour begins to show itself. Alcohol is then to be added in small quantities at a time, continuing to triturate the mass until the mixture has assumed a deep rose-colour. It is then to be diluted with alcohol, and the insoluble portion collected on a filter and washed, first with alcohol, then with water. If this residue be dissolved in a tepid concentrated solution of potash, black needles of *potassic indinate* ($\text{C}_{16}\text{H}_9\text{KN}_2\text{O}_2$) are deposited. They must be washed with absolute alcohol, and decomposed with a weak solution of hydrochloric acid. Pure pulverulent indin is left on washing the insoluble residue. *Dinitrindin*, $\text{C}_{16}\text{H}_8(\text{NO}_2)_2\text{N}_2\text{O}_2$, *dichlorindin* ($\text{C}_{16}\text{H}_8\text{Cl}_2\text{N}_2\text{O}_2$), and *tetrachlorindin* ($\text{C}_{16}\text{H}_6\text{Cl}_4\text{N}_2\text{O}_2$) are substitution-compounds obtainable from indin.

Hydrindin 2 ($\text{C}_{16}\text{H}_{11}\text{N}_2\text{O}_2$), H_2O .—This substance appears to stand to indin in a relation similar to that of reduced indigo to blue indigo. When the black solution of potassic indinate is heated with an excess of an alcoholic solution of the alkali, the colour gradually changes into a pale yellow, and the liquid on cooling deposits crystals of *potassic hydrindinate*. Water decomposes them, and leaves hydrindin in the form of a white powder, insoluble in water, and sparingly soluble in hot alcohol.

A number of other compounds have been obtained from indigo; they are described by Laurent, *Ann. de Chimie*, III. iii. 463, and by Erdmann, *Journ. für prakt. Chemie*, vols. xix., xxii., and xxiv.

(1523) 2. COLOURING MATTERS OF THE LICHENS.—Many of the lichens afford colouring matters which are of considerable importance. A yellow lichen common on old walls (*Parmelia parietina*) contains a colouring matter identical with that of the rhubarb root (1501), and the different varieties of *Usnea* and *Evernia* furnish an analogous, straw-yellow, crystalline substance, termed *usnic acid* ($\text{HC}_{19}\text{H}_{15}\text{O}_7?$), which is easily dissolved by ether; it yields red compounds with the alkalies. When boiled with an excess of alkali it furnishes a substance termed by Stenhouse beta-orcin ($\text{C}_8\text{H}_{10}\text{O}_2$). The same compound is obtained by

the distillation of usnie acid. These acids are unimportant as colouring matters, and need not be further noticed here.

(1524) The red, violet, and blue colours which are known in commerce under the names of archil, cudbear, and litmus, are supplied by different species of *Roccella*, *Variolaria*, and *Lecanora*. The *Roccella* tribe grow upon rocks on the sea-coast, in the Canary Islands, in Sardinia, and in Corsica, at the Cape of Good Hope, on the western coast of South America, and in various other parts of the world. The *Variolaria* abounds in certain parts of the Pyrenees, and of the Alps; and the *Lecanora tartarea* is abundant on the Swedish mountains.

In no case do these lichens furnish the colouring matter ready formed; but they contain from 7 to 12 per cent. of various colourless acids, such as the erythric ($C_{20}H_{22}O_{10}$), evernie ($C_{17}H_{16}O_7$?), and orsellie acids ($C_8H_8O_4$); these bodies under the influence of alkalis are readily decomposed into new acids (which are characterized by the production of a violet colour with chloride of lime), and into a colourless neutral substance, termed orein ($C_7H_5O_2$). Orein is the true colour-producing body; under the influence of ammonia it absorbs oxygen, and is converted into orein ($C_7H_7NO_3$), an azotised compound possessed of high tinctorial power.

In the preparation of *Cudbear*, the lichens (chiefly *Lecanora tartarea*) are first freed as far as may be from earthy impurities, and are made up into a paste with a solution of ammonia of sp. gr. about 0.990; formerly stale urine to which a quantity of lime had been added, for the purpose of liberating its ammonia, was used: the mixture is then exposed for some weeks to the air, moistening it from time to time with fresh quantities of the ammoniacal liquid. A paste is thus obtained of an offensive odour and of an intense violet-red colour; when dried and reduced to powder it constitutes the eudbear of commerce. The colouring matter of this dye-stuff consists mainly of orein. Cudbear is employed chiefly for woollen and silken goods, to which it imparts a brilliant but not very permanent dye, of various shades of violet, lilac, and purple. *Archil* is prepared by digesting the lichens in a hot solution of ammonia, allowing it to stand for a few hours, and exposing the clear solution which is drawn off from the lichen in deep jars to the air for about 3 weeks; the solution when concentrated by evaporation forms the archil liquor of commerce.

(1525) *Litmus* is obtained principally from the *Roccella tinctoria*: it is prepared by a process similar to that used for archil, but it is moistened with a mixture of carbonates of ammonium

and potassium,—the addition of sodic or potassic carbonate being essential to the development of the blue colour. During its preparation the mass at first assumes a red colour, but it ultimately becomes of an intense blue. It is made up with chalk or plaster of Paris into small cakes for the market. A small portion only of the colouring matter of litmus is soluble in water and in alcohol, but it is nearly all soluble in alkaline liquids. V. Luynes has succeeded in obtaining the essential colouring matter of litmus in a pure form by acting upon orcein (1530); 1 part of orcein, 25 of crystallized sodic carbonate, 5 of water, and 1 part of a strong solution of ammonia, are digested in a partially closed flask for 4 or 5 days, at a temperature of from 140° to 167° (60° to 75° C.) with frequent agitation. The blue liquid thus obtained is to be diluted with water, and hydrochloric acid added in slight excess. The colouring matter is thus precipitated, and after washing and drying furnishes pure litmus in irregular fragments, which assume a metallic lustre when pressed. It is scarcely soluble in cold water, benzol, or oil of turpentine, but readily soluble in alcohol, with which it furnishes a red solution, which, when neutralized with an alkali becomes blue, and reddens again with very slight traces of free acid.

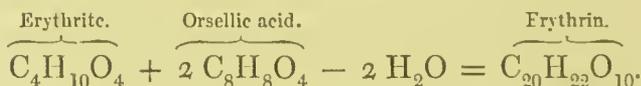
(1526) *Assay of Lichens for Colouring Matter.*—The different lichens contain variable amounts of colour-producing ingredients; consequently their commercial value is liable to great variation. Stenhouse estimates the comparative value of different samples by means of a standard solution of chloride of soda. A given weight of the lichens in powder is digested with dilute caustic soda in order to extract the colorific acid, and on adding chloride of soda to this liquid a red colour is produced, which disappears in a few minutes, leaving a brownish-yellow tint; fresh quantities of the chloride are added so long as this red coloration is produced by it. Another method also suggested by the same chemist consists in adding an acid to the solution of the lichen acids in lime water, and collecting and weighing the precipitate of the lichen acids. The colour-producing acids may be extracted by the following method (Stenhouse):—The pulverized lichens are mixed with water, and, after standing for an hour, a quantity of slaked lime is added, and the mixture is allowed to digest for some time; it is then placed in a linen filter supported in a tin vessel with a perforated bottom, and the liquid is gradually displaced by the cautious addition of water, the washing being continued so long as the filtrate yields the characteristic purple-red colour with solution of chloride of lime. On the addition of hydrochloric acid to the filtered solution, the lichen acids are precipitated in the form of a white gelatinous deposit, from which the water may be removed by pressure. The acids may then be crystallized from warm alcohol, but they must not be boiled with alcohol, otherwise compound ethers would be formed, into the composition of which the acids enter. This remarkable power of etherifying alcohol is a striking chemical peculiarity of the lichen acids.

The formulæ which indicate the composition of the numerous derivatives of the lichens are at present variously represented by

different chemists.* They are founded chiefly upon the analyses of Schunck and of Stenhouse, and the formulæ except the first four are those proposed by Gerhardt:—

| | | |
|--------------------------------------|-----------------------|-----------|
| Usnic acid | $C_{19}H_{16}O_7$ | Stenhouse |
| Erythrin | $C_{20}H_{22}O_{10}$ | V. Luynes |
| Picro-erythrin | $C_{12}H_{16}O_7$ | Do. |
| Erythrite | $C_4H_{10}O_4$ | Do. |
| Roccellinin | $C_{18}H_{16}O_7$ | Stenhouse |
| Evernie acid | $C_{17}H_{16}O_7$ | Do. |
| Evernesic acid | $C_9H_{10}O_4$ | Do. |
| Lecanorie or orsellie acid | $C_8H_8O_4$ | Do. |
| Orsellie (lecanoric) ether | $C_2H_5, C_8H_7O_4$ | |
| Parellie acid | $C_9H_6O_4$ | Schunck |
| Gyrophoric acid | $C_{36}H_{36}O_{15}?$ | Stenhouse |
| Orcin | $C_7H_8O_2, H_2O$ | Do. |
| Beta-orcin | $C_8H_{10}O_2$ | Do. |
| Orcin | $C_7H_7NO_3$ | |

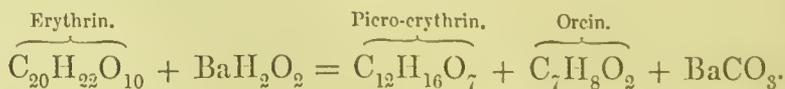
(1527) *Erythric Acid*, or *Erythrin* ($C_{20}H_{22}O_{10}$).—This compound appears to be present in most of the lichens which yield archil. Berthelot and V. Luynes regard erythrin as the diorcellie ether of the tetratomic alcohol erythrite (1243):—



Erythrin is soluble in about 240 parts of boiling water, but is nearly insoluble in cold water; hot alcohol also dissolves it, and deposits the acid in stellate groups of needles. It is likewise soluble in ether. When heated in a tube it is decomposed, and orcin is sublimed. The alkalis dissolve it with facility. When boiled with baryta, barie carbonate is formed, whilst erythrite and orcin are liberated:—



If the decomposition be arrested before it is complete, the body termed picro-erythrin is obtained:—



Picro-erythrin ($C_{12}H_{16}O_7$) is a colourless substance which is

* See Schunck (*Liebig's Annal.*, xli. 157; liv. 257; lxi. 64); Rochleder and Heldt (*Ib.* xlvi. 1); Stenhouse (*Phil. Trans.*, 1848, p. 63; 1849, p. 393); V. Luynes (*Ann. de Chimie*, IV. ii. 385, vi. 184).

sparingly soluble in cold water, but very soluble in boiling water, from which, on evaporation, it may be obtained in confused crystals. Picro-erythrin may be regarded as the monorsellie ether of erythrite (V. Luynes). It has a very bitter taste. Its solutions give a preeipitate with basic plumbic acetate, but none with the normal acetate: with ferric chloride it produces a beautiful purple colour. If heated alone in a tube it yields a sublimate of orcin. Alkalies dissolve it readily without the aid of heat. Its ammoniacal solution quickly becomes red by exposure to the air. When boiled with milk of lime or with baryta water it is decomposed, calcic or baric carbonate is formed, while orcin and erythrite are produced:—



(1528) *Evernic acid* ($\text{HC}_{17}\text{H}_{15}\text{O}_7$?) occurs associated with usnic acid in the *Evernia prunastri*. It is scarcely soluble in water, even when at a temperature of 212° , but is readily soluble in alcohol and in ether; with potassium and barium it yields soluble crystallizable salts. When boiled with lime or baryta in excess, orcin is formed, and a new acid termed *evernesic acid*:—



Evernesic acid does not yield orcin; ammonia does not produce any red colour with it; nor does chloride of lime yield with it a red or violet colour.

(1529) *Lecanoric* or *Orsellic Acid* ($\text{HC}_8\text{H}_7\text{O}_4$).—If the *Lecanora tartarea* and some other lichens be treated with ether, and the solution be evaporated, white crystals of *orsellic acid* are deposited; this substance is nearly insoluble in cold water, but it is freely dissolved by hot alcohol and by ether; its solution reddens litmus. Ferric chloride strikes a dull purple red with its spirituous solution. If boiled with alcohol it produces a true compound ether. The caustic alkalies dissolve the acid, and deprive it of the elements of carbonic anhydride, leaving *orscin* in solution; $\text{C}_8\text{H}_8\text{O}_4 - \text{CO}_2 = \text{C}_7\text{H}_8\text{O}_2$. Orcin is also obtained by simply distilling the acid. If orsellic acid be treated with ammonia and exposed to the air, the acid combines with the elements of ammonia, and a purple colour is gradually developed, owing to the production of orcin.

When either orsellic or erythric acid is boiled with alcohol for some hours, orcin is separated, and a substance termed *pseudo-erythrin*, or *orsellic ether* ($\text{C}_2\text{H}_5, \text{C}_8\text{H}_7\text{O}_4$), is formed: it crystallizes in plates or needles, which may be purified by recrystallization first from benzol and then from boiling water. It is

sarcely dissolved by cold water, but is very soluble in alcohol and in ether, as well as in alkaline solutions, from which it is precipitated unaltered on the addition of an acid. Its ammoniacal solution, when exposed to the air, assumes a wine-red tint.

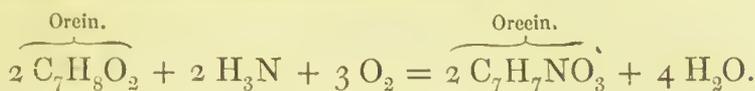
In certain cases Schunck found an acid which he terms *parellie acid* ($H_2C_{21}H_{14}O_{10}, H_2O?$), accompanying lecanoric acid: it is a fusible compound, which does not yield orcin when treated with alkalis. It crystallizes in brilliant, colourless, heavy needles, which are very sparingly soluble in cold water, but freely soluble in ether and in alcohol. The alcoholic solution has a very bitter taste; water precipitates the acid from it in a gelatinous form. It forms a white insoluble barium salt.

(1530) *Orcin* ($C_7H_8O_2, H_2O$; Gerhardt); *Sp. gr. of vap.* 4.20. —This substance appears to exist ready formed in several lichens, but it is generally procured by decomposing evernie, erythric, or orsellie acid, by boiling it with an alkali. Stenhouse prepares orcin by boiling the solution obtained by treating one of the varieties of the *Rocella* or *Lecanora* with lime for some hours, and concentrating it by evaporation. The excess of lime must then be removed by means of a current of carbonic anhydride, and the filtered liquid evaporated to the consistence of a syrup; this residue must be treated with boiling benzol, then agitated with water to separate the orcin from the benzol, and the aqueous solution allowed to crystallize: the red crystals of orcin thus obtained must be purified by recrystallization from their solution in benzol. Orcin is a substance with a sweet but mawkish taste, and, like sugar, it exerts an antiseptic influence on albuminoid compounds. It crystallizes with H_2O in colourless, quadrangular prisms, and is readily soluble in alcohol, ether, and water. When heated to 212° it melts and gives off its water of crystallization, and at $550^\circ.4$ (288° C.) it may be sublimed unchanged. It is not susceptible of the vinous fermentation. In its anhydrous form it is metameric with saligenin. With ferric salts it gives a dark red precipitate; it gives no precipitate with normal plumbic acetate, but with basic plumbic acetate a white precipitate is occasioned ($C_7H_6PbO_2, PbO$). With chloride of lime orcin gives a purple-red colour, which quickly changes to a deep yellow. Nitric acid converts orcin into oxalic acid, and a resinous substance. (V. Luynes, *Ann. de Chimie*, IV. vi. 184).

If orcin be acted upon by the oxychlorides of the acids, substitution-products, such as diacetyl orcin, $C_7H_6(C_2H_3O)_2O_2$, may be obtained. Orcin also forms unstable compounds with bases, and dissolves considerable quantities of baryta and lime. Fused potash dissolves without decomposing it.

Orcein ($C_7H_7NO_2$).—If orcin be exposed in a shallow dish under a bell-glass with air to the vapour of ammonia, it yields a

fine red colour; oxygen is absorbed, and a compound which has received the name of *orcein* is obtained:—



The aqueous solution of the result of the foregoing reaction contains ammoniac orceinate; it must be mixed with acetic acid, when orcein falls in red flocculi. Orcein is sparingly soluble in water, from which it is completely precipitated on the addition of a neutral salt. Alcohol dissolves it freely, forming a scarlet solution. It is sparingly soluble in ether. Potash and ammonia dissolve it readily, forming a splendid purple colour, which is the basis of the ordinary archil of commerce; the addition of common salt precipitates it from its solutions in the alkalies. With metallic salts alkaline solutions of orcein yield beautiful purple lakes. The addition of acids restores its red tint; hence its value in the form of litmus as a test for free acids. If a solution of orcein be treated with hydrochloric acid and zinc in closed vessels it becomes colourless, but it resumes its red colour on exposure to the air. If a solution of orcein in ether be saturated with dry ammoniacal gas, colourless octahedral crystals, containing from 11 to 12 per cent. of ammonia, separate on standing.

Resorcin ($\text{C}_6\text{H}_6\text{O}_2$; *Sp. gr. of vap.* 4.10) is the name given by Hlasiwetz and Barth to a homologue of orcein, which is one of the products obtained by fusing galbanum or ammoniacum resin with potassic hydrate. It is a white crystalline body, soluble in water, alcohol, and ether, which fuses at $210^{\circ}.2$ (99° C.), and boils at $519^{\circ}.8$ (271° C.).

Beta-orcin ($\text{C}_8\text{H}_{10}\text{O}_2$), the compound obtained by distillation of usnic acid (1523), is regarded by Gerhardt as another homologue of orcein: it is easily soluble in boiling water, alcohol, and ether; it has a slightly sweet taste. When mixed with ammonia it rapidly acquires a fine red tint. With caustic potash it yields a fine purple, and by chloride of lime its colour is instantly converted into a blood-red.

The orcins appear to be diatomic compounds connected with the phenols; they contain an atom more of oxygen than the corresponding phenols, but the true relation in constitution is not known.

| <i>Phenols.</i> | <i>Orcins.</i> |
|--|--|
| Phenol $\text{C}_6\text{H}_6\text{O}$ | Resorcin $\text{C}_6\text{H}_6\text{O}_2$ |
| Kresol $\text{C}_7\text{H}_8\text{O}$ | Orcin $\text{C}_7\text{H}_8\text{O}_2$ |
| Phlorol. . . . $\text{C}_8\text{H}_{10}\text{O}$ | Beta-orcin $\text{C}_8\text{H}_{10}\text{O}_2$ |

(1531) The vegetable colours are not the only ones which are used in dyeing; a beautiful blue is now prepared from potassic ferrocyanide and the ferric salts. A yellow is produced by plumbic chromate, and an orange upon woollen and silken goods by means of concentrated nitric acid.

A variety of colours are used by the artist as pigments; most

of them are obtained from the mineral kingdom: many of these mineral colours are wanting in transparency and brilliancy, but they are generally very durable. The pigments procured from the vegetable kingdom are more brilliant, but less permanent, and in the small number of cases in which colours are obtained from the animal creation they generally combine durability with brilliancy. Several of the pigments in common use, such as the preparations of lead, arsenicum, and copper, are poisonous. Many of the metallic colours, particularly those which contain lead, are injured by exposure to sulphuretted hydrogen, and become black. Vegetable colours are especially prone to fade under the influence of atmospheric oxygen, aided by a strong light.

(1532) *Colouring Matters of Plants and of Flowers.*—*Chlorophyll*, as the green colouring matter so generally diffused through the vegetable kingdom is termed (from $\chi\lambda\omega\rho\acute{o}\varsigma$, green, $\phi\acute{\upsilon}\lambda\lambda\omicron\nu$, a leaf), appears to be of a resinous nature. It is soluble in alcohol and in ether, but insoluble in water. The alcoholic solution is of a beautiful green colour, and on evaporation leaves the chlorophyll in an amorphous state. If the leaves be treated with ether, the colouring matter is dissolved, but it is accompanied by a wax-like body, which is insoluble in alcohol. When present in the leaf chlorophyll undergoes various changes of colour, according to the plant in which it occurs. In autumn, before the leaves fall, it generally passes into yellow, as may be seen in the lime, the poplar, the horse-chestnut, and the common laurel. In other cases the colour changes to red of various shades, as in the Virginia creeper, the Spanish chestnut, and the sumach. Chlorophyll, according to Fremy, consists of a blue colouring principle, *phyllocyanin* (from $\kappa\acute{\upsilon}\alpha\nu\omicron\varsigma$, blue), and a yellow one, *phylloxanthin* (from $\xi\alpha\nu\theta\acute{o}\varsigma$, yellow), and he attributes the yellow colour acquired by the fading leaves of autumn to the gradual destruction of the blue constituent. He found this yellow colouring matter to become green under the action of hydrochloric acid. Phylloxanthin was obtained by Kromayer as a fusible yellow body of butyraceous consistence, soluble in ether, alcohol, and carbon disulphide. Phyllocyanin he regards as an azotised body ($C_{34}H_{68}N_4O_{17}$?) of a dark blue colour, soluble in cold alcohol, but insoluble in water. Kromayer separated the two bodies by dissolving chlorophyll in alcohol, and boiling the solution for a few minutes with an alcoholic solution of potash; then, on neutralizing with hydrochloric acid, a yellow precipitate was obtained, leaving the supernatant liquid of a beautiful blue. On evaporation, this blue liquid deposited blue flocculi insoluble in water.

According to Stokes (*Proceed. Roy. Soc.*, xiii. 144), these results are due to the decomposition of the colouring matters by the reagents employed. He finds that there are four optically different colouring matters in chlorophyll. Two of these are green, and two are yellow. The solutions of the green colouring matters have a strong red fluorescence; they are readily destroyed by acids, or even by acid salts, such as hydric-potassic oxalate; and among their products of decomposition is Fremy's phyllocyanin.

Fremy and Cloez have examined the colouring matters of various flowers, and they consider that these tints may be referred to three distinct substances, one of which is of a blue or rose colour, while the other two are yellow. The blue or rose colour is produced by a compound which has been termed *cyanin*, the blue tint becoming red when exposed to the action of an acid. Red flowers have been observed to possess a juice the reaction of which is acid, whilst in blue flowers the juice is neutral. Cyanin may be obtained from the petals of the violet, or of the iris. *Xanthin* is the name given to the yellow matter which is insoluble in water: the petals of the sunflower contain xanthin in abundance. The yellow substance which is soluble in water is termed *xanthein*: it may be obtained from the yellow dahlia, and it becomes brown by the action of alkalies. Not one of these bodies, however, has been isolated in a pure condition, and there is considerable doubt whether the same colour in the flowers of different plants be due uniformly to the same materials. The yellow colouring matters, however, are clearly of a nature different from that of the blues and reds. Many red flowers become blue and green as they wither, but they never become yellow. Blue flowers are also sometimes observed to fade into red before the colour disappears, but they never become yellow; and on the other hand, a yellow flower as it withers never becomes blue.

Dyeing and Calico Printing.

(1533) *Use of Mordants.*—Of the various colouring matters used in dyeing, some, like indigo and safflower, are capable of being permanently attached to the fabric, and of fully communicating their colour to it without the intervention of any other substance, —these have hence been termed *substantive* colours; but the greater number of the colouring matters which are employed in the arts are removeable by washing. Such is the case when calico, for example, is boiled in the madder vat, or when flannel is heated with infusion of cochineal. Hence it becomes necessary, in order

to fix the colour upon the cloth, to employ various substances which possess a strong tendency to attach themselves to the fibres of the texture, and to combine chemically with the dye-stuff; they thus form the connecting link between the two. Bodies employed for this purpose are called *mordants*, and the colours which require such treatment are termed *adjective* colours. Various mordants are in use, some being better adapted to one dye, some to another. *Alumina*, in the shape of a mixture of alum and cream of tartar, is extensively employed for woollen goods and for silks; for calicoes aluminic acetate (1280), diluted till the solution has the sp. gr. 1.08, is much employed, especially for madder dyeing. It communicates to cloth impregnated with it a brown tint in the madder vat, if concentrated, and a red or pink if more dilute.

Ferric oxide is another mordant largely used; it is applied in the form of ferrous acetate, which is prepared by dissolving iron filings or nails to saturation in strong acetic acid, and the solution is then diluted till of the sp. gr. 1.05. When this mordant is used it is applied some time before the cloth is to be dyed; the cloth is afterwards hung up for several days in rooms fitted up with open lath floors and lath supports provided with hooks, from which it is suspended in folds; during this process of *ageing*, the air has free access to it, and the ferrous salt, by absorbing oxygen, is converted into a ferric salt, which is precipitated upon the cloth, in a form which is insoluble, owing to the want of acid. In this form, without any further addition, it gives a buff colour. Ferric oxide is also largely used as a mordant, both for madder and logwood. *Stannic oxide* is another valuable mordant; it is generally mixed with the colour, both being put into the bath at once. Oxide of manganese, chromic oxide, and some other metallic oxides are also applied as mordants for particular purposes.

(1534) *Dyeing*.—The process of *dyeing* generally consists in the immersion of the mordanted goods in a solution of the colouring matter, the temperature of which is gradually raised to ebullition by the injection of steam, the cloth being *wined* through the mixture, by placing it upon a revolving spindle or windlass; each portion of the cloth is thus alternately raised out of and replunged into the bath, and a uniform application of the colour to every part is insured. In woollen goods the richest colours are obtained by dyeing the yarn before it is woven, since in this form it absorbs the colouring material much more readily than after it has been subjected to the mechanical operations of weaving and dressing; but this method of proceeding is more expensive than dyeing in the piece.

The following outline of the process adopted in dyeing Turkey red, abridged from the account given by Dr. Thomson, will afford some idea of the complicated, and apparently trivial circumstances requisite to produce a good dye:—

In order to remove the weavers' dressing, the cloth is first steeped for twenty-four hours at 122° (50° C.), in a weak alkaline ley, containing 4lb. of potash to every 100lb. of cloth. It is then boiled with a solution of sodic carbonate, after which it is digested in an imperfect soap ley, composed of Gallipoli oil, sheep's dung, and a mixture of pearlash and sodic carbonate, in quantity much too small to saponify the whole of the oil. This oiling is repeated four or five times, allowing the cloth to become dry in the air between each immersion. The goods are next subjected to the action of a weak alkaline ley, in order to remove the excess of oil, and to prepare them for the operation of *galling*. Every 100lb. of cloth is then immersed in a bath containing twenty-five gallons of water, with 9lb. of nut galls, and $16\frac{1}{2}$ lb. of sumach. Having been *galled*, the cloth next undergoes the process of mordanting; for this purpose a solution of alum of sp. gr. 1.04, to which an equivalent of sodic carbonate has been added, is employed, and in this liquor the cloth is steeped for twelve hours, at a temperature of 100° (37° .8 C.). It is then dried and washed. The true process of dyeing is next performed in the madder vat, and a proportion of madder varying from 100lb. to 300lb. is used for every 100lb. of cloth. A quantity of chalk is added to the vat, and a certain proportion of bullock's blood is employed to clarify the liquid. The next operation is the *clearing*, or boiling the dyed goods with a weak solution of soap and soda, with the view of discharging the brown tint. The cloth is afterwards boiled under pressure, with a solution of stannous chloride, in order to brighten the colour; and finally it is thoroughly rinsed, and dried by exposure on the grass.

(1535) *Calico-Printing*.—It is not necessary in woven goods that the whole cloth should receive the mordant: if the latter be mixed into a paste with British gum, it may be applied to the calico in patterns, by means of suitable machinery. When cloth thus prepared, after being allowed to dry, is passed through the dye-vat, and afterwards well washed, the mordanted portions alone will receive the colour. This kind of pattern dyeing is principally practised with cotton goods, and constitutes a very extensive branch of industry, under the title of calico-printing.

The same mordant with different dyes produces different tints. Cloth mordanted with alum gives a red in a madder bath; but if immersed in a bath containing logwood, it is dyed black.

Different mordants produce different tints from the same colouring material; for example, in a madder bath, a piece of calico mordanted with iron gives a fine purple; but if it be mordanted with alum, it yields a pink or red colour; and a mixed mordant, consisting of iron and alum, in suitable proportions, gives a chocolate. If the colouring material employed in the bath consists of quercitron, cloth mordanted with alum will be dyed yellow; if mordanted with ferrous acetate, it will acquire a dark drab, and a mixed mordant of alum and iron will produce an olive.

The effects producible are susceptible of almost infinite varia-

tion, according to the method adopted. The cloth, for example, may be entirely dyed first, and the colour may afterwards be discharged in patterns. For instance, if a pattern be printed upon the dyed cloth with tartaric acid thickened with gum, and dried,—on passing it through a warm solution of chloride of lime, the chlorine will be disengaged upon the spots to which the acid was applied, and the colour will be removed at these parts of the cloth only. If the pattern discharged be required to be dyed again, the acid may be mixed with some suitable mordant—suppose it be plumbic acetate; and after washing out the solution of the chloride of lime, the cloth may be passed through another liquid, such as potassic dichromate; in this case a yellow pattern, due to the formation of plumbic chromate, would be produced. In some cases it is found to be more convenient to mordant the whole cloth in the first instance, and afterwards to discharge the mordant in patterns. Thus a piece of calico which has been mordanted by means of a mixture of alum and iron mordants may be discharged in patterns: by putting citric acid upon it, the mordant will be discharged upon those spots only; if it be then well washed and immersed in a logwood bath, it will come out dyed of a brown colour in every part except the places to which the citric acid was applied.

Occasionally with substantive colours, such as indigo, what are called *resist-pastes* are used: if, for instance, patterns be printed upon the cloth, with cupric nitrate properly thickened, and the goods thus prepared be passed through the indigo vat, the nitrate will act by oxidizing the indigo in the parts to which the salt is applied, and the dye-stuff will not soak into the cloth in its soluble form at those points: hence, the colouring matter may be readily washed away from the spots to which the resist-paste was applied, whilst it remains fixed firmly everywhere else.

A peculiar modification of the mode of fixing the colours has received the name of *steam-colour printing*. For steam colours stannic oxide is generally employed as the mordant. The stannic chloride is decomposed by an excess of potash, which dissolves the precipitated stannic oxide, and into this solution, when properly diluted, the cloth is dipped, and allowed to dry. After this it is immersed in very dilute sulphuric acid, to neutralize the potash, whilst the stannic oxide remains attached to the fibre: the colours, properly thickened, are then printed on in patterns, and the whole exposed to the action of steam. At this temperature the colour combines completely with the mordant, producing a brilliant effect.

CHAPTER IX.

PRODUCTS OF DESTRUCTIVE DISTILLATION.

(1536) (a) *Products of the Distillation of Wood and of Resins.*—

The substances which are formed during the destructive distillation of wood in closed vessels are very numerous. They vary with the nature of the wood operated on, and the temperature at which the distillation is effected. The decomposition commences slowly at a temperature of about 284° (140° C.). The volatile portion of the products includes substances which are gaseous, as well as those which are liquid or solid, whilst a considerable residue is left in the form of charcoal in the retort. Amongst the gaseous products of the distillation, the most abundant are carbonic anhydride, carbonic oxide, and hydrogen. Of the liquid products one portion is soluble in water; the other portion is insoluble, and is of an oily consistence. The soluble portion consists of acetic acid, wood spirit, methyl acetate, and acetone, accompanied by water, and by other bodies but imperfectly known. The insoluble portion which constitutes *wood tar*, is composed of a mixture of various liquids holding solid matters in solution, or in suspension: its most important constituents are several forms of hydrocarbon, such as toluol, xylol, cymol,—and other bodies, such as eupion, which have been less perfectly examined, besides a number of oxidized compounds including kreasote, picamar, and kapnomor. Amongst the solid portions are resinous matters more or less resembling colophony, and a waxy body, which has been termed paraffin; there are also many other compounds, such as naphthalin, cedriret, pittaéal, retene, thrysene, and pyroxanthin.

The products of the distillation of wood obtained at the lowest temperature are those into the composition of which oxygen enters abundantly, such, for example, as water, acetic and carbonic acids. As the temperature rises, compounds containing less oxygen are gradually formed, such as wood spirit, acetone, and kreasote; at a still more elevated temperature various hydrocarbons, such as toluol, xylol, eupion, and the different forms of paraffin, are produced, whilst as the temperature approaches to redness, pure hydrogen predominates.

In the distillation in iron cylinders of air-dried hard woods, such as oak or beech, the charcoal reaches about 25 per cent. of the weight of the wood employed, or about three-fifths of the

quantity of carbon present in the wood. The liquid portion, amounting to about 53 per cent., contains about one-fifth of the entire quantity of carbon in the wood; and the remaining portion of the distillate, consisting of uncondensed gases, carries off the remainder of the carbon. Among the liquid products acetic acid amounts to between 3 and 4 per cent. of the weight of the harder woods, naphtha to about 1 per cent., and the tar to 7.5 per cent.

Stockholm tar, so largely used in ship-building, is obtained by a rude kind of distillation of the resinous wood of the pine. A conical cavity is formed in the side of a hillock, the apex of the cone being below, and terminating in an aperture that opens into a trough which leads to a reservoir for the tar. The kiln is filled with wood, and covered over incompletely with turf; the pile is lighted at the top, and the combustion regulated by covering it in more or less completely; the wood is thus charred from above downwards, and the tar flows off at the bottom, charged with a considerable quantity of resin, and mixed with acetic acid and oil of turpentine. When heated, an impure essence of turpentine is distilled, leaving a black resinous substance, which constitutes ordinary *pitch*. The specific gravity of the ordinary wood tar of commerce is about 1.040.

In preparing pyroligneous acid, wood which contains but little resin is used. The distillation is conducted in iron cylinders, and the condensation is more complete. The tar is of a different kind, and contains a variety of products, which have been already enumerated.

(1537) *Paraffin* (C_nH_{2n+2}).—It is probable that most of the substances termed paraffin consist of a mixture of several homologous hydrocarbons, which form the higher terms of the series to which marsh gas belongs; the melting point of different bodies presenting the appearance and properties of paraffin varying between 110° and 149° ($43^\circ.3$ and 65° C.). It is, however, very difficult to determine by mere analysis of the higher terms of the series, whether their formula should be C_nH_{2n} or (C_nH_{2n+2}), which latter hypothesis their chemical properties render most probable.

The name paraffin was originally given by Reichenbach to a crystalline substance first found among the solid constituents of wood tar, and particularly in beech tar. It comes over during the last stages of the distillation, when the crude tar is rectified. Reichenbach also states that he found it in the tar of both animal and vegetable substances, as well as in that of pit-coal. A similar hydrocarbon is an abundant constituent of Rangoon

petroleum, and it is likewise obtained in considerable quantity from the products of the distillation of peat, as well as of certain forms of lignite, and of some varieties of bituminous shale. A large proportion of the solid paraffin of commerce is obtained from the distillate of the bituminiferous substance known as *Boghead Cannel* (note, p. 144).

At ordinary temperatures beechwood paraffin is a hard crystalline white substance, without either taste or odour, of sp. gr. 0·87, somewhat brittle, and resembling spermaceti both to the touch and in appearance. It fuses at $110^{\circ}\cdot7$ ($43^{\circ}\cdot8$ C.) to a colourless oily liquid, which remains transparent after solidification, and at a higher heat may be distilled unchanged.

Paraffin is an excellent insulator of electricity. It is insoluble in water. It does not dissolve camphor, naphthalin, or pitch when fused with them, but may readily be mixed with stearin, spermaceti, bees' wax, and common resin. Cold olive oil dissolves it sparingly till heated with it, but the hot oil dissolves it freely. Oil of turpentine and benzol dissolve it abundantly; so also does ether. Boiling absolute alcohol does not take up more than 3·45 per cent. of its weight, and deposits the greater part on cooling in crystalline plates. It burns with a bright smokeless flame; candles made of it burn like those made of the finest wax. The strongest sulphuric and hydrochloric acids, the alkalies, and even chlorine, unless at a high temperature, are without effect upon it; hence it received its name, *paraffin* (from *parum*, little, *affinis*, akin), but it may be slowly oxidized by treatment with fuming nitric acid, or with a mixture of potassic dichromate and sulphuric acid.

In order to isolate the paraffin from wood tar, the heaviest portion of the tar oils is gradually mixed with from $\frac{1}{4}$ to $\frac{1}{2}$ its weight of oil of vitriol. The temperature rises rapidly, and a black liquid is formed, which emits sulphurous acid. The temperature must be raised to 212° , if it does not reach that point spontaneously; the mixture must then be maintained at rest in a place the temperature of which is not allowed to fall below 122° (50° C.). A colourless liquid rises to the surface; it must be allowed to cool, when it will become solid. If now it be washed and submitted to pressure, a liquid oil will be removed, and the paraffin may be purified by boiling with a solution of caustic soda, from which it separates on standing, and solidifies on cooling.

The bodies termed *cerene* and *melene*, which Brodie obtained during the distillation of wax (1226), are very similar to this substance.

Paraffin Oil.—Among the products of the distillation of Boghead Cannel, and of certain other bituminous shales, is a large quantity of an oily matter, the proportion of which is greater, the lower the temperature at which the distillation is effected. The oil is almost entirely free from oxygen. When rectified, a volatile portion may be separated from it, which, according to G. Williams, contains several hydrocarbons of the form (C_nH_{2n+2}) , including C_8H_{18} and $C_{10}H_{22}$. For practical purposes the less volatile products may be separated into three portions, one of which remains liquid at very low temperatures: the sp. gr. of this is about 0.820, and it boils at about 419° (215° C.) or upwards: it is largely used in lamps as a source of light as *paraffin oil*, and also under a variety of other names. The second portion, which is distilled at a higher temperature, deposits crystals of a solid hydrocarbon (one of the forms of paraffin), when exposed to a great reduction of temperature; and the last portions of the distillate are semi-solid at ordinary temperatures. The less volatile liquid portion of the oil still retains solid paraffin in solution. This oil is frequently used for the purpose of lubricating machinery, to which use it is well adapted, since it does not become oxidized or thickened by exposure to the air, and it evaporates but slowly.

(1538) *Pyrene and Chrysene.*—In the latter stages of the distillation of fatty and of resinous bodies, and in that of coal tar, a yellow powder is sublimed, which contains two substances termed by Laurent, pyrene and chrysene. *Pyrene* ($C_{16}H_{12}$), so called from $\pi\upsilon\rho$, fire, to indicate its origin from the action of heat, is soluble in hot ether, and may be separated from chrysene by means of this solvent, which at a low temperature deposits it in microscopic rhomboidal plates. It is insoluble in water, and is destitute of odour; it fuses at about $350^\circ.6$ (177° C.), and may be distilled unaltered. *Chrysene* ($C_{18}H_{14}$)[?] is a crystalline substance of a beautiful yellow colour, whence its name, from $\chi\rho\upsilon\sigma\epsilon\omicron\varsigma$, golden. It is inodorous, insoluble in water and alcohol, and only slightly soluble in ether: boiling oil of turpentine dissolves it more readily than ether. It fuses at about 450° ($232^\circ.2$ C.), and is partially decomposed when distilled.

(1539) *Pyroxanthin* ($C_{21}H_{18}O_4$)[?] Gregory); *Fusing pt.* $291^\circ.2$ (144° C.).—This substance was discovered by Seanlan among the products of the action of caustic potash upon erude wood-spirit. When erude wood-spirit is rectified with lime, a dark brown residue remains in the retort, and this, when treated with hydrochloric acid leaves a brown insoluble matter, consisting of pyroxanthin and a resinous substance. If this residue be boiled in alcohol it is in great measure dissolved, and as the liquid cools, crystals of pyroxanthin are deposited in long yellow needles; hence its name—from $\pi\upsilon\rho$, fire, $\xi\alpha\rho\theta\omicron\varsigma$, yellow. It is insoluble in water and in alkaline solutions, but soluble in hot alcohol, ether, and acetic acid. It may be sublimed in a current of air at 273° (134° C.). If it be sublimed in a closed tube it undergoes partial decomposition. It is soluble in sulphuric acid with a deep bluish red colour, and in hydrochloric acid with a fine purple, which soon passes into dark brown. Pyroxanthin appears to be the result of the action of potash upon one of the tar oils, which Voelekel has hence termed *pyroxanthogen*.

(1540) *Eupion*.—When the tar of hard woods is submitted to distillation, an acid liquid comes over, upon the surface of which a light yellowish oil floats; and on continuing the distillation a volatile oil, heavier than water, passes over. The most volatile portion of the lighter oil consists principally of a hydrocarbon, to which Reichenbach gave the name of *eupion* (from εὔς, good, λίον, fat); *Sp. gr.* 0·740 at 68° (20° C.). He did not submit it to ultimate analysis, and it is probable that more than one body has been described as eupion (1207). Wood-tar eupion boils at 336°·2 (169° C.). It burns with a brilliant luminous flame, is soluble in hot absolute alcohol in all proportions, but at ordinary temperatures the alcohol will not retain more than a third of its bulk of eupion. Oil of turpentine and the fixed oils also mix with it in all proportions, and so does carbon disulphide. Eupion readily dissolves camphor, naphthalin, paraffin, and spermaceti, and caoutchouc also at an elevated temperature.

The less volatile portions of the lighter tar oil contain wood-spirit, acetone, and the hydrocarbons benzol, toluol, and xylol; these hydrocarbons may be removed by agitation with sulphuric acid, with which they form colligated acids. The heavier oil, which is of a yellow colour, also contains small quantities of the foregoing compounds: it is partially soluble in solution of caustic potash, and amongst the constituents of the portion which thus combines with the alkali are kreasote and kapnomor.

(1541) *Kreasote* ($C_{12}H_{16}O_2$? Gorup-Besanez; or $C_8H_{10}O_2$, Hugo Müller); *Sp. gr.* 1·057; *Boil. pt.* 398° (203°·3 C.).—Considerable doubt exists as to the exact composition of this interesting substance. Much of the kreasote of commerce is simply carbolic (phenic) acid; but the true kreasote of Reichenbach (*Pogg. Ann.* xxviii. 125, xxix. 62) is quite a distinct body. It is to this latter substance that wood-smoke owes its characteristic odour and antiseptic qualities. The name kreasote is derived from κρέας, flesh, σωτήρ, preserver, in reference to this antiseptic power.

Preparation.—The process of purifying kreasote is tedious. The heavier portions of the oil obtained from wood tar, after being washed with a solution of sodic carbonate, are submitted to distillation, by which they are further separated into a portion lighter than water, and into another which sinks in this liquid. This heavier oil is then treated with a solution of caustic potash of *sp. gr.* 1·12. By this means the kreasote is dissolved, and the greater part of the hydrocarbons which accompanied it are separated. The alkaline solution, after being decanted from the hydrocarbons,

is boiled gently in an open basin, with a view to oxidize a portion of the impurities. When cold, dilute sulphuric acid in slight excess is added to the liquid, by which means the kreasote is set at liberty. It is, however, far from being pure, and must be redistilled with water, again treated with concentrated solution of caustic potash, then with dilute sulphuric acid, and then redistilled with water. This series of operations is to be repeated so long as any separation of hydrocarbons is effected. Lastly, the kreasote must be digested upon calcic chloride, and distilled by itself. It may be regarded as pure if its boiling point be constant at 398° , and if it does not become brown when kept.*

Properties.—Kreasote, when pure, is a colourless oily liquid, of high refractive power. It is not easily inflamed, but when kindled it burns with a smoky flame. Its taste is burning, and its odour extremely pungent and peculiar; if swallowed in doses of more than a few drops it acts as a poison. Kreasote is sparingly soluble in water, to which it communicates its peculiar odour and pungent taste. It is soluble freely in acetic acid, alcohol, and ether, as well as in benzol and in carbon disulphide. It combines with potash, and forms a crystalline compound with it; solutions of the fixed alkalis and of ammonia also dissolve it. Kreasote produces the immediate coagulation of albumin. It is the most powerful antiseptic known. Meat that has been plunged into a solution containing 1 per cent. of kreasote gradually becomes dry and hard on exposure to the air, and acquires the flavour of smoked meat, but does not become putrid. A considerable portion of kreasote (from 1 to $1\frac{1}{2}$ per cent.) is held in solution in the crude pyroligneous acid obtained during the destructive distillation of wood; and on saturating this acid at 167° (75° C.) with effloresced sodic sulphate, an oily matter which contains a large proportion of kreasote is separated. Crude pyroligneous acid, on account of the kreasote which it contains, is frequently employed for preserving hams and salted provisions, to which it communicates the same flavour as if they had been exposed to wood-smoke.

Kreasote when largely diluted is sometimes given internally in order to check obstinate vomiting. If applied in a concentrated form to the exposed pulp of a carious tooth, it frequently affords instant relief in cases of acute toothache. It is also a

* By long boiling with a solution of caustic potash the kreasote appears to undergo oxidation, a portion of its hydrogen being removed, whilst the quantity of oxygen is increased (Gorup-Besanez).

valuable application, in a very diluted form, in some cases of fœtid ulcers, and in many cutaneous affections. If applied to the skin in a concentrated state it produces a white spot, the skin becomes disorganized, and peels off without any attendant inflammation. Kreasote dissolves many organic bodies, such as camphor, the fatty and volatile oils, and many of the resins.

H. Müller's researches seem to show that kreasote may be *methyloxykresylic* acid, so that its formula may be $\text{HC}_7(\text{CH}_3)\text{H}_6\text{O}_2$, or $\text{C}_8\text{H}_{10}\text{O}_2$. Phenic acid, when decomposed by a mixture of potassic chlorate and hydrochloric acid, yields perchloroquinone or chloranil (1337). Kreasote, when treated in a similar manner, furnishes a resinous mass, which, after digestion with cold alcohol, leaves a compound resembling chloranil in appearance and properties ($\text{C}_8\text{H}_4\text{Cl}_4\text{O}_2$; Gerhardt), and homologous with it, but containing 2CH_2 more than chloranil. This new body crystallizes in brilliant, golden-yellow plates; it is insoluble in water, sparingly soluble in cold alcohol, and freely soluble in ether; it may be sublimed at about $359^{\circ}\cdot6$ (182° C.).

(1542) *Kapnomor* ($\text{C}_{10}\text{H}_{11}\text{O}^?$ Voelckel; from *καπνός*, smoke, and *μοῖρα*, a part); *Sp. gr.* 0.995.—This is a colourless oil of peculiar odour, which boils at about $359^{\circ}\cdot6$ (182° C.). It is insoluble in water and in a solution of potash, but it is partially soluble in an alkaline solution of kreasote. It is soluble in sulphuric acid with a purplish red colour, and forms with it a colligated acid: nitric acid converts it into oxalic and carbazotic acids, and another crystallized body which has not been examined. *Kapnomor* is obtained by distilling the crude solution of kreasote in caustic potash with water: it passes over with the vapour of water.

Reichenbach has described various other compounds from tar, under the names of *pittacal*, from *πίττα*, pitch, *καλός*, beautiful, a solid compound of a deep blue colour; of *picamar*, an oily body of *sp. gr.* 1.10, which has a very bitter taste, whence its name (*pice, amarum*), it forms a crystalline compound with potash; and of *cedriret*, which crystallizes in a network of orange-red needles from a solution of ferric sulphate, and is dissolved with a blue colour in oil of vitriol; its name is derived from *cedrium*, an old term for the acid liquor of tar, and *rete*, a net: the properties of all these bodies have, however, been but incompletely examined.

(b) *Distillation of Peat.*

(1543) The distillation of peat has of late years been attempted on a considerable scale, and the results obtained are of sufficient interest to justify a brief notice in this place.

Attempts to effect the distillation of peat in closed cylinders in the manner practised for wood and coal, have failed in an economical point of view. The peat charcoal thus obtained is too bulky and too brittle to be commonly used with advantage as a fuel, whilst the percentage of ash which it yields is often extremely large. For some years, however, a process was in operation at Athy, near Kildare, in which the distillation of peat was carried on by the heat evolved during its own combustion. This operation was effected in furnaces, the con-

struction of which resembles that of an ordinary blast-furnace. The furnace when charged holds from 20 to 25 tons of peat. The head of the furnace is partially closed by an iron plate, with a circular opening in the centre, which can be closed by a conical valve. Above this valve is a hopper, furnished with two hinged lids, grooved, so as to form an air-tight cover when closed and fitted with lute. A charge having been introduced into the hopper, the conical valve is lowered, and the fuel falls into the furnace without allowing the gaseous products to escape. The valve is then closed by means of a counterpoised lever, and a fresh charge of peat is introduced into the hopper, and subsequently admitted to the furnace when necessary. The gases pass off from the upper part of the surface through the pipes, which conduct them to the hydraulic main, where the tar is deposited. The gases are then subjected to a series of powerful condensers constructed upon a principle similar to those employed for coal gas (Fig. 391), and the uncondensed products pass first through scrubbers and then into pipes, whence they are distributed to the various stills and boilers employed in purifying the liquid portions received by the condensers. By this arrangement the distillation is in reality effected in a current of heated steam, since during the combustion of the peat from 35 to 50 per cent. of water is given off, and this prevents the temperature of the escaping gases from rising above 392° (200° C.). The pressure of the blast used is about 1 lb. upon the square inch.

The crude products of the distillation consist of tar, above which a watery liquid condenses, whilst aqueous vapour and combustible gases escape mixed with nitrogen from the air which passes through the furnace. The ashes of the peat melt and form a slag, which runs off. The tar in its subsequent purification is not subjected to the direct action of the fire, but is submitted to distillation in cast-iron stills, into which superheated steam is injected, as in the distillation of fats. About one-fourth (A) of the distillate is liquid, that which follows (B) is nearly solid, and that which comes over at the end of the operation (C) becomes quite hard. The residue in the retort amounts to about 5 per cent. of the quantity of tar, and forms a shining black porous mass. The more solid portions (B) of the distillate contain the paraffin. In order to extract it the mass is heated in a tank by means of a jet of steam with a mixture of potassic dichromate and sulphuric acid, diluted with an equal bulk of water, which causes the separation of a considerable quantity of a resinoid matter. The partially purified product which rises to the surface is then drawn off, and is redistilled by the aid of steam heat, and the distilled product is allowed to cool and solidify in shallow iron trays; after which it is subjected to pressure in canvas: the solid residue constitutes crude paraffin, which is purified by a repetition of the treatment with the dichromate and sulphuric acid, and redistillation.

The liquid portion (A) of the tar, after treatment with oil of vitriol, is redistilled, and furnishes an oil employed for lubricating machinery, under the name of *paraffin oil*.

The aqueous portion of the distillate contains wood-spirit, acetic acid, and ammonia; but the expense of concentrating and purifying these different bodies has hitherto been too great to allow of their profitable extraction from this liquor.

(c) *Products of the Distillation of Pit-coal.*

(1544) The products of the distillation of pit-coal are still more numerous than those of wood; and they are invested with a special interest, owing to their intimate connexion with the manufacture of coal gas.

When a bituminous coal is burned in the open air, the prin-

cipal products of the combustion are carbonic anhydride and water, with small quantities of ammonia and sulphurous anhydride, derived from the azotised constituents, and the pyrites contained in the coal; a certain portion of carbon in a finely-divided form escapes combustion, and constitutes the soot or visible smoke of a coal fire. But when the decomposition of the coal is effected in vessels from which air is excluded, the products are much more numerous and complicated. A large amount of volatile matter is expelled, partly in the form of uncondensable gases, and partly in the form of vapours, which, when reduced to the ordinary temperature of the air, constitute liquids or solids; whilst a large proportion of the combustible material remains behind in the retort, and forms a light porous variety of coke, known as *gas coke*.

Amongst the gaseous products the most important are marsh gas, olefiant gas, acetylene, hydrogen, carbonic oxide, carbonic anhydride, sulphuretted hydrogen, and ammonia. The liquid portions contain water, and various forms of hydrocarbon, such as benzol, toluol, and cumol, which constitute the chief ingredients of the liquid termed *coal naphtha*; besides which there is a large quantity of a dark viscous matter, known as *coal tar*, the nature of which will be more particularly considered hereafter (1546).

When coal gas is to be employed for the purpose of illuminating the interior of a dwelling-house, it is not sufficient to condense the tar, the water, and other liquid products, but it becomes necessary to remove a number of gaseous compounds, before it can be burned with comfort, or even with safety to the health of the inmates. The impurities of which it is of most importance to deprive it are sulphuretted hydrogen and ammonia; in addition to which carbonic anhydride and a small quantity of cyanogen are always removed during the purification. This purification is effected by submitting the gas to the action of certain chemical agents, such as slaked lime, hydrated ferric oxide, and dilute sulphuric acid.

The illuminating power of coal gas is due chiefly to light carburetted hydrogen, olefiant gas, and to a small quantity of the vapour of naphtha and other volatile liquefiable compounds of carbon and hydrogen. The hydrogen and carbonic oxide are not only destitute themselves of any illuminating power, but they reduce the light of the gas with which they are mixed: there is, however, no means of getting rid of these useless gases; care should therefore be taken to produce as small an amount of them as possible during the process of carbonization.

(1545) *Manufacture and Purification of Coal Gas*.—The earliest attempts at illumination by means of coal gas were made by Mr.

Murdoch, during his residence in Cornwall, about the year 1792, and he subsequently further carried out his plan, so as to illuminate a large portion of the manufactory of Boulton and Watt at Soho, at the celebration of the peace of Amiens in 1802. Ten years afterwards the Chartered Gas Company, which made the first great experiment of lighting the streets by gas, was incorporated; and from that day to the present the employment of gas as a convenient and economical means of illumination has been steadily increasing. At the present time, upwards of a million tons of coal are converted into gas annually in London alone; in addition to which every large manufacturing town, and many of the smaller towns of Great Britain, are lighted by gas, and the use of gas is general in the principal cities of the Continent.

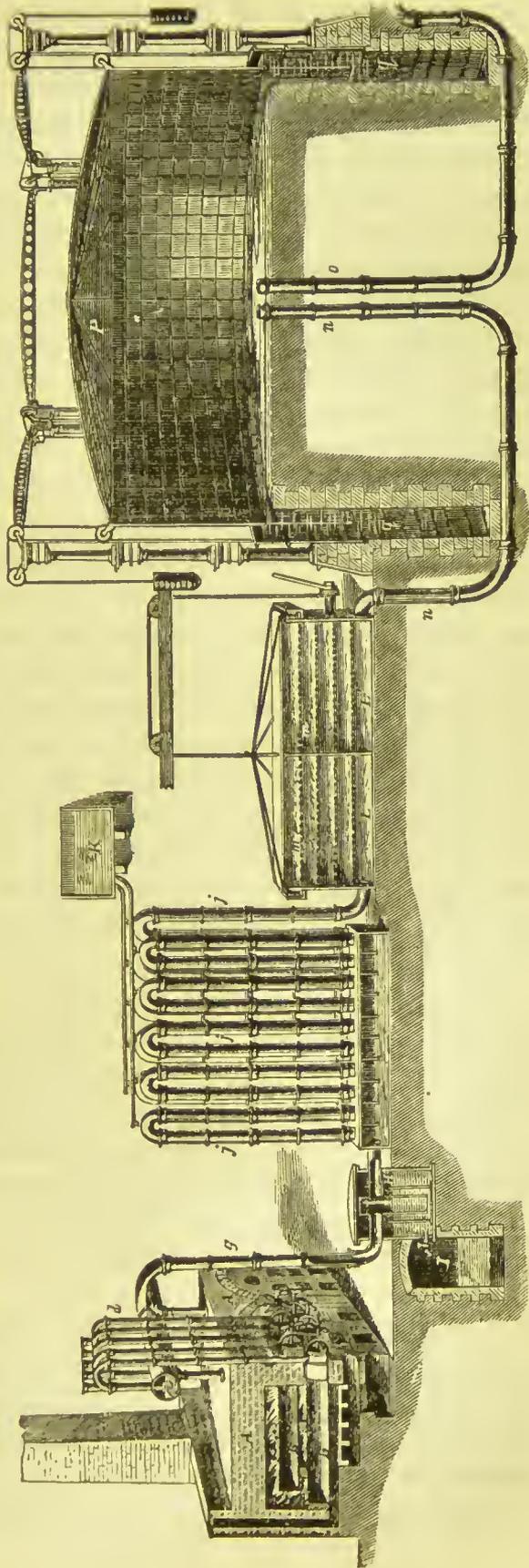
The proportion in which the different products of the distillation of coal are obtained, varies greatly, according to the kind of coal employed, and the temperature at which the distillation is conducted. The coal best suited to the manufacture of gas for illuminating purposes is of the variety known as bituminous (IIII). Anthracite is unfit for this use. The kind of coal employed in London for gas-making is principally that of the Durham coal field, or *Newcastle* coal, though it is not well adapted to the purpose, as it yields a gas of low illuminating power. A ton of good coal of this description yields on an average in London about 9250 cubic feet of gas of sp. gr. 0.410, and furnishes nearly a chaldron of coke weighing about 13 cwt. In coking, a quantity of fuel is required varying from 20 to 35 per cent. of the weight of the coal to be coked, according to the judgment shown in constructing the furnace. The Scotch coals furnish a gas of much higher illuminating power than that of the Newcastle coal, and of greater specific gravity, owing to the presence of a larger proportion of the denser hydrocarbons, but the volume of gas produced per ton is a little smaller, and the coke produced is of an inferior quality.

Fig. 391 gives a general view of the arrangement of the apparatus required in the manufacture and purification of coal gas; and the following is an outline of the process adopted:—

Pit-coal is heated in hollow flattened cylinders of iron or clay, B B, set in stacks of three or five, arranged in long brick furnaces, A A. The mouths, *c c*, of these cylinders or retorts project from the brickwork, and are fitted with moveable lids, which can be closed air-tight by means of clay luting. From the upper side of the projecting extremity of each retort, a tube, *d*, for the conveyance of the gas, passes vertically upwards for a few feet,

then forming an arch, dips downwards, terminating at *e*, beneath the level of the liquid contained in a long and wide pipe, *f*, called the *hydraulic main*, which passes horizontally along the front of the range of furnaces. This pipe is kept constantly half full of tar and condensed moisture. By this means the opening into each retort is effectually closed by a water valve, which permits a charge to be drawn and renewed in any one or more retorts, without interfering with the operation of those which are still in action. The tar, as it accumulates in the hydraulic main, flows over into the *tar wells*, *h*, *i*. In about four hours after charging the retort, the coal will have given off nearly all its gas, and a fresh charge of coal will be required; but it is not an unusual practice to charge the retorts only at intervals of six hours, since the gas, though poorer in quality, is increased in quantity, and the coke is improved by longer heating. When a charge is to be drawn, the mouth of the retort is opened, and the coke raked into

FIG. 391.



a large iron box, in which it is extinguished by pouring water over it. A fresh supply of coal is then introduced by means of a long scoop, so that the whole of the required quantity of coal is placed at once upon the floor of the retort, which is at a bright red heat. The door, which has been prepared with fresh luting upon its edges, is instantly replaced, and the distillation proceeded with. In large gas works the retorts are so arranged that a fresh set shall require charging every hour, in order that the gas which is produced shall at all times be nearly uniform in quality.*

Having deposited in the hydraulic main most of the tar and some water, containing in solution a good deal of ammoniac carbonate and sulphhydric, the gases pass next through the pipe, *g*, to the *refrigerators* or *condensers*, *j j*, a series of serpentine or contorted tubes; these are kept cool by the extent of surface which they expose to the air, and their temperature, when necessary, may be reduced still further, by allowing cold water from the cistern, *κ*, to flow over their exterior: here most of the remaining tar and aqueous vapour become separated. From the condenser the gas passes to the lime *purifiers* *L L'*, which consist of cast-iron vessels containing a number of horizontal perforated shelves, *m m*, arranged one above another; upon each of these shelves dry slaked lime is placed, to the depth of about five inches. The gas enters at the bottom of the purifiers, and rises on one side through each layer of lime in succession, descending on the other side of the purifier till it makes its exit at *n*. Sometimes the lime is made into a thin cream by admixture with water, and the gas is caused to stream in bubbles through the mixture, but

* The gas first given off is the best, and also the largest in quantity, the coal not having had time to rise to the full temperature of the retort. If the charge be exposed to heat for five hours, much of the gas in the last hour and a half consists of hydrogen and carbonic oxide, the coal having become thoroughly red hot throughout. The following details will illustrate these points. Two bushels of cannel coal, or the usual charge of a moderately-sized retort, were carbonized at a full cherry-red heat, and the quantity of gas produced was as follows:—

| | Cubic Feet. | Sp. Gr. |
|-----------------------------|---------------|---------|
| In the first hour | 345 | 0.677 |
| 2nd | 203 | 0.419 |
| 3rd | 118 | 0.400 |
| 4th | 54 | 0.322 |
| 5th | 20 | |

The gas amounted in all to 740 cubic feet; but it will be observed that the quantity of gas per hour, as well as the specific gravity, continued to diminish as the experiment proceeded. This was due to the diminution in quantity of the vapour of the heavy hydrocarbons, and the increase in the proportion of free hydrogen.

generally the lime is employed in the form of a slightly damp powder. In these purifiers the gas loses carbonic acid, sulphuretted hydrogen, sulphocyanogen, cyanogen, and traces of naphthalin which are still suspended in it; finally, it is caused to pass in bubbles through dilute sulphuric acid, with the view of removing the last portions of ammonia; but this part of the apparatus is not represented in the figure.

In most works the process of washing with acid is now superseded by the use of an apparatus termed a *scrubber*, consisting of a tower, the interior of which is filled with small coke resting upon perforated shelves; through this mass of porous material a constant supply of fresh water is maintained, and by this arrangement the gas, which enters at the bottom of the tower, is exposed to a large absorbent surface, and the ammonia is effectually removed. This washing, however, somewhat diminishes the illuminating power of the gas, by removing a portion of the vapour of some of the more condensable hydrocarbons which are held in suspension.

A mixture of hydrated ferric oxide and moistened sawdust is now generally substituted for slaked lime in the purifier (757); this mixture removes the sulphuretted hydrogen and cyanogen, but it has no effect on the carbonic acid, and the gas should therefore be made subsequently to pass through a lime purifier. Various other substances are also occasionally employed with a view of effectually arresting the sulphuretted and ammoniacal impurities. The gas, after it has been thus purified, is stored up for use in immense reservoirs or gasometers of metal, *p*, each consisting of a large bell of sheet iron, inverted in a brickwork tank, *q*, filled with water, in which the bell rises and falls. The bell is in some cases nearly counterpoised by weights attached to chains, which pass over pulleys suitably supported, or as is now more usual, is so constructed as to rise and fall by the admission or escape of the gas without the necessity for such counterpoises. The pressure, which is not ordinarily allowed to exceed that of a column of water two or three inches in height, drives the gas along the pipe or *main*, *o o*, by which it is distributed to the various consumers.

In the foregoing process one of the points of greatest importance is the due regulation of the temperature during the distillation. The retorts should be heated to a bright cherry-red. If they be insufficiently heated, the products contain a large quantity of the vapours of condensable hydrocarbons, which collect in the gasometers and the distributing pipes, and occasion

much loss and inconvenience; whilst if the temperature be too high, or if the gas after its production be allowed to remain long in contact with the highly heated surface of the retort, it undergoes partial decomposition; a portion of its carbon is deposited, in the form of a dense layer upon the interior of the retort, which it gradually chokes up, and at the same time the illuminating power of the gas is proportionately diminished by the loss of this carbon.

In addition to this inconvenience, carbon disulphide is apt to be formed in small quantity (the London gas contains from 7 to 10 grains in 100 cubic feet; Hofmann) if the distillation be conducted at too high a temperature. Dr. Angus Smith uses a solution of plumbic oxide in caustic soda diffused through sawdust for the purpose of absorbing the disulphide, and the plan is said to succeed on the large scale; and it has lately been proposed to use the ammoniacal liquor in a scrubber to absorb this impurity. When gas which contains carbon disulphide is burned, it gives rise to the production of a minute quantity of sulphuric acid, and this gradually accumulates on the furniture of the building, on the bindings of books, &c., and slowly corrodes and otherwise injures them.

(1546) *Compounds present in Coal-tar.*—Coal-tar varies in density from 1.120 to 1.150; the lightest tar containing the largest proportion of liquid oils. Of the substances contained in coal-tar some are basic, and some acid, but the principal portion consists of neutral or indifferent bodies.

The bases include ammonia, aniline, picoline, quinoline, and pyridine (1362 *et seq.*). Among the acids, the acetic is present in small amount, but the most important is phenic acid, the carbolic acid of Runge. This chemist also mentions two other acids, termed from their colour, which is respectively red and brown, *rosolic* ($C_{28}H_{18}O_4$) and *brunolic* acids; they require further examination.

The neutral substances contain several hydrocarbons, including benzol, toluol, cumol, and cymol, which are among the liquid constituents; whilst naphthalin, anthraene, anthraene hydride, chrysene, fluorene, retene, acenaphthene, and benzerythrene are among those which are solid at ordinary temperatures.

The distillation of coal-tar is conducted on an extensive scale, as a separate branch of trade. The operation is performed in large iron retorts upon quantities of several hundred gallons at a time. The first portions that are volatilized consist chiefly of ammonia, accompanied by some permanent gases which have been dissolved by the liquid hydrocarbons. As the temperature rises,

water charged with various ammoniacal salts comes over, and a fœtid brown oil gradually collects upon the surface of the water in the receiver. As the distillation proceeds, water ceases to pass over, and the quantity of this oil increases, its density continuing to augment until its specific gravity exceeds that of water. The light oil amounts generally to from 5 to 10 per cent. of the tar. This distillate may be freed from compounds which absorb oxygen rapidly and cause the distilled oil to become brown on keeping, by agitation with a small proportion of oil of vitriol, by which these oxidizable products are converted into a tenacious tarry mass denser than the rest of the oil, in which it is no longer soluble. The purified supernatant oil when again rectified constitutes *coal naphtha*. By continuing the distillation of the coal-tar, a yellow, heavy fœtid oil, technically known as *dead oil*, is obtained, the amount of which seldom exceeds 30 per cent. of the quantity of tar employed. In the latter stages of the operation, naphthalin is abundant in the distillate, and the oil becomes semi-solid as it cools. The black residue in the retort solidifies on cooling, and forms *pitch*, which is employed in the preparation of asphalt, and as a colouring ingredient in the production of a coarse black varnish, used for protecting iron-work from rust. If it be desired to carry the distillation further, a much higher temperature is required, when the pitch in its turn undergoes decomposition, and yields a product which, when cool, has the consistence of butter; it consists chiefly of anthracene, with various other hydrocarbons, which Berthelot has named *acenaphthene*, $C_{12}H_{10}$, *fluorene*, and *acenaphthene hydride*, $C_{12}H_{12}$. At a still more advanced stage of the process, the distillate acquires a yellow colour, and assumes the appearance of a resin; and as the temperature of the retort approaches a red heat the vapours produced become condensed in the form of a bright orange-coloured powder which is free from odour, and when pressed, agglutinates into a viscous mass. This substance consists chiefly of chrysenes, $C_{18}H_{12}$, with *benzerythrene*, and *retene* $C_{13}H_{18}$ (*Ann. de Chimie*, IV. xii. 141), the pyrene (?) of Laurent. The residue in the retort, after it has ceased to give off volatile matters, forms a hard porous coke which is difficult of combustion.

The heavy coal-oil, or dead oil, is seldom submitted to further purification. It contains phenic (carbolic) and kresylic acids, aniline, quinoline, and a variety of other bodies, consisting chiefly of hydrocarbons, which boil between 392° and 572° (200° and 300° C.), and which hold a considerable quantity of anthracene in solution. Heavy coal naphtha or dead oil is remarkable for its antiseptic qualities, and is employed for the preservation of timber

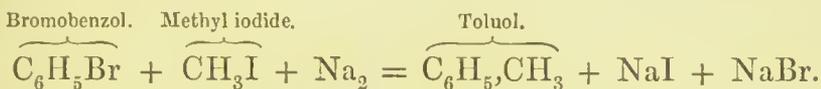
for railway sleepers, &c. It is also consumed as a fuel in common lamps, but it is chiefly used for burning into lampblack.

The light naphtha obtained in the foregoing process is submitted to rectification, by which it is separated into a more volatile portion, and an additional quantity of the heavy oil. It is usual to agitate the rectified portion with oil of vitriol; the acid thus acquires a deep red colour, and removes a large portion of the products which communicate to the crude distillate its offensive odour. The mixture on standing separates into two layers, the lighter of which is the purified naphtha. When this liquid is again submitted to distillation, the oil which comes over is free from naphthalin, and does not become coloured by exposure to the air. Coal naphtha thus purified and sold as 'highly rectified,' varies in specific gravity from about 0.860 to 0.900. It consists of a mixture of oils, which boil below 392° (200° C.), and may be separated from each other by distillation.

Mansfield (*Q. J. Chem. Soc.*, i. 252) made a careful examination of the constituents of this naphtha. In his experiments he employed the crude light oil, before it had been treated with oil of vitriol; and having freed it from basic and acid bodies by agitating it successively with dilute sulphuric acid and a weak solution of potash, he submitted it to a systematic process of fractionated distillation. He states that at least five distinct liquids may be separated from light coal naphtha. These liquids are:—1. An oil of a peculiar alliaceous odour, the boiling point of which lies between 140° and 158° (60° and 70° C.); this oil is present in small quantity, and has not been perfectly examined: it probably contains a mixture of alcohol radicles or of hydrocarbons of the marsh gas series. 2. An oil which boils at 176° (80° C.), consisting of benzol, C_6H_6 . 3. An oil which boils at about $235^{\circ}\cdot4$ (113° C.), and consists mainly of toluol, C_7H_8 . 4. An oil which boils between $287^{\circ}\cdot6$ and 293° (142° and 145° C.), presenting the characters of cumol, C_9H_{12} . And 5. An oil which possesses the odour and other properties of cymol, $C_{10}H_{14}$, boiling at from 338° to $341^{\circ}\cdot6$ (170° and 172° C.). The oil No. 5 is more abundant in those portions of coal naphtha which are heavier than water. It is however probable that No. 4 was mainly composed of xylol, which boils at $282^{\circ}\cdot2$ (139° C.), and No. 5 consisted only of impure cumol, a liquid which when pure boils at 329° (165° C.).

(1547) *Homologous Hydrocarbons from Coal Tar.*—Benzol, toluol, xylol, cumol, and cymol belong to a remarkably stable series of homologous hydrocarbons constituting the *aromatic group*. Fittig has succeeded in proving by synthetic experiments that the

several terms of the series which follow benzol are methylated derivatives of benzol, toluol being methyl-benzol, xylool dimethyl-benzol, coal-tar cumol trimethyl-benzol, and cymol methyl-propyl-benzol. The experimental mode of demonstrating these facts consists in taking a mixture of the bromide or iodide of the two radicles in equivalent proportions, and decomposing them by means of sodium, when the two radicles unite to form the hydrocarbon sought; for instance:—



Ethyl-benzol, which was obtained in a similar way, was found to be different from xylool, though isomeric with it. In a similar way Fittig has shown that *diphenyl* ($\text{C}_{12}\text{H}_{10}$), or *phenyl-benzol* ($\text{C}_6\text{H}_5\text{C}_6\text{H}_5$) may be obtained in crystalline fusible needles (*note*, p. 486).

It would be easy in connexion with these hydrocarbons, to form a table, of which the following is a fragment, constructed on the same principle as that given at pp. 38 and 39. The compounds of the various series of which it consists are at present undergoing careful study, and a recent digest of the subject will be found in Kekulé's *Organic Chemistry*, vol. ii. 493-744.

Homologous Derivatives of Coal-tar Hydrocarbons.

| Hydride. | Chloride. | Nitro-compound. | Dinitro-compound. | Amide base. | Acid. |
|---|---|---|---|---|--|
| $\text{C}_n\text{H}_{2n-7}\text{H}$ | $\text{C}_n\text{H}_{2n-7}\text{Cl}$ | $\text{C}_n\text{H}_{2n-7}\text{NO}_2$ | $\text{C}_n\text{H}_{2n-6}(\text{NO}_2)_2$ | $\text{C}_n\text{H}_{2n-7}\text{H}_2\text{N}$ | $\text{HC}_n\text{H}_{2n-7}\text{O}$ |
| Benzol. $\text{C}_6\text{H}_5\text{H}$ | Chlorobenzol. $\text{C}_6\text{H}_5\text{Cl}$ | Nitrobenzol. $\text{C}_6\text{H}_5\text{NO}_2$ | Dinitrobenzol. $\text{C}_6\text{H}_4(\text{NO}_2)_2$ | Aniline. $\text{C}_6\text{H}_5\text{H}_2\text{N}$ | Phenol. $\text{HC}_6\text{H}_5\text{O}$ |
| Toluol. $\text{C}_6\text{H}_5\text{CH}_3$ | Chlorotoluol. $\text{C}_7\text{H}_7\text{Cl}$ | Nitro-toluol. $\text{C}_7\text{H}_7\text{NO}_2$ | Dinitro-toluol. $\text{C}_7\text{H}_6(\text{NO}_2)_2$ | Toluidine. $\text{C}_7\text{H}_7\text{H}_2\text{N}$ | Kresol. $\text{HC}_7\text{H}_7\text{O}$ |
| Xylool. $\text{C}_8\text{H}_9(\text{CH}_3)_2$ | Chloroxylool. $\text{C}_8\text{H}_9\text{Cl}$ | Nitro-xylool. $\text{C}_8\text{H}_9\text{NO}_2$ | Dinitro-xylool. $\text{C}_8\text{H}_8(\text{NO}_2)_2$ | Xylidine. $\text{C}_8\text{H}_9\text{H}_2\text{N}$ | Phlorol. $\text{HC}_8\text{H}_9\text{O}$ |
| Coal tar Cumol. $\text{C}_9\text{H}_{11}(\text{CH}_3)_3$ | Chlorocumol. $\text{C}_9\text{H}_{11}\text{Cl}$ | Nitro-cumol. $\text{C}_9\text{H}_{11}\text{NO}_2$ | Dinitro-cumol. $\text{C}_9\text{H}_{10}(\text{NO}_2)_2$ | Cumidine. $\text{C}_9\text{H}_{11}\text{H}_2\text{N}$ | |
| Cymol. $\text{H}_4(\text{CH}_3)(\text{C}_3\text{H}_7)$ | Chlorocymol. $\text{C}_{10}\text{H}_{13}\text{Cl}$ | Nitro-cymol. $\text{C}_{10}\text{H}_{13}\text{NO}_2$ | Dinitro-cymol. $\text{C}_{10}\text{H}_{12}(\text{NO}_2)_2$ | Cymidine. $\text{C}_{10}\text{H}_{13}\text{H}_2\text{N}$ | Thymol. $\text{HC}_{10}\text{H}_{13}\text{O}$ |

Several isomerides of certain of the hydrocarbons enumerated in the first column of the foregoing table are known (p. 694). These isomerides yield products on gradual oxidation with a mixture of potassic dichromate and sulphuric acid, which differ

with the variation in constitution of the component hydrocarbons (1549).

Benzol is a compound of considerable interest and importance. It belongs to a group known as the *phenic* series. We shall, therefore, describe its properties, and those of some of its derivatives, including carbonic acid, and shall afterwards proceed to notice briefly some of the other hydrocarbons, among which naphthalin is the most remarkable.

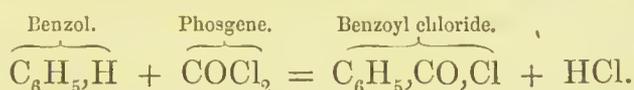
1. Benzol—Phenic Series.

(1548) BENZOL; *Benzine*, or *Phene* (C_6H_6); *Sp. gr. of liq.* 0.85 at 59° (15° C.); *of vap.* 2.77; *Rel. wt.* 39; *Fusing pt.* 40° ($4^\circ.4$ C.); *Boil. pt.* $177^\circ.8$ (81° C.).—This is a very limpid, colourless liquid, of a peculiar and rather agreeable odour. If exposed to a cold of 32° , it solidifies in transparent crystals, grouped like fern leaves, or in masses resembling camphor, which melt at 40° . It boils at $177^\circ.8$, and emits a highly inflammable vapour, which burns with a white smoky flame, depositing large quantities of carbon. If its vapour be transmitted through red-hot tubes it is decomposed, and a large quantity of carbon is deposited. It is not soluble in water, but is freely soluble in alcohol, ether, oil of turpentine, wood spirit, and acetone. When hot it dissolves sulphur, phosphorus, and iodine, and deposits the greater portion on cooling. It is also an excellent solvent for caoutchouc and gutta serena, and on evaporation it leaves them with their peculiar physical characters unaltered. Benzol also dissolves wax, camphor, and fatty bodies with facility. Its solvent power for fats and oils enables it to be used with advantage for removing grease stains from articles of silk or wool. Benzol does not dissolve copal or resins easily, but if these bodies be exposed to its vapour at a high temperature they are gradually dissolved by it.

Benzol was originally obtained by Faraday from the liquid produced by the compression of oil gas, and was named *bicarburet of hydrogen*. Subsequently the liquid procured by Mitscherlich from the distillation of benzoic acid, with an excess of lime, by him termed *benzine*, was found to yield the same body; $HC_7H_5O_2 + CaO = CaCO_3 + C_6H_6$; and more recently, Mansfield obtained it in large quantity from the more volatile portions of coal naphtha.* The name *phene* was proposed in allusion to its high value as an

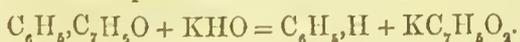
* Church found in light coal naphtha a hydrocarbon isomeric with benzol, which he terms *parabenzol*; it boils at $207^\circ.5$ ($97^\circ.5$ C.).

illuminating agent, from *φαίνω*, to emit light. Benzol may be obtained, mixed with other products, by several other processes, such as the distillation of phthalic acid with lime, and the dry distillation of quinic acid. It may also easily be procured in small quantities by exposing a mixture of one part of benzoic acid with three parts of quicklime to a moderate heat gradually applied; the distillate should be agitated with a weak solution of potash, and the benzol which rises to the surface be dried by digestion upon calcic chloride; after which it may be obtained pure by redistillation. Benzoic acid yields about a third of its weight of benzol.* When benzol is required in considerable quantity, its cheapest source is coal naphtha, although on a small scale its purification is tedious. Mansfield, after purifying it by repeated rectifications, took advantage of its power of solidifying at 32° , in order to free it from the hydrocarbons which accompany it, and which remain liquid at that temperature. By operating in this way upon two gallons of naphtha, a pint of pure benzol was procured. When benzol is acted upon by chloro-carbonic gas, hydrochloric acid is removed, and benzoyl chloride is formed:—



(1549) *Hydrocarbons homologous with Benzol, and their Isomerides.*—*Toluol* (C_7H_8), or *benzoene*, is one of the products of the distillation of balsam of tolu, and it appears to be identical with the *retinaphtha* obtained by Pelletier and Walter from the distillation of rosin (1481). Fittig and Tollens have shown it to be methyl-benzol. By oxidation with chromic acid it yields benzoic acid. *Xylol* (C_8H_{10}), which Fittig has proved to be dimethyl-benzol, was first found by Cahours, mixed with toluol, eumol, and eymol, among the oils which are separated from crude wood spirit by the action of water; hence its name, from *ξύλον*,

* If calcic benzoate be distilled with one-tenth of its weight of quicklime, it furnishes a red liquid which, when submitted to redistillation, first yields benzol; and when the temperature rises to 599° (315°C.) a compound termed *benzone* or *benzo-phenone* ($\text{C}_6\text{H}_5\text{C}_7\text{H}_5\text{O}$) passes over; this substance on cooling solidifies into a mass of straw-yellow crystals, which may be purified by recrystallization from ether. When pure it forms beautiful colourless crystals, belonging to the oblique system. It melts at $114^{\circ}8$ (46°C.), and boils at 599° ; it has an agreeable ethereal odour. Benzo-phenone may be regarded as a combination of benzoyl with phenyl; or as benzol, in which the place of an atom of hydrogen has been supplied by that of an atom of benzoyl. When heated with a mixture of caustic potash and lime, benzo-phenone is decomposed into benzol and potassic benzoate:—



wood. By oxidation with chromic acid it yields terephthalic acid ($\text{H}_2\text{C}_8\text{H}_4\text{O}_4$). *Cumol*, or *trimethyl-benzol* (C_9H_{12}), is one of the hydrocarbons obtained from coal tar. It is isomeric with *mesitylene*, a hydrocarbon derived from acetone, but not identical with it, as the products of oxidation of the two bodies are quite different; mesitylene yielding aetic, but no benzoic acid. The *eumol* obtained by the distillation of *euminic acid* with an excess of *quieklime* is isomeric if not identical with the *retinyl* of Pelletier and Walter. True *cumol* from *cuminic acid* yields benzoic acid by oxidation, and is viewed by Kekulé as *propyl-benzol*, $\text{C}_9\text{H}_{12} = \text{C}_6\text{H}_5\text{C}_3\text{H}_7$; and the *cymol* of Roman oil of *cumin* is, for analogous reasons, regarded as *propyl-methyl-benzol*, $\text{C}_{10}\text{H}_{14} = \text{C}_6\text{H}_4\text{C}_3\text{H}_7\text{CH}_3$; it yields terephthalic acid by oxidation with chromic acid. Another isomeric of this body has been prepared synthetically, viz., *tetramethyl-benzol*, $\text{C}_{10}\text{H}_{14} = \text{C}_6\text{H}_2(\text{CH}_3)_4$, which is distinguished from *cymol* by the products that it yields on oxidation. A metameride of *xytol*, *ethyl-benzol*, $\text{C}_8\text{H}_{10} = \text{C}_6\text{H}_5\text{C}_2\text{H}_5$, was also obtained synthetically by Fittig and Tollens; it yields benzoic acid when gradually oxidized by a mixture of potassic dichromate and sulphuric acid.

Isomeric Hydrocarbons of the Benzol Series.

| Empirical Formula. | Hydrocarbon. | Rational Formula. | Boiling Point. | | Specific Gravity. | |
|------------------------------|---|--|----------------|-------|-------------------|---------|
| | | | ° F. | ° C. | Liquid. | Vapour. |
| C_6H_6 | Benzol | C_6H_6 | 177·8 | 81 | 0·85 | 2·77 |
| C_7H_8 | Methyl benzol (toluol) . | $\text{C}_6\text{H}_5\text{CH}_3$ | 231·8 | 111 | 0·881 | 3·26 |
| C_8H_{10} | Dimethyl benzol (xytol) . | $\text{C}_6\text{H}_4(\text{CH}_3)_2$ | 282·2 | 139 | 0·867 | |
| | Ethyl benzol | $\text{C}_6\text{H}_5\text{C}_2\text{H}_5$ | 273·2 | 134 | 0·866 | |
| C_9H_{12} | Trimethyl benzol (coal tar cumol) | $\text{C}_6\text{H}_3(\text{CH}_3)_3$ | 329 | 165 | | 3·96 |
| | Methyl ethyl benzol . . | $\text{C}_6\text{H}_4\text{CH}_3\text{C}_2\text{H}_5$ | 320 | 160 | | |
| | Propyl benzol (true cumol) | $\text{C}_6\text{H}_5\text{C}_3\text{H}_7$ | 305·6 | 152 | | |
| $\text{C}_{10}\text{H}_{14}$ | Dimethyl ethyl benzol . | $\text{C}_6\text{H}_3(\text{CH}_3)_2\text{C}_2\text{H}_5$ | 362 | 183·5 | | |
| | Tetramethyl benzol . . | $\text{C}_6\text{H}_2(\text{CH}_3)_4$ | 379·4 | 193 | | |
| | Methyl propyl benzol (true cymol) | $\text{C}_6\text{H}_4\text{CH}_3\text{C}_3\text{H}_7$ | 347 | 175 | 0·861 | 4·59 |
| | Butyl benzol | $\text{C}_6\text{H}_5\text{C}_4\text{H}_9$ | | | | |
| | Diethyl benzol (camphor cymol) | $\text{C}_6\text{H}_4(\text{C}_2\text{H}_5)_2$ | 352·4 | 178 | | |
| $\text{C}_{11}\text{H}_{16}$ | Amyl benzol | $\text{C}_6\text{H}_5\text{C}_5\text{H}_{11}$ | 379·4 | 193 | 0·86 | |
| | Diethyl toluol | $\text{C}_6\text{H}_3(\text{C}_2\text{H}_5)_2\text{CH}_3$ | 352·4 | 178 | 0·8751 | 5·1107 |
| $\text{C}_{12}\text{H}_{18}$ | Amyl toluol | $\text{C}_6\text{H}_4\text{CH}_3\text{C}_5\text{H}_{11}$ | 415·4 | 213 | 0·8643 | |
| $\text{C}_{13}\text{H}_{20}$ | Amyl xytol | $\text{C}_6\text{H}_3(\text{CH}_3)_2\text{C}_5\text{H}_{11}$ | 450 | 232·2 | 0·8951 | |

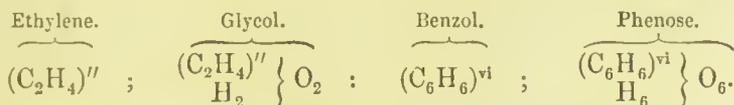
Cymol is present in essence of cumin, and it may also be obtained by distilling camphor with phosphoric anhydride, or with zincic chloride. These hydrocarbons are not, however, of sufficient importance to require any lengthened description in this work. In the preceding table their boiling points and densities are compared with those of benzol.

(1550) *Other Compounds of Benzol.*—Benzol yields direct compounds with chlorine and bromine, $C_6H_6Cl_6$ and $C_6H_6Br_6$, when exposed to the sun's light in contact with these halogens; and by the action of potassic dichromate and hydrochloric acid on the first, $C_6H_6Cl_3$, may be procured. These substances are crystallizable solids, which present a certain analogy with Dutch liquid, and the first two when decomposed by an alcoholic solution of potash, yield compounds which contain $C_6H_3Cl_3$ and $C_6H_3Br_3$.

Carius (*Liebig's Annal.*, cxxxvi. 324) has shown that by treating benzol with hypochlorous acid a compound is obtained ($C_6H_6, 3 HClO$), which he terms *trichlorhydrin of phenose*. It is obtained with difficulty in colourless thin crystalline plates, fusible at about 51° ($10^\circ.5$ C.); and this substance, if cautiously decomposed by alkalis, loses all its chlorine, and becomes converted into a non-fermentable sugar, *phenose*:—



The preparation of phenose is tedious and difficult; for the details the reader is referred to the memoir of Carius, above cited. Nitric acid converts phenose readily into oxalic acid; with sulphuric acid a colligated acid is produced which gives a soluble barium salt. No substitution-product resembling nitroglucose was obtainable from phenose. The conversion of benzol into this saccharoid substance lends additional probability to the view that glucose is hexatomic in structure; phenose being probably the hexatomic alcohol of benzol, to which it bears a relation analogous to that subsisting between glycol and ethylene:—



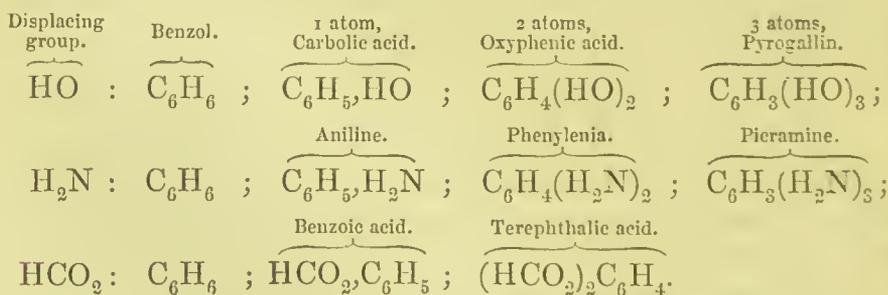
Benzol also furnishes with the halogens true substitution-products. Indeed the substitution-products which may be obtained from the aromatic hydrocarbons (C_nH_{2n-6}) of which benzol is the simplest member are very numerous and complicated. Benzol itself yields six such compounds with chlorine, in which one, two, or three, four, five, and even the whole six atoms of hydrogen have been displaced by a corresponding number of atoms of chlorine, the last three being solid crystallizable compounds. In the bromine series compounds are known in which one, two, three, four, and five atoms of hydrogen are displaced by a corresponding number of atoms of bromine; whilst with iodine the first 3 terms of the series only have been obtained. These different bodies have been recently studied by Fittig, Riche, Mayer, Jungfleisch, and others.

With nitroxyl benzol has as yet been found to furnish only two substitution-products, $C_6H_5NO_2$, and $C_6H_4(NO_2)_2$; but in the case of xylof a third product, $C_8H_7(NO_2)_3$ may easily be procured. In the benzol series mixed nitroxyl substitution-products may be obtained, such as *nitrotrichlorbenzol* $C_6H_2NO_2Cl_3$; *trinitrochlorbenzol*, $C_6H_2(NO_2)_3Cl$; and *dinitrotribrombenzol*, $C_6H(NO_2)_2Br_3$.

These substitution-compounds have lately acquired additional interest from the researches of Kekulé, who has by their aid been enabled to throw considerable light upon the molecular constitution of the benzol series.

He has succeeded in transforming bromobenzol into benzoic acid; and by a similar process he has converted bromotoluol into toluylie acid, and bromoxylof into xylylie acid. Sodie benzoate, for instance, is obtained by sending a slow current of carbonic anhydride through a mixture of bromobenzol and benzol in which lumps of sodium are suspended. Various compounds are formed in the operation; but the reaction which furnishes the benzoate is a simple one; $C_6H_5Br + Na_2 + CO_2 = NaC_7H_5O_2 + NaBr$. For further details the reader is referred to the paper of Kekulé, which will repay careful study (*Liebig's Annal.*, exxxvii. 129).

The hydrocarbons of the aromatic group exhibit a remarkable relation to several important series of compounds in which we may represent the displacement of one or more atoms of hydrogen by HO, H_2N , HCO_2 ; for example:—



Sulphuric acid forms a compound acid with benzol, termed *hyposulphobenzidic* or *sulphobenzolic acid* ($HC_6H_5SO_3$): it furnishes readily crystallizable salts. If benzol be treated with sulphuric anhydride a viscid mass is produced, which may be dissolved in a small quantity of water, but on the addition of a considerable amount of water, sulphobenzolic acid remains in the liquid, and a sparingly soluble crystalline body is separated. This crystalline body is termed *sulphobenzide* $(C_6H_5)_2SO_2$; it may be purified by crystallization from ether: it is fusible at 212° , and may be distilled unaltered at a much higher temperature. Hofmann and Buckton have lately obtained a sulpho-acid with a larger proportion of sulphuric acid, termed *disulphobenzolic acid* ($H_2C_6H_4S_2O_6$; p. 348), by heating benzonitrile with fuming sulphuric acid.

(1551) *Nitrobenzol*, or *Nitrobenzide* ($C_6H_5NO_2$); *Sp. gr.* of

liq., 1.209; *of vap.* 4.4; *Rel. wt.* 61.5; *Fusing pt.* 37° 4 (3° C.); *Boil. pt.* 415° 4 (213° C.).—Benzol is remarkable for the facility with which it yields substitution-compounds with nitroxyl. If benzol be added, in small portions at a time, to warm fuming nitric acid, it is dissolved, and on cooling, or on being diluted, nitrobenzol is separated in the form of a yellow oil, which may be purified by washing, first with water, and then with a weak solution of sodic carbonate.

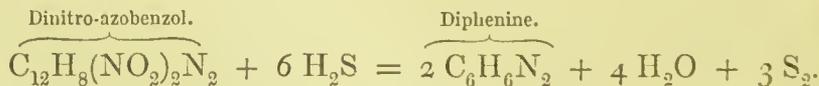
Nitrobenzol is a yellowish oil, which may be distilled unaltered; it crystallizes in needles when exposed to a temperature of 37° 4. It has a very sweet taste, and an odour resembling that of bitter almonds, which has led to its use in perfumery, under the name of *Essence of Mirbane*. Nitrobenzol is soluble in alcohol and in ether in all proportions. If its alcoholic solution be saturated with ammonia, and then with sulphuretted hydrogen, sulphur is deposited, and aniline is formed; aniline is also obtained from it still more readily by adding nitrobenzol to a mixture of equal parts of alcohol and hydrochloric acid, and introducing fragments of zinc, or by the process of Béchamp, with ferrous acetate (p. 483). The successive formation of nitrobenzol and of aniline may be employed as a test for the presence of benzol in oils:—A few drops of the suspected liquid are to be heated gently with fuming nitric acid in a test tube, and largely diluted with water, when oily drops of nitrobenzol are separated; if the liquid be agitated with ether, the nitrobenzol is dissolved, and may be decanted into a fresh tube: to this a mixture of equal parts of alcohol and hydrochloric acid are added, and a few fragments of granulated zinc. The nitrobenzol will thus be reduced to aniline, which may be liberated by the addition of caustic potash in excess: it must be again agitated with ether to dissolve the aniline, and if this ethereal solution be mixed with a solution of chloride of lime, the violet tint characteristic of aniline, will be developed.

Dinitrobenzol [$C_6H_4(NO_2)_2$].—If benzol be boiled with fuming nitric acid, or if it be allowed to fall, drop by drop, into a mixture of oil of vitriol and nitric acid so long as the liquids mix, dinitrobenzol is formed; the liquid must be boiled for a few minutes, and, on cooling, the dinitrobenzol is deposited in the form of a crystalline magma. It must be washed with water, and recrystallized from alcohol: it melts at a temperature below 212°. Dinitrobenzol represents benzol, in the molecule of which two atoms of nitroxyl have taken the place of two atoms of hydrogen. If its alcoholic solution be treated with ammoniac sulphhydride, a nitraniline (page 490) is produced.

When dinitrobenzol is dissolved in alcohol, and treated cautiously with hydrochloric acid, after introducing a plate of pure zinc, no gas is given off, but a crimson solution is formed. On supersaturating with an alkali, and treating with alcohol, a beautiful orange-red substance, termed *nitrosophenylin* ($C_6H_5N_2O$), is obtained. It is easily soluble in acids and in alcohol, but nearly insoluble in water and in benzol. Compounds homologous with dinitrobenzol yield by similar treatment bodies corresponding with nitrosophenylin.

(1552) *Derivatives of Nitrobenzol obtained by reduction.*—Nitrobenzol experiences a reduction of a different kind if it be treated with an alcoholic solution of potash; *azoxibenzol*, or *azoxibenzide* [$(C_6H_5)_2N_2O$; *fusing pt.* $96^{\circ}8$ ($36^{\circ}C.$)] is then formed, and may be obtained by distilling the liquid until it separates into two layers; the upper oily one, when washed with water, yields brown needles of azoxibenzol; they may be purified by dissolving them in alcohol, then transmitting a current of chlorine (to destroy the colouring matter), and recrystallizing. The brilliant crystals thus obtained are of a sulphur-yellow colour, and often exceed an inch in length. When distilled it yields aniline, and a new body termed *azobenzol*.

Azobenzol, or *Azobenzide* [$(C_6H_5)_2N_2$; *fusing pt.* 149° ($65^{\circ}C.$); *boil. pt.* $379^{\circ}4$ ($193^{\circ}C.$)], may also be procured by distilling nitrobenzol with an alcoholic solution of caustic potash; towards the end of the distillation, it passes over in the form of a red oil, which solidifies in large crystals: it may be purified by recrystallization from ether, and may be obtained in the form of orange-coloured plates, which are freely soluble in alcohol, but scarcely so in water. It is obtained still more easily by reducing an alcoholic solution of nitrobenzol by an amalgam of sodium, and is also formed in the preparation of aniline by Béchamp's method, distilling 1 part of nitrobenzol, 3 of iron filings, and 1 of acetic acid. The last portion of the distillate solidifies. It may be freed from aniline by washing with hydrochloric acid and recrystallizing from alcohol. When an alcoholic solution of azobenzol is treated with ammoniac sulphhydride, it yields *hydrazobenzol* (C_6H_5HN); if it be reduced with sulphurous acid, it is converted into the base called *benzidine* ($C_6H_5)_2H_2N_2$, isomeric with hydrazobenzol. The exact decompositions which attend the conversion of nitrobenzol successively into azoxibenzol, azobenzol, and benzidine, have not been clearly made out. If azobenzol be treated with nitric acid, it yields two substitution-compounds, $C_{12}H_9(NO_2)_2N_2$, and $C_{12}H_8(NO_2)_2N_2$ —the latter, *dinitroazobenzol*, when reduced by ammoniac sulphhydride, yields another base, termed *diphenine*, which is of a yellow colour; it is soluble in ether:—



(1553) *PHENIC*, or *Carbolic Acid*; *Phenyl Hydrate*; *Phenol* ($C_6H_6O = HC_6H_5O$); *Sp. gr. of liq.* 1.065; *Fusing pt.* about $105^{\circ}8$ ($41^{\circ}C.$); *Boil. pt.* $369^{\circ}5$ ($187^{\circ}5C.$).—This substance is the most abundant acid product of the distillation of pit-coal. It is also produced by the distillation of the salicylates of the alkalis and of the earths (1457). It is likewise found amongst the products of the distillation of gum benzoin, and of the resin of the *Xanthorrhæa hastilis*. Stædeler has found phenic acid in the urine of the cow, and of some other animals.

Laurent obtained phenic acid from the oil of coal tar by col-

lecting separately those portions which boil at between 302° and 392° , (150° and 200° C.), and mixing with this oil a hot saturated solution of caustic potash, adding a quantity of powdered potassic hydrate; a copious separation of white crystalline phenic acid immediately occurs.

The crystals of phenic acid melt at a temperature of about $105^{\circ}\cdot 8$ (41° C.), and the liquid enters into ebullition between 369° and 370° ($187^{\circ}\cdot 5$ C.). The presence of a small proportion of moisture is sufficient to cause the liquescence of the crystals. Crace Calvert (*Journ. Chem. Soc.*, 1865, p. 66) has described a crystallized hydrate of phenic acid, obtained by agitating four parts of carbolie acid with one of water, and exposing it to a temperature of $39^{\circ}\cdot 2$ (4° C.), when fine six-sided prisms $2(C_6H_6O), H_2O$, are formed; they liquefy at $60^{\circ}\cdot 8$ (16° C.), and if heated gradually lose water, the boiling point of the liquid rising until it reaches $369^{\circ}\cdot 5$ ($187^{\circ}\cdot 5$ C.).

Phenic acid requires 25 or 30 parts of water for solution, but it is dissolved by alcohol, ether, and concentrated acetic acid in all proportions. When agitated with solution of caustic potash of sp. gr. 1.060, the carbolie acid mixes freely with the alkaline ley, but a large portion of the acid separates on dilution. Phenic acid has a burning taste, and an odour of wood smoke resembling that of kreasote. Its vapour strongly attacks the skin of the lips and of the gums. Phenic acid possesses antiseptic properties similar to those of kreasote: indeed, much of the commercial kreasote consists solely of phenic acid. Its solutions do not redden litmus paper: a drop of it let fall upon paper produces a transient greasy stain. If a splinter of deal be dipped into a solution of phenic acid, and then into nitric or hydrochloric acid, the wood as it dries becomes blue.

Phenic acid, when heated with ammonia in a sealed tube, becomes partially converted into water and aniline; $C_6H_6O + H_3N = C_6H_5, H_2N + H_2O$. The acid combines with potash, and forms with it a crystalline compound; though it may be distilled unchanged from caustic potash, and from quicklime or caustic baryta in excess. Phenates of these bases may be obtained, but they are easily decomposed; with oxide of lead an insoluble compound (PbO, C_6H_6O) may be obtained. Phenic acid combines with sulphuric acid, with which it forms a colligated acid.*

* A beautiful orange-coloured dye, which is now used on a considerable scale under the name of *aurine*, is prepared by mixing together sulphuric and carbolie acids, heating in a glass vessel to 257° (125° C.), and then gradually adding oxalic acid nearly equal in weight to the quantity of sul-

Owing to its antiseptic power, carbolic acid is a valuable topical application in many surgical cases attended with offensive purulent or other discharges. Phenic acid has also lately been extensively used as a prophylactic against the spread of infectious diseases. It was extensively tried by Crookes, under the sanction of the Cattle Plague Commission; and he has given a careful report upon the subject, from which its efficacy in destroying the infectious matter would appear to be very high. As it is a volatile substance, it possesses the great advantage of being readily diffused through the air.

(1554) *Homologues of Phenic Acid.*—Phenic acid is accompanied in coal tar by other homologous bodies which greatly resemble it. By subjecting commercial coal-tar kreasote to fractionated distillation, Williamson obtained a liquid which boils at $397^{\circ}\cdot 4$ (203° C.), and which is nearly insoluble in solution of ammonia. *Kresylic acid*, *kresol*, or *methyl-phenol* ($\text{CH}_3\cdot\text{C}_6\text{H}_5\text{O}$) is soluble in oil of vitriol, producing a violet colour, and forming a compound acid. This substance is metameric with anisol (1467), and with benzyl alcohol (1438); it is the phenol of the toluic series. When treated with fuming nitric acid, it is oxidized with almost explosive violence, and a *trinitro-kresylic acid* [$\text{HC}_7\text{H}_4(\text{NO}_2)_3\text{O}$], homologous with carbazotic acid, is produced.

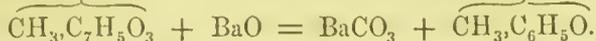
A third homologue, *xylyl phenol*, ($\text{HC}_8\text{H}_9\text{O}$), also occurs in coal-tar in small proportions. It is probably dimethyl-phenol ($(\text{CH}_3)_2\text{C}_6\text{H}_4\text{O}$), but it has not been accurately investigated. Isomeric with this body is *phlorol*, obtained by distilling calcic phlorctate with lime. It is a colourless, highly refractive oil, with a burning taste, and an odour recalling that of carbolic acid; *Sp. gr.* $1\cdot 0374$; *Boil. pt.* about 428° (220° C.). *Thymol* ($\text{C}_{10}\text{H}_{14}\text{O}$; 1421), also, according to Kekulé, is a homologue of carbolic acid; but this appears to be doubtful.

(1555) *Ethers of Phenic Acid.*—Phenic acid may be caused to furnish ethers with alcohol radicles by a process of double decomposition, which consists in distilling potassic methylsulphate, ethylsulphate, or amylsulphate with potassic phenate. These ethers may likewise be procured by heating potassic phenate with the iodide of methyl, of ethyl, or of amyl; they are also produced by the distillation of the salicylic ethers with caustic baryta,—the preparation of anisol by the latter process being represented by the equation:—

phuric acid employed. This operation requires to be performed very slowly and with great care. When the acid has all been added, the whole is thrown into cold water, when it solidifies as a green mass with a cantharides lustre. It is then well worked in boiling water till all excess of sulphuric acid is removed (Crace Calvert).

Methyl salicylate.

Methyl phenate.



Anisic acid, which is metameric with methyl salicylate, also by similar means yields methyl phenate, which is identical with anisol.

The ethers of phenic acid may thus be contrasted with the acid itself:—

| Phenic ether. | Formula. | Boiling Point. | | Specific gravity. Liquid. |
|------------------------------------|--|----------------|-------|---------------------------|
| | | ° F. | ° C. | |
| Phenic or carbohic acid (phenol) . | H, C ₆ H ₅ O | 369.5 | 187.5 | 1.065 |
| Methyl phenate (anisol) . . . | C H ₃ , C ₆ H ₅ O | 305.6 | 152 | 0.991 |
| Ethyl phenate (phenetol) . . . | C ₂ H ₅ , C ₆ H ₅ O | 341.6 | 172 | |
| Amyl phenate (phenamylol) . . | C ₅ H ₁₁ , C ₆ H ₅ O | 437 | 225 | |

Each of these ethers, when treated with nitric acid, yields substitution-compounds analogous to those furnished by anisol (1467), and when submitted to the action of ammoniac sulphhydride, bases are obtained analogous to anisidine, nitranisidine, and dinitranisidine.

(1556) *Products of the Decomposition of Phenic Acid.*—When phenic acid is distilled with phosphoric chloride, it reacts more like an alcohol than an acid, and yields *phenyl chloride*, or *chlorobenzol* (C₆H₅Cl), which is a colourless mobile liquid, with a fragrant smell, resembling that of bitter almonds: it boils at 276°·8 (136° C.). At the same time *triphenyl phosphate* [(C₆H₅)₃PO₄] is formed; it may be obtained at a low temperature in beautiful crystals. When melted it is slightly yellow, and has a fluorescent property. If phosphorous chloride be substituted for phosphoric chloride, phenyl chloride and phenyl phosphite are produced; and the latter, when distilled, yields benzol amongst other products (Williamson). Benzol, it will be remarked, contains one atom of oxygen less than phenic acid; the phosphorous acid in this case deoxidizes the phenic acid, and becomes converted into phosphoric acid. Other phenylic ethers have also been obtained, such as phenyl benzoate, C₆H₅.C₇H₅O₂, and phenyl acetate, C₆H₅.C₂H₃O₂.

Phenic acid gives rise by substitution to an unusual number of acid compounds, formed upon the type of phenic acid itself: such for example as the following:—

| | |
|---------------------------------------|--|
| Phenic (carbohic) acid | HC ₆ H ₅ O |
| Chlorophenic acid | HC ₆ H ₄ ClO |
| Dichlorophenic (chlorophenic) do. . . | HC ₆ H ₃ Cl ₂ O |
| Trichlorophenic (chlorophenic) do. . | HC ₆ H ₂ Cl ₃ O |
| Pentachlorophenic (chlorophenic) do. | HC ₆ Cl ₅ O |
| Bromophenic (bromophenic) do. . . | HC ₆ H ₄ BrO |
| Dibromophenic (bromophenic) do. . | HC ₆ H ₃ Br ₂ O |
| Tribromophenic (bromophenic) do. . | HC ₆ H ₂ Br ₃ O |
| Tetrabromophenic (bromophenic) do. | HC ₆ HBr ₄ O |
| Pentabromophenic (bromophenic) do. | HC ₆ Br ₅ O |
| Iodophenic do. (iodophenol) | HC ₆ H ₄ IO |
| Triiodophenic do. | HC ₆ H ₂ I ₃ O |
| Nitrophenic (nitrophenic) do. . . . | HC ₆ H ₄ (NO ₂) ₂ O |

| | |
|--|---|
| Dinitrophenic (nitrophenesic) acid | $\text{HC}_6\text{H}_2(\text{NO}_2)_2\text{O}$ |
| Trinitrophenic (nitrophenesic) do. | $\text{HC}_6\text{H}_2(\text{NO}_2)_3\text{O}$ |
| Dichloronitrophenic do. | $\text{HC}_6\text{H}_2\text{Cl}_2(\text{NO}_2)\text{O}$ |
| Diodo-nitrophenic do. | $\text{HC}_6\text{H}_2\text{I}_2(\text{NO}_2)\text{O}$ |
| Bromo-dinitrophenic do. | $\text{HC}_6\text{H}_2\text{Br}(\text{NO}_2)_2\text{O}$ |

All of these acids are monobasic, and form definite salts, many of which crystallize very beautifully.

A mixture of potassic chlorate and hydrochloric acid converts phenic acid into trichlorophenic acid ($\text{HC}_6\text{H}_2\text{Cl}_3\text{O}$), and by prolonging the action, chloranil ($\text{C}_6\text{Cl}_4\text{O}_2$) is produced.

Oil of vitriol dissolves phenic acid, without change of colour, and produces a compound monobasic acid, termed *sulphophenic acid* ($\text{HC}_6\text{H}_5\text{SO}_4$); it forms with barium a soluble salt, which crystallizes in tufts of needles.

If phenic acid be allowed to fall, drop by drop, into fuming nitric acid, it is attacked with great violence; each drop produces a hissing like that which accompanies the quenching of a hot iron; and upon boiling the mixture, carbazotic (*trinitrophenic*) [$\text{HC}_6\text{H}_2(\text{NO}_2)_3\text{O}$] acid is obtained. If the acid be more dilute, *nitrophenic acid* [$\text{HC}_6\text{H}_4(\text{NO}_2)\text{O}$], or *dinitrophenic acid* [$\text{HC}_6\text{H}_3(\text{NO}_2)_2\text{O}$] is produced. Both of these acids may readily be obtained in crystals: most of their salts crystallize with facility; they greatly resemble the carbazotates.

(1557) CARBAZOTIC, *Trinitrophenic*, *Nitrophenesic*, or *Picric Acid* [$\text{H}_2\text{C}_6\text{H}_2(\text{NO}_2)_3\text{O}$].—This is a frequent product of the action of nitric acid upon complex organic substances. Phenic acid, salicin, coumarin, phloridzin, silk, indigo, and a variety of resins yield it when treated with fuming nitric acid. The oil of tar, which distils over at a temperature between 302° and 392° (150° and 200° C.), is one of the best raw materials from which this acid can be procured. In preparing this acid on a large scale, Crace Calvert employs 42lb. of nitric acid, of sp. gr. 1.52, and allows 7lb. of carbolic acid to fall drop by drop into the nitric acid. After the lapse of about thirty-six hours, the whole of the carbolic acid having been introduced, heat is applied, and the acid liquor is concentrated to a fourth of its bulk; on cooling, it becomes solid. It is dissolved in water, which is boiled by the injection of steam. On allowing it to cool slowly, the acid crystallizes. The resin of the *Xanthorrhœa hastilis* is also a convenient source of carbazotic acid. In the latter case, in order to get rid of woody fibre, the resin should be purified by dissolving it in alcohol, and evaporating the solution to dryness. Care must be taken to act with nitric acid on the resin at a low tem-

perature, otherwise oxalic acid is formed in considerable quantity. The hot solution obtained by acting upon these bodies with nitric acid must be decanted from the undissolved portions, and the carbazotic acid, which is deposited as the liquor cools, may be purified by washing with cold water, and converting it into a salt of ammonium, which may be readily obtained in crystals; the ammoniac carbazotate when dissolved in boiling water may then be decomposed by dilute nitric acid, and crystals of carbazotic acid will be obtained as the liquid cools. If boiled with caustic potash in excess, the acid is decomposed, ammonia is expelled, and a brown resin is obtained in solution.

Carbazotic acid crystallizes in long, pale yellow, brilliant, rectangular plates, which are readily soluble in alcohol, in benzol, and in ether. It requires between 80 and 90 parts of cold water for its solution, forming a liquid of a bright yellow colour; it stains the skin yellow; if heated with a quantity of water insufficient to dissolve it, the acid melts to a yellowish transparent oil, which solidifies on cooling. The tinctorial power of this substance is so great that the aqueous solution may be diluted with several hundred times its bulk of water without losing its yellow colour. This acid has an intensely bitter taste, which has induced some persons fraudulently to substitute it in beer for a portion of the hops. Carbazotic acid is also employed for dyeing silk, to which it imparts a beautiful yellow colour, after the silk has been mordanted with alum, or with cream of tartar. On the application of heat carbazotic acid fuses to a yellowish oil, and if the temperature be gradually raised, it may be partially sublimed, but if suddenly heated it is decomposed with explosion. Concentrated sulphuric and nitric acids dissolve it unaltered, and deposit it on dilution. When gently heated with phosphoric chloride, *trinitrochlorobenzol* [$C_6H_2(NO_2)_3Cl$] is formed, with hydrochloric acid. Water reconverts this compound into carbazotic and hydrochloric acids, and it has been regarded as the oxychloride of picric acid, or *picryl chloride*.

The carbazotates generally crystallize with facility; they are bitter, and of a yellow colour: when heated they are decomposed with explosion. *Potassic carbazotate* is anhydrous; it is freely soluble in boiling water, but requires 260 parts of cold water for solution. *Ammonic carbazotate* is also anhydrous, but it is more soluble in water, and is somewhat soluble in alcohol. Strong hot solutions of these salts crystallize into a network of fine needles, which makes the solution appear to be semi-solid. The *sodium* salt is readily soluble in cold water. The carbazotates

of the metals of the alkaline earths, and of lead and silver, are freely soluble. Potassic carbazotate has recently been employed in France in the preparation of an explosive mixture intended to be used as a substitute for gunpowder in breech-loading firearms, the carbazotate being substituted for sulphur in the mixture of ordinary powder. The proportion of the carbazotate varies from 8 to 20 per cent. of the mass, according as it is to be employed for musketry or ordnance, musket powder containing the largest quantity of the carbazotate.

Carbazotic acid unites with several of the hydrocarbons, such as benzol, naphthalin, and anthracene, and forms with them crystalline compounds, often characteristic in form and colour (*Ann. de Chimie*, IV. xii. 189). The benzol compound, $C_6H_6, C_6H_3(NO_2)_3O$, is deposited in pale yellow transparent crystals when a hot saturated solution of the acid in benzol is allowed to cool. The crystals fuse at $300^{\circ} \cdot 2$ (149° C.). They gradually lose benzol when exposed to the air, but are permanent in an atmosphere saturated with benzol vapour.

Picrocyanic or *Isopurpuric Acid* ($C_8H_5N_5O_6$; Hlasiwetz).—The potassium salt of this acid, which is not known in the free state, may be obtained by dropping a hot solution of 1 part of carbazotic acid in 9 of water into a solution of 2 parts of potassic cyanide dissolved in 4 of water, at a temperature of about 140° (60° C.). Hydrocyanic acid and ammonia are evolved, and a deep blood-red solution is formed, which sets into a crystalline magma. It may be pressed, washed with a small quantity of cold water, and recrystallized from boiling water. It forms brown-red scaly crystals with a green lustre, sparingly soluble in cold water and in alcohol. Its solutions precipitate the salts of lead, silver, mercury, and baryta, but not those of calcium, strontium, zinc, or copper.

Chloropicrin [$CCl_3(NO_2)$; *Sp. gr.* 1.665; *Boil. pt.* $233^{\circ} \cdot 6$ (112° C.)] is the name given to a colourless transparent oil, of high refracting power, and of an excessively penetrating odour resembling that of oil of mustard; its vapour is not inflammable. This substance is produced by the action of chlorinating agents upon carbazotic (picric) acid. It is easily obtained by distilling the acid with 10 times its weight of chloride of lime, and rectifying the oil which comes over, from caustic magnesia. Alcoholic solutions of the alkalies decompose it into a chloride and a nitrate.

When nitrous derivatives of phenic acid are submitted to the reducing action of ammoniac sulphhydride, two red amidated acids are produced. The compound obtained from dinitrophenic acid is termed *nitro-phenamic acid* [$HC_6H_3(NO_2)_2H_2NO, 2H_2O$]; that from carbazotic acid is named *picramic acid* [$HC_6H_2(NO_2)_2H_2NO$].

(1558) *Oxyphenic acid*, or *pyrocatechin* ($C_6H_6O_2$), may be regarded as benzol, in which two atoms of hydroxyl have displaced two of its hydrogen, just as in phenol it may be supposed that one atom of hydroxyl has displaced one of hydrogen, and in pyrogallin three atoms of hydroxyl have displaced three of the hydrogen of benzol; as for example:—

| | |
|----------------------------------|----------------|
| Benzol | C_6H_6 |
| Phenol (carbolic acid) | $C_6H_5(OH)$ |
| Oxyphenic acid | $C_6H_4(OH)_2$ |
| Pyrogallin | $C_6H_3(OH)_3$ |

and Körner has recently succeeded in converting iodophenol C_6H_5IO into potassic oxyphenate by fusion with caustic potash; $C_6H_5IO + 2 KHO = KC_6H_5O_2 + KI + H_2O$: resorcin, an isomeride of oxyphenic acid, is also formed at the same time. The acid, however, is obtained most abundantly by the distillation of catechu (1332), of moritanic acid, or of gum of ammoniacum; the acid liquid which passes over during the operation must be decanted from tarry matters which accompany it, and be left to spontaneous evaporation. It is often mixed with hydroquinone (1337), another isomeride of oxyphenic acid. The crystals which are gradually deposited must be freed from the mother liquor by pressure between folds of filtering paper, and purified by sublimation.

Oxyphenic acid crystallizes in colourless rectangular prisms. It is very soluble in water and in alcohol, but is nearly insoluble in ether. It has a bitter taste, but scarcely any acid reaction. Its crystals fuse at about 232° (111° or 112° C.), and the liquid enters into ebullition between 464° and 473° (240° and 245° C.). Its solutions in the alkalis become first green, then brown, and finally black, whilst oxygen is absorbed. Its most characteristic reaction is the dark green colour which it produces on the addition of ferric chloride; on the addition of any alkaline solution this colour is changed to a deep red. With plumbic acetate it yields a white precipitate. Nitric acid decomposes oxyphenic acid, and oxalic acid is formed.

(1559) *Styphnic*, or *Oxyptic Acid* [$H_2C_6H(NO_2)_3O_2$].—The composition of this acid is such that it has been supposed to bear the same relation to oxyphenic acid that carbazotic acid does to phenic acid. This view, however, is not very probable, since the acid is dibasic, and it cannot be obtained from oxyphenic acid by the action of nitric acid upon it. It is the product of the action of nitric acid (sp. gr. 1.20) upon certain gum resins, such as ammoniacum, assafoetida, and sagapenum. The aqueous extract of Brazil-wood and of the *Morus tinctoria* also yield it when treated with nitric acid. Many of these substances furnish oxyphenic acid by distillation, extract of Brazil-wood yielding it abundantly by this process. Styphnic acid is sparingly soluble in cold water, but readily so in alcohol and in ether. It crystallizes in long prisms, which have a yellow colour. Its solution stains the skin permanently yellow. Styphnic acid reddens litmus, and decomposes the alkaline carbonates with effervescence. It also dissolves metallic iron and zinc with facility. Its taste is somewhat astringent, but not acid: the name is given in reference to this property, from *στυφνός*, astringent. The styphnates, like the carbazotates, are decomposed with explosion when gently heated. This acid forms two classes of salts, a normal and an acid one: many of its salts crystallize readily. It contains one atom of oxygen more than carbazotic acid.

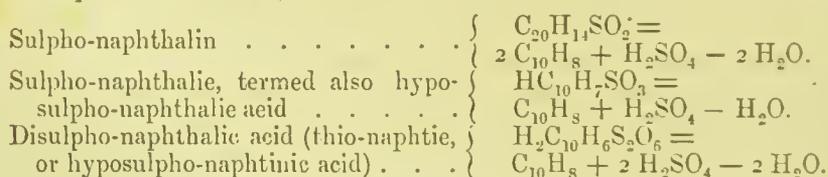
2. Naphthalic Series.

(1560) NAPHTHALIN ($C_{10}H_8$); *Sp. gr. of solid* 1.153; *of vap.* 4.528: *Fusing pt.* $174^\circ.2$ (79° C.); *Boil. pt.* 428° (220° C.).—Naphthalin is a constituent of the principal varieties of tar, but it is most abundant in coal tar, particularly in that obtained from the London gas-works. It is also produced when olefiant gas, paraffin, phenic acid, and some other constituents of coal tar, are transmitted slowly through red-hot tubes. Naphthalin is easily obtained from the last portions of the distillate from coal tar, which become semi-solid on cooling. The liquid constituents of this mass must be separated from it by pressure, and after recrystallization from hot alcohol it may be obtained perfectly pure by sublimation.

Naphthalin forms flaky crystals, consisting of rhombic plates, which feel unctuous to the touch and have a pearly lustre: its odour is peculiar, and its taste biting and somewhat aromatic. It gradually undergoes sublimation at ordinary temperatures, and is easily distilled over with the vapours of water. Naphthalin does not readily take fire, but when kindled it burns with a white smoky flame. It is insoluble in water, but is readily soluble in alcohol, ether, oil of turpentine, and the fixed oils. Potash is without action upon it. Melted naphthalin absorbs air copiously, and gives it off on solidification. It dissolves sulphur, phosphorus, and the sulphides of arsenicum, antimony, and tin, as well as oxalic, succinic, and benzoic acid, iodine and mercuric iodide.

(1561) *Action of Sulphuric Acid upon Naphthalin.*—Sulphuric acid when heated with naphthalin combines with it. If the naphthalin be in excess, the acid forms with it a neutral fusible compound termed *sulphonaphthalin*. If the sulphuric acid be in excess, and the temperature do not exceed 200° , a semi-solid acid compound is formed, the *sulphonaphthalic*. If a higher temperature be employed, especially if fuming sulphuric acid be used, *disulphonaphthalic acid* is also formed; it is a brown deliquescent compound, with a sour and bitter taste.

In all these cases the reaction of sulphuric acid upon naphthalin is attended with a separation of water; thus:—



Besides these two acids, a small quantity of a third acid is sometimes obtained, which is metameric with the sulpho-naphthalic; from the latter, this new acid is distinguished by the difference in the effect of heat upon its barium salt, which when burned in open air smoulders like tinder till the naphthalin is consumed, whilst the baric sulpho-naphthalate burns with a luminous flame. The sulpho-naphthalates are soluble in water, and many of them in alcohol also; they have a bitter, almost metallic, taste. If the disulphonaphthalates are fused with caustic potash, they are decomposed with formation of sulphite and sulphate, whilst a diatomic phenol of naphthalin ($\text{C}_{10}\text{H}_8\text{O}_2$) remains in combination with potash. It may be separated from potash by acids and crystallized in small rhombic plates, smelling like kreasote. A monatomic phenol of naphthalin *naphthol*, $\text{C}_{10}\text{H}_8\text{O}$, has also been obtained by other means.

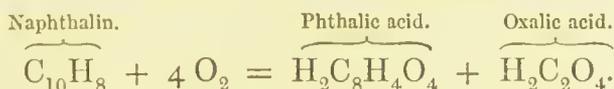
(1562) *Action of Nitric Acid upon Naphthalin.*—Nitric acid attacks naphthalin slowly at ordinary temperatures, and converts it into a sulphur-yellow compound, termed *nitro-naphthalin* [$\text{C}_{10}\text{H}_7(\text{NO}_2)$]; at higher temperatures *dinitro-naphthalin* [$\text{C}_{10}\text{H}_6(\text{NO}_2)_2$] and *trinitro-naphthalin* [$\text{C}_{10}\text{H}_5(\text{NO}_2)_3$] are pro-

duced. These different substitution-products of naphthalin crystallize beautifully from their alcoholic or their ethereal solutions. When solutions of these compounds are exposed to the reducing action of ammoniac sulphhydride, each compound yields an azotised base; *naphthalidine*, *naphthylia*, or *naphthylamine* ($C_{10}H_9N$) being that furnished from nitro-naphthalin, and *semi-naphthalidam*, or *dinaphthylia* ($C_{10}H_{10}N_2$), from dinitro-naphthalin: a third base was obtained by Laurent from trinitro-naphthalin.

A beautiful violet colour, *azodinaphthylidiamine* ($C_{20}H_{15}N_3$), or $(C_{10}H_7N'_2)_2$ } N_2 , rivalling that from aniline, has lately been obtained by oxidation of one of these bases.

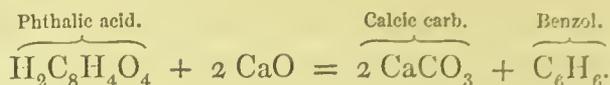
A very pure and beautiful yellow and orange colouring material is now prepared from *dinitronaphthol* [$C_{10}H_6(NO_2)_2O$] by adding to a dilute acid solution of naphthylia hydrochlorate ($C_{10}H_9N, HCl$) a dilute solution of potassic nitrite, until, on the addition of an alkali, a cherry-red precipitate of diazoamidonaphthol [$C_{10}H_5(H_2N)N_2$] is produced. Nitric acid is then added, and the temperature is gradually raised until the liquid boils. The liquid becomes turbid, from the deposition of yellow crystalline masses of dinitronaphthol, and a copious effervescence occurs. The precipitate is purified by solution in ammonia and recrystallization. This compound is soluble in boiling water, and crystallizes in needles. Dinitronaphthol is sparingly soluble even in boiling water, and soluble with difficulty in alcohol, in ether, and in benzol. Its compounds with the alkalies are of an orange or red-lead colour, soluble in water, and to a certain extent also in alcohol. Dinitronaphthol is used without any mordant for dyeing silk and wool of various shades, from bright lemon yellow to deep golden yellow. The sodium salt and calcium salt, $Ca\ 2\ [C_{10}H_5(NO_2)_2O, 3\ H_2O]$ are both largely manufactured.

Phthalic or *Naphthalic Acid* ($H_2C_8H_4O_4$), *fusing pt.* $363^{\circ} \cdot 2$ ($184^{\circ} C.$).—By prolonged boiling with nitric acid, naphthalin is converted into a mixture of oxalic and phthalic acids:—



Phthalic acid may also be obtained by the long-continued action of nitric acid upon naphthalin tetrachloride ($C_{10}H_8Cl_4$), and upon alizarin. The latter mode of its production is interesting, since it indicates a connexion between naphthalin and the colouring matter of madder. On evaporating the solution obtained by acting upon naphthalin with boiling nitric acid, phthalic acid is deposited in groups of lamellar crystals. It is sparingly soluble in cold water, and very soluble in alcohol and in ether. When exposed to a high temperature, water is expelled, and *phthalic anhydride* is sublimed: it fuses at $262^{\circ} \cdot 4$ ($128^{\circ} C.$), and boils at $528^{\circ} \cdot 8$ ($276^{\circ} C.$). By still further prolonging the action of nitric upon phthalic acid, a *nitro-phthalic acid* [$H_2C_8H_3(NO_2)O_4$] may be procured. If phthalic

acid be distilled with lime, calcie carbonate and benzol are the results:—



Phthalic acid is dibasic; it is isomeric with a product obtained by Hofmann from cuminic acid, by the oxidizing influence of nitric acid upon it; from its sparing solubility, he termed it *insolinic acid*. This body appears to be identical with the terephthalic acid obtained by oxidizing oil of turpentine with nitric acid (1415); this acid is also dibasic.

(1563) *Action of Chlorine on Naphthalin.*—When chlorine is brought into contact with naphthalin, the two bodies enter into direct combination: the naphthalin fuses, and a mixture of two compounds, presenting considerable analogy to Dutch liquid is formed. One of these compounds is *naphthalin dichloride* ($\text{C}_{10}\text{H}_8\text{Cl}_2$), and the other, *naphthalin tetrachloride* ($\text{C}_{10}\text{H}_5\text{Cl}_4 = \text{C}_{10}\text{H}_6\text{Cl}_2, 2 \text{HCl}$). The formation of small quantities of substitution derivatives of naphthalin also usually accompanies the production of these compounds.

Naphthalin dichloride ($\text{C}_{10}\text{H}_8\text{Cl}_2$) is an oily body, which is soluble in ether in all proportions. This circumstance is taken advantage of in effecting its partial separation from the tetrachloride, which is solid; but it is difficult to free it completely from this latter substance. *Naphthalin tetrachloride* ($\text{C}_{10}\text{H}_6\text{Cl}_4$) exists in two modifications, which have been distinguished by the letters α and β . These modifications are both formed simultaneously during the action of chlorine upon naphthalin. The *tetrachloride* α is sparingly soluble in boiling ether, from which, on cooling, it is deposited in crystals; or it may be purified still more advantageously by crystallization from boiling oil of petroleum. It is scarcely soluble in alcohol. The *tetrachloride* β is very soluble in alcohol, and still more so in ether. It is obtained by exposing the ethereal mother-liquor, from which the tetrachloride α has crystallized, to a low temperature for a few hours, and recrystallizing the deposit (which consists of a mixture of the modifications α and β), from ether: the liquid retains the modification β , which must be recrystallized until the crystals obtained are dissolved rapidly by cold ether. Corresponding compounds with bromine may be obtained, and other derivatives also may be formed, into the composition of which both chlorine and bromine enter. (See table on next page.)

Both the liquid chloride and the two modifications of the tetrachloride of naphthalin are decomposed by distillation. When treated with an alcoholic solution of potash, they are decomposed, potassic chloride is formed, and chlorinated derivatives of naphthalin are produced. In each atom of these new compounds the number of atoms of chlorine and hydrogen together is always equal to 8, which is the number of atoms of hydrogen in the compound atom of naphthalin.

The researches of Laurent have disclosed the existence of an exceedingly numerous series of substitution-compounds, formed upon the type of naphthalin, into the composition of which chlorine enters.

Corresponding compounds with bromine may also be formed; and another series may be obtained, in which the substitution is effected partly by chlorine and partly by bromine. It would be inconsistent with the plan of the present work to attempt to give any detailed account of these bodies. The table which follows will indicate the composition of the principal compounds of this series. These bodies are of little practical importance, but their investigation led Laurent to theoretical deductions regarding the molecular constitution of chemical compounds generally, which have exerted a remarkable influence upon the recent progress of organic chemistry.* Many of these bodies are isomorphous.

1. *Chlorides and Bromides of Naphthalin.*

| | I. | 2. |
|--------------------------------------|-------------------------|----------------------------|
| Liquid naphthalin dichloride . . . | $C_{10}H_8Cl_2$ | $C_{10}H_7Cl, HCl$ |
| Bronaphtase dichloride . . . | $C_{10}H_7Br, Cl_2$ | $C_{10}H_6Br, Cl, HCl$ |
| Naphthalin tetrachloride . . . | $C_{10}H_8Cl_4$ | $C_{10}H_6Cl_2, 2 HCl$ |
| Chlonaphtase tetrachloride . . . | $C_{10}H_7Cl, Cl_4$ | $C_{10}H_5Cl_3, 2 HCl$ |
| Naphthalin trichlorobromide . . . | $C_{10}H_8Cl_3Br$ | $C_{10}H_6Cl_2, HCl, HBr$ |
| Chlonaphtese tetrachloride . . . | $C_{10}H_6Cl_2, Cl_4$ | $C_{10}H_4Cl_4, 2 HCl$ |
| Bronaphtese tetrachloride . . . | $C_{10}H_6Br_2, Cl_4$ | $C_{10}H_4Cl_2Br_2, 2 HCl$ |
| Chlonaphtese tetrabromide . . . | $C_{10}H_6Cl_2, Br_4$ | $C_{10}H_4Cl_2Br_2, 2 HBr$ |
| Chlorabronaphtese tetrabromide . . . | $C_{10}H_6ClBr, Br_4$ | $C_{10}H_4ClBr_3, 2 HBr$ |
| Bronaphtese tetrabromide . . . | $C_{10}H_6Br_2, Br_4$ | $C_{10}H_4Br_4, 2 HBr$ |
| Bromechlonaphtise tetrabromide . . . | $C_{10}H_5Br_2Cl, Br_4$ | $C_{10}H_3Br_4Cl, 2 HBr$ |
| Bronaphtise tetrabromide . . . | $C_{10}H_5Br_3, Br_4$ | $C_{10}H_3Br_5, 2 HBr$ |

The compounds enumerated in the foregoing table are susceptible of decomposition by means of an alcoholic solution of potash, which effects the removal of a certain portion of chlorine

* The names proposed by Laurent, extraordinary and uncouth as many of them appear, are yet well adapted to represent the numerous substitution-compounds to which they refer. In the case of naphthalin, the compounds which contain chlorine are indicated by the prefix *chlo*, and end with a syllable in which the vowels *a*, *e*, *i*, *o*, and *u*, are intended respectively to indicate the displacement of 1, 2, 3, 4, or 5 atoms of hydrogen. In *chlonaphtase* 1 atom of hydrogen has been displaced by 1 atom of chlorine; in *chlonaphtose*, 4 atoms of hydrogen have been displaced by 4 of chlorine. If the number of atoms of hydrogen displaced exceed 5, a fresh syllable, such as *al*, is added to the word, and the vowels (beginning with *a*) are again employed as before. For instance, to express the substitution of 6 atoms of hydrogen by 6 of chlorine, the term *chlonaphtalase* is adopted. If bromine be the displacing body, the prefix *bro* is employed, and if both chlorine and bromine be present, the name employed indicates by the vowel in the concluding syllable the total number of atoms of hydrogen displaced, whilst the number of one of the halogens is indicated by a vowel attached to the prefix of the particular halogen to be represented. Thus *chloribronaphtose* indicates ($C_{10}H_4Cl_3Br$), or a compound in which 4 atoms of hydrogen have been displaced by 3 atoms of chlorine and 1 of bromine: the name *bromechlonaphtose* indicates that the 4 atoms of hydrogen displaced are represented by 2 atoms of bromine and 2 of chlorine.

or of bromine, and the body which is left is one of those represented in the following table:—

2. *Compounds formed upon the type* ($C_{10}H_8$).

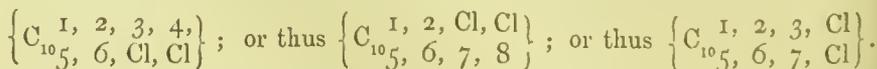
| | | | |
|-------------------------|-------------------|-------------------------|---------------------|
| Chlonaphtase . . . | $C_{10}H_7Cl$ | Chlonaphtose . . . | $C_{10}H_4Cl_4$ |
| Bronaphtase . . . | $C_{10}H_7Br$ | Chlorebronaphtose . . . | $C_{10}H_4Cl_2Br_2$ |
| Chlonaphtese . . . | $C_{10}H_6Cl_2$ | Chloribronaphtose . . . | $C_{10}H_4Cl_3Br$ |
| Bronaphtese . . . | $C_{10}H_6Br_2$ | Bronaphtose . . . | $C_{10}H_4Br_4$ |
| Chlonaphtise . . . | $C_{10}H_5Cl_3$ | Bromechlonaftase . . . | $C_{10}H_3Br_2Cl_3$ |
| Bronaphtise . . . | $C_{10}H_5Br_3$ | Chlonaphtalase . . . | $C_{10}H_2Cl_6$ |
| Chlorebronaphtise . . . | $C_{10}H_5Cl_2Br$ | Chlonaphtalise . . . | $C_{10}Cl_8$ |

From the results of this decomposition it appears to be probable that the formulæ given in the third column of the first table represent, more accurately than those of the second column, the true composition of the so-called chlorides and bromides of naphthalin.

It must not, however, be supposed that the foregoing tables indicate all the combinations of chlorine with naphthalin which may be formed by substitution or otherwise. Many of these different compounds exist in several distinct modifications. There are, for example, no fewer than seven distinct forms of *chlonaftese*, which Laurent has distinguished by the letters, *a*, *c*, *ad*, *e*, *f*, *x*, and *y*; four of them *a*, *c*, *f*, and *x*, are obtained by the distillation of naphthalin tetrachloride, and two of them, *ad* and *e*, by treating the same compound with potash, and *y* is the result of the action of chlorine upon dinitronaphthalin.

a and *x* are liquid at ordinary temperatures, *c* crystallizes in needles, which fuse at 122° (50° C.), *f* crystallizes in tables, fusible at 213.8° (101° C.), *ad* crystallizes in needles, which fuse at about 85° (29.5° C.), *e* fuses at 87.8° (31° C.); *y* fuses at 203° (95° C.), and may be sublimed in plates. Many of these bodies are also distinguished by differences in the degree of their solubility in alcohol and in ether, and by the different way in which they are attacked by chlorine and by bromine.

The existence of these remarkable modifications of chlonaftese was accounted for by Laurent, on the supposition that in the compound ($C_{10}H_8$), or naphthalin, each of the 8 atoms of hydrogen has its distinct or allotted position in the compound molecule. In chlonaftese 2 of these atoms of hydrogen are displaced by 2 atoms of chlorine, but it is not a matter of indifference which of the atoms are thus displaced. For example, if $\left\{ \begin{array}{cccc} 1. & 2. & 3. & 4. \\ C_{10} & 5. & 6. & 7. & 8. \end{array} \right\}$ represent the compound molecule of naphthalin, each numeral indicating a distinct atom of hydrogen, it is not a matter of indifference whether the displacement shall take place thus:—



In all these cases we should still have compounds which on analysis would exhibit a perfectly similar composition; and yet, from the different relative position of the atoms of chlorine in the compound, the properties of each might be different. It may be

shown by calculation, upon the principle of permutation, that twenty-eight such varieties of ehlonaphtese are possible; of these seven have been discovered. This idea of Laurent has been again handled in a very ingenious and interesting way by Kekulé in his paper on the aromatic hydrocarbons (1550).

Chlonaphtise has also been obtained in seven different forms, all of which are crystallizable solids. *Chlonaphthose* is known under four different modifications. The compounds which contain both chlorine and bromine of the type *naphthose*, in which 4 atoms of hydrogen have been displaced, may be formed in three different ways, and yield three metameric modifications, viz.:—1. *Chloribronaphthose*, which is obtained by exposing a mixture of bromine and chlonaphtise to the sun's rays; it forms six-sided prisms, which are fusible, and solidify at a temperature of about 221° (105° C.). 2. *Bromachlonaphthose α*, which is obtained by passing a current of chlorine over heated bronaphtese: it forms six-sided prisms of the consistence of wax, which after fusion solidify at 230° (110° C.). 3. *Bromachlonaphthose β*, which is obtained by the distillation of bronaphtese tetrachloride; it forms flattened oblique prisms. Several modifications of many of the other chlorides might be enumerated, but it is unnecessary to particularize further. This great variety of form admits of explanation upon the hypothesis already applied to account for the different forms of chlonaphtese. It is obvious that numerous as are the modifications of many of the forms of these derivatives of naphthalin, they constitute but a small number of the possible varieties which a permutation in the relative position of the elementary atoms of the compound would allow.

Naphthalin hydride ($C_{10}H_8, H_2$), *Boil. pt.* about 401° (205° C.).—If naphthalin be heated in a closed tube with 20 times its weight of concentrated hydriodic acid to about 536° (280° C.), the naphthalin disappears and is converted with some separation of a carbonaceous matter, into the hydride of naphthalin. It is a viscid liquid of a powerful and disagreeable odour: a small quantity of what appears to be a second hydride $C_{10}H_{12}$, boiling at 374° (190° C.), is formed at the same time. By a prolonged heating of the mixture of naphthalin and hydriodic acid, other hydrocarbons belonging to the benzol series—viz., benzol, ethylbenzol, and diethylbenzol are formed.

Dinaphthyl ($C_{10}H_7$)₂, *Fusing pt.* about 309°·2 (154° C.).—This is obtained mixed with phthalic acid and other substances, when naphthalin is treated with a mixture of finely-powdered manganese dioxide, and sulphuric acid diluted with twice its weight of water. It is soluble in alcohol, from which it crystallizes in octahedra. It is still more readily soluble in ether. It boils at a temperature above 662° (350 C.), and may be sublimed unaltered. Dinaphthyl forms with bromine, substitution-products, $C_{20}H_{12}Br_2$, and $C_{20}H_8Br_6$; other similar bodies may be obtained with chlorine or with nitroxyl.

(1564) *Anthracenc* ($C_{14}H_{10}$; Anderson), formerly called *Paranaphthalin*; *Sp. gr. of vap.* 0·741; *Fusing pt.* 415°·4 (213° C.).—This substance accom-

panies naphthalin in the last stages of the distillation of coal tar. It may be purified from naphthalin by means of alcohol, which dissolves the naphthalin, but leaves almost all the anthracene untouched. Anthracene is a white solid, which may be distilled without being decomposed, and it condenses in lamellar crystals. Its best solvent is oil of turpentine. An alcoholic solution of anthracene furnishes rusty red crystals if mixed with a hot alcoholic solution of carbazotic acid, and the same colour characterizes the compounds formed by the homologues of anthracene with the acid. Chlorine acts slowly upon anthracene, forming a substitution-compound ($C_{14}H_9Cl$). Chlorine also combines directly with anthracene, forming the compound $C_{14}H_{10}Cl_2$; with bromine its combination has the formula $C_{14}H_{10}Br_6$. Treated with nitric acid it yields *oxanthracene* $C_{14}H_8O_2$ which crystallizes in long needles. It is probable that coal tar contains other hydrocarbons homologous with anthracene (Berthelot), such as retene $C_{14}H_6(CH_3)_4$, or tetramethyl-anthracene. Anthracene has been formed synthetically by Limprieh from toluol.

Berthelot regards the paranaphthalin of Dumas as a mixture of several hydrocarbons.

(1565) *Metanaphthalin*, the *Retisterene* of Dumas [*Fusing pt.* $152^{\circ}6$ ($67^{\circ}C.$); *Boil. pt.* 617° ($325^{\circ}C.$)], is a compound polymeric with naphthalin: it was obtained by Pelletier and Walter during the distillation of resin. This body is sparingly soluble in cold alcohol, but is readily dissolved by boiling alcohol, as well as by ether, naphtha, and oil of turpentine. It does not appear to form any coupled acid when treated with oil of vitriol.

(1566) During the distillation of the bituminous shale of Dorsetshire, various products are obtained, which greatly resemble those contained in coal tar. The hydrocarbons appear to belong to the series of marsh gas (C_nH_{2n+2}). A portion of the oil, which boils between 392° and 482° (200° and $250^{\circ}C.$), furnishes a substance resembling kreasote, which Laurent termed *ampelin*: it is soluble to a considerable extent in water, but the addition of a few drops of an acid or of the solution of certain salts causes the separation of the ampelin. Ampelin is decomposed when the attempt to redistil it is made. By treating the oils of schist with nitric acid, Laurent obtained an acid metameric with the salicylic, and which he termed *ampelic acid*.

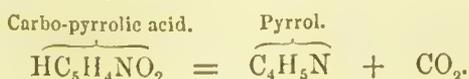
Shale tar is particularly rich in basic substances. G. Williams has detected in it, in addition to pyrrol, ammonia, pyridine, picoline, lutidine, collidine, and parvoline; besides two other bases as yet but imperfectly examined, which have been termed *carmidine* and *vertidine*. It is remarkable that aniline is not present amongst these bases. (*Q. J. Chem. Soc.*, vii. 97.)

The destructive distillation of bones, and of azotised animal matters generally, yields a substance commonly known as *Dippel's animal oil*. This oil comes over accompanied by an aqueous liquid, charged with carbonate, sulphide, and cyanide of ammonium. The oil itself is a complex mixture, consisting of a part which is soluble in acids, and of an insoluble portion; the latter

constitutes the larger part of the oil. In the portion soluble in acids, various volatile bases are present, including methyilia, ethyilia, tritylia, tetrylia, and amyilia,—aniline, pyridine, picoline, lutidine,—and the substance termed *pyrrol* by Runge. The portion insoluble in acids contains benzol, and a mixture of several nitriles.

(1567) *Pyrrrol* (C_4H_5N); *Sp. gr. of liq.* 1.077; *of vap.* 2.47; *Boil. pt.* $271^{\circ}.4$ (133° C.).—This body has been carefully examined by Anderson (*Edin. Phil. Trans.*, xxi. 586). Its purification is attended with considerable difficulties. During the distillation of the acid solution of the erude pyridine bases (1368) from Dippel's oil, a peculiar fœtid oil is obtained, which is colourless at first, but it becomes in a few days of a reddish colour, and ultimately nearly black. On subjecting this oil to fractionated distillation, a considerable portion is obtained between 266° and 293° (130° and 145° C.). If agitated with dilute sulphuric acid and dried over sticks of potash, it may be obtained nearly pure by repeated rectification. In order to purify it perfectly, it should be digested in a copper flask with 5 or 6 times its weight of caustic potash, allowing the liquid as it distils to fall back into the flask. Gradually the pyrrol enters into combination with the potash, and the heat may be raised nearly to redness without expelling any portion of the pyrrol. The residue thus obtained in the retort, after any traces of picoline have been expelled by heat, when thrown into water is decomposed, and pure colourless pyrrol rises to the surface.* This liquid has an odour faintly resembling that of chloroform, and a hot pungent taste. It becomes brown when exposed to the air. It is insoluble in alkaline solutions, but is slowly dissolved by acids. Its most remarkable reaction is the production of a pale pink colour, which gradually deepens to an intense carmine when a splinter of fir-wood moistened with hydrochloric acid is exposed to the vapour of pyrrol. When a solution of pyrrol in a dilute acid is heated, a red flocculent substance is deposited, and the liquid, if not extremely dilute, becomes of a gelatinous consistence; a similar change occurs in the acid solutions at ordinary temperatures if left for a few days. Alcoholic solutions of pyrrol precipitate

* Schwanert finds pyrrol among the products of the dry distillation of ammoniacal pyromucate ($H_4NC_5H_3O_3$), accompanied by a substance which he terms carbo-pyrrolamide $C_5H_6N_2O$, the amidated compound of an unstable acid, the *carbo-pyrrolic*, which readily breaks up into pyrrol and carbonic anhydride:—



solutions of corrosive sublimate, and of cadmic chloride, but not those of the metals in general.

The red substance obtained by the action of acids is supposed by Anderson to have the composition of $C_{12}H_{14}N_2O$, being formed from pyrrol by the elimination of the elements of ammonia and the assimilation of water, thus: $3C_4H_5N + H_2O = H_3N + C_{12}H_{14}N_2O$.

(1568) *Bitumen, Asphalt, and Petroleum*.—Closely connected with the products of destructive distillation are the different forms of bitumen, asphalt, and petroleum. Deposits of these substances are found in various localities, as, for example, at Trinidad, at Zante, and in some parts of the north of Italy, and also on the borders of the Caspian Sea, where petroleum occurs in beds of marl above coal measures. Petroleum is likewise abundant at Rangoon, and in several other localities of the kingdom of Burmah, where the naphtha is obtained from a pale blue clay, soaked with oil, which rests upon roofing slate, beneath which is coal containing much pyrites. The *petroleum* (*petri oleum*, rock oil) from the last-named locality has been made the subject of examination by De la Rue and H. Müller (*Proceed. Roy. Soc.*, viii. 221). It is obtained by sinking wells about 60 feet deep, in which the liquid is collected as it oozes from the soil. At common temperatures it has the consistence of goose fat; it is lighter than water, and has usually a greenish-brown colour; it has also a slight, peculiar, but not unpleasant odour. It is composed almost entirely of volatile constituents, about 11 per cent. of which come off below 212° . The fixed residue does not amount to more than 4 per cent. if it be distilled in a current of superheated steam. About 10 or 11 per cent. of the volatile matters consist of a body fusible at 149° (65° C.), but which is solid at ordinary temperatures (paraffin). When the liquid portion is agitated with oil of vitriol, some of its constituents enter into combination with the acid, but the greater part remains unaltered by this agent. In the portion which combines with the acid, benzol, toluol, xylol, and cumol have been identified,* and there are several basic substances which have not as yet been completely examined. The liquid from which the hydrocarbons of the benzol series have been removed by the action of oil of vitriol, after being rectified, constitutes *rock oil*, or *mineral naphtha*; it is a mixture of several hydrocarbons, and is the liquid in which potassium and sodium are preserved. In order to purify it for this purpose, the crude dis-

* Cumol also was found by Freund and Pebal in the rock oil from Boroslaw in Galicia.

tillate must be agitated several times with a fifth of its bulk of oil of vitriol; after which the undecomposed hydrocarbon is to be well washed with water, and rectified from quicklime. This liquid requires about eight times its bulk of alcohol for solution, but it is soluble in all proportions in ether and in the volatile oils. Hot naphtha dissolves phosphorus and sulphur, but deposits the greater portion of these bodies on cooling. It also dissolves caoutchouc, camphor, and fatty and resinous bodies generally. Warren and Storer have isolated from it a number of hydrocarbons of the olefine series; viz. *Rutylene*, $C_{10}H_{20}$; *Boil. pt.* 347° (175° C.); *Sp. gr. of liq.* 0.823; *of vap.* 5.08; *Endecylene*, $C_{11}H_{22}$; *Sp. gr. vap.* 5.47; *of liq.* 0.8938; *Boil. pt.* 383° (195° C.); *Laurylene*, $C_{12}H_{24}$; *Boil. pt.* about 419° (215° C.); *Sp. gr. of vap.* 6.00; *of liq.* 0.855; and *Cocinylene* $C_{13}H_{26}$; *Boil. pt.* 450° ($232^{\circ}.2$ C.); *Sp. gr. of vap.* 6.42; *of liq.* 0.8445. They also found small quantities of naphthalin among the constituents of Rangoon petroleum.

Pelouze and Cahours (*Ann. de Chimie*, IV. i. 5) have published an elaborate investigation upon the recently discovered American petroleum. The oil-wells of Pennsylvania are worked by boring into the oil-bearing strata to a depth of from 50 to 500 feet, and a mixture of oil and water is raised to the surface, usually by pumping; sometimes the oil overflows from the boring.

Four products are furnished for sale from these oils: 1st. A naphtha, used extensively as a solvent instead of oil of turpentine; 2nd. A heavier and less volatile oil, suitable for illuminating purposes; 3rd. A lubricating oil, used for machinery; and 4th. A still heavier oil, used for adulterating vegetable oils. These oils are furnished by the limestone rocks of the Silurian and Devonian formations.

The bulk of these oils, according to Pelouze and Cahours, consists of a mixture of various members of the marsh-gas series, including thirteen different compounds. Tetryl hydride, C_4H_{10} , is the lowest term of the series, and palmyl hydride, $C_{16}H_{34}$, the highest; the most abundant of these compounds is hexyl hydride, C_6H_{14} , and the next in amount heptyl hydride (1206).

In Canada also vast quantities of petroleum have been obtained, many of the oil-wells yielding 600 gallons of oil per day. According to Sterry Hunt this oil comes from the carboniferous limestone which crops out at Port Erie, and crosses the country to Lake Huron, being in parts overlaid by a thick bed of shale of the Hamilton group.

Asphalt is the term given to solid bitumen (1111). The

bitumens differ in the facility with which they are attacked by solvents. Generally they contain but little of any matter soluble in alcohol, but most of them are dissolved in great part by ether, and by oil of turpentine. When distilled they yield substances which resemble the paraffin oils in properties and consistence (1537).

CHAPTER X.

DERIVATIVES OF CYANOGEN—UREA—ORGANIC BASES OF ANIMAL ORIGIN—URIC ACID, PRODUCTS OF ITS DECOMPOSITION.

§ I. DERIVATIVES OF CYANOGEN.

(1569) IN describing some of the compounds of cyanogen (509), allusion was made to some important derivatives of this body (containing iron, cobalt, platinum, sulphur, and some other elements), which perform the functions of salt-radicles, or bodies which in their mode of combination present a certain analogy with the halogens. In the present chapter some of these compounds will be described; urea and some organic bases of animal origin will next be examined, after which uric acid and its more important derivatives will be considered.

(1570) Hydrocyanic acid in its anhydrous form combines with several of the anhydrous electro-negative chlorides, such as ferric chloride, stannic chloride, titanous chloride, and antimonous chloride, with which it forms compounds, the composition of which is represented by the formulæ $(4\text{HCy}, \text{Fe}_2\text{Cl}_6)$; $(2\text{HCy}, \text{SnCl}_4?)$; $(2\text{HCy}, \text{TiCl}_4)$; and $(3\text{HCy}, \text{SbCl}_5)$; but these compounds are all decomposed by water, and have no practical applications.

The general properties of the cyanides have been already discussed; some of these salts are of considerable practical importance, and may be now briefly described.

(1571) *Potassic Cyanide* ($\text{KCy} = 65.1$).—This salt is prepared in considerable quantities for the purpose of dissolving the salts of gold and silver in the processes of electrotyping; it is also employed in photography. It may be obtained by heating to dull redness, in a covered iron crucible, a mixture of 8 parts of anhydrous potassic ferrocyanide, and 3 of dried potassic carbonate,

until the fused mass has lost its yellow colour, and ceases to give off bubbles of gas. The iron is separated in the form of a metallic powder, and subsides to the bottom of the crucible; the fused cyanide can then be poured off, and solidifies on cooling to a milk-white mass. The cyanide thus obtained is, however, always mixed with a portion of cyanate, the reaction being such as is shown in the following equation:—

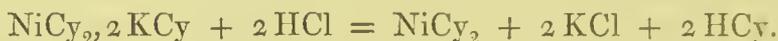


If the presence of the potassic cyanate be injurious, it may be got rid of by adding to the mixture of the carbonate and ferrocyanide, before fusion, one-eighth of its weight of charcoal, which at a red heat reduces the potassic cyanate to the form of cyanide: the fused salt, when decanted from the iron, will then have a black aspect, owing to the presence of particles of unconsumed charcoal. If it is to be used in solution immediately, it may be dissolved in water and filtered; but if required in the solid form it may be purified by treatment with boiling alcohol, from which, after filtration, it crystallizes on cooling. Potassic cyanide forms colourless cubes; it is deliquescent, has an alkaline reaction, and when moist emits an odour of hydrocyanic acid. It is highly poisonous.

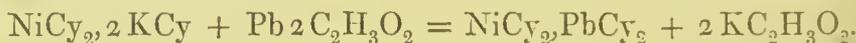
Potassic cyanide is a powerful and valuable reducing agent. The oxides of a large number of metals, including those of lead, copper, and iron, when thrown into the melted salt are immediately reduced to the metallic state, while potassic cyanate is formed. It may also be used in the laboratory as a reducing agent instead of black flux, in testing for arsenicum (846). Solutions of potassic cyanide dissolve metallic iron, zinc, nickel, and copper, with evolution of hydrogen, while potash is produced. Silver and gold are also dissolved by the solution of potassic cyanide, if air be allowed free access, and double cyanides of potassium with those metals are formed. Cupric sulphide is soluble in an excess of potassic cyanide, and may be thus easily separated from cadmic sulphide, which is insoluble in this reagent.

(1572) *Double Cyanides*.—Potassic cyanide, when mixed with metallic solutions, occasions a large number of precipitates, which in the majority of instances are soluble in an excess of the potassic cyanide; they generally form with it crystallizable double salts. The cyanides of the metals of the other alkalies and of the alkaline earths may be substituted for potassic cyanide, and they produce similar double cyanides. The double cyanides which are formed in these cases are of two kinds or classes. The

double salts of the first class are comparatively unstable, and are highly poisonous; they are decomposed by the addition of a diluted free acid, such as the hydrochloric. In such cases the potassic cyanide is decomposed, hydrocyanic acid is liberated, and the insoluble metallic cyanide is precipitated. The double salts which the cyanides of zinc, nickel, manganese, copper, and silver form with potassic cyanide belong to this class. When, for example, potassic nickel-cyanide is decomposed by hydrochloric acid, the following reaction occurs, and nickel cyanide is precipitated, since it is insoluble both in hydrocyanic and in hydrochloric acid:—

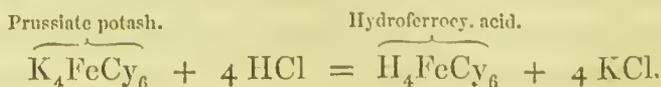


The alkalis do not occasion precipitates in the solutions of the double cyanides. When these double cyanides are mixed with a solution of a metallic salt which, like plumbic acetate or cupric sulphate, is capable of furnishing an insoluble cyanide, a double insoluble cyanide is formed; for example:—



The double cyanides of the second class are much more stable. The salts of this class do not possess the poisonous characters of the cyanides in general; on the addition of dilute acids no precipitation of an insoluble cyanide occurs; the more electro-negative metal appears to have entered into combination with the cyanogen in such a manner as to form a new salt-radicle, more or less analogous to chlorine and the halogens, in consequence of which the metal remains in solution.

The double salts which the cyanides of cobalt, of iron, of chromium, and of platinum, form with potassic cyanide, belong to this class, and they contain compounds to which the terms cobaltcyanogen, ferrocyanogen, ferrieyanogen, chromicyanogen, and platinocyanogen, have been applied: these radicles are distinguished by the property of yielding compounds with hydrogen which possess acid characters, and they contain a certain number of atoms of hydrogen in the place of the potassium of the double cyanide. For instance, the cyanide of potassium and iron, termed yellow potassic ferrocyanide, may be represented by the formula $(\text{K}_4\text{FeCy}_6)$; it yields, when decomposed by hydrochloric acid, a compound termed hydroferrocyanic acid $(\text{H}_4\text{FeCy}_6)$, which contains 4 atoms of hydrogen instead of the 4 of potassium in the yellow salt:—



The quantity of cyanogen in the simple cyanides may be determined by the following method proposed by Heisch (*Q. J. Chem. Soc.*, ii. 219). The substance for analysis is placed in a small flask with some pieces of pure zinc in a little water; the neck of the flask is fitted with a cork, through which are passed a tube funnel, and a second tube bent twice at right angles for carrying off the gas which is disengaged; sulphuric acid is poured into the funnel, and hydrogen is liberated; this gas at the moment of its liberation combines with the cyanogen, and carries it off in the form of hydrocyanic acid, which is arrested by causing it to pass through a solution of argentic nitrate. The argentic cyanide is afterwards collected upon a filter and weighed; but it is better, as practised by Liebig, to conduct the vapours of hydrocyanic acid into a solution of potash, and afterwards to add to the alkaline liquid (503) a standard solution of argentic nitrate, or of cupric sulphate.

(a) *Cyanides which do not contain Electro-negative Metallic Cyanides.*

(1573) The following are some of the principal insoluble metallic cyanides which yield double cyanides of the first class, *i.e.*, double salts which are decomposed and yield a precipitate on the addition of a dilute acid.

Zincic cyanide is white, and insoluble in water; with potassic cyanide it forms a soluble salt ($\text{ZnCy}_2, 2 \text{KCy}$), which may be obtained in large, regular, anhydrous, colourless octahedra: *sodic-zincic cyanide* ($2 \text{ZnCy}_2, 2 \text{NaCy}, 5 \text{H}_2\text{O}$) may be obtained in brilliant plates, if sodic cyanide is substituted for potassic cyanide. *Nickel cyanide* (NiCy_2) forms an apple-green precipitate, which is very soluble in potassic cyanide, forming a salt ($\text{NiCy}_2, 2 \text{KCy}, \text{H}_2\text{O}$) which crystallizes in oblique rhombic prisms of a yellow colour. *Manganous cyanide* falls as a bulky reddish-white precipitate, on mixing a solution of any manganous salt with one of potassic cyanide; it rapidly becomes brown by exposure to the air. This cyanide is soluble in excess of potassic cyanide, but the solution absorbs oxygen, and gradually deposits manganic oxide. *Cupreous cyanide*, Cu_2Cy_2 , is a white powder obtained by treating an acid solution of cupreous chloride with potassic cyanide; it is soluble in the dilute acids. Cupric sulphate yields with potassic cyanide a brownish-yellow precipitate (CuCy_2), which is only known in the hydrated form, and soon begins to give off cyanogen, becoming converted into a double cyanide ($\text{Cu}_2\text{Cy}_2, \text{CuCy}_2, 5 \text{H}_2\text{O}$). The same salt may be obtained in bright green crystals by adding hydrocyanic acid to a solution of cupric sulphate. Cupric cyanide (CuCy_2) is soluble in excess of potassic cyanide, with an evolution of cyanogen, and formation of cupreous cyanide; the cupreous cyanide forms two crystallized double salts ($\text{Cu}_2\text{Cy}_2, 2 \text{KCy}$), and ($\text{Cu}_2\text{Cy}_2, 6 \text{KCy}$). The latter is the more soluble salt of the two.

(1574) *Argentio cyanide*, or *cyanide of silver* ($\text{AgCy} = 134$; *Sp. gr.* 3.943) is precipitated in dense white flocculi when hydrocyanic acid or potassic cyanide is added to a solution of argentic nitrate. It is nearly insoluble in *dilute* nitric acid even at a boiling temperature, but it is soluble in ammonia, and is decomposed by strong boiling nitric acid and by hydrochloric acid. When heated gently it melts, and at a high temperature gives off cyanogen, leaving a residue of a grey colour, which retains a portion of cyanogen. Argentio cyanide is freely soluble in solu-

tions of the cyanides of potassium, sodium, barium, calcium, and strontium. These solutions give no precipitate with solutions of the metallic chlorides; indeed, argentic cyanide is dissolved by boiling solutions of the chlorides of the metals of the alkalis, and of the earths. It is also soluble in a solution of argentic nitrate, as well as in solutions of the ferrocyanide and ferriecyanide of potassium. When potassic ferrocyanide is used as the solvent, a dirty blue precipitate of ferrous cyanide is formed, and the liquid becomes strongly alkaline; $K_4FeCy_6 + 4AgCy = FeCy_2 + 4(AgCy, KCy)$. *Potassic-argentic cyanide* ($AgCy, KCy = 199$) is anhydrous, and may be obtained in octahedra or in six-sided plates. Occasionally it forms rhombic prisms $2(AgCy, KCy), H_2O$. This salt is freely soluble in water and in boiling alcohol. It is extensively employed for electro-silvering, since its solution, if mixed with an excess of potassic cyanide and then submitted to electrolysis, deposits silver in compact coherent plates (295).

(1575) *Mercuric Cyanide*, or *Cyanide of Mercury* ($HgCy_2 = 252$; *Sp. gr.* 3.77).—This salt may be prepared either by dissolving mercuric oxide in dilute hydrocyanic acid, in which the oxide is soluble with great facility, or by boiling a mixture of 4 parts of finely-powdered Prussian blue and 3 of mercuric oxide, also finely levigated, with 30 parts of water, until the undissolved portion has acquired a full brown colour: the filtrate on evaporation yields mercuric cyanide. It may also be procured by boiling 2 parts of mercuric sulphate with 1 part of potassic ferrocyanide and 8 of water:—



Mercuric cyanide crystallizes in anhydrous rectangular prisms, which are colourless and transparent. It has a nauseous, metallic taste, and is very poisonous. It requires about 8 parts of cold water for solution; it is less soluble in ordinary alcohol, and nearly insoluble in absolute alcohol. Mercuric cyanide is decomposed when heated; if perfectly dry it yields cyanogen gas, metallic mercury, and a residue of paracyanogen. If moist, carbonic anhydride, ammonia, and hydrocyanic acid are produced.

Mercuric cyanide dissolves mercuric oxide freely, and forms an *oxycyanide* ($HgO, HgCy_2$) which crystallizes in needles; it is sparingly soluble in cold water, and the liquid has an alkaline reaction. Mercuric cyanide does not give any precipitate of oxide of mercury on the addition of a free alkali. When heated with sulphuric or hydrochloric acid it is decomposed, and gives off hydrocyanic acid. It is also decomposed by sulphuretted

hydrogen. Mercuric cyanide enters into combination with a great number of chlorides, iodides, bromides, cyanides, nitrates, and various other salts, forming with them crystallizable double salts. It does not occasion precipitates when mixed with the solutions of salts of zinc, cobalt, nickel, manganese, and other metals which yield cyanides insoluble in water, with the exception of the salts of palladium; from which it would appear that mercury has a stronger attraction for cyanogen than any of the metals, excepting palladium.

(1576) *Cyanides of Gold*.—*Aurous cyanide* ($\text{AuCy} = 222.6$) is the only cyanide of gold which is accurately known. It may be obtained by several methods; the simplest consists in adding a solution of potassic cyanide to a dilute solution of auric chloride, so long as a precipitate is occasioned. It is a lemon-yellow powder, composed of microscopic hexagonal plates. It is decomposed by heat into cyanogen and metallic gold; boiling nitric, sulphuric, and hydrochloric acids do not decompose it unless very concentrated, and aqua regia acts upon it very slowly. It is soluble in sodic hyposulphite and in ammoniac sulphhydride; but its most important solvent is potassic cyanide, with which it forms a double salt ($\text{AuCy}, \text{KCy} = 287.6$): this compound crystallizes in colourless rhombic octahedra, or in pearly scales. It may be obtained by dissolving either aurous cyanide or auric oxide (precipitated from the trichloride by ammonia) in a solution of potassic cyanide. Aurous cyanide is also soluble in a solution of potassic ferrocyanide. The double cyanide is likewise formed by dissolving finely-divided metallic gold in a solution of potassic cyanide with exposure to the air. Auro-potassic cyanide is largely used for gilding by means of the galvanic battery (296).* Copper and silver articles may also be gilt by it without the aid of the battery, by mere immersion; portions of copper or of silver being dissolved during the operation.

(1577) *Palladious cyanide* ($\text{PdCy}_2 = 158.4$).—Palladium has a very powerful attraction for cyanogen; when a solution of a salt of palladium is mixed with one of mercuric cyanide, a yellowish-white precipitate of palladious cyanide is formed; this precipitate may be dissolved by means of potassic cyanide, with which it forms a double salt, which crystallizes in rhomboidal prisms ($2 \text{KCy}, \text{PdCy}_2, 3 \text{H}_2\text{O}$).

Plumbic cyanide (PbCy_2) is white: it is insoluble in water, and does not

* Böttger recovers the gold from the spent gilding solutions by evaporating them to dryness, mixing the residue with its own weight of finely-powdered litharge, and fusing the mass; the lead and the gold are reduced, and form a metallic button, which, when treated with nitric acid, leaves the gold in the form of a fine powder.

form a double cyanide with potassic cyanide; it is insoluble in an excess of a solution of this salt. Dilute sulphuric acid decomposes plumbic cyanide, and liberates hydrocyanic acid.

(b) *Electro-negative Metallic Cyanides.*

(1578) *Cyanides of Iron.*—Little is known accurately of the simple cyanides of iron. When potassic cyanide is mixed with ferrous sulphate free from ferric salt, a reddish-brown precipitate partially soluble in acids is formed, which appears to consist of hydrated *ferrous cyanide*. This precipitate is dissolved by an excess of potassic cyanide, and is thus converted into potassic ferrocyanide. The white compound obtained by decomposing Prussian blue by means of a current of sulphuretted hydrogen appears not to be a simple cyanide of iron, as was originally supposed by Robiquet. *Ferric cyanide* has not been procured in a separate form. When a solution of ferric chloride is mixed with one of potassic cyanide, hydrocyanic acid is liberated, potassic chloride is formed, and a precipitate of hydrated ferric oxide is obtained. *Prussian blue* ($\text{Fe}_7\text{Cy}_{18}, 18\text{H}_2\text{O}$; 1582), *Turnbull's blue* ($\text{Fe}_3\text{Cy}_{12}, 12\text{H}_2\text{O}$), and the substance ($\text{Fe}_3\text{Cy}_8, 4\text{H}_2\text{O}$), which Gmelin terms *Prussian green* (1584), are compound cyanides of iron.

(1579) 1. FERROCYANIDES.—The cyanides of iron, when in combination with other cyanides, give rise to two important classes of compounds, which are represented by the yellow prussiate of potash, or *potassic ferrocyanide* ($\text{K}_4\text{FeCy}_6, 3\text{H}_2\text{O}$), and the red prussiate of potash, or *potassic ferricyanide* (K_3FeCy_6).

| Ferrocyanogen (hypothetical). | = FeC_6N_6 . | or Fcy. |
|---|--|--|
| Hydro-ferrocyanic acid . . . | $\text{H}_4\text{C}_6\text{N}_6\text{Fe}$ | H_4Fcy |
| Potassic ferrocyanide . . . | $\text{K}_4\text{C}_6\text{N}_6\text{Fe}, 3\text{H}_2\text{O}$ | $\text{K}_4\text{Fcy}, 3\text{H}_2\text{O}$ |
| Sodic ferrocyanide . . . | $\text{Na}_4\text{C}_6\text{N}_6\text{Fe}, 12\text{H}_2\text{O}$ | $\text{Na}_4\text{Fcy}, 12\text{H}_2\text{O}$ |
| Everitt's white salt, or ferrocyanide of potassium and iron | $\text{K}_2\text{C}_6\text{N}_6\text{Fe}_2$ | { $\text{K}_2\text{Fe.Fcy}$, or { $\text{K}_4\text{Fcy}, 3\text{FeCy}_2$ |
| Ordinary Prussian blue . . . | $\text{C}_{18}\text{N}_{18}\text{Fe}_7, 18\text{H}_2\text{O}$ | $\text{Fe}_4\text{Fcy}_3, 18\text{H}_2\text{O}$ |
| Basic Prussian blue . . . | $\text{C}_{18}\text{N}_{18}\text{Fe}_9\text{O}_3, x\text{H}_2\text{O}$ | $\text{Fe}_4\text{Fcy}_3, \text{Fe}_2\text{O}_3, x\text{H}_2\text{O}$ |
| Baric dipotassie ferrocyanide | $\text{K}_2\text{BaC}_6\text{N}_6\text{Fe}, 3\text{H}_2\text{O}$ | $\text{K}_2\text{Ba.Fcy}, 3\text{H}_2\text{O}$ |
| Cupric ferrocyanide . . . | $\text{Cu}_2\text{C}_6\text{N}_6\text{Fe}, x\text{H}_2\text{O}$ | $\text{Cu}_2.\text{Fcy}, x\text{H}_2\text{O}$ |
| Cupric dipotassie ferrocyanide | $\text{K}_2\text{CuC}_6\text{N}_6\text{Fe}, 2\text{H}_2\text{O}$ | $\text{K}_2\text{Cu.Fcy}, 2\text{H}_2\text{O}$ |
| Plumbic ferrocyanide . . . | $\text{Pb}_2\text{C}_6\text{N}_6\text{Fe}, 3\text{H}_2\text{O}$ | $\text{Pb}_2.\text{Fcy}, 3\text{H}_2\text{O}$ |

Liebig considers that these two classes of salts contain two separate radicles, *ferrocyanogen* ($\text{FeCy}_6 = \text{Fcy}^{\text{iv}}$), and *ferricyanogen* ($\text{FeCy}_6 = \text{Fdcy}^{\text{v}}$). The first of these radicles is tetrabasic, the second tribasic; but neither of these bodies has been obtained in

a separate form. The hypothesis of their existence, however, affords a convenient mode of representing the composition of the double cyanides into which they are supposed to enter, and greatly facilitates the study of these salts, which are numerous and important. The preceding table shows the composition of some of the compounds of the ferrocyanogen series.

(1580) *Hydroferrocyanic Acid* (H_4FeCy_6).—This compound was originally obtained by Porrett, who decomposed the potassic ferrocyanide by means of tartaric acid. A better plan consists in forming a concentrated aqueous solution of the ferrocyanide, boiling it to expel the air, and then allowing it to cool in a vessel provided with a good cork to exclude air. Ether is now added, and an excess of hydrochloric acid, which has also been deprived of air by boiling. On agitating the mixture, potassic chloride is formed and remains in solution, and white scales of hydroferrocyanic acid are deposited; $K_4FeCy_6 + 4HCl = H_4FeCy_6 + 4KCl$. These crystals must be washed with a mixture of alcohol and ether, and dried *in vacuo* over sulphuric acid. Liebig adds by degrees to a cold saturated solution of potassic ferrocyanide an equal volume of hydrochloric acid; the white precipitate of hydroferrocyanic acid thus obtained must be washed with hydrochloric acid, dried *in vacuo* upon a tile, and caused to crystallize from its solution in alcohol by the addition of ether.

Hydroferrocyanic acid is tetrabasic. When exposed to the air, it absorbs oxygen and becomes blue; its solution, when boiled, evolves hydrocyanic acid, and deposits a white insoluble matter containing both iron and cyanogen. This body also becomes blue in the air. It is probably ferrous cyanide, and by exposure to air it absorbs oxygen, becoming converted into basic Prussian blue, which is a compound of ferric oxide and of true Prussian blue; $2(9FeCy_2) + 3O_2 = 2(Fe_7Cy_{18}, Fe_2O_3)$.

(1581) *Potassic Ferrocyanide, or Prussiate of Potash* ($K_4FeCy_6, 13H_2O = 368 + 54$).—This important salt is met with in commerce nearly in a state of purity. It is formed when azotised matters are heated to redness with potassic carbonate and iron. It is also formed when a ferrous salt is mixed with a solution of potash supersaturated with hydrocyanic acid. It is manufactured on a large scale by heating dried blood, horns, parings of hides, and other animal matters containing nitrogen, with an equal weight of potassic carbonate, and about one-third of their weight of iron filings, in a covered iron pot. Part of the carbon and nitrogen escapes in combination with oxygen and with hydrogen as carbonic anhydride and ammonia, while another portion (not exceeding,

however, from $\frac{1}{3}$ to $\frac{1}{4}$ of the whole) enters into combination with the potassium, and this when treated with water attacks the iron, forming a salt which may be obtained from its solution, in large lemon-yellow tabular crystals, which contain 3 atoms of water. The salt is tough, and splits into laminæ with facility.

The reactions by which the ferrocyanide is produced are complicated. When animal matter is heated with pearlsh and iron, cyanogen is formed, and this enters into combination with the potassium, forming potassic cyanide; but the temperature employed is too high to allow of the formation of ferrocyanide. A variable quantity of the iron is at the same time converted into sulphide, owing to the action of the dipotassic sulphide (produced by the reduction of the potassic sulphate in the pearlsh) upon the metal. When the mass is lixiviated, the potassic cyanide contained in the mixture attacks both the metallic iron and the ferrous sulphide, becoming converted into ferrocyanide in the following manner (Liebig):—A solution of potassic cyanide dissolves metallic iron with evolution of hydrogen, caustic potash being set at liberty, whilst potassic ferrocyanide is formed: $6 \text{KCy} + \text{Fe} + 2 \text{H}_2\text{O} = \text{K}_4\text{FeCy}_6 + \text{H}_2 + 2 \text{KHO}$: and the action of potassic cyanide upon ferrous sulphide may be thus represented; $6 \text{KCy} + \text{FeS} = \text{K}_4\text{FeCy}_6 + \text{K}_2\text{S}$. Ferrous oxide is also readily dissolved by a solution of potassic cyanide, while potassic ferrocyanide is formed as in the previous cases; $6 \text{KCy} + \text{FeO} + \text{H}_2\text{O} = \text{K}_4\text{FeCy}_6 + 2 \text{KHO}$. A knowledge of these reactions explains the formation of the ferrocyanide during the lixiviation practised in the course of the manufacture.

The iron in the ferrocyanide does not perform the part of a basyl; for when a solution of this salt is submitted to electrolysis, the iron accompanies the cyanogen to the negative electrode. The iron cannot be thrown down from an aqueous solution of the salt by the addition of any alkaline solution; but if the alkaline liquid be boiled with mercuric oxide, the iron is separated in the form of hydrated ferric oxide.

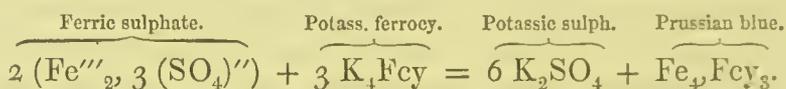
Potassic ferrocyanide is soluble in about 4 parts of cold water, and in 2 parts of boiling water; but it is insoluble in alcohol: the addition of a solution of potash to its aqueous solution causes the separation of a portion of the salt in crystalline flakes. Potassic ferrocyanide is not poisonous; it has a saline bitterish taste. When heated to 212° it loses the whole of its water of crystallization, and crumbles to a yellowish-white powder. When heated to redness in closed vessels it fuses, and at a full

and prolonged red heat undergoes partial decomposition, nitrogen being evolved, while potassic cyanide and carbide of iron are obtained. When dried and heated with red lead, or with manganese dioxide, potassic cyanate is formed (504).

Potassic ferrocyanide, when distilled with sulphuric acid, furnishes abundance of hydrocyanic acid; the decomposition which attends the reaction has been already explained (*note*, Part II. p. 284). When heated with concentrated oil of vitriol, the salt is decomposed into carbonic oxide, and a mixture of potassic, ammoniac, and ferrous sulphates (357). When fused with dry potassic carbonate the ferrocyanide furnishes a convenient source of potassic cyanide (1571). Potassic ferrocyanide is manufactured in large quantities for use in dyeing and calico-printing; it produces a beautiful bright blue colour, which, however, will not bear washing with alkaline solutions, or with soap. It is used also in the preparation of Prussian blue, as well as in the processes of electro-plating and electro-gilding. It is the source from which the compounds of cyanogen are usually obtained. An aqueous solution of potassic ferrocyanide produces characteristic precipitates with many of the metallic salts; it is, consequently, extensively employed as a qualitative test for indicating the presence of metallic bodies in solution. The precipitate generally consists of a ferrocyanide of the metal by which the precipitate is occasioned; usually the 4 atoms of potassium in the ferrocyanide are displaced by an equivalent amount of some other metal, such as cobalt, nickel, copper, or lead, yielding precipitates, Co_2FeCy_6 ; Ni_2FeCy_6 ; Cu_2FeCy_6 ; Pb_2FeCy_6 . These precipitates are apt to retain portions of potassic ferrocyanide, from which it is difficult to free them even by long-continued washing. In a few cases half the potassium only in the ferrocyanide is displaced by an equivalent of some other metal, with which it forms an insoluble precipitate, as happens when a salt of barium is precipitated by potassic ferrocyanide in excess; the yellowish-white precipitate consisting of $(\text{K}_2\text{Ba}, \text{FeCy}_6, 3\text{H}_2\text{O})$. The insoluble ferrocyanides cannot be precipitated in alkaline solutions; the liquid, in all cases, should be slightly but distinctly acid. Many of these precipitates are white, such as those of zinc, cadmium, nickel, manganese, tin, lead, bismuth, antimony, silver, and mercury; with the exception of those of cadmium and manganese, they are insoluble in dilute hydrochloric acid. The most characteristic precipitates occasioned by potassic ferrocyanide are the following:—With the salts of cobalt it gives a yellowish green; with ferrous salts a white, becoming blue; with ferric

salts a deep blue; with cupric salts a reddish brown; and with salts of uranium it also gives a brown precipitate.

(1582) The most important of these insoluble ferrocyanides is the compound largely employed as a pigment under the name of *Prussian blue* ($\text{Fe}_7\text{Cy}_{18}, 18\text{H}_2\text{O} = \text{Fe}_4\text{Fey}_3, 18\text{H}_2\text{O}$). Whenever potassic ferrocyanide is mixed with a soluble ferric salt, this beautiful blue precipitate is produced; 2 atoms of the ferric salt, ferric sulphate, for example, and 3 atoms of potassic ferrocyanide undergo decomposition, so that the place of the 12 atoms of potassium is supplied by 4 atoms of iron; potassic sulphate remains in solution, while the Prussian blue is precipitated:—



The composition of Prussian blue seems to be rather anomalous, but if taken as $(\text{Fe}''''_4, \text{Fcy}^{\text{iv}}_3)$, it corresponds to ferric chloride ($\text{Fe}''''_2\text{Cl}_6$), for if ferrocyanogen be a tetrabasic radicle, it will require 4 Fe instead of 2 Fe for its saturation. Gerhardt and Laurent, starting from the fact that iron is capable of entering into combination in two proportions, assumed that it possesses two different equivalent numbers: $\text{Fe}'' \textit{ferrosium} = 56$, and $\text{fe}'' \textit{ferricum} = \frac{2}{3}\text{Fe}$ or 37.3: and supposing that the portion of iron in Prussian blue which has displaced the potassium is in the form of fe, Prussian blue may be represented as a compound of the same order as potassic ferrocyanide, with the formula, $\text{fe}''_2, \text{Fcy}$.

When large quantities of Prussian blue are required, Liebig recommends that 11 parts of crystallized ferrous sulphate be dissolved in water, and divided into two equal portions; one part is then to be mixed with 2 parts of hydrochloric acid, and chloride of lime is gradually to be added until the whole of the ferrous salt is converted into a ferric salt; it is then to be mixed with the other portion of the solution, and a solution of 10 parts of potassic ferrocyanide is to be added. The compound thus obtained is not a pure substance. It may, however, be prepared in a state of perfect purity by mixing a solution of ferric chloride with one of hydroferrocyanic acid (Williamson). Commercial Prussian blue is generally contaminated with alumina, and sometimes with chalk, plaster of Paris, and starch. It always retains a portion of potassic ferrocyanide.

Prussian blue, as met with in commerce, occurs in eubical or irregular masses of a dark blue colour, which when pressed with a hard body acquire a coppery lustre resembling that of indigo. It is insoluble in water and in weak acids, and has neither taste nor smell. After it has been washed with dilute hydrochloric acid, it may, however, be rendered soluble by triturating it with one-sixth of its weight of crystallized oxalic acid. When this solution is diluted with forty or fifty parts of water, it forms a blue liquid,

which is used as a writing ink. Prussian blue is also soluble in a cold solution of ammonie tartrate, forming a violet-coloured liquid. It is decomposed when treated with alkalis or alkaline carbonates, hydrated ferrie oxide being liberated, and ferrocyanide of the alkaline metal remaining in solution. Oil of vitriol produces a white pasty mass when triturated with Prussian blue, but on the addition of water sulphuric acid is separated, and the blue pigment is reproduced. Prussian blue is decomposed when heated with concentrated sulphuric, nitric, or hydrochloric acid; it is also decomposed by the action of chlorine. When boiled with mercuric oxide, mercuric cyanide is produced and ferrie oxide is separated.

Prussian blue contains water, which cannot be expelled by heat without decomposing the compound. If heated in the open air it becomes kindled on the approach of an ignited body, and burns like tinder, leaving a residue of ferrie oxide.

Soluble Prussian blue may be obtained by pouring a solution of ferrie chloride into an excess of potassic ferrocyanide: the precipitate is insoluble in the saline liquid, and in solutions of salts generally, but it is freely soluble in pure water.

(1583) When a solution of a ferrous salt is mixed with one of potassic ferrocyanide, a greenish-white precipitate is formed, which appears to be the same as Everitt's white salt (501), and may be regarded as a double ferrocyanide of potassium and iron; $K_4FeCy_6 + FeCl_2 = K_2Fe''(FeCy_6)^{iv} + 2KCl$. When this white substance is exposed to the air, the ferrous cyanide becomes oxidized and turns blue, and a compound is formed termed *basic Prussian blue*; it consists of one atom of ferric oxide combined with one of Prussian blue: the potassic ferrocyanide originally present in the white compound may then be washed away. The change which occurs is probably the following, neglecting the potassic ferrocyanide of the precipitate, as it is not affected; $6Fe_2FeCy_6 + 3O_2 = 2(Fe_7Cy_{13}, Fe_2O_3)$. A strong acid removes the ferric oxide from basic Prussian blue, and converts it into ordinary Prussian blue.

(1584) 2. FERRICYANIDES, or *Ferridcyanides*.—*Potassic Ferricyanide*, or *Red Prussiate of Potash* ($K_3, FeCy_6 = 329$).—When a current of chlorine gas is passed through a dilute solution of potassic ferrocyanide, the liquid quickly changes colour and becomes of a deep red. If the current of the gas be arrested so soon as the liquid ceases to give a blue precipitate with the ferrie salts, the solution on evaporation yields magnificent ruby-red crystals of potassic ferricyanide. In this process the reaction which occurs is the following: $2K_4FeCy_6 + Cl_2 = 2K_3FeCy_6 + 2KCl$. The chlorine acts by withdrawing one-fourth of the potassium contained in the yellow salt; chloride and ferricyanide of potassium being the result. The ferricyanide may be obtained by a second crystallization in transparent anhydrous right rhombic

prisms of a beautiful red colour; and if the operation be performed on a large scale these crystals often attain a large size: they are soluble in about $2\frac{1}{2}$ parts of cold water and in $1\frac{1}{2}$ part of boiling water, but are insoluble in alcohol. If the action of the chlorine be too long continued, the red salt is in its turn partially decomposed, and a green compound is formed which interferes with the crystallization of the red salt. This green compound, according to the analysis of Pelouze, may be represented by the formula $(\text{FeCy}_2, \text{Fe}_2\text{Cy}_6, 4\text{H}_2\text{O})$, or it is the *magnetic cyanide*, corresponding to the magnetic oxide $(\text{FeO}, \text{Fe}_2\text{O}_3)$ of iron. Potassic ferrieyanide is prepared on the large scale for the use of the calico-printer; but it is then generally obtained by decomposing the solid yellow salt by exposing it in powder to the action of a current of chlorine gas. Potassic ferrieyanide may also be obtained in small quantities by decomposing a solution of the yellow ferrocyanide by means of the voltaic battery in a diaphragm cell (285); it is formed in the solution at the positive electrode. It may likewise be obtained by acting upon the yellow prussiate by various oxidizing agents.

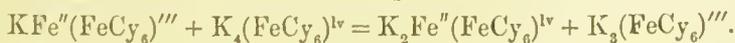
A solution of potassic ferrieyanide when mixed with an excess of potash furnishes a liquid possessed of considerable oxidizing power; it converts the hydrated protoxides of manganese, lead, and tin into peroxides of these metals, while the ferrieyanide passes into the condition of ferrocyanide of potassium; $2\text{K}_3\text{FeCy}_6 + 4\text{KHO} + \text{MnSO}_4 = 2\text{K}_4\text{FeCy}_6 + \text{K}_2\text{SO}_4 + \text{MnO}_2 + 2\text{H}_2\text{O}$. The same solution is employed by the calico-printer for the purpose of discharging the blue colour of indigo from calico (Mereer). The red prussiate burns with scintillation when introduced into the flame of a candle. Potassic ferrieyanide produces a large number of insoluble compounds when mixed with the salts of many of the metals; and as the colours of these precipitates are often characteristic, this salt is frequently employed in the laboratory as a qualitative test for the metals in neutral or feebly acid solutions. With salts of zinc it gives an orange precipitate, with those of cadmium a yellow, with nickel a yellowish green, with cobalt a dark reddish brown, with copper a yellowish green, with ferrous salts a brilliant blue, with manganeous salts a brown, with stannous salts a white, with silver salts an orange, and with mercurous salts a brownish red. These precipitates, with the exception of those with zinc and tin, are insoluble in dilute hydrochloric acid. The following table exhibits the composition of some of the ferrieyanides:—

| | | |
|--|-----------------------------------|-----------------------------|
| Ferricyanogen (hypothetical) | $(C_6N_6Fe)''$ | Fdcy |
| Hydroferricyanic acid | $H_3C_6N_6Fe$ | H_3Fdcy |
| Potassic ferricyanide | $K_3C_6N_6Fe$ | K_3Fdcy |
| Sodic ferricyanide | $Na_3C_6N_6Fe, H_2O$ | Na_3Fdcy, H_2O |
| Sodic-potassic ferricyanide | $K_3Na_3C_{12}N_{12}Fe_2, 6 H_2O$ | $K_3Fdcy, Na_3Fdcy, 6 H_2O$ |
| Baric-potassic ferricyanide | $KBa''C_6N_6Fe, 3 H_2O$ | $KBa''Fdcy, 3 H_2O$ |
| Ferrous ferricyanide (Turnbull's blue) | $C_{12}N_{12}Fe_5, x H_2O$ | $Fe''_3Fdcy_2, x H_2O$ |

Potassic ferricyanide gives no precipitate in the solutions of the ferric salts, but a splendid blue when mixed with those of the ferrous salts. It is a very delicate test for any ferrous salt when in solution. If ferrous sulphate be employed, the change which occurs is the following: $2 K_3Fdcy + 3 FeSO_4 = Fe_3Fdcy_2 + 3 K_2SO_4$. The hydrated precipitate which is thus formed constitutes a highly-valued and brilliant variety of Prussian blue, commercially known as *Turnbull's blue*. Turnbull's blue may be distinguished from ordinary Prussian blue by the action of a solution of potash upon it, which decomposes it into potassic ferrocyanide and magnetic oxide of iron, whilst the ordinary blue when similarly treated yields potassic ferrocyanide and ferric oxide.

Williamson finds that when Everitt's white salt ($K_2Fe, FeCy_6$) is treated with chlorine or with nitric acid it is decomposed, and a blue salt is formed (KFe'' , $FeCy_6, 9 H_2O$) corresponding in composition to Turnbull's blue, in which one third of the iron has been displaced by its equivalent of potassium. The formation of this substance is best effected by boiling the white precipitate with nitric acid, diluted with twenty parts of water; as the liquid approaches the boiling point a copious evolution of nitric oxide occurs: each atom of the white salt loses one atom of potassium, and the ferrous-potassic ferricyanide is formed. Care is required to prevent the action of the acid from proceeding too far, otherwise the compound acquires a green colour, owing to the formation of Pelouze's magnetic cyanide of iron.

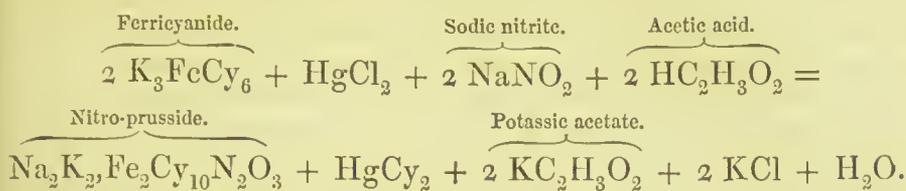
When this blue compound is treated with a solution of potassic ferrocyanide, it is reconverted into the original white compound, and pure potassic ferricyanide is obtained in the liquid, one atom of the yellow salt losing an atom of potassium, which is transferred to the blue compound:—



From the foregoing statements it will be seen that several different blue compounds containing iron and cyanogen may be procured. The composition of these bodies may be thus represented:—

| | | |
|---|--------------------------------|----------------------------------|
| Ordinary Prussian blue | $Fe_7Cy_{18}, 18 H_2O$ | $= Fe_4, Fcy_3, 18 H_2O$ |
| Basic ditto | $Fe_7Cy_{18}, Fe_2O_3, x H_2O$ | $= Fe_4, Fcy_3, Fe_2O_3, x H_2O$ |
| Turnbull's blue, or ferrous ferricyanide | $Fe_5Cy_{12}, x H_2O$ | $= Fe_3, Fdcy_2, x H_2O$ |
| Williamson's blue, or ferrous-potassic ferricyanide | $Fe_2KC_y_6, x H_2O$ | $= FeK, Fdcy, x H_2O$ |

adding a definite quantity of sodic nitrite. The reaction which occurs may be thus represented :—



A mixture of potassic and sodic nitro-prusside is formed, while the soluble potassic acetate remains in the liquid. If properly performed, a large portion of mercuric cyanide separates from the solution without difficulty, but the purification of the salt requires care: for the necessary details the reader is referred to Hadow's paper.

Sodic Nitro-prusside ($\text{Na}_4\text{Fe}_2\text{Cy}_{10}\text{N}_2\text{O}_3, 4\text{H}_2\text{O}$).—This salt crystallizes in fine prisms of a ruby-red colour, which require about $2\frac{1}{2}$ parts of cold water for solution. Its solution is decomposed by exposure to the sun's rays, Prussian blue being deposited, while nitric oxide escapes. *Baric nitro-prusside* ($\text{Ba}_2\text{Fe}_2\text{Cy}_{10}\text{N}_2\text{O}_3, 6\text{H}_2\text{O}$) crystallizes in fine octahedra of a dark red colour.

The nitro-prussides give a pale green precipitate with salts of copper, and a flesh-coloured precipitate with those of silver. With salts of zinc a salmon-coloured precipitate is produced; with salts of nickel, a dirty white; with salts of cobalt, a flesh-coloured precipitate; and with ferrous salts, a salmon-coloured precipitate is formed. The ferric salts, and the salts of lead, of mercury, and of tin, give no precipitates with the nitro-prussides. Chlorine is without effect upon solutions of the nitro-prussides; but they are decomposed when boiled with the alkalies, part of the iron being separated as a crystalline hydrated ferric oxide, while the solution becomes orange-coloured, owing to the formation of a new compound containing both cyanogen and iron. They are also decomposed by boiling oil of vitriol. If their solutions be boiled with mercuric oxide, nitric oxide is evolved, and mercuric cyanide is formed. Sulphuretted hydrogen also decomposes them. The most delicate and characteristic test for the nitro-prussides is the production of a magnificent purple colour when mixed with solutions of the alkaline monosulphides, such as K_2S or KHS . This coloration is extremely intense, and may be employed to indicate very minute traces either of a soluble sulphide or of a nitro-prusside. The colour, however, speedily disappears if any of the polysulphides are present. It appears to be due to the formation of a double salt of the nitro-prusside with the sulphide of the alkali-metal. By boiling the liquid, nitrosulphide of iron and of the alkali-metal is obtained.

Nitrosulphides of Iron.—A remarkable class of compounds may be obtained by the reaction of potassic nitrite and ammoniac sulphhydride upon the salts of iron (Roussin, *Ann. de Chimie*, III. lii. 285). If to a mixture of a solution of ammoniac sulphhydride and potassic nitrite a solution of ferrous sulphate or chloride be added drop by drop, keeping the mixture constantly agitated, it is found that on raising the liquid to the boiling point, the blackish precipitate which is at first formed is almost entirely redissolved. If the solution be boiled for a few minutes and then filtered, an extremely dark liquid runs through; this, on cooling, deposits hard, sandy, or needle-shaped crystals; the supernatant liquid presents only a slightly yellow tint. If a ferric salt be substituted for a ferrous salt, a similar result is obtained, but a considerable quantity of sulphur is left upon the filter.

The crystals thus formed are well-defined oblique prisms with a rhombic base. They are black and opaque, very heavy, sparingly soluble in cold water, but soluble in twice their weight of boiling water. Alcohol, wood-spirit, fousel oil, and concentrated acetic acid also dissolve them freely, but they are absolutely insoluble either in chloroform or in carbon disulphide. The effect of ether upon them is remarkable; they instantly become liquid if exposed to the vapour of ether, and are soluble in ether in almost unlimited quantity. Traces of ether or of alcohol in chloroform can be detected with certainty by agitating the specimen under trial with a few of the crystals. If pure the liquid will remain absolutely colourless, but the presence of one part of alcohol or of ether in 1000 will yield a coloured solution. These crystals have a brilliant metallic lustre: their taste is at first inky, followed by a persistent bitterness. The new salt is permanent in air containing a trace of ammonia; but, if the substance be in the least acid, gradual decomposition ensues, and ruddy fumes are seen in the bottle. It is not decomposed by a temperature of 212° , but if the heat be gradually increased, it is resolved at a little above 275° (135° C.) into sulphur, ammoniac sulphite, nitric acid, and ammoniac nitrate, leaving a residue of sulphide of iron. When heated sharply it deflagrates, emitting white fumes, which have an odour like that of burning gunpowder. The concentrated mineral acids immediately decompose the nitrosulphide; but acetic, hydrochloric, and oxalic acids have no effect upon it.

Solutions of caustic potash and ammonia, when added to its aqueous solutions, cause a deposition of the crystals, unaltered in composition, scarcely any of the compound being retained in the liquid. Chlorine and iodine decompose it, causing a separation of nitric oxide and of sulphur. It is also immediately decomposed by mercuric oxide with evolution of nitric oxide; with lead dioxide it yields plumbic nitrate and sulphur: it is likewise decomposed by potassic permanganate; solutions of argentic nitrate, corrosive sublimate, cupric sulphate, and ferric chloride decompose the solution of this compound, with evolution of nitric oxide and precipitation of black sulphides. Ferrous sulphate is without effect upon it. With plumbic nitrate it gradually deposits oblique rhomboidal prisms, which are sparingly soluble in water, soluble in ether, and deliquescent in ether vapour. Roussin attributes to the black crystals a composition represented by the following formula, $\text{Fe}_3\text{S}_5\text{H}_2(\text{NO})_4$:—

| | | By calculation. | | By expt. |
|------|---|-----------------|----------|----------|
| 3 Fe | = | 168 | or 37.35 | 37.36 |
| 5 S | = | 160 | 35.55 | 35.54 |
| 4 NO | = | 120 | 26.66 | 26.45 |
| 2 H | = | 2 | 0.44 | 0.45 |
| | | <hr/> | <hr/> | <hr/> |
| | | 450 | 100.00 | 99.80 |

The formula suggested by Roussin for this compound is $(\text{Fe}_2\text{S}_3\text{N}_2\text{O}_2, \text{FeS}_2\text{N}_2\text{O}_3)$,

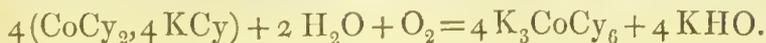
H_2S). One remarkable point in the composition of this substance, which has been called *dinitrosulphide of iron*, is that the iron is not indicated by any of the usual tests of the metal, such as ammonia, potassic ferrocyanide, or ammoniac sulphhydrate. If it be boiled with a concentrated solution of caustic soda, ammonia is disengaged in abundance, and crystallized ferric oxide is deposited. The solution now contains a new salt, which, on evaporation, is deposited in black, well-defined crystals, aggregated in inverted hollow square pyramids. This salt, *sulphuretted nitrosulphide of iron and sodium* ($3 Na_2S, Fe_2S_3N_2O_2$), is soluble in a solution of soda, but insoluble in caustic potash or ammonia. It is decomposed by metallic solutions, and by iodine, with evolution of nitric oxide, in a manner very similar to that in which the same compounds behave to the dinitrosulphide of iron. Acids decompose the new salt with facility at ordinary temperatures, and occasion the deposition of a red flocculent substance ($Fe_2S_3, N_2O_2, 4 H_2S?$) which readily subsides, and should be washed with a weak solution of sulphuretted hydrogen. By prolonged washing it loses a portion of its sulphuretted hydrogen.

This flocculent substance is soluble in alcohol and in ether; when dry it becomes slowly decomposed, emitting fumes of nitric oxide and ammonia, and leaving a residue of sulphide of iron. It is soluble in solutions of the alkalis as well as in those of their carbonates and sulphides, producing salts analogous to the compound with sodium already described.

Nitrosulphide of iron ($Fe_2S_3N_2O_2$).—This compound is obtained by decomposing the foregoing sodium compound ($3 Na_2S, Fe_2S_3N_2O_2$), by adding dilute sulphuric acid gradually to a boiling solution of the salt. Sulphuretted hydrogen is evolved in abundance, and the nitrosulphide of iron is precipitated in the form of a black heavy powder. It is insoluble in water, in alcohol, and in ether. It is permanent while moist, but if dried is gradually decomposed, with evolution of nitric oxide. When dry and freshly prepared it burns like tinder if touched with an ignited body. It is soluble in the alkalis, and in the sulphides of the alkali-metals, forming a new class of salts. The sodium compound ($Fe_2S_3N_2O_2, Na_2S, H_2O$) is easily obtained as an intensely dark red crystalline substance of metallic lustre, by dissolving nitrosulphide of iron in disodic sulphide, and allowing the solution to crystallize over sulphuric acid.

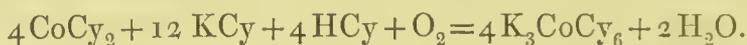
An interesting relation has been observed between the nitrosulphides and the nitroprussides. The crystals of both classes belong to the oblique prismatic system. If a solution of the nitrosulphide of iron and sodium be mixed with one of mercuric cyanide, mercuric sulphide is precipitated, and sodic nitroprusside is obtained in solution. On the other hand, if sodic nitroprusside in solution be mixed with an excess of an alkaline sulphide, a magnificent purple colour is produced, which passes on boiling into a reddish green, and nitrosulphide of iron and sodium is formed, while sulphocyanide of the alkali-metal remains in solution. Probably the formula of the nitrosulphides will require a modification similar to that proposed by Hadow for the nitroprussides.

(1586) 4. COBALTICYANIDES.—When potassic cyanide is added to a salt of cobalt, it gives a reddish-brown precipitate ($CoCy_2$), which is soluble in excess of potassic cyanide. The double cyanide of cobalt and potassium ($4 KCy, CoCy_2$) thus obtained is decomposed on the addition of hydrochloric acid, and cobaltous cyanide is precipitated; but if, previously to the addition of hydrochloric acid, it be exposed to the air, it absorbs oxygen, potash is liberated, and potassic cobalticyanide is produced:—



After this change has occurred, the addition of hydrochloric acid causes no precipitate. Potassic cobalticyanide corresponds in composition to the ferricyanide of the same metal. A *hydrocobalticyanic acid* (H_3CoCy_6) may be obtained by decomposing cupric cobalticyanide with sulphuretted hydrogen.

Potassic Cobalticyanide (K_3CoCy_6).—This salt was discovered by Gmelin. It crystallizes in yellowish flattened prisms, which are anhydrous, and isomorphous with those of potassic ferricyanide. It is sparingly soluble in water. This salt may be obtained either by dissolving cobaltous cyanide in an excess of potassic cyanide, and exposing it to the air; or by dissolving hydrated cobaltous oxide by the aid of a gentle heat in a solution of potash, supersaturated with hydrocyanic acid; in both cases oxygen is absorbed:—



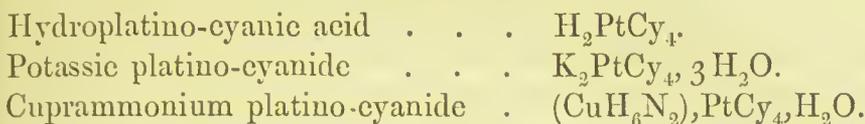
The corresponding salt of *sodium* ($Na_3CoCy_6, 2H_2O$) crystallizes in long, transparent, colourless needles; that of *barium* in efflorescent prisms ($Ba_3, 2CoCy_6, 22H_2O$). Solutions of these cobalticyanides occasion precipitates in a large number of metallic salts. Cobalticyanide of zinc is white; that of nickel is gelatinous, and of a pale blue; that of cobalt is of a pale red; that of copper, of a pale blue; the ferrous, manganous, and stannous, as well as mercurous and argentic cobalticyanides, are white: salts of lead give no precipitate with the soluble cobalticyanides.

(1587) 5. CHROMICYANIDES.—Chromic salts yield with potassic cyanide a pale bluish-grey precipitate ($CrCy_3$), which is not soluble in excess of the potassic cyanide; but if a mixture of hydrated chromic oxide with a solution of potash and an excess of hydrocyanic acid, be exposed to the air, the liquid acquires a reddish-brown colour, and a potassic chromicyanide is formed (Beckmann), corresponding to the ferricyanides and cobalticyanides. These salts are of small importance, and have been but little examined. *Potassic chromicyanide* (K_3CrCy_6) forms brownish-red anhydrous prisms; its solution precipitates argentic nitrate, white; salts of cobalt blue; and ferrous salts of a brick-red: but it gives no precipitate with ferric salts, or with plumbic nitrate.

6 and 7. OSMIO-CYANIDES and RUTHENIO-CYANIDES may, according to Claus, be obtained, corresponding in composition to the ferrocyanides, which they greatly resemble in the colour of the precipitates they form when mixed with salts of copper, iron, zinc, and lead.

(1588) 8. PLATINO-CYANIDES.—Gmelin ascertained that platinum is capable of entering into combination with cyanogen, and forming a series of double cyanides, which are amongst the most beautiful substances that are known: these compounds are analogous to the foregoing, but their composition differs from that

of any of the preceding series : for example, the following formulæ represent a few of the platino-cyanides :—



Potassic platino-cyanide is best formed by dissolving platinous chloride in a solution of potassic cyanide ; but it may also be obtained by fusing potassic ferrocyanide with spongy platinum ; or by heating a concentrated solution of platinic chloride with an excess of potassic cyanide. This beautiful salt forms long transparent rhombic prisms, which are yellow by transmitted, and blue by reflected light : it is very soluble in water, and more sparingly so in alcohol and in ether. *Magnesian platino-cyanide* is a beautiful salt which crystallizes in rosettes from its solution in a mixture of alcohol and ether : these crystals form square prisms, which are of a rich crimson by transmitted light, and green or blue by reflected light ; they are very soluble in water, and the solution is colourless.

The changes of colour which this salt experiences by change in its condition of hydration are very remarkable. The ordinary red salt ($\text{Mg}_2\text{PtCy}_4, 7\text{H}_2\text{O}$) when gently warmed, even under water, becomes yellow, and if crystallized at 160° , yellow crystals with $6\text{H}_2\text{O}$ are deposited. At 212° the salt still retains $2\text{H}_2\text{O}$ when it is white, and between 300° and 400° it becomes anhydrous, and is then yellow. These singular changes of colour may be strikingly displayed by allowing a strong solution of the salt to evaporate on a sheet of white paper. When dry, a crimson surface is obtained, but a drop of water upon any point destroys the colour at that spot instantly ; on drying, it again reappears. When heated, the red salt first becomes yellow ; as the temperature rises it is rendered white ; and by a somewhat stronger heat it again becomes yellow. By breathing on the paper, the salt resumes the water that it had lost, the yellow spot becoming successively white, yellow, and eventually crimson (Hadow).

The most characteristic tests of the platino-cyanides are the formation of a beautiful smalt-blue precipitate when a platino-cyanide is added to a solution of mercurous nitrate in excess, and a flocculent blue precipitate with cupric salts.

(1589) There is another very beautiful series of salts, commonly termed the *platini-cyanides*, which crystallize in prisms of a coppery lustre when viewed by reflected light, but they appear to be green by transmitted light, and polarize light powerfully ; their solutions, however, are colourless. These salts, when dissolved in water, produce a white precipitate with argentic and mercuric salts, a blue with the mercurous salts, and a greenish blue with the cupric salts. The platini-cyanides have been carefully examined by Hadow, who has shown that the usually received formula (M_2PtCy_5) is erroneous, and that they are more

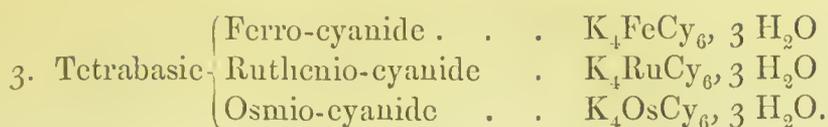
complicated in construction. The salt formerly known as potassic platini-cyanide is really a *chloroplatino-cyanide* $2 (K_6Pt_3Cy_{12}Cl)$, $21 H_2O = [5 K_2PtCy_4, K_2PtCy_4Cl_2 \cdot 3 H_2O, 18 H_2O]$; but salts exist which correspond in appearance with this, containing, in place of the 2 atoms of chlorine, either 2 atoms of bromine, or of NO_3 , or 1 atom of SO_4 . In order to prepare these compounds in a state of purity, Hadow converts the potassic platino-cyanide into the colourless perchloroplatino-cyanide ($K_2PtCy_4Cl_2$), or into the perbromoplatino-cyanide ($K_2PtCy_4Br_2$), by the use of an excess of chlorine or bromine, and crystallizing out the salt. He then mixes the compound so obtained, with the platino-cyanide, in the ratio of 5 atoms of the latter with 1 atom of the former; and, on crystallizing, the copper-coloured compound is obtained in a state of purity. The platini-cyanides, so called, appear to be double salts of the platino-cyanides with the perchloroplatino-cyanides. The platino-cyanides are, indeed, remarkable for their strong tendency to form double salts. Amongst others a very beautiful double salt of potassium and magnesium ($MgPtCy_4, K_2PtCy_4, 7 H_2O$) may be obtained. For further details respecting the platino-cyanides, see Knop, *Liebig's Annal.*, xliii. 111; Quadrat, *ib.* lxiii. 164, and lxx. 300; and Hadow, *Q. J. Chem. Soc.*, xiii. 106.

9 and 10. RHODI-CYANIDES and IRIDI-CYANIDES.—Both rhodium and iridium yield double cyanides analogous to the ferricyanides, but potassic rhodic cyanide is decomposed by acetic acid, with separation of the insoluble rhodic cyanide. This reaction may be employed in the separation of rhodium from iridium, since acetic acid does not decompose the iridium salt.

(1590) *Potassic iridi-cyanide* (K_3IrCy_6 ; Claus) forms four-sided colourless crystals, and is characterized by giving a deep indigo precipitate with the cupric salts, and a bright yellow with the ferric salts.

It appears from the foregoing statements, that cyanogen has a strong tendency to produce, with several of the metals, electro-negative compounds, which form with hydrogen a series of well-marked acids. The number of atoms of metal which are united with the cyanogen to constitute the radicals of these acids, varies with the nature of the metal; three different classes of these hydro-acids are known, the first class being dibasic, the second tribasic, and the third tetrabasic; the composition of their salts with potassium is exhibited as follows:—

| | | |
|-------------|-------------------------|---------------------|
| 1. Dibasic: | Platino-cyanide . . . | $K_2PtCy_4, 3 H_2O$ |
| | { Ferri-cyanide . . . | K_3FeCy_6 |
| | { Cobalti-cyanide . . . | K_3CoCy_6 |
| 2. Tribasic | { Chromi-cyanide . . . | K_3CrCy_6 |
| | { Iridi-cyanide . . . | K_3IrCy_6 |
| | { Rhodi-cyanide . . . | K_3RoCy_6 |



(1591) **SULPHOCYANIDES.**—When potassic cyanide is fused with sulphur, or even when a solution of the cyanide is boiled with flowers of sulphur, the two bodies enter into combination, and a new compound (KCyS) is formed: this compound is also readily prepared by calcining in a covered crucible at a dull red heat an intimate mixture of 3 parts of anhydrous potassic ferro-cyanide, 2 of flowers of sulphur, and 1 part of potassic carbonate. The melted mass when cold must be treated with boiling water, and the filtered liquid evaporated; on cooling, striated prismatic crystals of potassic sulphocyanide will be deposited: the salt may be obtained pure by recrystallization from alcohol. In this operation potassic cyanide is first formed, while metallic iron is separated; the latter is converted partially into ferrous sulphide, and potassic cyanide into sulphocyanide, which is separated from the iron by solution in water.

Potassic Sulphocyanide (KCyS=97) is anhydrous, but very deliquescent. It resembles nitre in appearance and in taste; it is not poisonous. Boiling alcohol dissolves it abundantly: it fuses on the application of heat. This salt is commonly supposed to contain a particular monobasic radicle to which the name of *sulpho-cyanogen* (CyS=Scy) has been given. The radicle is, however, not known in a separate condition, but it forms an acid compound with hydrogen, and yields numerous well-marked salts. Some chemists prefer to regard the sulphocyanides as representatives of the cyanates, in which the oxygen of the latter salts has had its place supplied by sulphur; and the decomposition of hydro-sulphocyanic acid by the aid of heat and acids resembles that of cyanic acid under similar circumstances:—

Hydrosulphocy. acid.



Cyanic acid.



Ammonic sulphocyanide indeed, by carefully heating it to 338° (170° C.) for 2 hours, may be converted into an isomeric sulphuretted urea, just as ammonic cyanate passes during evaporation into ordinary urea (Reynolds, *Q. J. Chem. Soc.*, 1869). The following table represents both views:—

| | | |
|---------------------------------------|------------------------------|-------------------------------|
| Hydrosulphocyanic acid | HCyS | H,Scy |
| Potassic sulphocyanide | KCyS | K,Scy |
| Sodic sulphocyanide | NaCyS | Na,Scy |
| Ammonic sulphocyanide | H ₄ NCyS | H ₄ N,Scy |
| Calcic sulphocyanide | Ca 2 CyS, 3 H ₂ O | Ca, 2 Scy, 3 H ₂ O |
| Cupric sulphocyanide | Cu 2 CyS | Cu, 2 Scy |
| Cupreous sulphocyanide | CuCyS | Cu,Scy |
| Plumbic sulphocyanide | Pb 2 CyS | Pb, 2 Scy |
| Argentio-potassic sulphocyanide . . . | AgCyS,KCyS | AgScy,KScy |
| Mercurio-potassic sulphocyanide . . . | HgCyS,KCyS | HgScy,KScy |
| Mercurous sulphocyanide | HgCyS | Hg,Scy |

The view which admits the existence of sulphocyanogen as the salt radicle of these compounds, renders a simple and satisfactory account of the metamorphoses to which the sulphocyanides are subject, and it will be made use of here.

The sulphocyanides of *sodium* and *ammonium* are anhydrous and deliquescent. Small quantities of one of these salts exist in the saliva of man and of the sheep. A considerable quantity of ammonic sulphocyanide is formed during the distillation of coal gas, and is arrested by the hydrated ferric oxide employed for absorbing sulphuretted hydrogen. Ferric and ammonic sulphocyanide may be extracted from the mixture by simple washing, and by distillation with nitric acid may be converted into hydrocyanic acid, which may be condensed in milk of lime; by then adding ferrous sulphate so long as the ferrous oxide at first precipitated is redissolved, calcic ferrocyanide is formed, and this may be converted into the potassium salt by the addition of potassic carbonate to the solution till it ceases to occasion a precipitate (Hadow, *Q. J. Chem. Soc.*, 1858, 177). The majority of the sulphocyanides are soluble both in water and in alcohol; their most eharacteristic property is the production of an intense blood-red colour when their solutions are mixed with one of the ferric salts: if the red liquid thus obtained be acidulated with hydrochloric acid, and fragments of zinc be added, sulphuretted hydrogen is disengaged, and the colour disappears. Ferric sulphocyanide does not form crystals. *Plumbic* sulphocyanide is sparingly soluble; it is slowly deposited in brilliant anhydrous crystals when solutions of plumbic acetate and potassic sulphocyanide are mixed. Basic plumbic acetate gives a white precipitate with the soluble sulphocyanides. The sulphocyanides also give a white precipitate of cupreous sulphocyanide (C_nCyS) when added to a mixture of a ferrous salt with a salt of copper: with mercurous salts and with the salts of silver and of gold, they produce white precipitates.

(1592) *Hydrosulphocyanic Acid* (HCyS); *Fusing pt.* $10^{\circ}.4$ (-12° C.); *Boiling pt.* $215^{\circ}.6$ (102° C.)—When dry mercurous sulphocyanide ($HgCyS$) is decomposed by exposure to a current of sulphuretted hydrogen, mercurous sulphide is produced, and a colourless oily liquid is formed; it consists of *hydrosulphocyanic acid*. This acid crystallizes into a radiated mass at $10^{\circ}.4$. Its odour is pungent, and resembles that of acetic acid. It is a dangerous poison, and has a strongly acid taste. In its concentrated form it soon undergoes decomposition into hydrocyanic acid and hydropersulphocyanic acid ($H_2Cy_2S_3$), since $3 HgCyS = Hg_3 + H_2Cy_2S_3$.

Hydrosulphocyanic acid may be obtained in solution by suspending the sulphocyanide of copper, of mercury, or of silver in water, and decomposing it by means of a current of sulphuretted hydrogen. When its diluted solutions are boiled, it gradually undergoes decomposition, ammonia, carbon disulphide, and carbonic anhydride being formed. If it be in a more concentrated state it is resolved into hydrocyanic and hydropersulphocyanic acid; and these changes occur more quickly in the presence of other acids.

Solutions of hydrosulphocyanic acid, and of the sulphocyanides are decomposed by the action of nitric acid, and of chlorine, a bright yellow precipitate being occasioned, which was formerly supposed to be sulphocyanogen (CyS); the composition of this precipitate, however, is not known with certainty, but it has been found to contain hydrogen as well as sulphur and cyanogen: it is soluble in a solution of potash. When this substance is exposed to a strong heat in a retort, it gives off carbon disulphide and sulphur, and an orange-yellow residue is left, consisting of carbon and nitrogen only: this residue bears a dull red heat without decomposition, and constitutes in a crude form the substance to which Liebig gave the arbitrary name of *mellon*, C_9N_{13} ; but if the temperature be raised still further it is converted into a mixture of 3 volumes of cyanogen and 1 volume of nitrogen.

If a saturated solution of potassic sulphocyanide be mixed with 8 or 10 times its weight of concentrated hydrochloric acid, it is decomposed, hydrocyanic acid is evolved, and the solution becomes semi-solid from the separation of *hydropersulphocyanic acid* ($H_2Cy_2S_3$) in crystalline needles. These crystals are sparingly soluble even in boiling water, and as the solution cools it deposits the acid in beautiful orange-coloured needles.

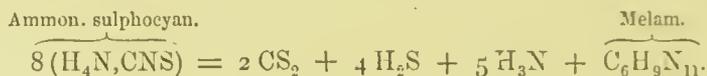
Than has lately shown that the sulphocyanide is partially decomposed into a new compound, *carbon oxysulphide*, COS (*Liebig's Annal. supp. bd.*, v. 236) when treated with a mixture of 5 measures of sulphuric acid and 4 of water; $2 KCNS + 2 H_2O + 2 H_2SO_4 = 2 COS + K_2SO_4 + (H_4N)_2SO_4$; the hydrosulphocyanic acid is thus decomposed into ammonia and the carbon oxysulphide, just as under analogous circumstances cyanic acid is decomposed into ammonia and carbonic anhydride (504).

(1593) *Mellon* (C_9N_{13} ; Liebig).—This anomalous compound was originally supposed by Liebig to contain C_3N_4 , but he has since repeated and varied his experiments upon it, and has altered its formula as above. Mellon is not known in an isolated form in a state of purity, but it constitutes the principal portion of the solid residue obtained by heating the yellow precipitate occasioned by chlorine in solutions of the sulphocyanides. Mellon appears to be a tribasic radicle, which forms with hydrogen an acid termed *hydromellonic acid* ($H_3C_9N_{13}$); this latter is an unstable compound which yields three salts with potassium; a normal mellonide,

$K_3C_9N_{13} \cdot 5H_2O$; a soluble acid mellonide, $K_2H_2C_9N_{13} \cdot 3H_2O$; and an insoluble acid mellonide, $KH_2C_9N_{13}$. The normal mellonide is usually formed as a secondary product during the preparation of potassic sulphocyanide; but it is more plentifully obtained by fusing three parts of pure potassic sulphocyanide, and gradually adding about one part of crude mellon; it is very soluble in hot water, from which it crystallizes on cooling with $5H_2O$. Its solution has an intensely bitter taste. A solution of potassic mellonide produces white insoluble mellonides when mixed with solutions of argentic nitrate, of corrosive sublimate, and of plumbic acetate.

When potassic mellonide is boiled with an excess of caustic potash, it is decomposed, and a new tribasic acid, the *cyameluric* ($H_3C_6N_7O_3$) is formed: various other compounds are also obtained by its decomposition, for details regarding which the reader is referred to Liebig's paper (*Liebig's Annal.*, xev. 257).

(1594) *Melam*.—When ammoniac sulphocyanide is submitted to distillation it undergoes decomposition, and yields a mixture of carbon disulphide, sulphuretted hydrogen, and ammonia, whilst there remains in the retort a grey insoluble residue, which Liebig has called *melam* ($C_6H_9N_{11}$, Liebig; or $C_5H_6N_8$, Gerhardt, calculating from Voelckel's analysis):—

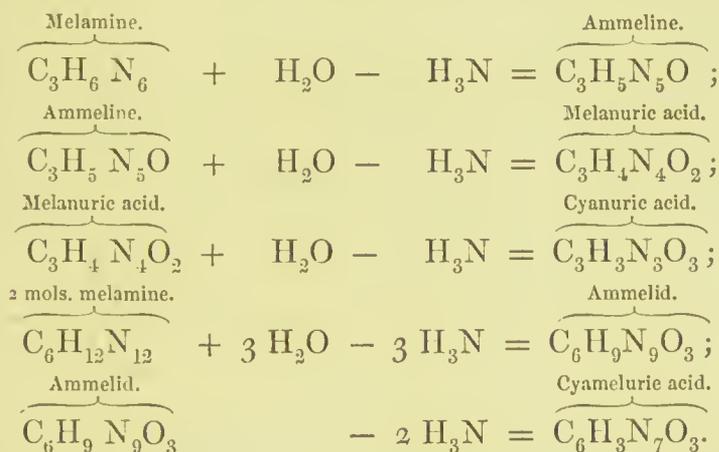


The same substance may be procured by heating an intimate mixture of equal parts of potassic sulphocyanide and sal-ammoniac. In this process potassic chloride and ammoniac sulphocyanide are formed, and the sulphocyanide is decomposed by the high temperature, as before, leaving melam, from which the potassic chloride may be removed by washing.

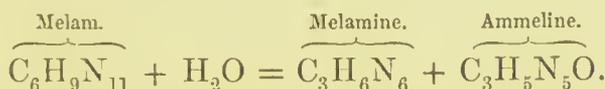
Melam is a greyish-white granular powder, insoluble in cold water, and in alcohol and ether. Boiling water dissolves it sparingly, and deposits it in the form of a white voluminous powder. When boiled with a solution of potash it is dissolved, and a series of compounds are formed, all of which are closely related. The first of these bodies has been called *melamine* ($C_3H_6N_6$). It is possessed of basic powers, and is deposited in brilliant, colourless, rhombic octahedra; it forms crystallizable salts. A solution of melamine precipitates the oxides of zinc, iron, manganese, and copper from their salts; with argentic nitrate it gives a white crystalline precipitate ($AgC_3H_6N_6 \cdot NO_3$). Melamine is polymeric with cyanamide (1600), and isomeric with cyanuramide, $(H_2N)_3C_3N_3$, if not identical with it. If the mother-liquid from which the melamine has been deposited be neutralized with acetic acid, a voluminous white precipitate of *ammeline* ($C_3H_5N_5O$) is produced: this substance is a feeble base, which forms a crystallizable salt with nitric acid.

When either melamine or ammeline is dissolved in strong sulphuric acid, or when melam is treated with hot nitric acid, and the solution is diluted with twice its bulk of water, and then with alcohol, a white powder termed *ammelid* ($C_6H_9N_9O_3$) is precipitated. It is insoluble in water, but is easily soluble, by the aid of heat, in solutions of potash and of ammonia. When either melam, melamine, ammeline, or ammelid is dissolved in concentrated sulphuric acid, and maintained at a temperature just short of boiling for two or three days, until on dilution it ceases to give a precipitate when neutralized with ammonia, it under-

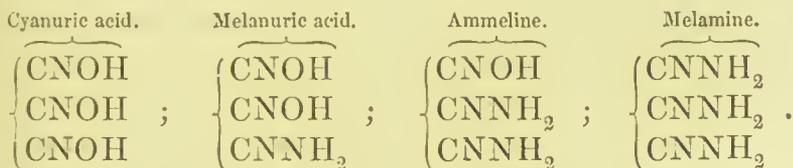
goes a change, in consequence of which the elements of ammonia are removed, and those of water are assimilated: and on evaporating the liquid, *cyanuric acid* ($H_3C_3N_3O_3$) is obtained in crystals. In fact, melamine, ammeline, and ammellid may be viewed as amidated derivatives of cyanuric acid, although they have not as yet been obtained directly by acting upon the compounds of cyanuric acid with ammonia. Two other bodies of acid character, viz., the melanuric* and cyameluric acids, also belong to the same group, as may be seen by the following equations, illustrative of the relation in composition which they all bear to cyanuric acid, and of the successive stages by which they are produced:—



The formation of melamine and of ammeline from melam is readily explained, since



Kekulé has represented the relations of some of these bodies by the following formulæ:—

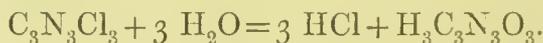


Cyanuric acid contains a triple cyanic acid [CN(OH)], and in the other three compounds compared with it, each group in succession is displaced by an atom of cyanamide, in which the hydroxyl (OH) of the cyanic acid is displaced by amidogen NH_2 .

(1595) *Cyanuric Acid* ($H_3C_3N_3O_3, 2 H_2O$). — This polyamide of cyanic acid may be obtained in various ways. 1. By the action of sulphuric acid upon melam or its derivatives, as just described. 2. By the action of a current of dry chlorine upon fused urea; sal-ammoniac, nitrogen, and hydrochloric acid, are thus produced, and cyanuric acid is formed in abundance; $6 CH_4N_2O + 3 Cl_2 = N_2 + 2 HCl + 4 H_4NCl + 2 H_3C_3N_3O_3$: the sal-ammoniac may be removed by washing with cold water, and the

* Melanuric acid is obtained by heating urea beyond its point of fusion; $4 CH_4N_2O = C_3H_4N_4O_2 + 4 H_3N + CO_2$.

cyanuric acid may be crystallized from boiling water. 3. By decomposing urea hydrochlorate by heat: if the compound formed by transmitting dry hydrochloric acid gas over powdered urea be heated to 293° (145° C.) in an oil bath, rapid decomposition occurs, sal-ammoniac is sublimed, and pure cyanuric acid may be obtained by crystallizing the residue from boiling water; $3(\text{CH}_4\text{N}_2\text{O}, \text{HCl}) = 3 \text{H}_4\text{NCl} + \text{H}_3\text{C}_3\text{N}_3\text{O}_3$. 4. By heating urea beyond its fusing point until it has become converted into a dry greyish mass, resembling ammeliid in appearance and properties: when this residue, which consists of melanuric acid ($\text{C}_3\text{H}_4\text{N}_4\text{O}_2$), is dissolved in hot oil of vitriol, to which a small quantity of nitric acid has been added for the purpose of removing the colour, it combines with the elements of water, and at the same time ammonia and cyanuric acid are formed; for $\text{C}_3\text{H}_4\text{N}_4\text{O}_2 + \text{H}_2\text{O} = \text{H}_3\text{N} + \text{H}_3\text{C}_3\text{N}_3\text{O}_3$: the cyanuric acid is deposited on diluting the liquid moderately with water. 5. By the destructive distillation of uric acid; cyanuric acid being one of the products obtained in this operation. 6. By decomposing solid cyanogen chloride by prolonged boiling with water, or by dissolving the solid chloride in hydrated alcohol: in the latter case the liquid becomes hot, emits hydrochloric acid, and slowly deposits cyanuric acid in cubes:—

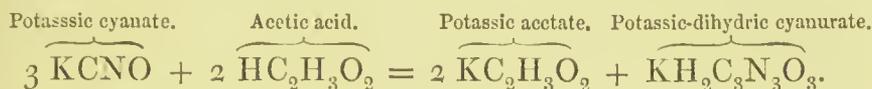


Cyanuric acid is deposited from its aqueous solution in colourless rhombic prisms, which are efflorescent. It is sparingly soluble in cold water, more freely so in boiling water, and is also somewhat soluble in boiling alcohol. When crystallized from hot hydrochloric or nitric acid, it is deposited in square-based anhydrous octahedra. By long boiling with the concentrated acids it is decomposed into carbonic anhydride and ammonia. When crystallized cyanuric acid is distilled, it is converted into normal cyanic acid, and this hydrate in a few minutes begins to undergo a spontaneous change into the white insoluble compound known as *cyamelid* (504), while the temperature rises spontaneously, owing to the solidification of the mass.

Cyanuric acid is generally considered to be tribasic;* its salts with lead and with silver contain 3 equivalents of metal. Most of the cyanurates are sparingly soluble in water. Those formed from the alkalis and from the alkaline earths contain only two equivalents of metal. An acid *ammonic* cyanurate (H_4N

* Wöhler, however, regards cyanuric acid as dibasic, and considers that part of the hydrogen above reckoned as basic enters into the composition of the acid. (*Liebig's Annal.*, lxii. 241.)

$H_2C_3N_3O_3, H_2O$) may be obtained in brilliant efflorescent prisms; and a corresponding acid *potassic cyanurate* ($KH_2C_3N_3O_3$) is deposited in anhydrous cubes, when acetic acid is added in small quantities at a time to a solution of potassic cyanate; three molecules of cyanic acid coalescing to form one molecule of the polymeric cyanuric acid:—



When a solution of a salt of copper, after being saturated with ammonia, is mixed with a solution of cyanuric acid, a characteristic violet precipitate, which is insoluble in cold water, is formed.

Argentio cyanurate ($Ag_3C_3N_3O_3$) is white, and insoluble in water, but soluble in dilute nitric acid. A remarkable acid cyanurate of silver (hydric-diargentic cyanurate), $Ag_2HC_3N_3O_3$, may also be obtained.

(1596) *Isomerides of Cyanuric Acid*.—Sometimes during the preparation of cyanuric acid, by boiling crude mellon (1593) with nitric acid, crystals of an acid isomeric with the cyanuric are formed. It crystallizes in long oblique rhomboidal prisms, which are efflorescent: it resembles cyanuric acid, but is distinguished from the latter by its greater solubility; Liebig terms it *cyanilic acid*.

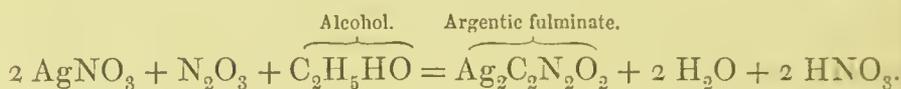
(1597) *Fulminic Acid*.—This remarkable body has not hitherto been isolated. When a solution of nitrate of silver or of mercury in an excess of nitric acid is heated with alcohol, a decomposition attended with a copious evolution of gas occurs, and a crystalline deposit of a metallic fulminate is formed.

Fulminic acid is generally assumed to be dibasic, but its power of saturating bases differs from that of dibasic acids in general. Fulminates may be obtained with 2 equivalents of a monad metal; or with 1 equivalent of metal, and 1 equivalent of hydrogen, in which latter case the compound has an acid reaction. The 2 equivalents of basyl may consist of 2 equivalents of the same metal, or they may consist of two different metals: for example, fulminates containing 2 equivalents of silver, 2 of mercury, or 2 of copper may be obtained, or double fulminates of copper and mercury, or of mercury and silver, may be procured; double fulminates of any of these metals with the metals of the alkalis, or of the alkaline earths may also be obtained, but no fulminates are known in which both atoms of the basyl consist of the metal of an alkali or alkaline earth. If fulminate of silver or of mercury be mixed with a solution of potash in excess, one half only of the silver or mercury is precipitated in the form of oxide, leaving a double fulminate of the alkali-metal and silver, or alkali-metal and mercury in solution.

Argentio Fulminate [$Ag_2C_2N_2O_2 = Ag_2C(NO_2)CN$].—In order

to prepare this salt 1 part of silver is dissolved at a gentle heat in 10 parts of nitric acid of sp. gr. 1.36, and the solution poured into 20 parts of alcohol of sp. gr. 0.840. On the application of a very gentle heat, an appearance of ebullition commences, the liquid becomes turbid, and on cooling, deposits the crystallized fulminate, which may be washed with cold water, and dried at a very gentle heat. During the preparation of the salt, vapours of nitrous ether, mixed with fumes of nitrous acid, and of aldehyd, as well as of acetic and formic acids, are liberated, and the solution is found to contain oxalic acid.

Argentie fulminate may also be obtained by transmitting vapours of nitrous anhydride into an alcoholic solution of argentic nitrate. In this case crystals of the fulminate are deposited without any disengagement of gas during the reaction illustrated by the following equation:—



Argentie fulminate is sparingly soluble in cold water, but soluble in 36 parts of boiling water. Its most remarkable property is its extremely explosive nature. When quite dry, a blow or even very slight friction between two hard bodies is sufficient to cause its decomposition, attended with a detonation of extraordinary violence. Even when moist, or under water, pressure with a hard body will often produce a similar effect. The addition of a drop of oil of vitriol, or an elevation of temperature somewhat over 266° (130° C.), also causes its explosion. The contact of gaseous chlorine likewise determines its explosion. It is decomposed with effervescence by dilute sulphuric or by oxalic acid, oxalic acid and ammonia being formed and hydrocyanic acid liberated. Dilute hydrochloric acid also decomposes it, giving rise to a peculiar chlorinated acid, the silver being precipitated wholly in the form of chloride. Sulphuretted hydrogen converts the salt into argentic sulphide and liberates cyanic acid, which, if the sulphuretted hydrogen be in excess, is converted into sulphocyanic acid.

Solutions of the alkaline chlorides, even when employed in excess, precipitate only one-half of the silver in the form of chloride, producing double salts, such as the *argentie-potassic fulminate* ($\text{AgKC}_2\text{N}_2\text{O}_2$?) which is soluble in about 8 parts of boiling water. It is a highly explosive compound, and crystallizes in elongated brilliant leaflets.

A *hydric-argentie fulminate* ($\text{HAgC}_2\text{N}_2\text{O}_2$?) may be obtained in the form of a white powder by the cautious addition of nitric acid to one of these double fulminates. It is soluble in boiling water, and crystallizes on cooling. If boiled with mercuric oxide it dissolves the oxide, forming a mercuric-diargentie fulminate ($\text{HgAg}_2 \cdot 2 \text{C}_2\text{N}_2\text{O}_2$).

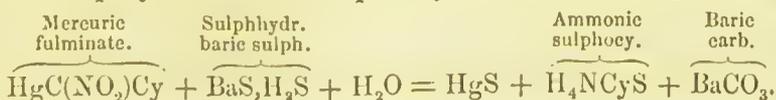
If a solution of argentic fulminate be boiled with metallic mercury, or copper, the whole of the silver is precipitated, and a fulminate of mercury or of copper is formed.

Mercuric Fulminate ($\text{HgC}_2\text{N}_2\text{O}_3, x\text{H}_2\text{O}$) ; *Sp. gr.* 4.4018.—The best method of preparing this salt, according to Liebig, consists in dissolving 3 parts of mercury in 36 of nitric acid, of sp. gr. 1.34, without the aid of heat, in a flask capable of containing 18 times the bulk of the acid. The solution is then to be poured into a large vessel containing 17 parts of alcohol, of sp. gr. 0.830, and immediately to be retransferred to the flask which is still full of nitrous vapours, and with which it is to be agitated to effect their absorption. In a few minutes an effervescence commences; this becomes extremely violent, and is attended with a deposit of metallic mercury, which is gradually redissolved. The reaction must be moderated by the gradual addition of 17 parts more of alcohol; and, on cooling, crystals of the fulminate, amounting to 4.6 parts, are deposited. The reaction is attended with the formation of the same products as when silver is used. Glycolic acid is also found in the mother-liquor.

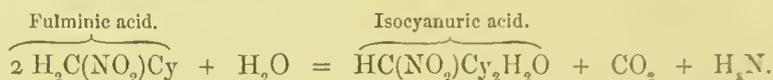
Mercuric fulminate forms white silky needles, which have a metallic sweetish taste. It is sparingly soluble in cold water, but much more soluble in boiling water, and in solution of ammonia. It may be handled without much danger while moist, but if when dry it be exposed to the electric spark, or if it be heated to about 356° (180°C.), it explodes; and if it be struck by a hard body, or touched with concentrated sulphuric or with nitric acid, detonation occurs, but the suddenness of the explosion is decidedly less than that of argentic fulminate. The priming of the ordinary percussion cap consists of a mixture of 1 part of mercuric fulminate with 6 parts of nitre, or of a mixture of 3 parts of the fulminate, 5 of potassic chlorate, 1 of sulphur, and 1 of ground glass. It is applied in the form of a dry powder, and is made to adhere to the cap by the subsequent application of a drop of shell-lac varnish.

When either zinc or copper is boiled with mercuric fulminate suspended in water, the whole of the mercury is displaced by the metal which is employed, and fulminate of zinc, or of copper, is formed.

The nitrogen in the fulminates appears to be in two different conditions, since these compounds when decomposed yield products containing ammonia and cyanogen; mercuric fulminate, for example, when decomposed by boiling it with a solution of sulphhydrate of baric sulphide, yielding the following compounds:—

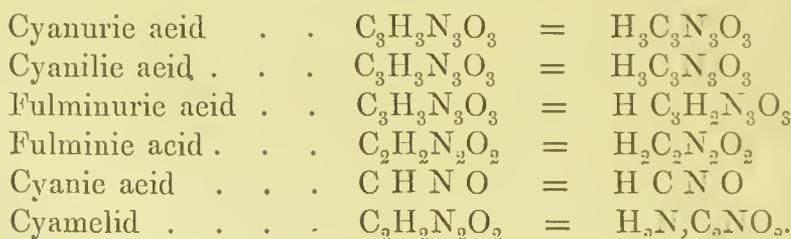


(1598) *Fulminuric* or *Isocyanuric Acid* ($\text{HC}_3\text{N}_3\text{H}_2\text{O}_2$).—This is an acid which was discovered at about the same time by Liebig and by Schischkoff. Fulminuric acid contains the same elements as the cyanuric, but it is a monobasic acid, two of the atoms of hydrogen being united with cyanogen and with oxygen to form the radicle of the acid. The salts of fulminuric acid are obtained by boiling one of the fulminates, such as mercuric fulminate, with a solution of one of the soluble chlorides. When mercuric fulminate is thus boiled with potassic chloride, it is gradually dissolved, and a yellow compound containing mercury is separated: during the first part of the operation, the liquid appears to be turbid, but as soon as this appearance ceases it is filtered, and on being evaporated it yields brilliant crystals of potassic fulminurate. The general result of the reaction may be thus represented (Kekulé):—



In short, the elements of 2 molecules of fulminic acid become split up into 1 of fulminuric acid, 1 of carbonic anhydride, and 1 of ammonia. The fulminurates crystallize with great facility; they possess a high lustre, and exert a great dispersive power on light; they are decomposed by heat with a feeble explosion.

It thus appears (supposing isolated fulminic acid to be capable of existing) that not less than 6 compounds polymeric with cyanuric acid might be produced, viz. :—



It is a remarkable peculiarity of cyanogen, both when free and when in combination, that it exhibits a strong tendency to form new compounds by condensation; for instance paracyanogen is formed by the condensation of several molecules of cyanogen into a single more complex molecule; in like manner the liquid and solid chlorides of cyanogen are produced by the condensation of two or more molecules of the gaseous chloride into one, and the molecule of cyanuric acid may be obtained by the condensation of three molecules of cyanic acid into one complex molecule.

(1599) The action of ammonia upon the oxygen acids of cyanogen has not been fully studied: the group of bodies derived from melam appears to be intimately related to the amides of cyanuric acid, and would well repay further investigation. The compounds of cyanic acid with ammonia are still more interesting, since they include the remarkable substance known as urea. This substance has the composition of ammonic cyanate, and it is always produced when a solution of ammonic cyanate is evaporated. True ammonic cyanate may be obtained by transmit-

ting the vapour of cyanic acid into gaseous ammonia, when it is condensed in the form of a white voluminous crystalline powder, which is very soluble in water. This solution, when freshly prepared, disengages ammonia on the addition of caustic potash; but if kept for a few days, or if the solution be evaporated at a gentle heat, it is converted into urea.

Urea, however, on account of the important relation which it bears to some of the most interesting chemical changes which occur within the living body, will be better considered (1601) in connexion with other substances by which it is usually accompanied in the animal organization.

(1600) *Cyanamide* (CH_2N_2); *Fusing pt.* 104° (40° C.).—Before quitting the subject of the compounds of cyanogen, mention may be made of the true amide of cyanic acid. The most convenient method of preparing it consists in transmitting a current of gaseous cyanogen chloride into ether saturated with ammonia; the ammonia hydrochlorate which is deposited during the process, having been separated by filtration, pure cyanamide is left on evaporating the ethereal solution. It forms a white crystallizable substance, which is soluble without alteration in alcohol. Water dissolves cyanamide freely, but the residue obtained on evaporating the liquid is found to consist almost wholly of its polymeride melamine (1594). Cyanamide fuses at 104° , and if heated to 302° (150° C.) it suddenly becomes solid, with a considerable evolution of heat, and is converted into melamine. The addition of nitric acid to an ethereal solution of cyanamide, converts it into urea nitrate; each molecule of cyanamide, by the assimilation of water in the proportion of H_2O , becoming changed into one of urea; $\text{CH}_2\text{N}_2 + \text{H}_2\text{O} = \text{CH}_4\text{N}_2\text{O}$.

§ II. BASES OF ANIMAL ORIGIN.

In the present section the following compounds and some of their derivatives will be described:—

| | |
|-------------------------|--|
| Urea | $\text{C H}_4\text{N}_2\text{O}$ |
| Kreatine | $\text{C}_4\text{H}_9\text{N}_3\text{O}_2, \text{H}_2\text{O}$ |
| Kreatinine | $\text{C}_4\text{H}_7\text{N}_3\text{O}$ |
| Sarkosine | $\text{C}_3\text{H}_7\text{NO}_2$ |
| Methyluramine | $\text{C}_2\text{H}_7\text{N}_3$ |
| Guanine | $\text{C}_5\text{H}_5\text{N}_5\text{O}$ |
| Xanthine | $\text{C}_5\text{H}_4\text{N}_4\text{O}_2$ |
| Hypoxanthine | $\text{C}_5\text{H}_4\text{N}_4\text{O}$ |
| Guanidine | $\text{C H}_5\text{N}_3$ |
| Glycocine | $\text{C}_2\text{H}_5\text{NO}_2$ |
| Alanine* | $\text{C}_3\text{H}_7\text{NO}_2$ |
| Leucine | $\text{C}_6\text{H}_{13}\text{NO}_2$ |
| Tyrosine | $\text{C}_9\text{H}_{11}\text{NO}_3$ |

* Alanine is an artificial, and not an animal product, but is described here from its homology with glycocine and leucine.

(1601) UREA ($\text{CH}_4\text{N}_2\text{O} = 60$; *Sp. gr.* 1.30).—This important compound is an essential constituent of the urine of animals; it is abundant in that of the mammalia, and particularly so in the urine of the carnivora; but it has also been met with in the urine of birds, and of amphibia. Urea is the principal outlet for the nitrogen of the system, after the materials which compose the animal tissues have experienced oxidation under the influence of the respired air, a healthy human adult excreting nearly an ounce and a quarter of urea daily. Dumas made many fruitless attempts to effect the direct conversion of the azotised constituents of the body into urea; but Béchamp states that he has succeeded in obtaining this result by subjecting albumin to the oxidizing action of potassic permanganate. The correctness of this observation has since been denied by Städler, who obtained benzoic acid abundantly by Béchamp's method, and this he thinks must have been mistaken for urea. Urea is not formed in the kidneys; these glands appearing to act somewhat in the manner of filters, by means of which the urea is separated from the mass of the blood, where it exists already formed before reaching the kidneys.

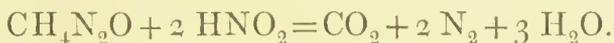
Urea may be obtained artificially in a variety of ways: one of the most remarkable of these was discovered by Wöhler, who showed that a solution of ammoniac cyanate, which is metameric with urea, when evaporated at a gentle heat, furnishes urea; since $\text{H}_4\text{N}_2\text{CNO} = \text{CH}_4\text{N}_2\text{O}$.

This conversion of the cyanate into urea occurs whether it be formed by the direct union of cyanic acid with ammonia, or by the double decomposition of a metallic cyanate, such as potassic or plumbic cyanate, with a salt of ammonium. Neither cyanic acid nor ammonia can, however, be discovered in the compound obtained; but if a solution containing a mixture of argentic nitrate and urea be boiled for some time, it is partly resolved into argentic cyanate and ammoniac nitrate.

Urea is likewise formed during the action of lead dioxide and other oxidizing agents upon uric acid; by the action of alkalis upon alloxan, and upon kreatine; as well as by the action of sulphuretted hydrogen upon the double fulminate of copper and ammonium. It is also obtained as a product of the action of phosgene gas (COCl_2) upon ammonia, and by the reaction of ammonia upon carbonic ether, at a temperature of $359^{\circ}6$ (182° C.) (1161; Natanson). Urea is metameric with carbamide, if not identical with it (1604).

Preparation.—1. Urea is readily procured by concentrating urine to the consistence of syrup, decanting from the deposited

salts, and adding an equal bulk of pure colourless nitric acid, of sp. gr. 1.25. The mixture becomes nearly solid from the deposition of flaky crystals of urea nitrate, the quantity of which is increased by immersing the vessel in a freezing mixture. The mother-liquor is then pressed out, and the crystals diffused through water, to which baric carbonate in powder has been added. Effervescence takes place from the expulsion of carbonic anhydride, baric nitrate is formed, whilst urea is set free, and is dissolved. If the mixture of baric nitrate and urea, obtained by evaporation, be treated with boiling alcohol, urea only is dissolved, and it is deposited on cooling or during evaporation in long, slender, striated, colourless prisms. When an aqueous solution of urea containing not less than one-thirtieth of its weight of urea is mingled with an equal bulk of pure nitric acid, an abundant deposition of needles of urea nitrate occurs ($\text{CH}_4\text{N}_2\text{O}, \text{HNO}_3$). The nitric acid employed must be quite free from nitrous acid, since urea is completely decomposed by nitrous acid, into carbonic anhydride, nitrogen, and water:—

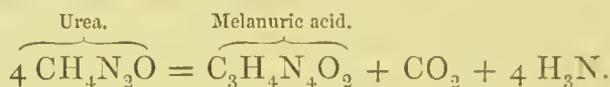


2. Oxalic acid may be substituted for the nitric in the foregoing process; the urea oxalate thus formed may be decomposed by calcic carbonate, and the urea may then be separated from the calcic oxalate and carbonate, by water; on evaporating the aqueous solution, crystals of urea are obtained.

3. Urea, however, is more easily and abundantly obtained from potassic cyanate, procured by heating an intimate mixture of 56 parts of potassic ferrocyanide, which has been completely dried at 212° , with 28 parts of carefully-dried finely-powdered black oxide of manganese. The mixture is placed upon a plate of sheet-iron and heated to dull redness, when it slowly smoulders, care being taken to stir the mass from time to time. The residue of this operation when cold is to be digested in cold water, and 41 parts of ammonic sulphate are to be added to the solution; double decomposition then ensues, ammonic cyanate and potassic sulphate being formed: the ammonic cyanate may be dissolved by means of alcohol; it thus becomes converted into urea, which crystallizes as the solution cools.

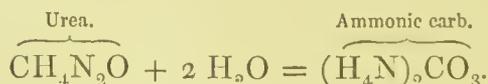
It is still better obtained as follows:—Potassic cyanide is fused at a very low red heat in a shallow iron dish, and red lead in fine powder is added gradually till it ceases to be decomposed. When cold the mass is treated with cold water, filtered, and baric nitrate added to separate the carbonic acid; plumbic nitrate is now added to the filtrate, and insoluble plumbic cyanate is precipitated; this must be well washed, and decomposed with an equivalent of ammonic sulphate (J. Williams).

Properties.—Pure urea is colourless; it crystallizes in slender striated prisms, which are slightly deliquescent. Its solution has a cooling bitterish taste, and is neutral to test papers. It is very soluble in water and in hot alcohol, but very sparingly so in ether. It forms no definite compound with water, but it deprives many salts, such as sodic sulphate, of their water of crystallization when triturated with them, producing a soft semi-fluid magma. Urea melts at about 248° (120° C.), but at a temperature a little above this it is decomposed, yielding ammonia, with cyanate and carbonate of ammonium, cyanuric acid being left in the retort; this, if the temperature be raised further, in its turn undergoes decomposition, and a white amorphous residue, consisting of melanuric acid, is obtained:—



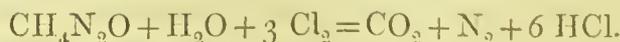
Previously to the completion of this change, a substance termed biuret ($\text{C}_2\text{H}_5\text{N}_3\text{O}_2, \text{H}_2\text{O}$) is formed (1606). By a still further elevation of temperature melanuric acid is decomposed and mellon is formed.

A solution of urea, if pure, may be kept at ordinary temperatures without alteration, and it may even be boiled without undergoing decomposition; but if heated in a sealed tube to about 284° (140° C.), each molecule of urea combines with 2 molecules of water, and is converted into normal ammonic carbonate:—



The same change takes place slowly at ordinary temperatures in the presence of the mucus of the bladder, the ammoniacal odour acquired by urine after keeping it for a few days being due to this alteration. A similar decomposition into carbonic anhydride and ammonia occurs when urea is fused with caustic potash, or treated with concentrated sulphuric acid.

Chlorine, when transmitted into an aqueous solution of urea, resolves the latter into carbonic anhydride and nitrogen, whilst hydrochloric acid is formed:—



Urea does not possess well-marked basic properties, but it combines with certain acids, and yields crystallizable compounds, which preserve a strong acid reaction. It absorbs hydrochloric

acid gas, forming a deliquescent substance ($\text{CH}_4\text{N}_2\text{O}, \text{HCl}$) which fuses at a gentle heat to a yellowish oil, and solidifies to a crystalline radiated mass as it cools; water decomposes it immediately. The most important salts of urea are those which it forms with nitric and oxalic acids. In combining with the monobasic oxyacids, each molecule of urea unites with 1 of acid, no separation of water occurring. *Urea nitrate* ($\text{CH}_4\text{N}_2\text{O}, \text{HNO}_3$) is such a compound; it crystallizes in rhombic prisms, or in brilliant leaflets, which are sparingly soluble in water, especially if it contain excess of nitric acid. It is sparingly soluble in alcohol. *Urea oxalate* [$2 \text{CH}_4\text{N}_2\text{O}, \text{H}_2\text{C}_2\text{O}_4$] crystallizes in long, thin, transparent, sparingly soluble prisms. It is almost insoluble in a saturated aqueous solution of oxalic acid.

(1602) *Compounds of Urea with Salts, and with Metallic Oxides.*

—Urea forms definite compounds with certain metallic oxides, such as those of silver and of mercury. Its compound with silver oxide ($3 \text{Ag}_2\text{O}, 2 \text{CH}_4\text{N}_2\text{O}$) is produced by digesting at a gentle heat freshly-precipitated argentic oxide in an excess of a solution of urea; a grey or yellowish crystalline powder is thus formed. Three such compounds may be obtained with mercuric oxide, viz., $\text{CH}_4\text{N}_2\text{O}, \text{HgO}$; $2 \text{CH}_4\text{N}_2\text{O}, 3 \text{HgO}$; and $\text{CH}_4\text{N}_2\text{O}, 2 \text{HgO}$. The first of these compounds ($\text{CH}_4\text{N}_2\text{O}, \text{HgO}$) is formed, if successive portions of mercuric oxide suspended in water be mixed with a warm solution of urea; at first the oxide is completely dissolved, but the compound in question is gradually deposited as a white powder, which becomes yellowish on drying. The compound ($2 \text{CH}_4\text{N}_2\text{O}, 3 \text{HgO}$) is obtained by adding to a solution of urea rendered alkaline by potash, a solution of corrosive sublimate, taking care to maintain an excess of alkali; a white gelatinous precipitate is formed, which when well washed is converted by boiling water into a pale yellow granular powder, having the composition above indicated; and the compound ($\text{CH}_4\text{N}_2\text{O}, 2 \text{HgO}$) is obtained by precipitating a solution of mercuric nitrate by adding it to an alkaline solution of urea. (Liebig, *Chem. Gaz.*, xii. 41.)

When a solution of mercuric nitrate is mixed with one of urea, the urea enters into combination with the salt in several proportions. If warm dilute solutions of urea and of mercuric nitrate be mixed, a crystalline precipitate ($4 \text{HgO}, \text{N}_2\text{O}_5, 2 \text{CH}_4\text{N}_2\text{O}$) falls as a heavy granular powder, which consists of concentric groups of minute needles. But if a dilute solution of mercuric nitrate be added to a solution of urea so long as a precipitate is formed, and the whole be maintained at a temperature of

from 104° to 122° (40° to 50° C.), the precipitate is principally composed of six-sided prisms, consisting of $(3\text{HgO},\text{N}_2\text{O}_5, 2\text{CH}_4\text{N}_2\text{O})$. If a solution of urea nitrate be poured into a somewhat dilute solution of mercuric nitrate, slightly acidulated with nitric acid, until a permanent turbidity appears, on filtering the liquid and allowing it to stand, crystalline crusts of small shining rectangular tables are gradually formed $(2\text{HgO},\text{N}_2\text{O}_5, 2\text{CH}_4\text{N}_2\text{O})$.

Argentie nitrate forms two similar compounds $(\text{AgNO}_3, \text{CH}_4\text{N}_2\text{O})$, and $[2\text{AgNO}_3, \text{CH}_4\text{N}_2\text{O}]$, which crystallize readily when a mixture of a solution of urea and of argentic nitrate is evaporated *in vacuo* over sulphuric acid. Urea also combines with other salts, but the compounds which it forms with them are of little importance.

(1603) *Liebig's method of determining Chlorides and Urea in Urine.*—The foregoing observations are due to Liebig, who has founded upon them a method of determining the quantity of chlorine and of urea in urine, which is valuable when such analyses are numerous, since it enables a large number of comparative experiments to be made in a short time.

1. *For the Chlorine.*—A solution of urea is not precipitated by a solution of corrosive sublimate, but it is immediately precipitated by mercuric nitrate. Solutions of the chlorides of the metals belonging to the groups of the alkalis and alkaline earths, when mixed with mercuric nitrate, become decomposed into corrosive sublimate, and a nitrate of the metal of the alkali or earth; hence, when a solution of sodic chloride is mixed with one of urea, no precipitate is occasioned in this liquid on the addition of mercuric nitrate, until the whole of the sodic chloride has been decomposed by the mercurial salt; $2\text{NaCl} + \text{Hg}_2\text{NO}_3$ becoming $2\text{NaNO}_3 + \text{HgCl}_2$. After this point has been reached, every fresh addition of mercuric nitrate occasions a precipitate of the compound $(4\text{HgO},\text{N}_2\text{O}_5, 2\text{CH}_4\text{N}_2\text{O})$; and if a solution of the mercurial salt of known strength and free from excess of acid be prepared, it is easy to determine the quantity of chlorides present by measuring the volume of this solution which it is necessary to add to a given volume of urine before it begins to occasion a precipitate.

2. *For the Urea.*—Having ascertained the number of divisions of the mercurial solution which are consumed before a precipitate begins to be formed, a measured volume of a standard solution of argentic nitrate, sufficient exactly to effect precipitation of the chlorine thus indicated, is added, and afterwards the urea is determined by means of the solution of mercuric nitrate. The following are the details of the operation:—

1. *Preparation of the Solution of Mercuric Nitrate No. 1, employed for determining the Chlorine.*—Crystals of pure mercurous nitrate are to be dissolved in moderately strong nitric acid, and the solution is to be heated until a sample is no longer rendered turbid by sodic chloride, which indicates that the whole has been converted into a mercuric salt. The solution is next to be evaporated on a water-bath to a syrupy consistence, diluted with about ten times its bulk of water, and neutralized by the addition of precipitated yellow oxide of mercury so long as the oxide is dissolved; it is then set aside for twenty-four hours, and, if necessary, filtered. In order to graduate the solution, it is requisite to procure a saturated solution of pure sodic chloride, prepared by digesting a large excess of the salt in cold water, with frequent agitation, for twenty-four hours: 100 cub. centim. of such a solution contain 31.84 grammes of sodic chloride. 10 c.c. of this solution (= 3.184 grms. of sodic chloride) are poured into a small beaker, and mixed with 3 c.c. of a solution of urea, containing about 4 per cent. of urea, and also with 5 c.c. of a cold saturated solution of pure sodic sulphate; the solution of mercuric nitrate is then to be added to this mixture from a burette, with constant stirring, until a distinct and permanent precipitate is formed. The number of cubic centimetres of the solution poured from the burette indicates the amount of the liquid which corresponds to 3.184 grms. of sodic chloride. The strength of the mercurial solution having been thus ascertained, such a proportion of water must be added to it, that 100 cub. cent. may correspond to 1 gramme of sodic chloride.

2. *Preparation of the Solution of Argentic Nitrate employed for removing the Chlorine.*—17.436 grms. of fused argentic nitrate are dissolved in water, and diluted until the liquid amounts to 600 c.c.; 100 c.c. of this solution correspond to 1 gram. of sodic chloride.

3. *Preparation of the Solution of Mercuric Nitrate No. 2, for determining the Urea.*—A concentrated solution of mercuric nitrate, containing about 2.5 grms. of the salt in 18 c.c., is prepared according to the directions already given. In order to graduate this solution, 5 grms. of pure urea are to be dissolved in water, and diluted till the volume of the solution amounts exactly to 250 c.c.: 10 c.c. of this liquid are to be poured into a beaker, and the mercurial solution is to be added from a burette, till a few drops in a watch-glass produce a distinct yellow colour with sodic carbonate. If the solution were of the exact strength desired, it would require 20 c.c. of the mercurial solution; but if the latter be prepared of the strength above directed, a somewhat smaller quantity will be requisite, and a quantity of water exactly sufficient to reduce it to this strength must be added to the solution.

It will be found convenient, in executing analyses of urine by this method, to be provided, 1. with a pipette capable of delivering exactly 15 c.c. from a mark upon its stem, for measuring off the diluted urine; 2. with a small burette divided into tenths of a cubic centimetre, and capable of measuring 5 c.c., for the mercurial solution No. 1; and 3. with an ordinary alkalimeter burette, divided to c.c., for the mercurial solution No. 2.

Before proceeding to determine the amount of the urea in urine, it is necessary to remove the phosphoric acid contained in the liquid. This is effected by means of a mixture of two volumes of cold saturated baryta water, and one volume of a cold saturated solution of baric nitrate. A glass cylinder of about

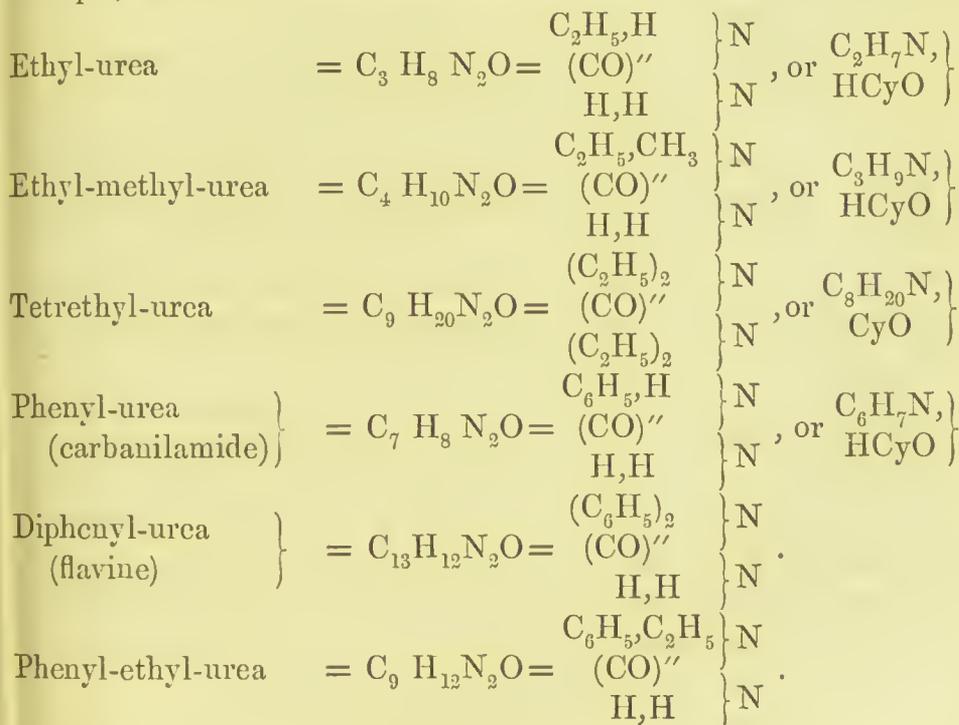
30 c.c. in capacity is filled to overflowing with urine, the excess being removed by causing a glass plate to slide over the mouth of the cylinder; two such cylinderfuls are to be poured into a beaker, and mixed with one cylinderful of the baryta solution. The precipitate thus formed is to be filtered off, and the amount of sodie chloride in 15 e.e. of the filtrate (=10 c.c. of urine) is to be determined by *faintly* acidulating by the addition of nitric acid, and then adding the standard solution of mercury No. 1, till a cloudiness appears: 30 e.c. more of the filtrate (=20 c.c. of urine) are then to be measured off into a separate vessel, and mixed with a quantity of the standard solution of silver, equal to twice that of the mercurial solution employed in the preceding experiment. The liquid is to be filtered, and a bulk of the filtrate, equal to 15 e.e. + half the volume of silver solution used, is to be employed for the determination of the urea. This quantity, which corresponds to 10 e.e. of urine, is to be poured into a beaker, and the graduated mercurial solution No. 2 added from a burette with frequent stirring, until no further increase of the precipitate is perceptible. In order to ascertain whether a sufficient quantity of the mercurial solution has been added, a few drops of the turbid liquid are to be removed with a pipette into a watch-glass, and 2 or 3 drops of a solution of sodie carbonate allowed to flow from the edge of the glass into the liquid. If, after some minutes, the mixture retain its white colour, a further quantity of the mercurial solution is to be added, until a fresh sample plainly exhibits the yellow colour after the addition of the sodie carbonate.

Picard has successfully applied a modification of this method to the detection of urea in healthy blood, and he has even succeeded in estimating the difference in the quantity of urea contained in the blood of the renal artery, and in that of the renal vein after the blood has undergone the depurating influence of the kidney. (*Comptes Rendus*, Sept. 8, 1856.)

(1604) *Compound Ureas*.—A remarkable series of compounds may be obtained from urea by the displacement of a certain number of the atoms of hydrogen which it contains. The formation of these compounds is readily explained upon the hypothesis that urea is the diamide (1346) of carbonic acid: (CO)'' would then occupy the place of H₂ in the double molecule of ammonia; thus

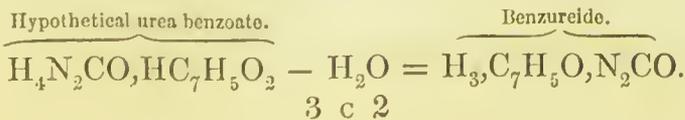
urea $\text{CH}_4\text{N}_2\text{O} = \begin{array}{l} \text{H}_2\text{H} \\ \text{H}_2\text{H} \end{array} \left. \begin{array}{l} \text{N} \\ \text{N} \end{array} \right\}$, and each of its four atoms of hydrogen would admit of displacement by an equivalent amount of

some organic radicle. Compounds of this kind are readily formed in most cases by the action of cyanic acid upon the base which they represent, just as ordinary urea is formed from ammonia, by acting upon it with cyanic acid. They may also be obtained by decomposing the cyanic ethers with ammonia. The compound ureas combine, like ordinary urea, with acids, and form crystallizable salts. Examples of the formation of these compounds have already been cited in the case of the alcohol radicles (1164); for example, we have:—



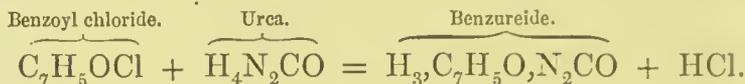
It is obvious that this class of compounds admits of being multiplied and varied as extensively as the allied group of artificial bases. Some of the natural organic bases, such as nicotylia and conylia, when made to act upon the cyanic ethers, also react like ammonia, and give rise to bodies belonging to the class of ureas (1388).

(1605) *Ureides*.—Urea likewise gives rise to the formation of another class of compounds analogous to the amides, forming substances which have been called *ureides*; that is to say, these bodies may be represented as salts of urea from which the elements of water have been abstracted, or they may be regarded as compounds in which one or more of the atoms of hydrogen in urea have been displaced by an equivalent amount of the radicle of an acid:—



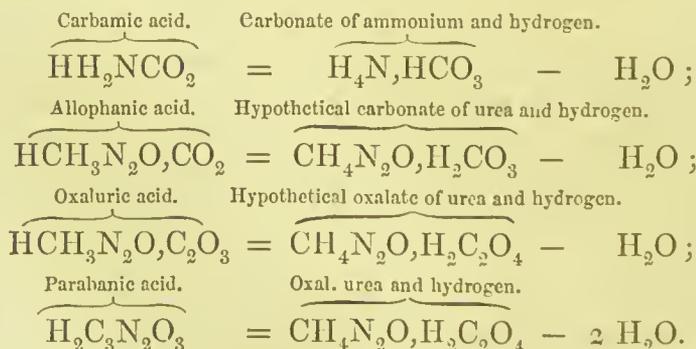
Benzureido.

When, for instance, a mixture of an atom of urea with an atom of one of the oxychlorides of the acids (1266) is heated, decomposition occurs, and a ureide is formed. For example, if urea be heated to about 311° (155° C.), and then gradually mixed with benzoyl chloride, taking care that the temperature shall not exceed 320° (160° C.), the mass becomes pasty, the odour of benzoyl chloride disappears, and *benzureide*, or benzoyl urea, is left in the form of a crystalline powder, which is soluble in alcohol, but insoluble in ether:—

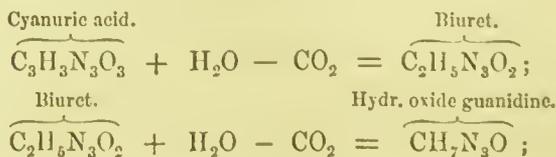


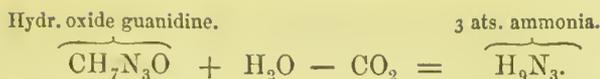
Acetyl chloride, butyryl chloride, and valeryl chloride may be made in like manner to yield respectively *acatureide* [$\text{H}_3\text{C}_2\text{H}_5\text{O}_2\text{N}_2\text{CO}$]; *butyrureide* [$\text{H}_3\text{C}_4\text{H}_7\text{O}_2\text{N}_2\text{CO}$]; and *valerureide* [$\text{H}_3\text{C}_5\text{H}_9\text{O}_2\text{N}_2\text{CO}$]. (Zinin.) These bodies, in fact, belong to the class of secondary diamides (1346), and may be regarded as urea in which one of the atoms of hydrogen has been displaced by the acid radicle benzoyl, acetyl, or valeryl.

Besides these ureides, there are various compounds known which bear a relation to urea similar to that of the amidated acids to ammonia:—for example, allophanic acid, known, however, only in its salts (1165; $\text{HC}_2\text{H}_3\text{N}_2\text{O}_3$), may be regarded as *carbureic acid*, analogous to carbamic acid: oxaluric acid (1626) may in like manner be viewed as *oxalureic acid*; whilst parabanic acid (1625) would represent the imide corresponding to oxaluric acid (Gerhardt), as indicated by the following equations:—



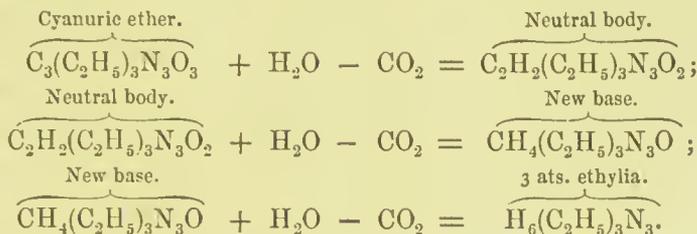
(1606) *Biuret* ($\text{C}_2\text{H}_5\text{N}_3\text{O}_2, \text{H}_2\text{O}$).—This compound has the composition due to ammonic dicyanate; but it appears to be really a derivative from cyanuric acid, and to form one of a series, the relations of which may be thus represented (Hofmann):—





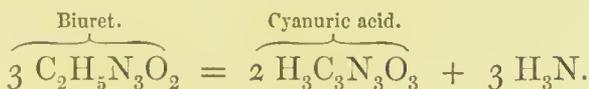
And Finckh has indeed shown that biuret may be converted into a salt of guanidine (1611) by the prolonged action of gaseous hydrochloric acid at a temperature of 338° (170° C.).

Parallel with this series runs one derived from cyanuric ether, which indicates the successive stages by which this ether is converted into ethylia (1165):—



(Hofmann, *Proceed. Roy. Soc.*, xi. 285.)

Biuret is prepared by melting urea for some time in an oil bath at a temperature between 302° and 338° (150° and 170° C.). When the disengagement of ammonia has ceased and the mass has assumed a pasty consistence, it is treated with a small quantity of boiling water, and the solution, after filtration, is mixed with a solution of basic plumbic acetate; plumbic cyanurate and melanurate are thus precipitated; the excess of lead is removed by sulphuretted hydrogen, and the filtered liquid, on evaporation, yields granular crystals of biuret. This compound is very soluble both in water and in alcohol. It may be obtained from its alcoholic solution in long, anhydrous, foliated crystals. It is a remarkably stable substance, since it may be dissolved by concentrated sulphuric or nitric acid without being decomposed. A characteristic reaction of biuret is the formation of an intensely red liquid when a few drops of a solution of a cupric salt are added to its aqueous solution, and then a slight excess of caustic potash. When heated strongly, it is decomposed into ammonia and pure cyanuric acid:—



(1607) Urea is accompanied in urine by small quantities of two other crystallizable principles, which have received the names of *kreatine* and *kreatinine*. The alkaline properties of the first are extremely feeble. In order to prepare these bodies from urine, the liquid is to be neutralized by lime, and a solution of calcic chloride added, so long as it produces a precipitate. The filtered liquid is to be evaporated by a water heat, until the salts crystallize on cooling; the mother-liquor is then to be decanted, and mixed with one-twentieth of its bulk of a saturated solution of zincic chloride. In the course of three or four days a deposit of rounded yellow crystalline grains of the zinc chloride of kreatinine, mixed with crystals of kreatine, occurs. These crystalline masses must be washed with cold water, and then dissolved in boiling water, after which hydrated plumbic oxide is to be added, till the liquid is distinctly alkaline. The hydrochloric

acid and zinc are thus precipitated from the hot liquid, in the form of hydrated zincic oxide and plumbic oxychloride. The filtered solution is digested with animal charcoal, in order to remove adhering colouring matter, and, on evaporating the solution, mixed crystals of kreatine and kreatinine are deposited. Hot alcohol dissolves the kreatinine, and during evaporation yields it in crystals. The undissolved portion is kreatine. If, instead of employing fresh urine for the extraction of kreatine and kreatinine, it be taken after putrefaction has commenced, the kreatine, according to Liebig, will have disappeared, while the kreatinine remains unchanged. Both kreatine and kreatinine were originally discovered among the constituents of the fluids contained in the muscular tissue. There can be little doubt but that, like urea, they are products of disintegration of the muscular tissue, and that they are destined either for ulterior change in the economy, or for immediate rejection as excrementitious matter; and this view is strengthened by the fact that the proportion of kreatine is greater in the muscles of animals killed in the chase than in the same animals killed otherwise.

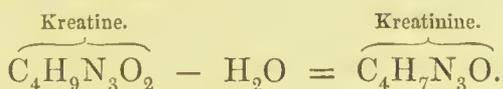
Kreatine ($C_4H_9N_3O_2, H_2O = 131 + 18$).—Kreatine is present in the juice of the flesh in very small proportion, whence the name, from κρέας, flesh, given to it by its discoverer, Chevreul. A pound of flesh yields on an average, according to Gregory, about 5 grains of kreatine; the quantity, however, varies in the flesh of different animals. The flesh of the common fowl was found by Gregory to contain more kreatine than that of any animal upon which his experiments were made; but cod fish is its cheapest source: 10,000 parts of fresh cod furnish from 9 to 17 parts of kreatine, while the same weight of fowl furnishes 32 parts: and Neubauer found in ox flesh on the average 20 parts. The best process consists in chopping up raw cod finely, mixing it with an equal weight of water, and expressing the liquid. This liquid is next heated sufficiently to coagulate the albumin, taking care to avoid ebullition, after which it is filtered. Baryta water is then added cautiously, so long as it occasions a precipitate; the liquid is again filtered, to separate baric phosphate; and the filtrate, on being evaporated to a very small bulk, yields crystals of nearly pure kreatine. It may be rendered quite pure by a second crystallization.

Kreatine crystallizes in colourless, transparent, brilliant, oblique prisms, which, when heated to 212° , become opaque, and lose their water of crystallization. Kreatine is sparingly soluble in cold water, of which it requires 75 times its weight for solu-

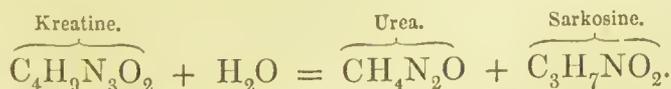
tion: it is freely dissolved by boiling water. Alcohol, when cold, scarcely dissolves it; it is insoluble in ether. The aqueous solution has a weak, bitterish taste. Although kreatine is neutral to test papers, it yields definite compounds with some of the acids. *Kreatine hydrochlorate* ($C_4H_9N_3O_2, HCl$) forms colourless, well-defined crystals, which are soluble in water. It may be prepared by mixing solutions of equivalent quantities of hydrochloric acid and kreatine, and evaporating *in vacuo*, or by a temperature not exceeding $89^{\circ}6$ ($32^{\circ}C.$). The *sulphate* ($2C_4H_9N_3O_2, H_2SO_4$) may be obtained in a similar manner; the *nitrate* ($C_4H_9N_3O_2, HNO_3$) may also be obtained in brilliant crystals, which have a very sour taste.

When kreatine is boiled with mercuric oxide, the oxide is reduced, and a basic substance is formed, which Dessaignes calls methyluramine ($C_2H_7N_3$; 1610). The same substance may be obtained by boiling kreatine with sulphuric acid and lead dioxide. When a current of nitric oxide is transmitted through a solution of kreatine nitrate, an abundant disengagement of gas occurs; on neutralizing with caustic potash, separating the nitre by crystallization, and adding argentic nitrate, a crystalline compound is obtained ($C_3H_5N, AgNO_3$), in which the argentic nitrate is combined with a new base, to which Dessaignes assigns the formula C_3H_5N .

If kreatine be boiled with either sulphuric, hydrochloric, nitric, or phosphoric acid, it is decomposed, each molecule losing a molecule of water; while kreatinine is formed, and enters into combination with the acid:—



Alkaline bodies produce with kreatine a different result. If, for instance, to a boiling solution of kreatine, crystallized baric hydrate, equal in weight to ten times that of the kreatine, be added, the kreatine is gradually decomposed, another new alkali termed *sarkosine* is formed, and urea is found in the liquid; one atom of hydrated kreatine furnishing the elements of one molecule of sarkosine and one of urea:—



By continued boiling with baryta, the urea itself is decomposed into ammonia, which is expelled during the ebullition, and carbonic anhydride, which combines with the baryta.

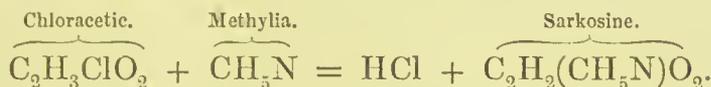
(1608) *Kreatinine* ($C_4H_7N_3O=113$).—This base may be pro-

eured from urine by the method already described (1607). It may also be obtained by boiling kreatine with hydrochloric acid; kreatinine hydrochlorate is thus formed, and from this the acid may be separated by boiling it with hydrated plumbic oxide in excess; a yellow, insoluble plumbic oxyehloride is formed, and the kreatinine remains in solution. Its crystals require about 12 parts of cold water for solution, and they are still more soluble in hot water; kreatinine is also dissolved abundantly by boiling alcohol, and it crystallizes on cooling. Its aqueous solution restores the blue colour to reddened litmus, and it expels ammonia when heated with solutions of ammoniacal salts. It has a strong tendency to form basic double salts: for example, if a solution of argentic nitrate, moderately concentrated, be mixed with one of kreatinine, it becomes converted into a magma of white needles, which are very soluble in boiling water; and a similar compound is formed when a solution of corrosive sublimate is substituted for that of the silver salt. The zinc chloride of kreatinine $[(C_4H_7N_3O)_2ZnCl_2]$ is also sparingly soluble. With the salts of copper, kreatinine forms a blue crystallizable compound. Both the sulphate and the hydrochlorate of kreatinine may readily be obtained in crystals.

By prolonged digestion with bases, as with milk of lime for example, kreatinine recombines with the elements of water, and forms kreatine.

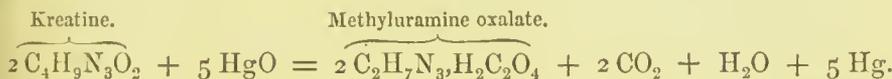
(1609) *Sarkosine*, from σαρκίξ, flesh ($C_3H_7NO_2 = 89$).—In order to prepare this alkali, the solution of kreatine must be boiled with 10 times its weight of baric hydrate until all odour of ammonia shall have disappeared. The excess of baryta is to be removed by a current of gaseous carbonic anhydride; the solution is to be boiled, filtered, and evaporated to the consistence of syrup, from which the sarkosine may be obtained in foliated crystals. In order to ensure its purity it may be converted into the form of sulphate, the aqueous solution of which may be decomposed by pure baric carbonate. Sarkosine crystallizes in right rhombic, perfectly transparent, colourless prisms, which are freely soluble in water, sparingly so in alcohol, and insoluble in ether. At a temperature a little above 212° they melt, and may be sublimed unchanged. Its aqueous solution has a sharp, sweetish, somewhat metallic taste, but has no action on vegetable colours. It forms crystallizable salts, which have an acid reaction. The sulphate ($2C_3H_7NO_2, H_2SO_4, H_2O$) crystallizes in colourless cubes. With platinum chloride sarkosine gives a double salt, which by spontaneous evaporation may be obtained in large yellow flattened octahedra $[(C_3H_7NO_2)_2, 2HCl, PtCl_4, 2H_2O]$. Sarkosine is isomeric

with alanine and carbamic ether (urethane), as well as with lactamide, but quite distinct from all these bodies in properties, and is distinguished from them by its insolubility in ether and in alcohol. From its reactions Strecker considers it to be *methyl-glycocine*, $C_2H_2(CH_3)(H_2N)O_2$ (1615); and Volhard (*Liebig's Annal.*, exxiii. 261) has experimentally confirmed this view by preparing sarkosine directly by heating an excess of methylin with chloracetic acid in a sealed tube to about 266° (130° C.).

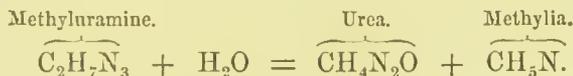


It is worthy of remark, that both kreatine and sarkosine yield methylin when distilled with a mixture of sodic hydrate and lime; and sarkosine, when heated with sulphuric acid, is decomposed with effervescence, emitting vapours of a peculiar, stupefying odour, whilst methylin sulphate is formed in the liquid.

(1610) *Methyluramine* ($C_2H_7N_3 = 73$).—When an aqueous solution of kreatine or of kreatinine is boiled with mercuric oxide, carbonic anhydride is evolved, the oxide is reduced, and on evaporating the solution a copious crystallization of methyluramine oxalate takes place:—



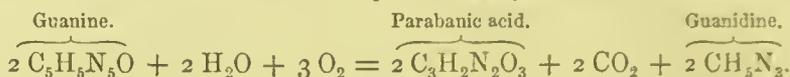
When the oxalate of the base is decomposed by milk of lime, methyluramine is liberated, and may be obtained in the form of a colourless deliquescent mass, by evaporating the solution *in vacuo*. It is powerfully alkaline, and absorbs carbonic acid rapidly from the air. It has a caustic, somewhat ammoniacal taste. When heated on platinum foil it is almost wholly volatilized. If boiled with baryta water it is decomposed, and vapours of methylin are evolved. Hydrated methyluramine, in fact, contains the elements of methylin and of urea:—



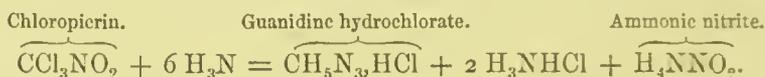
Methyluramine oxalate ($2C_2H_7N_3, H_2C_2O_4, 2H_2O$) crystallizes in flattened, double prisms, which are very soluble in water. It is easy to prepare other salts of the base, such as the hydrochlorate, the nitrate, and the sulphate, by decomposing the oxalate with a solution containing an equivalent quantity of calcic hydrochlorate, nitrate, or sulphate.

(1611) *Guanine* ($C_5H_5N_5O = 151$) was obtained by Unger from guano; it is also found to constitute the principal portion of the excrement of the garden spider (*Epeira diadema*), and it was found by Seherer in the pancreas of the horse. In order to obtain it from guano, this substance must be boiled with milk of lime until the liquid shall have acquired a yellowish-green tint instead of a brown colour. The liquid must then be filtered, and neutralized with hydrochloric acid. The guanine is slowly deposited, mixed with uric acid, and assumes the form of a flesh-coloured precipitate. This precipitate, when boiled with hydrochloric acid, gives up the guanine, and on cooling, a compound of this body with hydrochloric acid is obtained in crystals: the acid may be removed by digestion with ammonia. Certain specimens of guano were found to yield nearly 6 per cent. of this substance. Guanine forms a yellow powder which is insoluble in water, alcohol, and ether. It appears to possess the properties of a feeble base, and is soluble in hot dilute acids, forming unstable compounds with them. Guanine

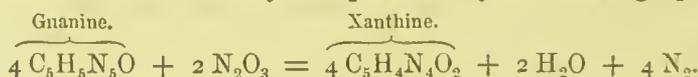
forms both normal and acid salts, the normal compound with hydrochloric acid being $[(C_5H_5N_5O, HCl), H_2O ?]$, and the acid salt $(C_5H_5N_5O, 2 HCl)$; both of them lose the whole of their acid on being heated to 392° (200° C.). Other salts of guanine contain three atoms of the base and four of acid. Guanine forms a crystallizable double chloride with platinic chloride $[(C_5H_5N_5O, HCl), PtCl_4, 2 H_2O]$. Guanine also combines with the alkalis, and is more soluble in alkaline solutions than in the acids. It is readily oxidized by a mixture of potassic chlorate and hydrochloric acid, yielding numerous products, among which are parabanic acid, oxaluric acid, and urea, the result of the decomposition of parabanic acid (1625), as well as a new base termed *guanidine* by Strecker:—



Guanidine (CH_5N_3) is homologous with methyluramine ($C_2H_7N_2$). It is possibly, as Hofmann supposes, a triammonia formed from 3 atoms of ammonia, in which 4 atoms of hydrogen have been displaced by 1 of carbon $C^{iv}H_5N_2$, or *carbortriammonia*. By heating chloropierin in sealed tubes with an alcoholic solution of ammonia for some days to the temperature of boiling water, Hofmann succeeded in obtaining guanidine hydrochlorate, mixed with ammonic nitrite and hydrochlorate, while gaseous nitrogen is liberated owing to the decomposition of the ammonic nitrite:—



Among the products of the oxidation of guanine is xanthine in small quantity, the formation of which is best observed when guanine is treated with nitrous acid; the relation of the two bodies may be represented by the following equation:—



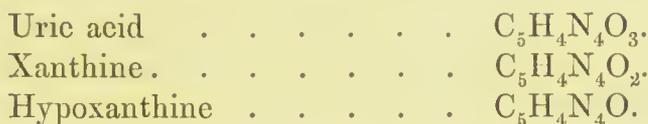
(1612) *Xanthine*, or *xanthic oxide* ($C_5H_4N_4O_2$), was discovered by Marcet as the principal constituent of a very rare variety of urinary calculus. Göbel has since found it in some oriental bezoars extracted from the intestines of certain ruminating animals. The concretions which contain xanthine are of a pale brown colour; they have a polished surface and a lamellar fracture. These calculi are readily soluble in a solution of potash; and on neutralizing the alkaline solution with an acid, xanthine is precipitated in the form of a white powder, which is insoluble in water, alcohol, and ether. It acquires a waxy lustre on friction with a hard body. The caustic alkalis, particularly ammonia, dissolve it freely. Hydrochloric acid dissolves it very sparingly, but it is soluble in nitric acid without effervescence: the solution, when evaporated, leaves a lemon-coloured residue, hence the name *xanthine*, from $\xiανθός$, yellow. This residue does not become red by the action of ammonia. When distilled, xanthic oxide yields hydrocyanic acid and ammonic carbonate, but no urea. It contains one atom of oxygen less than normal uric acid. Stædeler found xanthine diffused pretty extensively through different organs of the body, such as the liver, spleen, and pancreas, as well as the brain and muscular tissue. It may be separated from other bodies with which it is associated, by the insolubility of the com-

* Nitroxanthine is formed at the same time. It may be reduced to the condition of xanthine by dissolving the mass in ammonia, and reducing by ferrous sulphate, evaporating to dryness, washing the residue with water, and then extracting the xanthine by solution of ammonia, which, on evaporation, leaves xanthine in crystals (Strecker).

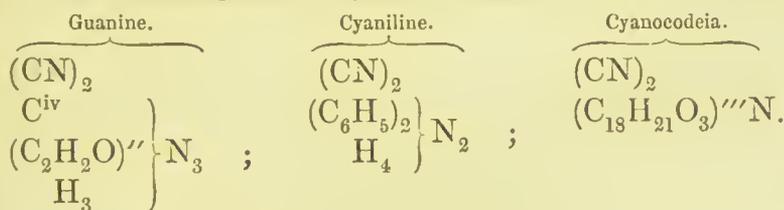
pound with mercuric oxide, which is formed on adding mercuric acetate to a solution of xanthine; it also gives a precipitate with basic plumbic acetate.

(1613) *Hypoxanthine* ($C_5H_4N_4O$) contains one atom of oxygen less than the preceding compound. It was found by Scherer in the liquid contained in the substance of the spleen both of man and of the cow. Hypoxanthine has also been found in the thyroid and thymus glands; and it appears to be identical with the base obtained from muscular tissue by Strecker, and called by him *sarkine*. Hypoxanthine is a white powder, which is nearly insoluble in water, but soluble in a dilute solution of potash, as well as in dilute hydrochloric acid; this acid may indeed be made use of in order to separate the base from xanthine. It is attacked by nitric acid with evolution of gas, yielding xanthine, and leaving a bright yellow crystalline residue.

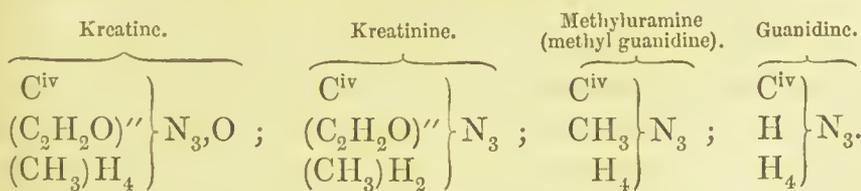
Strecker (*Liebig's Annal.*, cxviii. 151) has pointed out the close relations which exist between several of the bases which have been just described; and experiments made by Rchneck (*Lieb. Annal.*, cxxxi. 121) have shown that uric acid, when reduced by a very dilute amalgam of sodium, yields both xanthine and hypoxanthine:—



Guanine is regarded by Strecker as a cyanuretted compound triatomic base analogous to cyaniline and to cyanocodeia:—



If kreatine be the hydrated ammonium base corresponding to kreatinine, we should have the following series:—

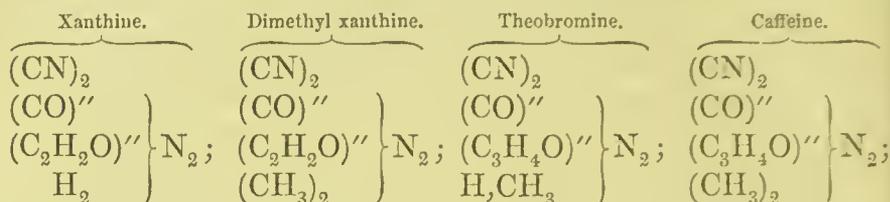


The formula of xanthine would also allow of its being considered as forming one of a series homologous with theobromine and caffeine; for



But direct experiments have shown that caffeine is a methyl-derivative of theobromine (1408), and these two bodies stand in a relation similar to that of ethylia to diethylia; whilst as yet

the experiments on the conversion of xanthine into theobromine have been unsuccessful; for xanthine, when treated with methyl iodide, yields a new methylated base metameric with theobromine, but not identical with it. The constitution of these bases may possibly be thus represented (Strecker):—



xanthine, kreatine, and kreatinine containing *glycolyl* (C₂H₂O)'', the radicle of glycolic acid, while theobromine and caffeine contain *lactyl* (C₃H₄O)'', the radicle of lactic acid.

(1614) *Bases homologous with Glycocine.*—The three bases glycocine, alanine, and leucine, are homologous bodies; when submitted to the action of nitrous acid, they are all decomposed according to the following formula, and furnish acids which are also homologous with each other:—



The relation of these bases and acids to each other may be thus represented:—

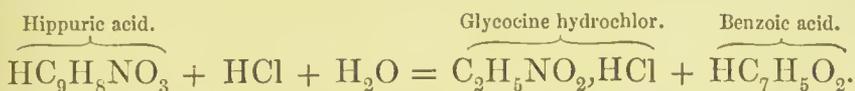
| Bases (C _n H _{2n+1} NO ₂). | Acids (HC _n H _{2n-1} O ₃). |
|---|--|
| Glycocine . . . C ₂ H ₅ NO ₂ | Glycolic . . . HC ₂ H ₃ O ₃ |
| Alanine . . . C ₃ H ₇ NO ₂ | Lactic . . . HC ₃ H ₅ O ₃ |
| Leucine . . . C ₆ H ₁₃ NO ₂ | Leucic . . . HC ₆ H ₁₁ O ₃ |

The azotised bodies contained in this series possess but very feeble basic power, although they form crystallized compounds with the acids. There can be little doubt that they are the representatives of a class of compounds co-extensive with the volatile fatty acids; and probably the missing terms of the series might be obtained by processes similar to those which furnish alanine and leucine, viz., by acting upon a mixture of hydrocyanic acid with the corresponding aldehyd-ammonia, by means of hydrochloric acid. Glycocine, alanine, and leucine are isomeric with the amides of glycolic, lactic, and leucic acids; but they are not the amides themselves: glycolamide and lactamide may be obtained by acting upon the glycolic and lactic ethers with an alcoholic solution of ammonia, but they differ in properties from glycocine and alanine. Indeed, the true amides are all decomposed into salts of ammonium when boiled with dilute acids, whereas the compounds of the glycocine series may be boiled with dilute

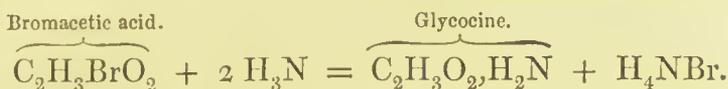
acids for hours without decomposition. These bases when submitted to dry distillation yield carbonic anhydride, and methyilia, ethyilia, and amyilia respectively: for example:—



(1615) *Glycocine*, or *Glycocoll* ($\text{C}_2\text{H}_5\text{NO}_2=75$).—This substance is one of the products of the decomposition of gelatin when boiled with dilute sulphuric acid, and hence the name glycocoll, from $\gamma\lambda\upsilon\kappa\upsilon\varsigma$, sweet, $\kappa\acute{o}\lambda\lambda\alpha$, glue; after removing the acid by means of baric carbonate, the glycocine may be procured in crystals on evaporating the solution. It may also be obtained by heating gelatin with a solution of potash or of soda. But it is most easily isolated in a state of purity by boiling hippuric acid for half an hour, with hydrochloric acid (1442); as the liquid cools, benzoic acid is separated in abundance, and glycocine remains in combination with hydrochloric acid:—



On the addition of absolute alcohol, after the solution has been concentrated by evaporation and supersaturated with ammonia, pure glycocine is deposited in minute crystals. Glycocine may likewise be obtained from glycocholic acid, one of the resinous acids of the bile (1693), when it is decomposed by ebullition with hydrochloric acid. Perkin and Duppa have also obtained glycocine (*Q. J. Chem. Soc.*, xi. 31) by acting upon an alcoholic solution of ammonia with bromacetic acid, exposing the mixture to heat in a sealed tube; the reaction is represented as follows:—



Glycocine, in fact, bears the same relation to acetic acid that amido-benzoic does to benzoic acid, and it may therefore be viewed as amido-acetic acid:—



Pure glycocine has a sweet taste, which is less intense than that of cane-sugar: it is soluble in about 400 parts of cold water, and is less soluble in rectified alcohol; it is insoluble in absolute alcohol and in ether. Glycocine crystallizes readily by spontaneous evaporation of its aqueous solution. It is not susceptible

of the alcoholic fermentation. Its solution has the power of reddening litmus feebly. It throws down metallic mercury from a solution of mercurous nitrate. Glycocine has a strong tendency to combine with the acids, with some of which, such as the sulphuric and hydrochloric, it combines in 2 or 3 different proportions, without, however, neutralizing them; many of these compounds, such as the nitrate ($C_2H_5NO_2, HNO_3$), crystallize readily; the sulphate, the oxalate, and the hydrochlorate may also be obtained in crystals. A large number of the metallic oxides also combine with glycocine, displacing an equivalent of water from it, and forming with it soluble compounds, which may be obtained in crystals; this is the case with the oxides of zinc, copper, lead, barium, and silver. These compounds may be obtained by heating the hydrated oxides of the metals with a solution of glycocine. When glycocine is boiled with cupric acetate, acetic acid is expelled, and a compound of glycocine with cupric oxide is obtained in solution. If glycocine be heated with a strong solution of potash it gives a fleeting, beautiful fiery red colour, ammonia is expelled, and oxalic and hydrocyanic acids are formed in the solution. Indeed, few substances enter so readily into combination as glycocine. In addition to its compounds with acids and with bases, it unites with many salts, and forms bodies which crystallize with great regularity and brilliancy.

If a mixture of glycocine with sulphuric acid and manganese or lead dioxide be submitted to distillation, a brisk effervescence occurs, owing to the escape of carbonic anhydride, and pure hydrocyanic acid distils over:—

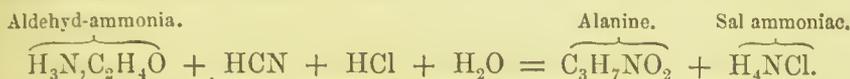


When nitrous acid is transmitted through an aqueous solution of glycocine, mutual decomposition occurs, nitrogen is disengaged, and on agitating the mixture with ether, decanting the ethereal liquid after it has risen to the surface, and submitting it to evaporation, glycolic acid (1308) is left in the form of a syrup which is freely soluble in alcohol:—

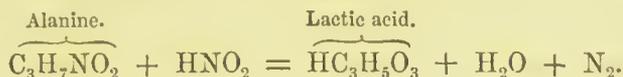


(1616) *Alanine* ($C_3H_7NO_2$).—The interest attaching to this base arises from its homologous relation to glycocine, and to its connexion with lactic acid. It is isomeric with laetamide, with sarkosine, and with urethane, but is perfectly distinct from all of them, being, in fact, *amidopropionic acid* [$HC_3H_4(H_3N)O_2$]. Alanine, as it was arbitrarily named by Strecker, is obtained by distilling an aqueous solution containing two parts of aldehyd-ammonia (1249) and one of hydrocyanic acid with an excess of hydrochloric acid. Traces of hydrocyanic

and formic acids pass over with the excess of hydrochloric, but no aldehyd. The liquid in the retort is concentrated by evaporation, and a considerable proportion of ammonia hydrochlorate is separated in crystals. The mother-liquor retains alanine hydrochlorate: it must be boiled with hydrated plumbic oxide, which is to be added in small portions to the boiling liquid until it ceases to occasion a disengagement of ammonia. The liquid is then to be decanted from the precipitate, treated with sulphuretted hydrogen to remove the excess of lead, filtered and evaporated. Alanine crystallizes out, and if the mother-liquor be mixed with alcohol, it furnishes an additional quantity. The reaction by which alanine is formed may be thus represented:—



Alanine crystallizes in groups of colourless prisms, which are soluble in between 4 and 5 parts of cold water, but are very sparingly soluble in alcohol, and insoluble in ether. Its aqueous solution has a very sweet taste: it is without action upon test-papers. Alanine may be partially sublimed at a temperature a little above 401° (205° C.). If heated suddenly, it melts and is decomposed, becoming converted into ethylia and carbonic anhydride: when heated on platinum foil it burns with a violet flame. Caustic potash decomposes it, ammonia and hydrogen are disengaged, while potassic acetate and cyanide are obtained. When distilled with dilute sulphuric acid and lead dioxide, carbonic anhydride, aldehyd, and ammonia are formed. But its most interesting metamorphosis is that which it undergoes when the aqueous solution is treated with nitrous acid, in which case lactic acid is formed, while nitrogen is liberated:—

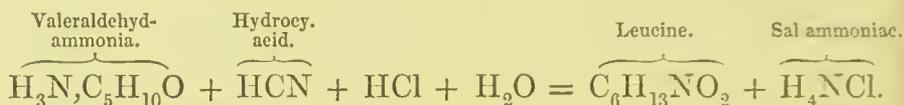


Alanine, like glycocine, forms numerous compounds both with acids and with bases; many of them may be obtained in crystals, but they are all very soluble.

The compounds ($\text{C}_4\text{H}_9\text{NO}_2$) and ($\text{C}_5\text{H}_{11}\text{NO}_2$), intermediate between alanine and leucine, in the glycocine series, or amido-butyric and amido-valeric acids, have not as yet been prepared synthetically, but according to Gorup-Besanez the butyric compound accompanies leucine in the pancreas of the ox.

(1617) *Leucine* ($\text{C}_6\text{H}_{13}\text{NO}_2$).—Various decompositions give rise to the formation of this body, which may be viewed as amido-caproic acid [$\text{C}_6\text{H}_{11}(\text{H}_2\text{N})\text{O}_2$]. It is one of the products of the putrefaction of casein, or of cheese, of muscle, and of gluten, in the presence of water; and it is also among the compounds obtained by the action either of sulphuric acid diluted with 3 or 4 parts of water, or of caustic potash, upon gelatin, muscular tissue, the yellow elastic tissue of the *ligamentum nuchæ*, white of egg, horn, and wool. One of the best methods of obtaining leucine consists in fusing dried casein or any other albuminoid substance with its own weight of caustic potash; during this operation ammonia is evolved, and a disgusting fæcal odour is emitted: as soon as hydrogen begins to come off, which is indicated by the change of colour from dark brown to yellow, the mass must be allowed to cool; and on treating it with hot water, a highly alkaline liquid is obtained, which contains in solution

leucine and *tyrosine* (Bopp, *Liebig's Annal.*, lxi. 21). On slightly supersaturating the liquid with acetic acid, tyrosine is deposited in concentric groups of needles; and on further evaporation of the mother-liquid, leucine is obtained in pearly colourless plates, which may be purified by washing them with alcohol, and recrystallizing the residue from boiling dilute alcohol. Limpricht has also succeeded in obtaining leucine artificially, by boiling the compound of valeric aldehyde and ammonia with an excess of hydrocyanic and hydrochloric acids, until the oily liquid produced by the fusion of the valeraldehyde-ammonia has disappeared: in this manner sal ammoniac and leucine are obtained:—



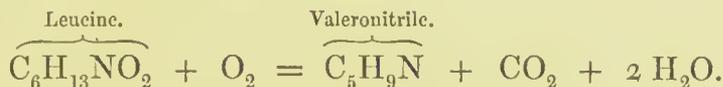
The excess of hydrochloric acid may be removed by means of plumbic oxide, and the traces of lead may be separated by hydrosulphuric acid, after which the liquid is evaporated in a water-bath: boiling dilute alcohol then dissolves leucine from the residue, and deposits it in plates as it cools.

Cloetta has made the interesting observation that leucine is one of the normal constituents of the pulmonary tissue; and by operating upon considerable masses of bullocks' lungs he procured it associated with taurin, inosin, and uric acid. It has also been found as a normal constituent of the spleen (Stædeler) and pancreas, and has been obtained from the urine in cases of typhus and affections of the spinal cord.

Leucine somewhat resembles cholesterol in appearance, and derives its name from λευκός, white; it has an unctuous feel, and is lighter than water. When heated cautiously, leucine may be sublimed before it melts, without undergoing decomposition, and may be collected in the form of woolly flocculi. At a higher temperature it becomes brown, and melts at about 338° (170° C.), and when heated a little beyond this point it furnishes a distillate composed of a yellow oily liquid, containing free ammoniac carbonate, whilst a brown resinous substance remains in the retort. The oily distillate consists chiefly of amylin. Leucine is sparingly soluble in cold water, but freely so in boiling water. The presence of acetic acid or of potassic acetate favours its solution both in water and in alcohol. Cold absolute alcohol dissolves it very sparingly, and it is insoluble in ether. It is, however, easily soluble in dilute solutions of the acids, with many of which it forms crystallizable compounds; leucine *hydrochlorate* (C₆H₁₃NO₂.HCl) is very soluble in water; the *nitrate* or *nitro-*

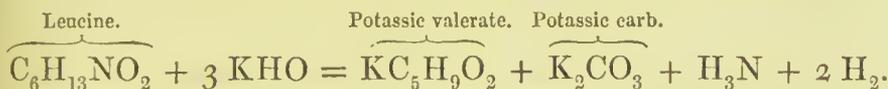
leucic acid ($C_6H_{13}NO_2, HNO_3$) crystallizes in colourless needles. An aqueous solution of leucine occasions a white precipitate with basic plumbic acetate; and if to a boiling solution of leucine mixed with the normal plumbic acetate, ammonia be cautiously added, pearly scales ($PbO, 2C_6H_{13}NO_2$) are deposited. Leucine also precipitates mercurous nitrate (Braconnot), but no other metallic solutions.

Leucine, when distilled with lead dioxide, furnishes ammonia and butyric aldehyd. If it be distilled with dilute sulphuric acid and manganese dioxide, valeronitrile with carbonic anhydride and water is produced:—



If a solution of leucine be treated with chlorine in excess, carbonic anhydride is liberated, and a mixture of valeronitrile and chlorvaleronitrile is obtained, which is separated in the form of volatile oily drops, whilst a quantity of leucine hydrochlorate is formed in the retort (Schwanert).

If leucine be fused with caustic potash it yields potassic valerate and carbonate, whilst ammonia and hydrogen are liberated:—



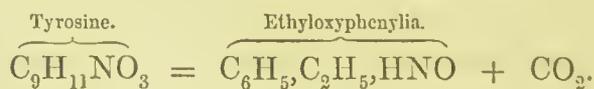
Pure leucine is stated also to undergo a similar decomposition when caused to ferment, by the addition of a small quantity of muscular fibre, or of albumin. When an aqueous solution of leucine is submitted to the action of nitrous acid, the leucine is decomposed with liberation of nitrogen and the formation of leucic acid ($HC_6H_{11}O_3$), just as glycolic and lactic acids are formed from glycocine and alanine under similar circumstances.

(1618) *Tyrosine* ($C_9H_{11}NO_3$; Hinterberger).—This substance was obtained by Liebig from the products of the fusion with caustic potash of well-dried fibrin, albumin, or cheese (hence its name, from *τυρὸς*, cheese): the process must be conducted in the manner described when treating of the preparation of leucine. The crude crystals of tyrosine must be redissolved in a solution of potash, and precipitated with acetic acid. If coloured it must be converted into hydrochlorate, digested with animal charcoal, and the filtered liquid must be mixed while boiling with potassic acetate; potassic chloride is thus formed, and tyrosine, free from acetic acid, is deposited in long fibrous crystals. Tyrosine is also found among the products of the putrefaction of albumin, fibrin, and casein; and it is produced, together with leucine, when

these albuminoid bodies are boiled for some hours with dilute sulphuric or hydrochloric acid. Horn, feathers, and hair, also yield it by this treatment:—one part of horn, 4 of oil of vitriol, and 12 of water, if boiled for forty hours, furnish a dark brown fluid, which at the end of that time must be rendered alkaline by the addition of milk of lime, then heated and filtered: sulphuric acid must now be added to neutralization, and on evaporation, crystals of tyrosine will be deposited; they may be purified in the manner already directed.

Tyrosine in certain cases is a direct product of the chemical actions in the living animal; it was found by De la Rue ready formed in the cochineal insect, and has been met with in the pancreas and other internal organs of the higher animals, as well as in the urine in typhus, and in certain spinal affections.

Tyrosine forms long fibrous crystals, which are very sparingly soluble in cold water, and nearly insoluble in alcohol and in ether; boiling water dissolves it in considerable quantity. Although its solutions are neutral to test paper, it is freely soluble both in acid and in alkaline solutions; it combines with bases such as baryta and zinc, forming unstable compounds which are decomposed on attempting to recrystallize them. With sulphuric acid it forms a colligated crystallizable acid; if this be neutralized with lime, and mixed with ferric chloride, it gives a characteristic violet solution. By cautious distillation tyrosine may be almost wholly converted into ethyloxyphenylia and carbonic anhydride (Schmitt and Nasse):—



When treated with hot nitric acid, tyrosine yields oxalic acid; and if cold dilute nitric acid be employed, *nitrotyrosine nitrate* [$\text{C}_9\text{H}_{10}(\text{NO}_2)\text{NO}_3, \text{HNO}_3$] is formed. A very delicate test of the presence of tyrosine is afforded by the formation of a red flocculent precipitate when its solution is heated with a nearly neutral solution of mercuric nitrate, and if the solution be very dilute a rose-red colour is developed in the liquid (R. Hoffman). Tyrosine is probably the ethylo-amidic acid of paroxybenzoic acid (Barth). Potassic paroxybenzoate may be obtained by fusing tyrosine with an excess of caustic potash. The relation between tyrosine and paroxybenzoic acid is seen by comparing the formulae which follow:—



§ III. URIC ACID AND ITS DERIVATIVES.

(1619) URIC ACID ($\text{H}_2\text{C}_5\text{H}_2\text{N}_4\text{O}_3 = 168$).—This important excrementitious product occurs in small quantity in human urine. It is much more abundantly contained in the white, semi-solid excretions of birds; and, in combination with ammonia, it constitutes almost the whole of the excrement of serpents, such as the boa. The beds of *guano* found in the rainless islands of the Pacific, and formed of the accumulated excrements of countless generations of sea-fowl, consist chiefly of ammoniacal urate, which has undergone decomposition more or less extensive. When uric acid is secreted in excess in man, it is often deposited from the urine in the form of hard crystalline grains, forming what is commonly termed red gravel; or it collects into larger masses which, if retained in the bladder, generally acquire considerable size, and constitute the most usual variety of urinary calculus. In gouty patients also uric acid not unfrequently accumulates around the joints affected; and in combination principally with sodium, forms the white friable concretions often improperly called *chalk stones*.

Uric acid is best prepared from the dried urine of the boa by dissolving 1 part of the powdered mass in from 40 to 50 parts of boiling water, to which an excess of caustic potash is added, sufficient to bring the whole of the acid into solution: during this operation ammonia escapes abundantly. The heat must be continued until the ammoniacal odour has disappeared. The brownish liquid thus procured contains an impure potassic urate, which must be filtered while hot, and decomposed by adding a slight excess of hydrochloric acid. Uric acid is immediately separated in minute white crystals; these must be washed with cold water, dissolved a second time in solution of potash, and once more precipitated by hydrochloric acid; the product, after being thoroughly washed, and then dried, is quite pure. Uric acid crystallizes in rhombic tables, the outlines of which are frequently rounded; but when it is deposited from animal fluids, the form of the crystals is often much modified. If a cold saturated solution of potassic urate be decomposed by hydrochloric acid, large crystals of the acid are obtained with $2\text{H}_2\text{O}$. This water is expelled when the acid is heated to 212° .

When uric acid is long boiled with a solution of potash, the elements of water are assimilated, and *potassic uroxanate* ($\text{K}_2\text{C}_5\text{H}_8\text{N}_4\text{O}_6, 3\text{H}_2\text{O}$) is formed in small quantity. On the addi-

tion of a strong acid, uroxic acid is separated in sparingly soluble, microscopic, tetrahedral crystals ($H_2C_5H_8N_4O_6$).

Pure uric acid is a white crystalline powder requiring 10,000 parts of cold water for solution, to which, however, it imparts a feebly acid reaction. Uric acid is insoluble in alcohol and in ether, but it is dissolved by concentrated sulphuric acid, and is deposited in a hydrated condition on diluting the solution. The urates of potassium and of ammonium are more soluble than the free acid. The acid urates of ammonium, of sodium, and of calcium are frequent ingredients of urinary calculi; but the proportion of the calcium salt is always very small. The reaction of uric acid with nitric acid and ammonia is highly characteristic, and it enables the acid to be detected in very minute quantities; the method of proceeding will be described under the head of murexid (1638). By the action of reducing agents, such as a very dilute amalgam of sodium, Strecker found that first one atom of oxygen, and then a second atom could be removed from uric acid, xanthine being first obtained, and then hypoxanthine in considerable quantity (1613).

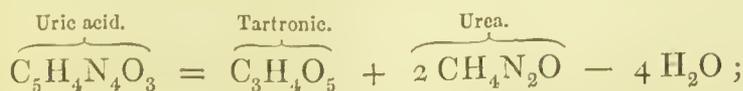
(1620) *Urates*.—Uric acid is dibasic. Its salts have been carefully examined by Benseh (*Liebig's Annal.*, liv. 189, and lxx. 181). All the urates are but sparingly soluble in water; they are much more soluble in alkaline solutions, especially when heated. They are also freely soluble in solutions of borax. Two urates of potassium may be formed: the *acid* salt ($KHC_5H_2N_4O_3$) is the one best known. It is precipitated in a granular form when carbonic anhydride is transmitted through a solution of the normal salt. It is soluble in about 80 parts of boiling water, from which, on cooling, it is deposited in amorphous flocculi; it requires about 800 parts of cold water for solution. *Normal potassic urate* ($K_2C_5H_2N_4O_3$) is obtained by saturating a cold dilute solution of potash, free from carbonate, with uric acid suspended in water, and boiling down the solution in a retort. At a certain degree of concentration the salt is deposited in fine anhydrous needles: the clear liquid must be decanted from them, and they must be washed with dilute alcohol. The salt requires about 44 parts of cold water for solution, and 35 of boiling water. Its solution is slowly decomposed by ebullition. This salt has a caustic taste, and absorbs carbonic acid rapidly from the air.

There are two *urates of sodium*; the normal urate being ($Na_2C_5H_2N_4O_3, H_2O$), the acid urate being ($NaHC_5H_2N_4O_3$); they are each somewhat less soluble than the corresponding potassium salts. The *acid ammonic urate* ($H_4NH, C_5H_2N_4O_3$) is the only

urate of ammonium which is known. It usually forms a white amorphous mass, which is soluble in 1800 parts of cold, and 240 of boiling water; it is deposited in fine needles from a boiling aqueous solution of it, even when it contains an excess of ammonia. *Lithic urate* is more soluble than any other of these salts. Hence lithia water is occasionally prescribed to gouty patients, and to others who suffer from a superabundance of uric acid. Only the *acid magnesian urate* ($\text{MgH}_2, 2\text{C}_5\text{H}_2\text{N}_4\text{O}_3, 6\text{H}_2\text{O}$) is known; but both a normal ($\text{CaC}_5\text{H}_2\text{N}_4\text{O}_3$) and an acid urate of calcium ($\text{CaH}_2, 2\text{C}_5\text{H}_2\text{N}_4\text{O}_3, 2\text{H}_2\text{O}$) may be obtained.

(1621) *Products of the Decomposition of Uric Acid*.—When uric acid is submitted to distillation it does not fuse, but undergoes decomposition, producing ammoniac carbonate, hydrocyanic acid, cyanuric acid, urea, and some empyreumatic products. Uric acid is decomposed when heated with fused caustic potash, ammonia is evolved, and the residue contains potassic cyanide mixed with potassic carbonate and oxalate: we have already referred to the action of reducing agents upon it. But the most remarkable chemical peculiarity of uric acid is the facility with which it is altered by oxidizing agents, and the number of definite and crystallizable compounds to which it gives rise. These products were first investigated by Liebig and Wöhler (*Liebig's Annal.*, xxvi. 241); and the importance of the acid as an excrementitious product has led to further minute investigations by others subsequently, particularly by Schlieper, by Strecker, and still more fully by Baeyer (*Liebig's Annal.*, cxxvii., cxxx., and cxxxi.). The oxidation of uric acid may be effected in various ways, such as by means of nitric acid, by lead dioxide, and by potassic ferricyanide mixed with caustic potash; the products of oxidation differing with the energy of the action according to the nature of the agent employed.

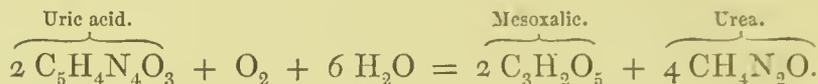
But notwithstanding the numerous researches of which uric acid has been the subject, the exact mode of its construction still remains unknown; for it has never been broken up into the actual molecules of the bodies from which it was formed, nor have the attempts to produce it synthetically been hitherto attended with success. Gerhardt proposed to regard uric acid as the diureide of tartronic acid, in accordance with the equation:—



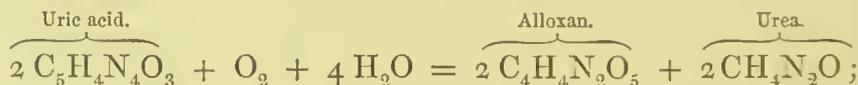
but it is doubtful whether this supposition is correct, inasmuch as the uric acids are very unstable, whilst the uric acid is not

so; besides which, it has not as yet been possible to obtain uric acid from tartronic acid and urea.

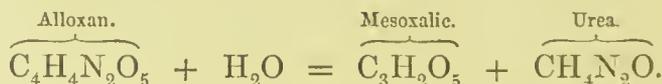
It is, however, certain that when uric acid is subjected to oxidation in the presence of water, the nitrogen is wholly removed in the form of urea, which often breaks up, owing to the action of the acids or alkalis employed in the process; whilst the remaining non-azotised constituents of the uric acid furnish either mesoxalic acid, or a product of its decomposition by further oxidation:—



The abstraction of urea from uric acid is, however, generally effected in two stages, the first portion being removed more easily than the second. If one atom of urea only is got rid of, alloxan is formed; if both atoms are removed, mesoxalic acid is the product. When, for instance, dilute nitric acid acts upon uric acid, alloxan is obtained:—

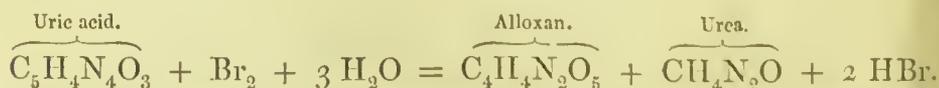


while the second atom of urea is removed when the alloxan is boiled with baryta water:—



In both cases the urea, in the act of liberation, is in great measure decomposed by the action of the acid and of the alkali, neither of which is represented in the equations. The last equation shows that alloxan may itself be regarded as the monureide of mesoxalic acid, since the alloxan would be derived from the action of one molecule of the acid upon one of urea, with elimination of an atom of water.

The decomposition of uric acid, according to Hardy, may be effected at common temperatures by means of bromine, which is to be gradually added in excess, to finely-divided uric acid suspended in water. Under these circumstances the uric acid is wholly resolved into alloxan and urea, while hydrobromic acid is formed by the removal of two atoms of hydrogen from one of uric acid:—



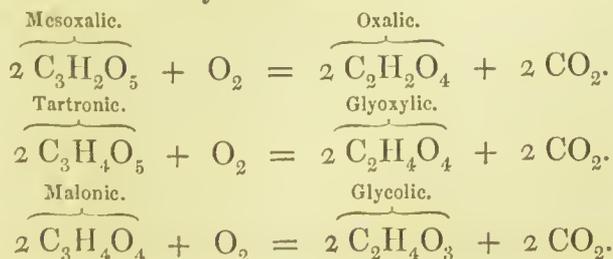
The following table contains a list of the most important derivatives of uric acid:—

| | | |
|----------------------------------|--|--|
| Uric acid | $\text{H}_2\text{C}_6\text{H}_2\text{N}_4\text{O}_3$ | |
| Pseudo-uric acid | $\text{H C}_5\text{H}_5\text{N}_4\text{O}_4$ | |
| Uroxic acid | $\text{H}_2\text{C}_5\text{H}_8\text{N}_4\text{O}_6$ | |
| Alloxan | $\text{C}_4\text{H}_4\text{N}_2\text{O}_5$ | $= \text{C H}_2(\text{C}_3\text{O}_3)\text{N}_2\text{O}, \text{H}_2\text{O}$ |
| Alloxanic acid | $\text{H}_2\text{C}_4\text{H}_2\text{N}_2\text{O}_5$ | $= \text{C}_4\text{H}_2(\text{HO})_2\text{N}_2\text{O}_3$ |
| Alloxantin | $\text{C}_8\text{H}_4\text{N}_4\text{O}_7, 3 \text{H}_2\text{O}$ | $= \text{C}_4\text{H}_2(\text{C}_4\text{H}_2\text{N}_2\text{O}_4)\text{N}_2\text{O}_3, 3 \text{H}_2\text{O}$ |
| Dibromobarbituric acid | $\text{C}_4\text{H}_2\text{Br}_2\text{N}_2\text{O}_3$ | $= \text{C}_4\text{H}_2(\text{Br})_2\text{N}_2\text{O}_3$ |
| Bromobarbituric acid | $\text{H C}_4\text{H}_2\text{Br N}_2\text{O}_3$ | $= \text{C}_4\text{H}_3(\text{Br})\text{N}_2\text{O}_3$ |
| Barbituric acid | $\text{H}_2\text{C}_4\text{H}_2\text{N}_2\text{O}_3, 2 \text{H}_2\text{O}$ | $= \text{C}_4\text{H}_3(\text{H})\text{N}_2\text{O}_3, 2 \text{H}_2\text{O}$ |
| Violuric acid | $\text{H C}_4\text{H}_2\text{N}_3\text{O}_4$ | $= \text{C}_4\text{H}_3(\text{NO})\text{N}_2\text{O}_3$ |
| Dilituric acid | $\text{H C}_4\text{H}_2\text{N}_3\text{O}_5, 3 \text{H}_2\text{O}$ | $= \text{C}_4\text{H}_3(\text{NO}_2)\text{N}_2\text{O}_3, 3 \text{H}_2\text{O}$ |
| Violantin | $\text{C}_8\text{H}_6\text{N}_6\text{O}_9$ | $= \text{C}_4\text{H}_3\text{N}_3\text{O}_4, \text{C}_4\text{H}_3\text{N}_3\text{O}_5$ |
| Dialuric acid | $\text{H C}_4\text{H}_3\text{N}_2\text{O}_4$ | $= \text{C}_4\text{H}_3(\text{HO})\text{N}_2\text{O}_3$ |
| Uramil | $\text{C}_4\text{H}_5\text{N}_3\text{O}_3$ | $= \text{C}_4\text{H}_3(\text{H}_2\text{N})\text{N}_2\text{O}_3$ |
| Thionuric acid | $\text{H}_2\text{C}_4\text{H}_3\text{N}_3\text{O}_6\text{S}$ | $= \text{C}_4\text{H}_3(\text{H}_2\text{NSO}_3)\text{N}_2\text{O}_3$ |
| Hydurilic acid | $\text{H}_2\text{C}_8\text{H}_4\text{N}_4\text{O}_6, 2 \text{H}_2\text{O}$ | $= \text{C}_4\text{H}_2(\text{C}_4\text{H}_4\text{N}_2\text{O}_3)\text{N}_2\text{O}_3, 2 \text{H}_2\text{O}$ |
| Allantoin | $\text{C}_4\text{H}_6\text{N}_4\text{O}_3$ | |
| Glycoluril | $\text{C}_4\text{H}_6\text{N}_4\text{O}_2$ | |
| Mykomelinic acid | $\text{H C}_4\text{H}_3\text{N}_4\text{O}_2$ | |
| Oxaluric acid | $\text{H C}_3\text{H}_3\text{N}_2\text{O}_4$ | |
| Allanturic acid | $\text{H C}_3\text{H}_3\text{N}_2\text{O}_3$ | |
| Hydantoin | $\text{C}_3\text{H}_4\text{N}_2\text{O}_2$ | |
| Hydantoic acid | $\text{H C}_3\text{H}_6\text{N}_2\text{O}_3$ | |
| Allituric acid | $\text{H C}_6\text{H}_6\text{N}_4\text{O}_4$ | |
| Leucoturic acid | $\text{H C}_6\text{H}_3\text{N}_4\text{O}_5$ | |
| Parabanic acid | $\text{H}_2\text{C}_3\text{N}_2\text{O}_3$ | |
| Dibarbituric acid | $\text{H}_2\text{C}_8\text{H}_4\text{N}_4\text{O}_5$ | |
| Murexid | $\text{C}_8\text{H}_8\text{N}_6\text{O}_6$ | |
| Mesoxalic acid | $\text{H}_2\text{C}_3\text{O}_5$ | |

Mesoxalic acid may be made to furnish the key to the greater number of compounds enumerated in the following table. If submitted to the action of reducing agents, such as sodium-amalgam, the mesoxalic combines with 2 additional atoms of hydrogen, and yields tartronic acid, and tartronic acid, by a further reducing action, is converted into malonic acid:—

| | |
|--------------------------|----------------------------------|
| Mesoxalic acid | $\text{C}_3\text{H}_2\text{O}_5$ |
| Tartronic acid | $\text{C}_3\text{H}_4\text{O}_5$ |
| Malonic acid | $\text{C}_3\text{H}_4\text{O}_4$ |

If each of these three acids be submitted to oxidizing agents, it loses one molecule of carbonic oxide, and furnishes a new acid containing two atoms only of carbon:—



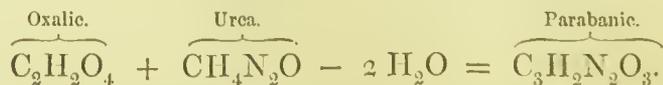
Now each of the six acids just mentioned is susceptible of being combined with one or with two atoms of urea while the elements of water are separated. Compounds so obtained constitute what Baeyer terms *monureides*, when a single molecule of urea enters into their formation; when two atoms of urea unite with the elements of each atom of the acid *diureides* are formed. In the following table the numerous uric compounds of this kind are arranged so as to indicate their mutual relations.

| Non-azotised Acids. | Monureides with loss of | | Diureides with loss of | |
|---------------------------------------|---|---|--|--|
| | H ₂ O. | 2 H ₂ O. | H ₂ O. | 2 H ₂ O. |
| Mesoxalic. $\overbrace{C_3H_2O_5}$ | Alloxan. $\overbrace{C_4H_4N_2O_5}$ | | | |
| Tartronic. $\overbrace{C_5H_4O_5}$ | | Dialuric. $\overbrace{C_4H_4N_2O_4}$ | Pseudo-uric. $\overbrace{C_5H_6N_4O_4}$ | Uric. $\overbrace{C_5H_4N_4O_2}$ |
| Malonic. $\overbrace{C_3H_4O_4}$ | | Barbituric. $\overbrace{C_4H_4N_2O_3}$ | | |
| Oxalic. $\overbrace{C_2H_2O_4}$ | Oxaluric. $\overbrace{C_3H_4N_2O_4}$ | Parabanic. $\overbrace{C_3H_2N_2O_3}$ | | |
| Glyoxylic. $\overbrace{C_2H_4O_4}$ | | Lantanuric. $\overbrace{C_3H_4N_2O_3}$ | Allantoin. $\overbrace{C_4H_6N_4O_3}$ | Mykomelinic. $\overbrace{C_4H_4N_4O_2}$ |
| Glycolic. $\overbrace{C_2H_4O_3}$ | Glycoluric. $\overbrace{C_3H_6N_2O_3}$ | Hydantoin. $\overbrace{C_3H_4N_2O_2}$ | Glycoluril. $\overbrace{C_4H_6N_4O_2}$ | |
| Acetic. $\overbrace{C_2H_4O_2}$ | Acetylurea. $\overbrace{C_3H_6N_2O_2}$ | | | |

In the first column are the generating acids; in the second the corresponding monureides formed by the union of the acid with one atom of urea, and elimination of a single atom of water, as in the formation of oxaluric acid from oxalic acid:—



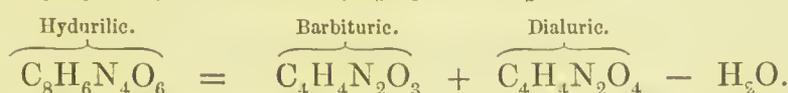
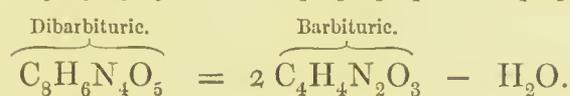
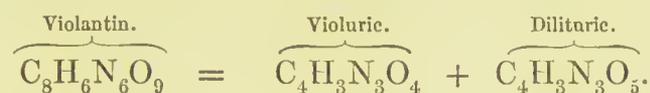
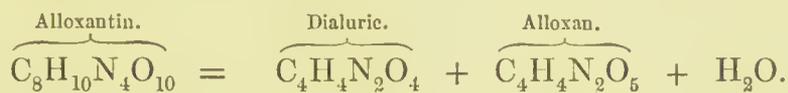
In the third column are the more numerous monureides formed by the action of the acid in the same horizontal line upon one molecule of urea, with elimination of two atoms of water; as in the formation of parabanic from oxalic acid:—



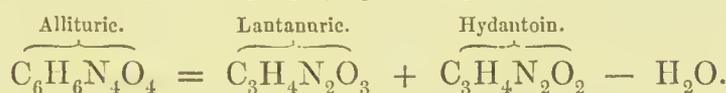
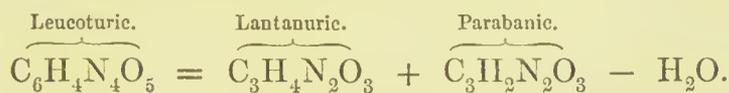
The fourth column indicates diureides formed with the acid and

2 molecules of urea, with elimination of 1 atom of water; while the fifth column shows the diurcides formed from the action of the acid upon 2 atoms of urea, with elimination of 2 atoms of water. Many of the blanks at present existing will doubtless hereafter be filled up.

Several of the more complex uric acid products are formed by the coalescence of two of the newly-formed bodies, with or without separation of water: such, for example, are those exhibited in the following equations:—



Among the derivatives of the 3 carbon products of uric acid are the following, which are thus formed by coalescence:—



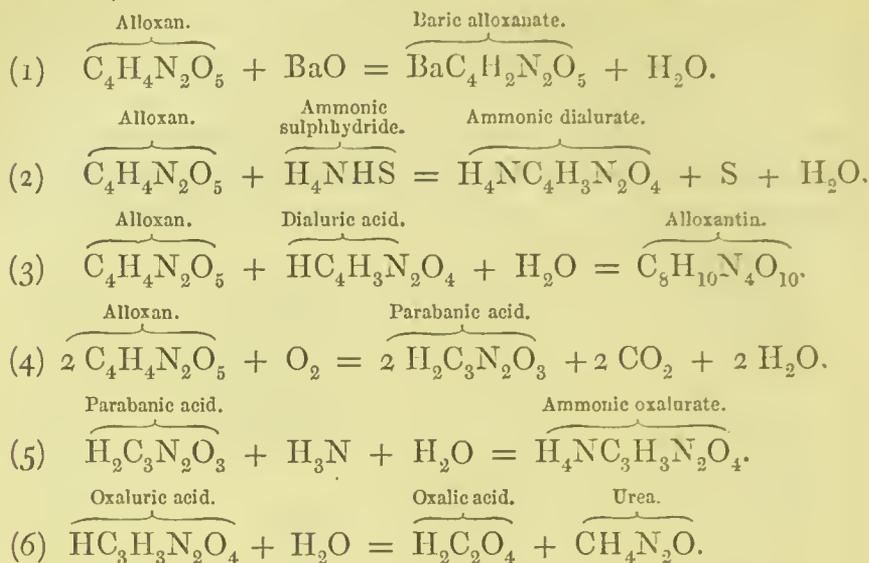
A large number of the remaining compounds in the table at p. 775 may be referred to barbituric acid, of which they may be viewed as derivatives by substitution, but these will be better understood after the methods of preparing them, and their properties, have been described (1629 *et seq.*).

We shall commence with alloxan, the most important of the monurcides.

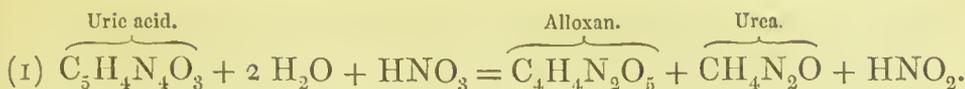
Alloxan is itself susceptible of various transformations, which give rise to several interesting compounds, of which the most important are the following:—

Alloxanic Acid, which in its normal state is metameric with the octahedral form of alloxan (1); *Dialuric Acid*, which may be regarded as a hydride of alloxan (2); *Alloxantin*, a compound of alloxan with dialuric acid (3). If alloxan be treated with nitric acid it yields *Parabanic Acid* (4); and this acid, under the influence of bases, assimilates the elements of water, and is converted into *Oxaluric Acid* (5); while the solution of oxaluric acid,

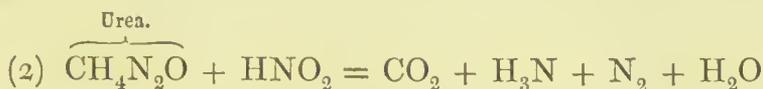
if boiled, also combines with water, and breaks up into oxalic acid and urea (5), as may be seen by the annexed equations:—



(1622) *Alloxan* ($\text{C}_4\text{H}_4\text{N}_2\text{O}_5, 3\text{H}_2\text{O}$).—This name is a compound from allantoin and oxalic acid, and was given under the idea that it contained derivatives from both these compounds. Alloxan is easily obtained by adding to nitric acid (of sp. gr. 1.42) pure uric acid in small portions at a time, waiting till the effervescence produced by the addition of each separate quantity has subsided, and taking care to moderate the heat generated by the reaction, by immersing the vessel in cold water if necessary. The temperature must not be allowed to rise much above 122° (50° C.). During this operation, carbonic anhydride and nitrogen escape abundantly. Uric acid must be added until crystals begin to be formed; the liquid must then be allowed to cool, when an abundant deposit of octahedral crystals of alloxan will occur. These crystals must be drained in a funnel partially obstructed with asbestos, washed with ice-cold water, and dried on a tile. In this form alloxan was regarded as anhydrous by Liebig and Wöhler, but Gmelin finds that if it be heated to from 302° to 320° (150° to 160° C.), it loses 11.3 per cent., or 1 atom of water: probably this is a conversion into a different and dehydrated body, which reproduces alloxan when redissolved. If the octahedral crystals be redissolved in water at 122° , they yield on evaporation transparent prisms containing 3 atoms more of water than the octahedral form. The changes which attend the formation of alloxan from uric acid by the action of nitric acid, may be represented as occurring in two consecutive stages, though the decompositions appear to take place simultaneously:—



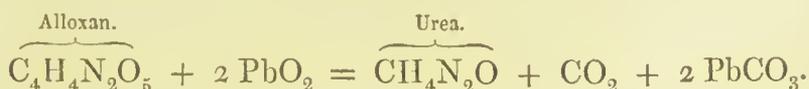
But, since urea and nitrous acid immediately decompose each other, nitrogen and carbonic anhydride are disengaged with effervescence, while water and ammonia are formed in the liquid with alloxan :—



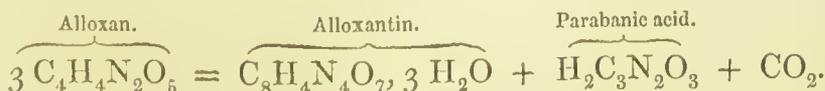
Alloxan may be more economically prepared by Schlicper's method of mixing 4 parts of uric acid with 8 of commercial hydrochloric acid, and gradually adding 1 part of powdered potassic chlorate. Under these circumstances no effervescence occurs, and the whole of the urea is found in solution. The temperature must be carefully prevented from rising too high. Alloxan has been found by Liebig among the constituents of urine in small quantity.

Gmelin's anhydrous alloxan ($\text{C}_4\text{H}_2\text{N}_2\text{O}_4$) may be regarded as mesoxal-urea [$\text{CH}_2(\text{C}_3\text{O}_3)''\text{N}_2\text{O}$], or urea in which 2 atoms of hydrogen have been displaced by the dyad radicle mesoxalyl C_3O_3 .

Alloxan is freely soluble in water; it stains the skin pink, and gives it a sickly odour, and, though not possessed of acid properties, it reddens litmus paper. In its octahedral condition it is a stable and definite substance; but in its prismatic form it often becomes spontaneously decomposed into parabanic and oxaluric acids. When alloxan is boiled with lead dioxide it yields urea and carbonic anhydride, the lead dioxide being converted into carbonate of the metal :—



A characteristic property of alloxan is the formation of an intensely violet purple-coloured liquid on admixture with a solution of a ferrous salt. Long-continued boiling decomposes a solution of alloxan, carbonic anhydride is given off, and the solution contains a mixture of parabanic acid and alloxantin :—



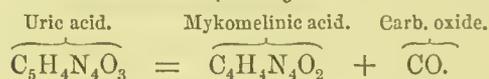
(1623) *Alloxanic Acid* ($\text{H}_2\text{C}_4\text{H}_2\text{N}_2\text{O}_5$).—By treating alloxan with baryta water, so long as the precipitate produced is redissolved on agitation, and gently heating the mixture, two atoms of hydrogen are displaced by one of barium, and a salt is formed which crystallizes as the liquid cools. This is *baric alloxanate*,

from which the acid may be separated by the cautious addition of sulphuric acid, and may be obtained in crystals by evaporation.

A solution of alloxan in ammonia is nearly colourless, but if heated gently it becomes yellow, and on cooling forms a semi-solid transparent gelatinous mass of *ammonic mykomelinate*, while the liquid retains urea in solution, with alloxanate and mesoxalate of ammonium; these are probably the results of secondary actions. Mykomelinic acid contains the elements of 1 atom of alloxan and 2 of ammonia, from which 3 atoms of water have been separated:—



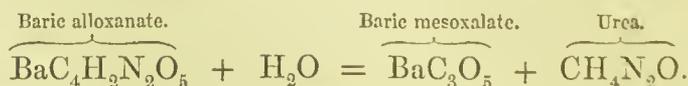
Hlasiwetz states that when uric acid is heated to 356° or 374° (180° or 190° C.) with water under pressure, it is dissolved, with evolution of a quantity of gas, while mykomelinic acid remains in solution; and he suggests that certain yellow sediments which have been regarded as ammonic urate may really consist of this acid, which evolves ammonia when heated with potash, and yields murexid when treated with nitric acid (*Liebig's Annal.*, ciii. 216):—



If alloxanic acid be neutralized by ammonia it gives with argentic nitrate a white precipitate, which, by boiling, first becomes yellow, by conversion into argentic mesoxalate, and is afterwards reduced with effervescence.

Alloxanic acid is an unstable compound. If its aqueous solution be boiled, carbonic anhydride is emitted; and if the solution be rapidly reduced to the consistence of a syrup, and then diluted with water, it is only partially dissolved; the white insoluble portion is named by Schlieper *leucoturic acid* ($\text{HC}_6\text{H}_2\text{N}_4\text{O}_5$); the solution contains a white deliquescent body, hence termed *diffuan* ($\text{C}_6\text{H}_5\text{N}_4\text{O}_5$), from *fluo*, to flow. Nitric acid reconverts the latter into alloxan, and caustic potash decomposes it with evolution of ammonia and formation of potassic oxalate.

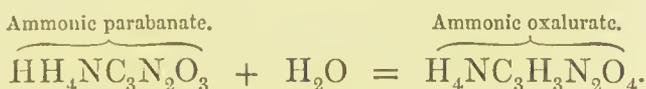
(1624) *Mesoxalic Acid* ($\text{H}_2\text{C}_3\text{O}_5$).—When baric alloxanate is subjected to prolonged boiling it is decomposed; urea is liberated, and a yellowish precipitate is formed, consisting of a mixture of baric carbonate and a sparingly soluble baric mesoxalate, the baric carbonate being the result of a secondary decomposition of the urca. The following equation shows the process of the transformation of a salt of alloxanic into one of mesoxalic acid:—



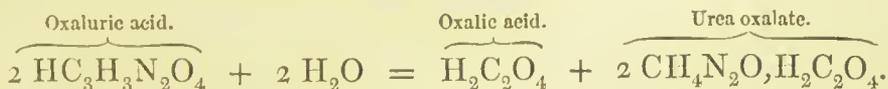
Mesoxalic acid may be procured in a free state by the addition of sulphuric acid to the barium salt; the solution when evaporated yields crystals, which are very soluble in water; it fuses at 239° (115° C.) without loss of water; it is powerfully acid, and has a very sour taste. The most characteristic reaction of mesoxalic acid is the formation of a yellow precipitate of argentic mesoxalate, when a solution of ammonic mesoxalate is mixed with one of argentic nitrate: this precipitate when heated is decomposed with a brisk effervescence, owing to the escape of carbonic

anhydride and carbonic oxide, while metallic silver is left: $\text{Ag}_2\text{C}_3\text{O}_5 = \text{Ag}_2 + 2\text{CO}_2 + \text{CO}$. When to a boiling solution of alloxan a boiling solution of plumbic acetate is added, a yellow, heavy, insoluble precipitate of plumbic mesoxalate is formed, from which it is said the acid may be obtained by decomposing the precipitate by means of sulphuretted hydrogen. Deichsel has made the interesting observation that if a dilute aqueous solution of mesoxalic acid be treated with sodium amalgam, sodic tartrate is obtained (p. 775); $\text{H}_2\text{C}_3\text{O}_5 + \text{Na}_2 = \text{Na}_2\text{C}_3\text{H}_2\text{O}_5$.

(1625) *Parabanic Acid* ($\text{H}_2\text{C}_3\text{N}_2\text{O}_3$) may be obtained by concentrating the acid mother-liquor of alloxan, till on cooling it forms a soft crystalline mass; $\text{C}_4\text{H}_4\text{N}_2\text{O}_5 + \text{HNO}_3 = \text{H}_2\text{C}_3\text{N}_2\text{O}_3 + \text{CO}_2 + \text{HNO}_2 + \text{H}_2\text{O}$. This is to be dried on a tile, redissolved in water, and recrystallized, when it forms thin, colourless, six-sided prisms: it is a powerful acid, very permanent in its uncombined condition, and very soluble in water. It may be viewed as oxalyl urea $\text{CH}_2(\text{C}_2\text{O}_2)''\text{N}_2\text{O}$. At a heat of 212° it acquires a reddish tint: at a higher temperature it undergoes partial sublimation, but a portion of it is decomposed, and furnishes hydrocyanic acid. Parabanic acid forms salts which are exceedingly unstable; argentic parabanate being the only salt which is permanent. All the other parabanates during evaporation combine with the elements of one atom of water, and become converted into oxalurates: ammoniac parabanate, for instance, when boiled furnishes brilliant crystals of ammoniac oxalurate:—



(1626) *Oxaluric Acid* ($\text{HC}_3\text{H}_3\text{N}_2\text{O}_4$).—This acid, so named because it breaks up easily into oxalic acid and urea, is best obtained from ammoniac oxalurate: a hot saturated solution of this salt when mixed with dilute sulphuric acid, and cooled rapidly, yields pure oxaluric acid as a sparingly soluble heavy white powder. By long boiling with water this acid is decomposed into oxalic acid and urea oxalate:—



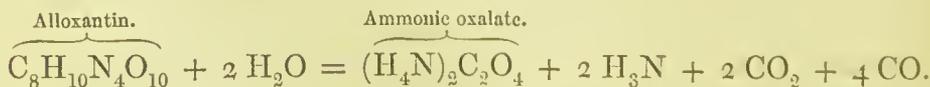
Argentic oxalurate is a white salt, soluble in hot water, from which it crystallizes in beautiful silky needles as the solution cools.

(1627) *Alloxantin* ($\text{C}_8\text{H}_4\text{N}_4\text{O}_7, 3\text{H}_2\text{O}$).—This compound may be regarded as a combination of dialuric acid with alloxan, since it may be formed by mixing solutions of these two bodies in equivalent proportions:—

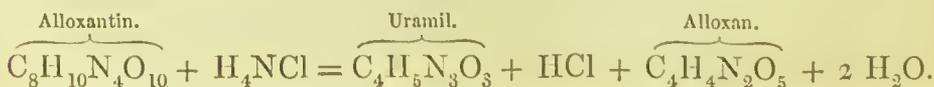


the crystals of alloxantin are slowly deposited from the mixture. Alloxantin may also be obtained by the action of deoxidizing agents upon alloxan. If alloxan be dissolved in water, and a current of sulphuretted hydrogen be transmitted, the liquid in a short time becomes turbid, from the separation of sulphur, and crystals of alloxantin are gradually deposited. The acid mother-liquor which remains after the preparation of alloxan by nitric acid is well adapted for furnishing alloxantin; it should be neutralized with chalk, and submitted to the action of a current of sulphuretted hydrogen gas. Many other processes may, however, be adopted for preparing alloxantin; for example, if stannous chloride be mixed with a solution of alloxan, crystals of alloxantin are deposited. Also, if a solution of alloxan be acidulated with hydrochloric acid, and a bar of zinc be introduced, hydrogen is evolved, and crystalline crusts of alloxantin are slowly produced.

Alloxantin forms small white, hard, brilliant, prismatic crystals, which become pink by exposure to an atmosphere containing ammonia. It is very sparingly dissolved by cold water, but more freely by boiling water; its solution reddens litmus. Crystallized alloxantin may be heated to 212° without losing weight, but at a higher temperature it gives off 15.4 per cent of water. Baryta water, when added to its solution, causes a characteristic violet precipitate, which becomes white if boiled in the liquid. A solution of alloxantin reduces the salts of silver, and is converted into alloxan; thus affording an instance of the facility with which oxidizing agents reconvert it into alloxan. Hlasiwetz found that when alloxantin is heated under pressure with water to 356° or 365° (about 180° or 185° C.), it is slowly decomposed, evolving gas in large quantity, whilst ammoniacal oxalate is formed, probably owing to the following reaction:—



If a boiling solution of alloxantin be mixed with a solution of ammonia hydrochlorate, also at a boiling temperature, and the mixture be allowed to cool in a well-corked vessel, crystals of *uramil* (dialuramide) are deposited, while the liquid retains alloxan and free hydrochloric acid in solution:—



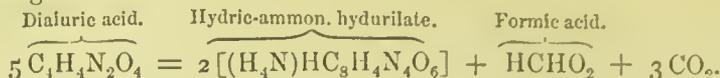
When alloxantin is boiled with hydrochloric acid it is gradually decomposed, alloxan and parabanic acid are formed, accompanied by two compounds, termed by Schlieper *allituristic acid* ($C_6H_6N_4O_4$) and *dilituristic acid* ($C_4H_3N_3O_5, 3H_2O$).

(1628) *Dialuric Acid* ($HC_4H_3N_2O_4$).—If a stream of sulphuretted hydrogen be transmitted in excess through a hot solution of alloxan or of alloxantin, sulphur is deposited, and the liquid becomes strongly acid, owing to the formation of *dialuric acid*. If this acid liquid be neutralized with ammonia, ammoniac dialurate is deposited in silky needles ($H_4N, C_4H_3N_2O_4$). The same salt may be obtained by reducing alloxan by means of zinc and hydrochloric acid, and adding a sufficient excess of ammonia to redissolve the oxide of zinc, which is at first precipitated by the ammonia.

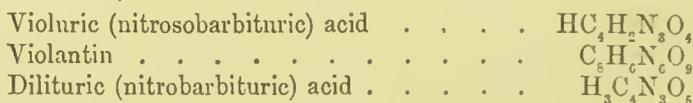
If ammoniac dialurate be added to hot hydrochloric acid, so long as it is dissolved, and the liquid be allowed to cool, long needles of dialuric acid are deposited. They become red by exposure to the air, and are gradually converted into alloxantin. Dialuric acid forms a sparingly soluble salt with *potassium*, which may be obtained by adding a solution of potassic cyanide to one of alloxan: the brown-yellow precipitate thus obtained must be dissolved in a weak potash ley, and neutralized by acetic acid, when it falls as a white precipitate. In this case, however, half the alloxan passes into the form of *oxaluramide* ($H_2N, C_3H_3N_2O_3$) mixed with potassic oxalurate. If a magma of alloxantin and water be treated with amalgam of sodium, *sodic dialurate* is formed; $C_8H_{10}N_4O_{10} + Na_2 = 2NaC_4H_3N_2O_4 + 2H_2O$; and from a hot solution of this salt the acid crystallizes on adding hydrochloric acid in excess. A still better process, according to Baeyer, consists in reducing alloxan by means of excess of stannous chloride in a larger excess of hydrochloric acid. The *ammoniac dialurate* is white at the moment of its formation, but as it dries it becomes of a splendid pink or blood-red colour. This salt is freely soluble in boiling water. It occasions a white precipitate with the salts of barium, and a yellow one with salts of lead. Argentic nitrate is reduced by it to the metallic state.

(1629) *Hydurilic Acid* ($H_2C_8H_4N_4O_6, 2H_2O$).—If 9 parts of dry dialuric acid be mixed with 5 of concentrated glycerin, and heated gradually, by means of an oil bath, to 284° (140° C.) in a capacious flask, a brisk and steady disengagement of carbonic anhydride takes place; the contents of the flask gradually become solid, and the disengagement of gas ceases; during the operation the temperature may be gradually raised to 320° (160° C.): the mass is then allowed to cool, and the glycerin containing formic acid is to be washed out with

cold water, when a yellowish-white granular mass of acid ammoniac hydrurate is left. The glycerin merely supplies a means of equalizing the temperature, while the following reaction occurs:—

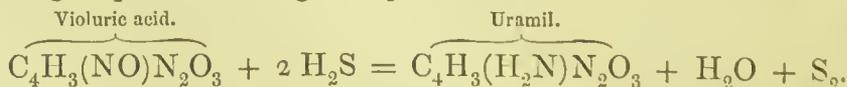


If this acid ammoniac salt be neutralized with ammonia and mixed with cupric sulphate, the liquid becomes of a dark-green colour, and gradually deposits from a hot solution black, anhydrous, or, from a cold solution, red hydrated crystals of normal cupric hydrurate. From this salt hydrochloric acid sets free white crystalline hydruric acid, which is sparingly soluble, and crystallizes from a hot solution in small four-sided prisms. It is best recognized by the beautiful green colour produced on mixing solutions of the acid or its salts with ferric chloride. The colour passes into red when heated, whilst hydruric acid is decomposed. If treated with fuming nitric acid, hydruric acid is converted into alloxan, but if the acid be used in a less concentrated form, three nitro-substitution products are formed in succession, viz.:—

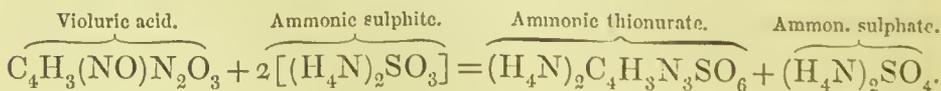


Diluric acid is not further decomposed by the nitric acid.

(1630) *Violuric Acid* crystallizes from hot water in brilliant transparent rhombic octahedra. Its salts are very beautiful, and brilliant in colour: potassic violurate crystallizes in blue prisms, giving a violet solution, which becomes red when potash is added in excess; the magnesian salt yields purple-red crystals; the calcic salt is brick red. Baric violurate crystallizes in brilliant square tables with truncated angles: it is of a beautiful red colour, and nearly insoluble in cold water. An aqueous solution of violuric acid is decomposed if boiled; and from its behaviour when heated with soda-lime there is no doubt that it is a nitrosyl (NO) substitution-compound: reducing agents like sulphuretted hydrogen and hydriodic acid convert it into uramil, changing the nitric oxide group into amidogen, e.g.:—



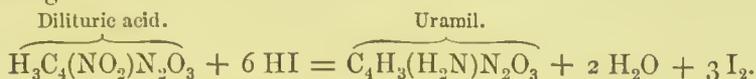
If boiled with ammoniac sulphite, violuric acid becomes converted into ammoniac thionurate:—



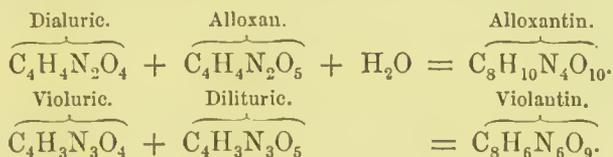
(1631) *Diluric Acid* (H₃C₄N₃O₅, 3 H₂O) is the final result of the action of nitric acid of moderate strength upon hydruric acid. It crystallizes in colourless square prisms and plates which effloresce in the air, and are soluble freely in hot water, less soluble in cold water, furnishing an intensely yellow solution. When heated it is decomposed, emitting nitrous fumes. The acid appears to be tribasic (Bayer), but it most usually forms salts containing 1 atom of a metallic monad, like the potassic-dihydric salt (KH₂C₄N₃O₅). These acid salts are very stable: they do not give up their basyl when treated with a dilute mineral acid, and they

usually have a yellow colour. The *hydric-dipotassic* salt ($\text{HK}_2\text{C}_4\text{N}_3\text{O}_5$) is anhydrous, and explodes feebly when heated, or when moistened with oil of vitriol. Many other diluturates, such as the ferric, cupric, and argentic salts, explode when heated. The soluble diluturates yield white precipitates with salts of ammonium, white needle-shaped crystals with solution of ferrous sulphate, and a lemon-yellow precipitate with silver acetate, the last consisting of $\text{Ag}_3\text{C}_4\text{N}_3\text{O}_5$.

Dilituric acid is a compound of nitroxyl (NO_2) or it is *nitrobarbituric acid*; it may be reduced to uramil by the action of hydriodic acid, but not by sulphuretted hydrogen:—

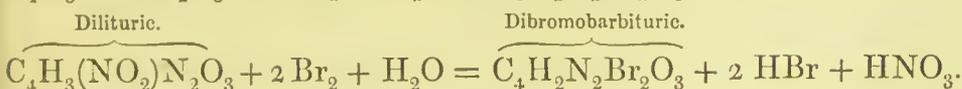
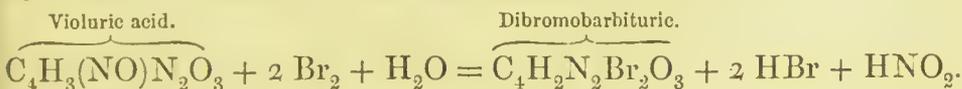


When a mixture of strong solutions of violuric and dilituric acids is made, a compound of the two bodies, *violantin*, crystallizes out. It bears a relation to violuric and dilituric acids somewhat similar to that which exists between alloxantin, and the dialuric acid and alloxan:—



Violantin is an unstable compound, and separates into its constituents when it is attempted to purify it by recrystallization.

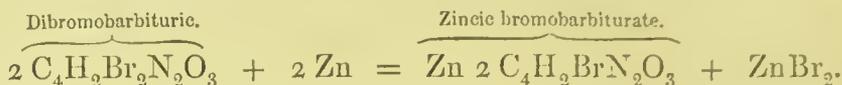
(1632) *Dibromobarbituric Acid*.—This arbitrary name was given by Bacyer to a substance at first called by him *bromalloxan* ($\text{C}_4\text{H}_2\text{Br}_2\text{N}_2\text{O}_3$). It is best prepared by triturating hydurilic with nitric acid into a paste, and adding bromine gradually, so long as it enters into combination. If the mixture is then heated, the crystals which had formed become dissolved, with evolution of nitrous fumes; and dibromobarbituric acid crystallizes as it cools in colourless brilliant plates. In this operation the hydurilic passes first into violuric or dilituric acid, and then the bromine displaces the nitrosyl or the nitroxyl, together with part of the hydrogen, as shown by the following equations:—



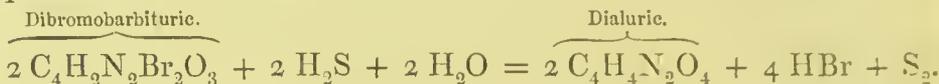
Dibromobarbituric acid crystallizes in colourless brilliant plates or prisms, which are soluble in water, and very soluble in absolute alcohol and in ether. If the aqueous solution is boiled, it is quickly decomposed into hydrobromic acid and alloxan, but it may be crystallized easily from nitric acid, which does not decompose it. Dibromobarbituric acid is readily soluble in alkalies, and furnishes compounds which are easily decomposed by heat, with loss of part of their bromine. It appears to be a dibrominated acid, which, by means of reducing agents, may be converted

into its corresponding simple acid, the barbituric of Baeyer ($\text{H}_2\text{C}_4\text{H}_2\text{N}_2\text{O}_3$).

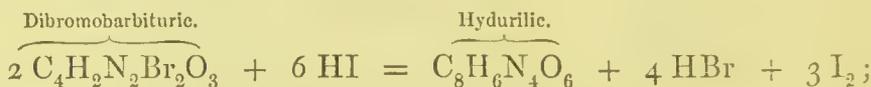
If a solution of dibromobarbituric acid be digested upon metallic zinc, it loses half its bromine and furnishes zincic bromobarbiturate:—



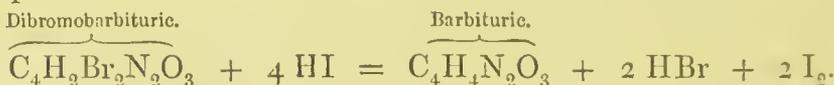
By sulphuretted hydrogen it is reduced to dialuric acid in the presence of water:—



If a small proportion of hydriodic acid be employed, hydurilic acid is the result:—



and if heated with hydriodic acid in excess, the reduction proceeds a step further:—

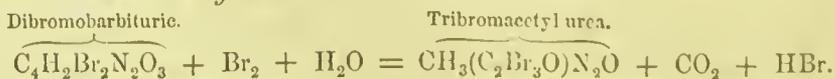


(1633) *Barbituric Acid* ($\text{H}_2\text{C}_4\text{H}_2\text{N}_2\text{O}_3, 2\text{H}_2\text{O}$) crystallizes in beautiful prisms, or sometimes in plates, or needles, which are sparingly soluble in cold water, but readily soluble in hot water. Fuming nitric acid converts it into dilituric acid, potassic nitrite into potassic violurate, and bromine into dibromobarbituric acid.

If boiled with caustic potash, ammonia is expelled, and potassic malonate ($\text{K}_2\text{C}_3\text{H}_2\text{O}_4$) is formed, from which Baeyer concludes that barbituric acid is *malonyl urea* $\text{CH}_2(\text{C}_3\text{H}_2\text{O}_2)''\text{N}_2\text{O}$, or urea in which 2 atoms of hydrogen have been displaced by the dyad radicle malonyl ($\text{C}_3\text{H}_2\text{O}_2$)''.

If heated to 302° (150° C.) in glycerin, barbituric acid loses the elements of water, and the residues of two molecules of the acid coalesce and form a new compound, *dibarbituric acid*; $2 \text{C}_4\text{H}_4\text{N}_2\text{O}_3 - \text{H}_2\text{O} = \text{H}_2\text{C}_8\text{H}_4\text{N}_4\text{O}_6$. The decomposition is always attended with the formation of some secondary products, among which is ammonia.

(1634) If a hot saturated solution of dibromobarbituric acid be treated with bromine in excess, carbonic anhydride is expelled, and long colourless prismatic needles of *tribromacetyl urea* are obtained:—



This substance is sparingly soluble in cold water, but readily soluble in hot alcohol, from which it crystallizes in brilliant tufts of needles on cooling. If heated to $298^\circ.4$ (148° C.), it melts without decomposition to a colourless liquid, which solidifies to a crystalline mass on cooling. When its solution is boiled it is decomposed, bromoform (CHBr_3) being produced, while pungent vapours

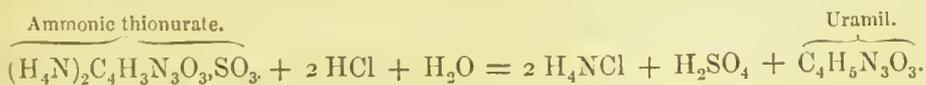
which attack the eyes are evolved. The powdered tribromacetyl urea exerts a very irritating effect upon the mucous membranes of the eyes and nose.

Acetyl urea [$\text{CH}_3(\text{C}_2\text{H}_3\text{O})\text{N}_2\text{O}$] or acetureide has been already mentioned (1605).

(1635) *Review of the derivatives of Barbituric Acid.*—From the details above given it will be easy to trace the connexion between several of the foregoing compounds. Barbituric acid may itself be derived from malonic acid and urea, being malonyl urea. If one of the atoms of hydrogen in the acid be displaced by bromine, we have bromobarbituric acid; if a second atom of hydrogen be displaced, we arrive at dibromobarbituric acid. If two atoms of hydroxyl be introduced in the place of the two of bromine, the formula indicates the composition of alloxanic acid. Violuric acid is barbituric acid in which an atom of hydrogen has been displaced by nitrosyl (NO); dilituric acid the same compound in which nitroxyl (NO_2) has taken the place of one atom of hydrogen, and dialuric acid is the compound in which an atom of hydroxyl (HO) has taken the place of the same atom of hydrogen; whilst in uramil an atom of amidogen may be regarded as having taken the place of the atom of hydrogen, as is represented in the following table:—

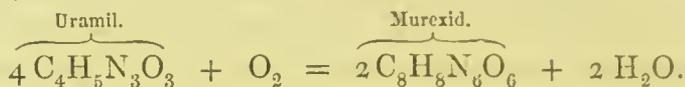
| | |
|----------------------------------|--|
| Barbituric acid | $\text{C}_4\text{H}_2(\text{H})[\text{H}]\text{N}_2\text{O}_3$ |
| Bromobarbituric acid | $\text{C}_4\text{H}_2(\text{H})[\text{Br}]\text{N}_2\text{O}_3$ |
| Dibromobarbituric acid | $\text{C}_4\text{H}_2(\text{Br}_2)\text{N}_2\text{O}_3$ |
| Alloxanic acid | $\text{C}_4\text{H}_2(\text{HO})_2\text{N}_2\text{O}_3$ |
| Violuric acid | $\text{C}_4\text{H}_2(\text{H})[\text{NO}]\text{N}_2\text{O}_3$ |
| Dilituric acid | $\text{C}_4\text{H}_2(\text{H})[\text{NO}_2]\text{N}_2\text{O}_3$ |
| Dialuric acid | $\text{C}_4\text{H}_2(\text{H})[\text{HO}]\text{N}_2\text{O}_3$ |
| Uramil | $\text{C}_4\text{H}_2(\text{H})[\text{H}_2\text{N}]\text{N}_2\text{O}_3$ |

(1636) *Uramil*, or *Dialuramide* ($\text{H}_2\text{N}, \text{C}_4\text{H}_3\text{N}_2\text{O}_3$).—This compound may be obtained by decomposing ammoniac thionurate (1637) by boiling it for a few minutes with an acid:—



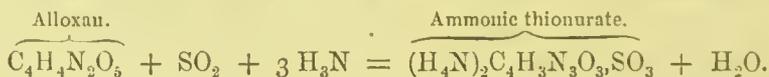
It may also be procured by mixing boiling solutions of alloxantin and sal ammoniac freed from air (1627); as well as by the reducing action of sulphuretted hydrogen upon violuric acid (1630), or that of hydriodic upon dilituric acid (1631). Uramil crystallizes in penniform groups of brilliant hard needles, which are insoluble in cold water, and sparingly soluble even in boiling water. When exposed to an atmosphere containing traces of ammonia it acquires a rose tint. Uramil is freely soluble in dilute alkaline solutions at ordinary temperatures, and is deposited

from them unaltered on adding an acid. But if its solution in ammonia be boiled, it absorbs oxygen, gradually acquiring a rich purple colour, and on cooling deposits crystals of murexid. If uramil be boiled for some time with mercuric or argentic oxide, a similar change occurs; the metallic oxide is reduced, and if the liquid be filtered while hot, beautiful crystals of pure murexid are deposited:—



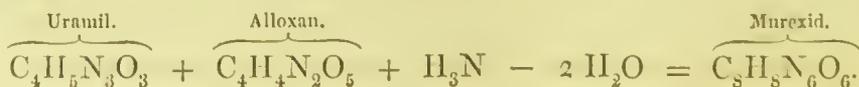
An excess of the metallic oxide must be carefully avoided, otherwise the purple colour disappears, and ammoniacal alloxanate is formed in the liquid. A solution of uramil in caustic potash evolves ammonia when heated; at ordinary temperatures it absorbs oxygen slowly from the air, acquiring a fine purple colour, and depositing crystals of potassic purpurate; the liquid becomes neutral, and contains potassic alloxanate and mesoxalate.

(1637) *Thionuric Acid* ($\text{H}_2\text{C}_4\text{H}_3\text{N}_3\text{O}_3\text{SO}_3$).—If an aqueous solution of alloxan be added to a solution of ammoniacal sulphite containing a considerable quantity of free ammonia, and the mixture be boiled for a few minutes, the ammonia and sulphurous acid unite with the elements of alloxan; hence the name, which indicates its connexion with $\theta\epsilon\tilde{\iota}\omega\nu$, sulphur, and uric acid. As the liquid cools, a beautiful salt, termed *ammonic thionurate*, is deposited:—



By adding a solution of plumbic acetate to the solution of this salt, an insoluble gelatinous plumbic thionurate is procured, which on standing becomes converted into concentric groups of delicate needles. This precipitate, on being decomposed by sulphuretted hydrogen, gives pure thionuric acid, which may be obtained by evaporation at a gentle heat, crystallized in slender needles. Its aqueous solution may be preserved unchanged at ordinary temperatures, but it undergoes decomposition when boiled; sulphuric acid being formed, while silky crystals of uramil are deposited. Ammonic thionurate gives a pale yellowish-brown precipitate with salts of copper. It gives no precipitate in acid solutions with salts of barium, but a white one in neutral solutions: when mixed with argentic nitrate the metal is gradually reduced, and forms a mirror-like coating on the sides of the vessel which contains it.

(1638) *Murexid*, or *Ammonic Purpurate* ($\text{C}_8\text{H}_8\text{N}_6\text{O}_6$).—This beautiful compound derives its name from *murex*, the shell-fish from which the celebrated Tyrian purple was obtained. There are several modes of preparing it. The decomposition of uramil by ammonia under the influence of oxygen, and by the action of mercuric oxide, has been already mentioned (1636). Another advantageous method of preparing murexid consists in adding alloxan to an ammoniacal solution of uramil:—



Murexid may also be obtained by adding a solution of ammoniac carbonate, drop by drop, to a boiling solution of alloxan, until the liquid has a slightly ammoniacal odour; the solution then acquires a beautiful purple tint, becomes turbid, and on cooling deposits 4-sided prismatic crystals of murexid. Murexid may also be prepared on a small scale by dissolving 4 grains of alloxantin with 7 of hydrated alloxan, in half an ounce of boiling water, and mixing the solution whilst hot with 80 grains of a cold saturated solution of ammoniac sesquicarbonate; brisk effervescence ensues, and a splendid purple liquid is produced, which on cooling deposits magnificent green crystals of murexid, with a golden lustre. These crystals, when heated to 212° , lose water to the extent of 3 or 4 per cent. The brilliant colour of the compound is speedily destroyed by sulphuretted hydrogen, as well as by free ammonia. Murexid is but sparingly soluble in cold water, to which, however, it communicates its intense purple colour: hot water takes it up more freely.

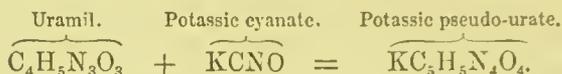
When the solution of murexid is mixed with one of a salt of lead, of barium, or of silver, it yields a purple precipitate. Corrosive sublimate slowly but completely decolorizes a solution of murexid, giving a beautiful purple precipitate. A solution of zincic acetate yields a golden-yellow precipitate in a solution of murexid, and forms a brilliant iridescent film in which green and yellow tints predominate. Dilute acids decompose the crystals of murexid, and cause the separation of scales of a sparingly soluble yellowish substance, termed *murexan*, which, in all probability, is an impure form of uramil; the solution contains a mixture of alloxan and alloxantin.

The colouring principle of murexid has lately been applied successfully to the dyeing of silks and cotton, and less perfectly to wool. Silk may be dyed by simple immersion in a concentrated solution of corrosive sublimate mixed with murexid. Cotton goods are mordanted with lead. Plumbic nitrate is thickened and mixed with a proportion of murexid sufficient to give the desired shade: it is then printed, the cloth dried and immersed in a bath containing 1 part of corrosive sublimate, 1 of sodic acetate, and 100 of water (Lauth). Dyeing on wool with murexid may be effected if the fabric be first mordanted with 'pink salt,' the double chloride of tin and ammonium ($2\text{H}_4\text{NCl}, \text{SnCl}_4$).

Test for Uric Acid.—Advantage is taken of the formation of murexid, in order to detect very minute quantities of uric acid by the action of nitric acid. In applying this test, the substance supposed to contain uric acid is heated on a slip of glass with a

drop of nitric acid, and evaporated cautiously to dryness. If uric acid be present, the residue has a red colour, which is converted by exposure to the vapour of ammonia into a fine crimson; further, the addition of a drop of a solution of potash develops a splendid purple colour, which disappears on the application of heat, with extrication of ammonia.

(1639) *Pseudo-Uric Acid* ($\text{HC}_5\text{H}_5\text{N}_4\text{O}_4$).—If uramil be boiled with a concentrated solution of potassic cyanate until it no longer becomes red on exposure to the air, a solution is obtained which deposits a yellow crystalline powder on cooling (Baeyer), consisting of potassic pseudo-urate:—



If this salt be dissolved in excess of potash and decomposed by hydrochloric acid, a white crystalline deposit of pseudo-uric acid, $\text{C}_5\text{H}_6\text{N}_4\text{O}_4$, is obtained. Sodio pseudo-urate is rather soluble in hot water, from which it crystallizes in tufts of prisms with $2\text{H}_2\text{O}$. The ammoniac salt crystallizes in voluminous plates and needles with H_2O , and easily becomes red when heated. The potassium salt resembles it in composition and in appearance. Pseudo-uric is a monobasic acid, the molecule of which contains the elements of uric acid with one additional atom of water. When oxidized with lead dioxide it does not, however, yield allantoin, but carbonic, oxalic, and oxaluric acids, whilst urea is liberated.

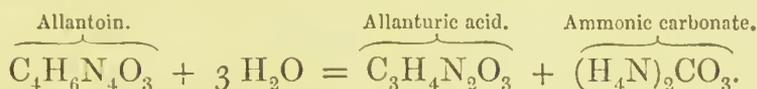
(1640) *Allantoin* ($\text{C}_4\text{H}_6\text{N}_4\text{O}_3$).—This is a body which occurs in the allantoinic fluid of the cow, or in the urine of the foetal calf, but it may also be procured by the oxidation of uric acid. For this purpose, 1 part of uric acid must be suspended in 20 parts of water, and raised to the boiling point: finely-levigated lead dioxide is then to be added in small quantities at a time to the boiling liquid, until the oxide ceases to change colour. The dioxide of lead is reduced to the state of protoxide, and a brisk effervescence occurs, owing to the escape of carbonic anhydride, while plumbic oxalate is precipitated; the supernatant liquid is colourless, and on filtering it and allowing it to cool, hard, brilliant, rhombic prisms of allantoin are deposited. Upon further concentration of the solution, fresh crystals of allantoin are obtained, and when the mother-liquid has been evaporated until it acquires a syrupy consistence, crystals of urea are deposited.

Allantoin is a neutral, tasteless substance, sparingly soluble in cold water, but freely soluble in boiling water. It shows but small tendency to combine with other bodies; but a silver compound of allantoin may be obtained by mixing a boiling solution of allantoin with one of argentic nitrate, and adding ammonia drop by drop: a white precipitate ($\text{C}_4\text{H}_5\text{AgN}_4\text{O}_3$) is thus occasioned. Allantoin undergoes fermentation in the presence of yeast, furnishing urea, ammoniac oxalate, and an unexamined acid (Wöhler). When allantoin is boiled with solutions of the

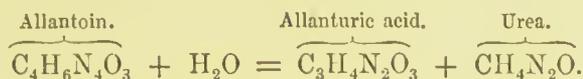
alkalies, it undergoes decomposition, ammonia being evolved whilst an oxalate of the alkali-metal is formed:—



Allantoin is readily decomposed by simple elevation of temperature: when its aqueous solution is heated in a closed tube to about 284° (140° C.), it is resolved into a new acid, the *allanturic acid* of Pelouze ($\text{C}_3\text{H}_4\text{N}_2\text{O}_3$), and into ammonic carbonate; both these substances being produced from the elements of allantoin by the assimilation of the elements of water:—



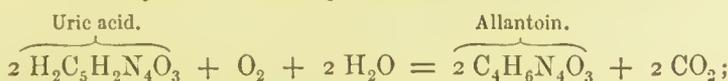
Allantoin also assimilates water and is transformed into allanturic acid by heating it gently with nitric acid, or with hydrochloric acid, and urea is at the same time formed:—



Pelouze considers that the urea found in the mother-liquor, obtained during the preparation of allantoin from uric acid by means of lead dioxide, is due to this secondary action; this, however, is very doubtful.

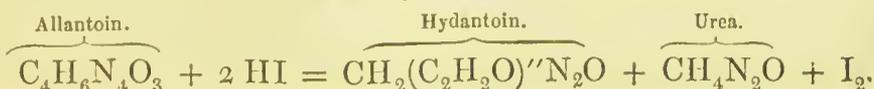
Allanturic acid is a white deliquescent substance, which gives white precipitates with argentic nitrate and with the acetates of lead; these precipitates are soluble in an excess of these salts, as well as in free allanturic acid. Baeyer regards allanturic acid as glyoxal-urea [$\text{CH}_3(\text{C}_2\text{HO}_2)\text{N}_2\text{O}$].

Lantanuric Acid is the name given by Schlieper to a result obtained by adding the powdered uric acid to a solution of potassic ferricyanide and caustic potash at ordinary temperatures. Under these circumstances the ferricyanide is rapidly converted into the ferrocyanide of potassium, while nascent oxygen attacks the uric acid; $4 \text{K}_3\text{FeCy}_6 + 4 \text{KHO} = 4 \text{K}_4\text{FeCy}_6 + 2 \text{H}_2\text{O} + \text{O}_2$. Allantoin and carbonic anhydride are first produced:—

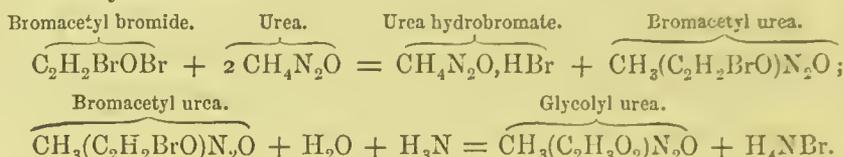


and the allantoin combining with an additional quantity of water is resolved into lantanuric acid and urea. It is probable that lantanuric acid is identical with the allanturic acid of Pelouze: it is a deliquescent substance, which forms a white insoluble salt with plumbic oxide, and its properties agree very closely with those ascribed by Pelouze to allanturic acid, respecting the analysis of which he has published no details.

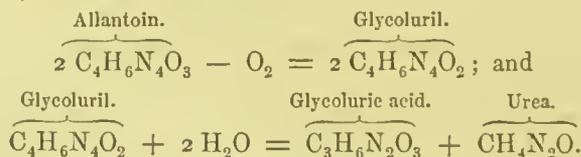
(1641) *Hydantoin* ($\text{C}_3\text{H}_4\text{N}_2\text{O}_2$).—There are several methods by which this body may be obtained: one consists in heating an excess of concentrated hydriodic acid with allantoin, then diluting, removing the excess of iodine by means of sulphuretted hydrogen, and the hydriodic acid by plumbic carbonate. On evaporation hydantoin is obtained in warty masses of crystals:—



Hydantoin crystallizes indistinctly; it is moderately soluble in cold water, has a slightly sweet taste, and is neutral to litmus: it fuses at $402^{\circ}8$ (200° C.). When boiled with baryta water, it is converted with assimilation of an atom of water into hydantonic, or glycoluric acid. Baeyer has, indeed, succeeded in synthetically producing hydantoin by a process which shows it to be really glycolyl urea:—by acting on urea with bromacetyl bromide he first obtains bromacetyl urea, and by heating this for some hours with an alcoholic solution of ammonia he obtains hydantoin:—



(1642) *Glycoluril* ($\text{C}_4\text{H}_6\text{N}_4\text{O}_2$).—If a hot solution of allantoin, in about 30 parts of water, is acidulated with sulphuric acid, and treated with an amalgam of sodium, containing about 1 per cent. of sodium, *glycoluril* is deposited in octahedral crystals. This compound contains 1 atom of oxygen less than allantoin. If heated with baryta water, ammonia escapes, baric carbonate is deposited, and baric glycolurate is obtained in solution, from which *glycoluric acid* ($\text{HC}_3\text{H}_5\text{N}_2\text{O}_3$) may be procured in transparent crystals after the removal of the barium by the cautious addition of sulphuric acid. This appears to be identical with the *hydantonic acid* of Schlicper and Baeyer. When dilute glycoluric acid is treated with argentic oxide in excess, it furnishes an alkaline liquid, which gradually deposits a characteristic salt in fine pearly scales, and warty white tufts of needles; but on acidulating with nitric acid, or adding argentic nitrate, these pearly scales ($\text{AgC}_3\text{H}_5\text{N}_2\text{O}_3$) are deposited immediately (Rheineck, *Lieb. Annal.*, cxxxiv. 218). The formation of glycoluril and glycoluric acid from allantoin is easily traced by the following equations:—



The urea breaks up in the presence of baryta into carbonic acid and ammonia.

(1643) Two other substances which have been sometimes found in urine—viz., cystin and kynurenic acid, will be noticed here.

Cystin, or *Cystic Oxide* ($\text{C}_3\text{H}_6\text{NO}_2\text{S}$).—This substance constitutes a rare form of urinary calculus; its name is derived from $\kappa\acute{\upsilon}\sigma\tau\iota\varsigma$, the bladder. Calculi composed of cystin are semi-transparent and of a brownish-yellow colour, and crystalline texture. Cystin is insoluble in water, alcohol, and ether, but it is dissolved by the stronger acids, such as the sulphuric, nitric, hydrochloric, and phosphoric. It is also freely soluble in alkaline solutions, whether caustic or carbonated, from which it can be precipitated by the addition of an acid such as the acetic. It may readily be obtained crystallized in hexagonal plates, by allowing its ammoniacal solution to evaporate spontaneously. When heated it does not melt, but is decomposed, emitting a peculiar foetid odour. Cystin contains 25.5 per cent. of sulphur.

(1644) *Kynurenic Acid* (from *κύων*, a dog) is the name given by Liebig to a peculiar acid found in the urine of the dog. It forms very light, silky, colourless, delicate needles, which are soluble in alkaline solutions, nearly insoluble in water, and insoluble in alcohol and ether. It is soluble in hot dilute acid solutions, and is deposited from them on cooling. With the metals of the alkalies it forms soluble crystalline salts. Kynurenic acid does not appear to contain nitrogen. Its composition has not been ascertained. When heated in a small tube it yields a crystalline sublimate, and leaves scarcely a trace of any carbonaceous residue.

CHAPTER XI.

ALBUMINOID AND GELATIGENOUS PRINCIPLES.

(1645) THE greater number of the compounds of organic origin which have hitherto occupied our attention are destitute of organic structure; they contain in each of their constituent or equivalent molecules only a moderate number of elementary atoms, and in this respect they differ from the compounds which remain to be described, since the latter are of a much more complex constitution. These bodies enter into the formation of the organized textures, and are destitute of crystalline character. The most important of them—viz., fibrin and albumin, occur both in plants and in animals; and though they form but a small proportion of the solid and liquid components of the organs of plants, they are never entirely wanting in some portion or other of their organism. They are most abundant in the seed. These substances abound, however, in the animal tissues, and constitute their most remarkable and distinctive ingredients. Owing to the complexity of their composition no satisfactory rational formula can at present be assigned to any of these azotised bodies; and, owing to their indisposition to crystallize, great difficulty is experienced in obtaining them in a state of purity, and of ascertaining when they are really free from foreign admixture. All of them contain sulphur amongst their components, though the proportion of this element never exceeds 2 per cent.

These azotised compounds may be subdivided into two groups; of these the more important is termed the *albuminoid* group, owing to the general resemblance of its members to albumin, or white of egg; it comprises albumin, fibrin, casein, and legumin, in which the proportion of carbon to nitrogen is that of four atoms of the former to one of the latter. The second group is the *gelatigenous*; it comprises gelatin, chondrin, and ossein.

(1646) *Products of Oxidation of the Albuminoid and Gelatigenous Groups.*—When these azotised substances are submitted to the gradual action of oxidizing agents, they furnish a great variety of products, which, however, belong to three principal groups; viz., to the acetic, the benzoic, and the cyanic series. Amongst the volatile bodies furnished by treating albuminoid substances with a mixture of potassic dichromate and sulphuric acid, or with a mixture of manganese dioxide and sulphuric acid, Guekelberger (*Liebig's Annal.*, lxiv. 39) obtained the following products, besides others which have not been specially identified:—

| | | |
|----------------|-------------------|------------------|
| Formic acid | Acetic aldehyd | Benzoic acid |
| Acetic acid | Propionic aldehyd | Benzoyl hydride |
| Propionic acid | Butyric aldehyd | ———— |
| Butyric acid | ———— | Hydrocyanic acid |
| Valeric acid | | Valeronitrile. |
| Caproic acid | | |

The volatile products of oxidation are the only ones which have as yet been fully examined. The most abundant of these products are the monobasic fatty acids: next to these the products of the benzoic series occur in the largest quantity, while the hydrocyanic is obtained in the smallest amount. The proportion in which these substances are formed varies according as casein, fibrin, albumin, or gelatin has been the body submitted to oxidation. Gelatin yields the largest quantity of formic, acetic, and valeric acids (Schlieper, *Liebig's Annal.*, lix. 1); fibrin gives the largest proportion of butyric acid, and casein yields the compounds of benzoyl in greatest abundance. There can be no doubt that these bodies originate in more complex organic products, which are the first results of the breaking up of these complicated azotised substances. For example, leucine and tyrosine are among the products obtained in an early stage of the reaction, and they break up into valeric acid, ammonia, and probably other compounds. When the albuminoid and gelatigenous substances are fused with caustic potash, they yield leucine and tyrosine, together with variable quantities of acetate, valerate, and other salts of potassium, which belong to the series of fatty acids.

§ I. THE ALBUMINOID GROUP.

(1647) It has been already stated that the more important members of this group are albumin, fibrin, casein, and legumin, but it comprises several modifications of these bodies of minor importance, such as globulin and vitellin. The different forms of mucus also exhibit a close relationship to the compounds of this division.

Albumin is the characteristic ingredient of white of egg, and of the serous portion of the blood. *Fibrin* is the principal constituent of muscular tissue, and is that component of the blood which occasions its spontaneous coagulation; *casein* is the constituent of milk which is separated in the form of curd on the addition of an acid; it is the essential component of cheese. *Legumin* is abundant in the seeds of the leguminous plants, such as peas, beans, and lentils. Liebig regards legumin as identical with casein; but many other chemists consider that it has hitherto been found only in the vegetable kingdom, and casein only in the animal: albumin and fibrin are, however, generally admitted to occur in both divisions of the organic creation. No animal can continue to subsist upon food in which these azotised substances are entirely wanting. This circumstance is explained by the important observations of Liebig, who first clearly insisted upon the fact that none of these albuminoid principles are ever produced by the animal organism; they are elaborated in the growing plant, and are merely assimilated by the animal in the process of digestion. The albuminoid principles furnish those essential ingredients of the blood which are concerned in repairing the soft azotised portions of the body, such as the muscular and nervous tissues, as they become effete: hence the albuminoid principles have been termed the *plastic* materials of nutrition, in order to distinguish them from other portions of the food which, like starch and fatty matters, are especially needed for maintaining other functions, and which Liebig termed the *respiratory* materials of the food. It will, however, be necessary to consider the components of food more in detail (1719), after the properties of the albuminoid principles have been discussed.

The albuminoid principles may be preserved in a dry state for an indefinite period without change, but if exposed to the air while moist, they gradually putrefy and emit a sickening odour. According to Lehmann, among the products of their putrefaction are always to be found carbonate, butyrate, valerate, and sulphide of ammonium, together with leucine and tyrosine. The readiness with which the albuminoid bodies putrefy and undergo spontaneous chemical changes when moist is one of their most striking characters. Synaptase, diastase, pepsin, and other ferments are considered by Liebig to be modifications of albumin in particular states of decay; and he supposed yeast itself, although an organized structure, to owe a part of its remarkable power of exciting fermentation to the presence of azotised matter which is undergoing definite transformation, although the nature of the change

is but little understood. If albuminoid matters be heated in closed vessels, they first swell up and fuse, then blacken, and emit a large quantity of fœtid empyreumatic products, among which ammonia and sulphuretted hydrogen are always present; and they leave in the retort a porous, brilliant, carbonaceous mass. When incinerated they furnish a notable amount of ash: this varies in quantity in different cases, but it always contains calcic phosphate.

(1648) *Properties and Composition of the Albuminoid Principles.*—All of these albuminoid substances are capable of existing both in a soluble and an insoluble form; they belong to the class of compounds which Graham has distinguished as colloids (62). In the animal fluids they occur in the soluble modification, whilst in the solid parts they frequently are found in the insoluble condition. The power of thus existing either in the solid or in the liquid state is of the greatest importance to the operations of animal life. It is necessary that these essential constituents of our frame should be able to exist in solution, in order that by the circulation of the blood they may be carried into every part of the body; and it is also necessary that they should be able to assume a solid form, to prevent the circulating fluids in their course from dissolving and washing away the delicate organs through which they pass.

These albuminoid principles, either in their soluble or their insoluble condition, are readily dissolved by the aid of a gentle heat in a solution of potash or of soda: the addition of an acid to the liquid so obtained causes the separation of a greyish flocculent precipitate, termed by Mulder *protein*, whilst a slight odour of sulphuretted hydrogen is emitted, and a small quantity of phosphoric acid is also found in the solution. This precipitation is best effected by means of acetic acid, since the mineral acids are obstinately retained by the flocculi: excess of acetic acid redissolves the precipitate. When either of these principles, in its soluble form, is evaporated at a gentle heat, it yields a semi-transparent friable mass, nearly insoluble in alcohol and in ether. Indeed, the addition of alcohol to the aqueous solutions causes their coagulation. Their aqueous solutions are also precipitated by the addition of solutions of the salts of copper, of lead, and of mercury, as well as by infusion of galls.

Concentrated sulphuric acid dissolves the albuminoid substances with a brownish-red colour, but the most characteristic tests for the albuminoid bodies are afforded by nitric and hydrochloric acids. Concentrated nitric acid produces in their solutions a

coagulum of a bright orange colour, and gradually dissolves it with effervescence; or if they be in the insoluble condition, the tissue is stained yellow, and is slowly dissolved. Mulder considers this yellow substance to be a distinct compound, and names it *xanthoproteic acid*. Concentrated hydrochloric acid when gently warmed with albuminoid solutions produces a milk-white coagulum, which it dissolves slowly, forming a blue or violet-coloured liquid. It may farther be stated that acids generally produce coagulation of albuminoid substances when in solution, but that (with the exception of the metaphosphoric) when added in excess they redissolve the coagulum. On diluting these acid liquids with a moderate quantity of water, a precipitate occurs, but it disappears if the dilution be carried still farther. These acid solutions give a precipitate with the ferrocyanide and with the ferricyanide of potassium, though the aqueous solution does not. Millon proposed to test for the protein-compounds by moistening the tissues supposed to contain them with a solution of two parts of mercury in four of nitric acid, of sp. gr. 1.40. On the application of a temperature a little below that of boiling water, an intense red colour is developed, which is not destroyed by boiling with water, nor by exposure to the air. The gelatinous tissues, however, exhibit a similar coloration when similarly treated. This red colour is so intense that it may be perceived on adding the mercurial solution to a liquid containing not more than $\frac{1}{100000}$ of its weight of albumin.

Both albumin and fibrin contain a small quantity (less than 2 per cent.) of sulphur and of phosphorus; casein likewise contains sulphur, but phosphorus is absent. It is owing to the presence of sulphur that putrid eggs possess their peculiarly offensive odour. The sulphur is in the unoxidized condition, and this probably is also the case with the phosphorus. By the action of a solution of potash, both these elements are in great measure removed from the organic body, and when the alkaline liquid is neutralized with an acid, the so-called protein is precipitated, while the phosphorus and most of the sulphur remain in the solution. The presence of unoxidized sulphur in the supernatant liquid may be shown by adding to the cold solution of one of these compounds in potash (albumin for example), a few drops of a clear solution of plumbic oxide in potash, formed by adding an excess of potash to a solution of plumbic acetate. On applying heat to the solution, the albumin is decomposed, its sulphur is removed, while sulphide and hyposulphite of potassium are produced; $S_4 + 6KHO = 2K_2S + 2H_2O + K_2S_2H_2O_4$: the sulphide immediately shows itself by forming a brown precipitate of plumbic sulphide, which renders

the liquid dark-coloured and opaque: $\text{PbO} + \text{K}_2\text{S} + \text{H}_2\text{O} = \text{PbS} + 2\text{KHO}$. The phosphorus becomes oxidized and converted into phosphoric acid; it remains in the liquid, in which it may be discovered by the appropriate tests.

Many chemists, and Gerhardt among the number, regard all the substances of the albuminoid group as chemically identical, and as resulting from the combination of a single principle, which presents the characters of a feeble acid; the modifications in properties which it exhibits under the various forms of albumin, fibrin, and casein, being due to its combination with different bases, or saline bodies. This hypothesis, however, though probable, has not been actually proved to be true, and in the present state of science it is necessary to regard these bodies as distinct substances, which are convertible by vital processes one into the other, but each of which has its own peculiar functions in the organism.

The original view of Mulder was, that albumin, fibrin, and casein were derivatives of one fundamental azotised principle, which he termed *protein*, from $\pi\rho\omega\tau\omicron\varsigma$, first, in allusion to its supposed importance; and that this substance, by its union with different proportions of sulphur and of phosphorus, gave rise to the different modifications of the albuminoid group. Liebig has since shown that Mulder's protein always retains a small but variable amount of sulphur, and he denies the existence of protein as a separate body. It appears to be most likely that the substance termed protein by Mulder is merely the original body which was operated upon, but slightly modified in the course of the experiments by the action of potash.

| Constituents. | Mulder. | | | | | Gobley. | Dumas and Cahours. | Bence Jones. |
|---------------|-----------------------|--------------------------|---------|---------|-----------|---------------------------|--------------------|---------------------|
| | Protein from Albumin. | Albumin from hens' eggs. | Fibrin. | Casein. | Globulin. | Vitellin from hens' eggs. | Legumin from peas. | Legumin from beans. |
| Carbon . . | 53·7 | 53·5 | 52·7 | 53·83 | 54·5 | 52·26 | 50·53 | 55·05 |
| Hydrogen . . | 7·0 | 7·0 | 6·9 | 7·15 | 6·9 | 7·25 | 6·91 | 7·59 |
| Nitrogen . . | 14·2 | 15·5 | 15·4 | 15·65 | 16·5 | 15·06 | 18·15 | 15·89 |
| Oxygen . . | 23·5 | 22·0 | 23·5 | 22·52 | } 22·1 | 23·24 | } 24·41 | } 21·47 |
| Sulphur . . | 1·6 | 1·6 | 1·2 | 0·85 | | 1·17 | | |
| Phosphorus | | 0·4 | 0·3 | | | 1·02 | | |
| | 100·0 | 100·0 | 100·0 | 100·0 | 100·0 | 100·00 | 100·00 | 100·00 |

The preceding table indicates the composition of 100 parts of protein according to the analysis of Mulder, and it gives a comparative view of the results of the analysis of albumin, fibrin, and casein, by the same chemist; from which it is appa-

rent that the composition of these bodies is such that mere ultimate analyses are insufficient to distinguish between them. The analyses of legumin are discordant, and it is very doubtful whether Dumas and Cahours operated on a homogeneous substance (1659). In all cases the ashes have been deducted before calculating the composition in 100 parts.

The numerous experiments upon fibrin, albumin, and casein, made subsequently to these, by various chemists, completely confirm the accuracy of the results obtained by Mulder with these substances.

(1649) *Protein?* ($C_{18}H_{25}N_4O_5, H_2O?$).—Mulder still maintains the existence of a substance free from sulphur, which he terms protein, and to which he assigns the formula above given. It has, however, never been procured free from sulphur. The gelatinous flocculi, obtained on neutralizing an alkaline solution of any albuminoid substance, if well washed and dried, furnish a yellowish, horny-looking, semi-transparent mass, which has, according to Mulder, the same composition, whether it be prepared from albumin, from fibrin, or from casein. Protein is destitute of taste and smell: it is insoluble in water, alcohol, and ether; but in water it swells up and becomes gelatinous in appearance. The alkalis dissolve it, and deposit it unaltered on neutralizing the solution with an acid. In the mineral acids it swells up and forms a jelly which retains a portion of acid; this acid jelly is insoluble in water, though an excess of the acid dissolves it, and deposits it unaltered on dilution. Diluted sulphuric acid if digested upon protein at 212° for some hours gradually decomposes it, and produces amongst other compounds a quantity of leucine.

When protein, or any compound which furnishes it, is boiled in water for several consecutive hours, the protein gradually combines with oxygen, and becomes converted into a soluble substance, termed by Mulder, *ammoniacal trioxide of protein*, ($H_3N, C_{36}H_{50}N_8O_{13}, 2 H_2O?$): this compound is insoluble in alcohol and in ether. Its aqueous solution is precipitated by the mineral acids, by solutions of chlorine, of tannic acid, and by the salts of lead, of silver, of zinc, and of iron; but not by potassic ferrocyanide, or by salts of barium. It forms neutral compounds with the alkalis; but if boiled with an excess of potash or of soda it emits ammonia. It is very probable that much of the material which figures in the analyses of animal products as 'watery extractive animal matter' consists of this body: and if so, it forms an important substance in connexion with the metamorphosis of albumin and of fibrin into the products which are carried off by excretion from the system.

When a current of chlorine is transmitted through a dilute solution of albumin, a compound is separated in white flocculi, which Mulder regards as a definite compound of chlorous acid with protein. This substance, when decomposed by ammonia, yields the ammoniacal trioxide of protein just described. This ammoniacal trioxide appears to exist in the *buffy coat* of the blood, which is formed upon the surface of the coagulum in blood drawn from patients suffering from certain acute inflammatory affections. In such cases, it is associated with an insoluble compound, described by Mulder as the *dioxide* of protein. The same chemist also regards this insoluble dioxide as forming the principal constituent of the hair: it is of a yellowish colour, is soluble in alkalis, and is sparingly so in acetic acid. Mulder states that it is this compound which constitutes the insoluble residue obtained from fibrin after it has been boiled for many hours in water. It is probably similar to that found in horn; but the

nature of this substance, and its relations to albumin, require further examination. Indeed, the existence of the whole of these protein compounds, as distinct principles, must be admitted to be very problematical.

(1650) ALBUMIN.—The properties of this body when in solution are subject to considerable modification, according to the nature of the substances with which it is associated. The reactions of albumin from the white of the hen's egg (*ovalbumin*), therefore, differ in some respects from those afforded by albumin contained in the serum of blood (*seralbumin*), and this again from soluble albumin freed as far as possible from saline mixture; and all of these forms of albumin differ slightly from the albumin contained in the urine as excreted in Bright's disease.

Soluble albumin, in an aqueous solution, is a tasteless, somewhat glairy, colourless liquid, which exerts a left-handed rotatory action upon a ray of polarized light. A solution of albumin is readily coagulated by heat, and by the addition of various saline and acid liquids. It may be evaporated to dryness at a temperature not exceeding 122° (50° C.), and may be preserved in the form of a yellowish, brittle, transparent mass, which is insoluble in alcohol and in ether; but it may be slowly redissolved in lukewarm water; the solution being greatly promoted by the addition of a small quantity of sodic chloride or of any other salt of the alkali-metals. A considerable portion of the albumin is, however, always left in the insoluble form. If white of egg, or serum, be evaporated to dryness *in vacuo*, then powdered and digested in a small quantity of cold water, the greater portion of the soluble salts is dissolved, and at the same time a considerable quantity of albumin is found in the liquid; the residue, after being thus freed from its soluble salts, is almost insoluble. Albumin, in its purest form, has a slightly acid reaction upon litmus.

The most remarkable peculiarity of albumin is its power of solidifying on the application of heat, and of becoming insoluble. This coagulation begins at 140° (60° C.); the solution, if concentrated, sets into a gelatinous mass, as is seen in the common process of boiling an egg hard; but when the liquid is very dilute, it simply becomes turbid. The albumin may, however, be separated by ebullition, provided that the solution be neutral or slightly acid; it then collects into flakes, which can be separated by filtration. Nothing is known of the cause of the coagulation of albumin by heat. When a solution of albumin containing alkali, such as serum or white of egg, is heated, a small quantity of sulphur is separated, and the liquid becomes rather more alkaline from the liberation of a portion of the soda from the

coagulated mass. Seralbumin does not form so solid a coagulum as ovalbumin.

Coagulated albumin, when dried, forms hard, horny, transparent masses, of a yellowish colour. When plunged into cold water it absorbs four or five times its bulk of this liquid, and becomes opaque and elastic. It is not soluble in water, but by long boiling in open vessels it undergoes gradual decomposition, and a soluble compound is obtained, which has the composition of the ammoniacal trioxide of protein (1649). If heated to 302° (150° C.), with a small quantity of water, in a sealed tube, the albumin is redissolved, and furnishes a liquid which does not coagulate by heat, but which when acidulated with acetic acid gives a precipitate with potassic ferrocyanide.

Strong alcohol precipitates albumin from its aqueous solution ; but if the alcohol be rendered slightly alkaline by the addition of potash, no coagulation ensues. Ether, if free from alcohol, does not occasion the coagulation of seralbumin, although it renders the concentrated solution of ovalbumin viscid, and gradually effects its complete coagulation. Kreasote occasions its immediate coagulation. The concentrated mineral acids precipitate albumin in a coagulated form, but gradually decompose and dissolve it, acting upon it as they do upon the compounds of protein generally: oil of vitriol dissolves it with a brownish-red colour, nitric acid produces with it a lemon-yellow, and warm hydrochloric acid a violet-coloured solution after some hours' digestion. Nitric acid precipitates it, and when dilute does not redissolve the precipitate. Hydrochloric acid precipitates it and redissolves the coagulum ; the solution when poured into a small quantity of water becomes milky, but is rendered clear by the further addition of water. The solution of coagulated albumin in strong hydrochloric acid furnishes syntonin, the same substance which is produced by the action of the dilute acid on muscular fibre (1656). Dilute sulphuric acid produces no precipitate till the liquid is boiled ; the clear solution in concentrated sulphuric acid is not precipitated when diluted with water. Metaphosphoric acid causes an immediate coagulation of albumin ; but the other varieties of phosphoric acid produce no such effect. Acetic acid, and the organic acids generally, except the modification of tannic acid contained in the gall-nut, do not produce any precipitate in solutions of albumin.

The solutions of albumin in the organic acids are not coagulated by boiling, but a pellicle is gradually formed over the surface during evaporation ; the addition of a solution of some salt, such

as sodic sulphate or chloride, causes the albumin to separate from these solutions. The precipitates from the unboiled solutions are generally soluble in pure water; *precipitated* albumin is, therefore, not necessarily in the *coagulated* form. If a solution of white of egg be rendered accurately neutral by the addition of acetic acid, and then be diluted, flocculi of albumin are precipitated, but they are redissolved when treated with a solution of common salt or of nitre.

Solutions of alum, and of many of the metallic salts, such as those of copper, lead, mercury, or silver, precipitate solutions of albumin. It is, therefore, useful to administer whites of eggs in the liquid form in cases where poisoning from swallowing any of the salts of these metals is suspected to have occurred; the remedy is a safe one, whilst if the poison have really been taken, the albumin decomposes the salt, and generally enters into combination both with the acid and the base; the albumin sheathing the stomach from the influence of the poison, whilst other measures are in preparation for effecting its removal from the system.

(1651) *Effect of Bases on Albumin.*—The presence of an alkali in liquids containing albumin considerably modifies the reactions; if the alkali be present in large quantity, the solution does not coagulate when heated, but a pellicle is formed over the surface during the evaporation, an appearance being thus produced similar to that observed when milk and other solutions of casein are exposed to the air whilst hot.

Albumin forms definite compounds with the alkalies and other metallic oxides. Coagulated albumin is dissolved freely by solutions of the alkalies, and in certain proportions it even neutralizes their action upon test paper. If a concentrated solution of albumin be mixed with one of potash, a gelatinous mass of *potassic albuminate* is formed, from which, by washing with cold water, the excess of alkali may be removed; it retains 5.4 per cent. of potash (Lieberkühn). If the gelatinous mass be washed with alcohol and then with water, it is insoluble in boiling water and also in boiling alcohol; but if it be washed with cold water only, the residue is soluble both in boiling water and in boiling alcohol. The aqueous solution of potassic albuminate is not coagulated by boiling it, but on the addition of a small quantity of acetic, tartaric, or phosphoric acid, a white coagulum is produced, which is readily dissolved by an excess of the acid. These characters resemble those of casein, and some chemists have supposed that casein is simply an albuminate of potassium. The coagulum obtained by the addition of acetic acid to the solution of potassic

albuminate, when well washed, furnishes nearly pure albumin. It leaves scarcely any ash on incineration.

Sodic albuminate resembles the potassic compound, and may be formed in a similar manner. The animal fluids in which albumin occurs, such as the white of the egg and the serum of the blood, are very slightly alkaline, the proportion of alkali not exceeding 1.58 per cent. in ovalbumin (Lehmann). Even this small proportion renders the albumin more soluble, and prevents its complete coagulation on boiling, a portion of albumin remaining dissolved and forming sodic albuminate: and that portion of the albumin which does coagulate does not collect into flocculi. Sodic albuminate may be readily decomposed by neutralizing it with acetic acid; on afterwards boiling it, the albumin is separated in coherent flocks. It is also to be remarked that the albumin may be made to separate from the slightly alkaline liquid by boiling it after the addition of a neutral salt, such as sodic sulphate, common salt, or hydrochlorate of ammonia. These are points which require attention in the analysis of animal liquids, in which the quantitative separation of albumin is necessary. Gerhardt is disposed to view serum and the white of eggs as containing a definite hydric-sodic albuminate; and adopting Lieberkuhn's formula for albumin (*Poggend. Annal.*, lxxxv. 117, 298), it would be $(\text{HNaC}_{72}\text{H}_{110}\text{N}_{18}\text{SO}_{22}, \text{H}_2\text{O})$. Such formulæ, however, can only be regarded as approximations.

According to Lieberkuhn, the compound of albumin with *silver* is $(\text{AgHC}_{72}\text{H}_{110}\text{N}_{18}\text{SO}_{22}, \text{H}_2\text{O})$; that of *copper* $(\text{CuC}_{72}\text{H}_{110}\text{N}_{18}\text{SO}_{22}, \text{H}_2\text{O})$; the copper compound is soluble in an excess of solution of cupric sulphate, as well as in an excess of a solution of potash; in the latter case a deep blue liquid is formed resembling that obtained by adding ammonia in excess to the salts of copper. The presence of albumin in a solution consequently prevents the precipitation of the cupric salts by the alkalies, and a similar observation has been made in the case of the ferric salts. The compound of albumin with *lead* is obtained by adding basic plumbic acetate to a solution of albumin; it is readily decomposed by all the acids. The albuminate of *mercury* is formed when a solution of white of egg is mixed with one of corrosive sublimate: it is very insoluble in pure water, but it is dissolved by a solution of common salt.

Preparation.—The preparation of pure albumin in the *coagulated form* may be effected by precipitating white of egg by means of hydrochloric acid, washing with the same acid in a diluted form, and then dissolving in water: this solution is precipitated by

ammonie carbonate; the coagulum is washed, dried, and subsequently powdered, after which it is digested in alcohol and in ether, in order to remove traces of adhering fatty matters. Pure coagulated albumin may also be obtained by decomposing potassic albuminate by means of acetic acid.

Wurtz considers that a pure *soluble* albumin may be obtained in the following manner: white of egg is well agitated with twice its volume of water, and strained through linen in order to remove the membranous floeculi: the filtered portion is then mixed with a solution of basic plumbic acetate, in quantity insufficient to throw down the whole of the albumin. The copious precipitate thus obtained must be well washed, suspended in water, and decomposed by means of a current of gaseous carbonic anhydride, when the lead is separated in the form of carbonate, and the liberated albumin becomes dissolved. The solution is filtered through paper freed from saline matter by washing with a weak acid. It however retains traces of lead, which may be removed by transmitting sulphuretted hydrogen and heating the liquid to 140° (60° C.) when the first floeculi of coagulated albumin which are thus formed carry with them the whole of the sulphide of lead, and may be removed by filtration. The liquid is finally evaporated at a temperature below 122° (50° C.). Graham obtains albumin free from saline impurities by acidulating white of egg with acetic acid, and submitting it to the process of dialysis.

No method is known by which the absolute purity of albumin can be ascertained. Its combining proportion is also uncertain, since it forms no definite compound upon the purity of which a decided opinion can be formed.

(1652) *Sources of Albumin.*—Albumin is a very abundant constituent of the animal body: it constitutes about 7 per cent. of the entire mass of the blood; it is an essential component both of lymph and of chyle; and it is abundant in all serous exudations, although it is found in these fluids in smaller proportion than in the serum of the blood. It is also contained in large proportion in many of the soft solids of the body, as for example, in the brain, the kidneys, the liver, and the pancreas, in all of which it exists in the uncoagulated form. The liquid of the pancreas appears to be the only secretion in which it occurs in health. It is never found in the excreta except under the influence of disease: thus it is occasionally poured out from the mucous membrane of the bowels in cases of intestinal catarrh, and has been repeatedly found in the alvine dejections in cases of dysentery, as well as in those of Asiatic cholera. It is likewise

often met with in the urine in acute febrile disorders, as well as in some chronic affections of the heart, liver, and kidneys, especially in cases of fatty degeneration of the kidneys. Its occurrence in the ovum is general, and is familiarly illustrated in the case of the eggs of birds.

The juice of many plants, such as that of carrots, turnips, and cabbages, when heated, becomes turbid, from the coagulation of a substance which analysis shows to have the same composition as albumin, and with which it coincides in all important particulars. Wheat flour likewise contains an azotised substance soluble in cold water, forming a solution which yields greyish flocculi of albumin on evaporation.

Paralbumin is the name given by Scherer to a substance obtained from the liquid of ovarian dropsy. Its solution is precipitated by acetic acid, which redissolves it if added in excess; with alcohol it also gives a precipitate, but the flocculi are redissolved by water at 100° ($37^{\circ}.8$ C.), and it is only imperfectly coagulated by heat. Many other varieties of albumin which have been described probably arise from the modifying effects of salts upon albumin.

(1653) *Globulin*, or *Crystallin*, is a substance which closely resembles albumin. It occurs mixed with albumin in the cells of the crystalline lens in a very concentrated solution, forming, according to Simon, from 10 to 14 per cent. of the dry lens.* It also enters largely into the composition of the red globules of the blood, and has hence received its name. Globulin has not been obtained in the soluble form free from salts. It may be extracted from the crystalline lens by rubbing up the lens in a mortar to break up the cells, evaporating to dryness at 212° , washing with ether and dilute alcohol to remove the fat, and then dissolving the crystallin out with hot alcohol, of sp. gr. 0.915. A large portion of crystallin separates on cooling; after it has been dried it is insoluble in water, and it is precipitated from its alcoholic solution by diluting it with water. It is dissolved readily by a concentrated solution of common salt. When washed muscular tissue is digested with a mixture of 1 part of saturated solution of common salt and 2 of water, a solution of a substance resembling globulin is obtained, and is precipitated on largely diluting with water. It has been called *myosin*.

Globulin is distinguished from the soluble protein-compounds by the circumstance that it is precipitated both from acid and alkaline solutions on exactly neutralizing them. It putrefies rapidly, and its solution when boiled emits ammonia. Its reactions with the mineral acids and with kreasote resemble those of albumin.

(1654) *Vitellin* is the name which has been given to the albuminoid constituent of the yolk of the egg; the yellow colour of the yolk is, however, due to an oil containing phosphoric acid, which is dissolved readily by ether, while the vitellin is coagulated. This reaction with ether, and the fact that its aqueous solution is not precipitated by salts of lead and of copper, are the principal characters by which vitellin is distinguished from albumin. By ultimate analysis it is found to contain less carbon and more hydrogen and oxygen than albumin

* Lehmann, in his experiments upon this substance, appears not to have separated the albumin, and hence the description which he gives of it differs from that of Simon, who removed this impurity.

(see Table, p. 798). The yolk of the egg contains 16 or 17 per cent. of this substance. According to the experiments of Valenciennes and Fremy, the composition of the azotised constituent of the yolk of the egg varies in different classes of animals. These chemists have termed that obtained from the eggs of cartilaginous fishes, such as the ray, *Ichlin* (from *ἰχθῦς*, a fish), and that obtained from the eggs of the turtle, *Emydin*.

(1655) FIBRIN.—This substance, like albumin, occurs in two distinct states, the solid and the liquid, during the life of the plant or animal, but on removing it from the living organism it undergoes speedy, and so-called spontaneous, coagulation—a circumstance by which fibrin is at once distinguished from all other analogous substances. It is contained in the blood in the liquid state, in a proportion not generally exceeding 2·5 parts in 1000, though it is liable to considerable variation in quantity under the influence of disease, being greatly increased in febrile and acute inflammatory affections, especially in rheumatism and pneumonia, where it has been found as high as 11·8 parts in 1000. In anæmic diseases, in typhus, chlorosis, &c., it is frequently, but not uniformly, slightly diminished, though by long fasting it is somewhat increased in quantity. Lymph does not usually contain more than 0·4 or 0·5 parts per 1000. In the chyle of animals it has been found to vary from 0·7 to 7·0 per 1000.

Fibrin, in the form of muscular tissue, constitutes a large proportion of the soft parts of animals. It occurs in muscle arranged in bundles of fibres, and from this circumstance the name of fibrin derives its origin. Muscular fibrin, however, presents several points of difference from the fibrin obtained from the blood. According to Liebig, fibrin may also be obtained from the juice of plants, and it exists in the gluten of wheat.

Preparation.—*Blood-fibrin* may be obtained in a state of tolerable purity by whipping up freshly-drawn blood with a bundle of twigs: in the act of coagulation the fibrin attaches itself in soft, white, opaque, elastic strings to the twigs, and may be afterwards washed clean by maceration and kneading in water till it is free from colour. When dry, fibrin forms a horny, yellowish, or grey solid.

The reactions of blood-fibrin in the solid form are similar to those of coagulated albumin, except that fibrin decomposes peroxide of hydrogen with effervescence, whilst albumin produces no such effect; but fibrin by long boiling in water is also rendered equally inert. When fibrin is heated to 302° (150° C.) with a small quantity of water, in a sealed tube, it is redissolved, and forms a solution which becomes coagulated by acids, and resembles that

formed by albumin under similar circumstances. The coagulation of fibrin is prevented by allowing the blood, at the moment of its efflux from the body, to mix with solutions of certain salts, such as potassic carbonate or nitrate, and sodic acetate, sulphate, or chloride. The fibrin of venous blood, before exposure to the oxygen of the air, is freely soluble in a solution containing about one-sixth of its weight of nitre, as well as in similar solutions of the alkaline sulphates, acetates, phosphates, and chlorides. This solution becomes coagulated like albumin when heated, but is precipitated by acetic acid; when exposed to the air, the solution absorbs oxygen and deposits insoluble flocculi. If blood be drawn into a vessel containing a concentrated solution of sodic sulphate, it remains liquid, and the red globules subside on standing. If the clear liquid be now diluted with ten times its bulk of water, in many cases the fibrin will be gradually coagulated, and by washing may be obtained in a pure form. Fibrin is freely soluble in dilute solutions of potash or of soda, and the alkaline liquid presents many of the characters of sodic albuminate, but on neutralizing the solution with acetic or phosphoric acid, the fibrin is reprecipitated: if the alkaline solution be mixed with metallic salts, it yields precipitates similar to those formed by the same salts with albumin. The solutions both of fibrin and of albumin in acetic acid are precipitated on the addition of potassic ferrocyanide, a character by which they are at once distinguished from gelatin, which gives no precipitate under similar circumstances. If the acetic solution of fibrin be neutralized by potash, it is precipitated by the same reagents as albumin, but it does not become coagulated when heated. There is a marked difference between the action of oxygen upon albumin and fibrin. Scherer found that when freshly-drawn serum, or white of egg, is exposed to the action of oxygen gas, confined over mercury, scarcely any absorption of the gas occurs, and little or no carbonic anhydride is evolved; coagulated fibrin, on the other hand, when exposed in a moist state to the air, gradually absorbs oxygen, and emits carbonic anhydride, and in a few days becomes putrid. By long boiling in water it is gradually dissolved, and becomes oxidized. Albumin is similarly altered. Analysis appears to prove that fibrin is a body which is more highly oxidized than albumin (see Table, p. 798); and coagulated fibrin, as it exists in muscle, is also more fully oxidized than that which separates from the blood on standing. Lehmann's view, that blood-fibrin is a state of transition between albuminous matter and the animal tissues, is thus rendered highly probable. Fibrin appears also, from the

analysis of Dumas and others, to contain about 1 per cent. more of nitrogen than albumin.

(1656) *Varieties of Fibrin*.—The observations of Liebig on the different forms of fibrin are interesting. He finds that moist *blood-fibrin*, if left under water in a warm place in a vessel loosely covered, putrefies, and gradually becomes dissolved; in one of his experiments, after the fibrin had been macerating for a fortnight, a liquid was obtained which coagulated when heated and presented many of the characters of a solution of albumin. The solution likewise contained leucine, and acetic and valeric acids, besides some other acid substances, which have been but incompletely examined. Sulphide of ammonium was also formed. If the water in which the fibrin is digested be previously mixed with one-tenth of its bulk of hydrochloric acid, blood-fibrin swells up slowly into a gelatinous mass, which, on the addition of a stronger acid, shrinks to nearly its original volume, and again swells up when put into water, but it does not form a true solution.

The *fibrin of muscle*, on the contrary, after it has been well washed and pressed, to free it from soluble matters, is dissolved more or less completely by dilute hydrochloric acid (1 part in 1000). If the acid contained in this solution be exactly neutralized by an alkali, a coagulum occurs which is readily dissolved by an excess of alkali, or even by lime water; this latter solution becomes coagulated, on boiling, like white of egg. On the addition of ammonia to the solution of fibrin in hydrochloric acid, the muscle fibrin is precipitated, forming *syntonin*, and may be purified by successive washings in water, alcohol, and ether. Syntonin is distinguished from myosin by its insolubility in a solution of sodic chloride. The muscle of different animals varies in insolubility in dilute acid; that of the fowl and of beef was found to be almost wholly soluble, that of mutton was less so, whilst in the muscular fibrin of veal the insoluble portion amounted to nearly one-half; this residue contained the fat and the vascular portions, besides a quantity of fibrin which resembled blood-fibrin in characters. The soluble portion was found to contain less nitrogen than the blood-fibrin. When fibrin is treated with acetic acid, and viewed by the microscope, it is found to consist of two portions, one of which is granular, and soluble in acetic acid, while the other is fibrous and insoluble. The proportion of these two components differs widely in different specimens. The ultimate composition of these two constituents appears to be very nearly the same.

The portion of the gluten of wheat flour which is insoluble in hot alcohol and in ether is regarded by Liebig and by Dumas as

coagulated fibrin. It is soluble in very dilute hydrochloric acid, like the fibrin of muscle.

(1657) CASEIN is found abundantly in milk, of which it constitutes nearly 3 per cent. Its solutions do not become coagulated by boiling; they, however, present a reaction nearly as characteristic: the hot liquid absorbs oxygen gradually, and in consequence, a pellicle, which is insoluble in water, is slowly formed upon the surface.

Preparation.—Casein, in the *soluble* form, as found in milk, appears to owe its solubility to the presence of a certain proportion of free alkali. It has not been obtained free from salts. If skimmed milk be evaporated to dryness at a gentle heat, and then digested with ether to remove the fat, on treating the residue with water, the lactose and a portion of the casein are redissolved, and, on the addition of alcohol, a considerable portion of the lactose is separated. The alcoholic liquid contains casein, still contaminated with lactose and with salts.

Casein may be obtained in the *coagulated* form nearly pure by the following process:—Skimmed milk is to be curdled with dilute sulphuric acid. The curd, after being well washed with water, is to be dissolved in sodic carbonate, and suffered to stand undisturbed for twenty-four hours or more, to allow the oil to rise to the surface; this is to be skimmed off, and the casein again precipitated by an acid, and well washed; after repeating this operation a second time, the coagulum is to be digested in alcohol and in ether, and again dried; but it cannot be perfectly freed from the saline matters, which adhere to it with great tenacity.

Casein may also be obtained by coagulating skimmed milk by means of hydrochloric acid, and washing the curd first with water, then with water acidulated with 2 or 3 per cent. of hydrochloric acid, and finally with pure water; a glutinous mass is thus obtained, which is slowly dissolved by digestion at 110° ($43^{\circ}.3$ C.) in a large quantity of water. The solution, after being filtered, is precipitated by the cautious addition of ammoniac carbonate, the coagulum is washed with water, and then digested successively with alcohol and ether.

Properties.—Casein in solution is immediately coagulated by acids. An excess of acetic or of oxalic acid dissolves the coagulum, but it is reprecipitated from its acetic solution on the addition of one of the mineral acids. According to Bouchardat, water, containing 1-2000th of its weight of hydrochloric acid, forms with casein a colourless solution, which produces left-

handed rotation of a ray of polarized light. If these acid solutions be evaporated at a high temperature, a pellicle of insoluble casein is formed over their surface. Mulder considers that when the mineral acids are employed to coagulate casein, they form definite compounds with it; the acid may, however, be entirely removed by washing. With strong nitric, sulphuric and hydrochloric acids, casein produces the same reactions as albumin; and its acetic solution gives a similar precipitate with potassic ferrocyanide. Soluble casein is sparingly dissolved by cold alcohol, but more freely by hot alcohol. The stronger acids produce no precipitate in this alcoholic solution, which, however, is immediately coagulated by infusion of galls. The solubility of casein in water is not destroyed by the action of alcohol, for the residue obtained on evaporating both the aqueous and the alcoholic solutions to dryness may be redissolved in water.

(1658) *Action of Bases and of Salts.*—Coagulated casein is readily dissolved by solutions of the alkalies, and of the alkaline carbonates; and if the solution be very feebly alkaline, the alkaline reaction may be completely neutralized by the casein. Solutions of common salt, of potassic nitrate, and of sal ammoniac, likewise dissolve casein with facility, and these solutions, when evaporated by the aid of heat, become covered with an insoluble pellicle. Casein also unites with the alkaline earths and forms compounds which are insoluble in water. If a piece of poor cheese, which consists principally of casein, be reduced to a paste with water, and mixed with slaked lime, it produces a tenacious lute, which sets very hard, and may be used for cementing pieces of broken earthenware. In consequence of the tendency to the formation of these insoluble compounds, a solution of casein is precipitated by salts of calcium or by magnesian sulphate, upon the application of heat to the mixture; this reaction is very characteristic of casein. Most of the metallic salts, such, for instance, as the neutral and basic acetates of lead, cupric sulphate, mercurous nitrate, and corrosive sublimate, occasion precipitates in the cold with solutions of casein.

But the most important and remarkable form under which the coagulation of casein occurs is that which is produced by the secretion from the mucous membrane of the stomach. Advantage is taken of this in the manufacture of cheese, which consists essentially of the coagulated casein of milk. The coagulation is effected by means of the substance called *rennet*, the inner membrane of the fourth stomach of the calf, after it has been salted and dried. When milk is maintained for a few hours

at a gentle heat in contact with rennet (or with an infusion of rennet prepared at a low temperature), the casein becomes entirely coagulated, carrying with it the fatty matters which were held in suspension by the milk, and leaving a clear straw-coloured liquid known as *whey*. It was at one time supposed that the rennet acts by converting the sugar of milk into lactic acid, and that the lactic acid is the real agent in effecting the coagulation, but this view is no longer tenable, for it appears that the coagulation occurs equally well with milk which has been purposely rendered slightly alkaline (Selmi, Heintz), and with an aqueous solution of casein; the action of rennet is therefore as yet unexplained. The coagulum, or *curd* thus obtained, when submitted to strong pressure, forms cheese. This curd is dissolved with difficulty by alkaline solutions. New cheese has but little flavour; when kept for some time, the fatty and nitrogenous substances undergo partial decomposition, and furnish ammonia, with valeric and butyric acids, and other compounds which impart pungency to old cheese.

Casein has not been detected with certainty anywhere but in the milk of animals, which contains it in very variable quantity, the amount depending greatly upon the period of lactation at which the milk is examined. Its amount also varies greatly in the milk of different species of animals. In the milk of the human female it has been found to constitute from 31 to 35 parts in 1000; in that of the cow, from 30 to 41; in that of the dog, from 80 to 146, and in that of the ass, from 19 to 23 parts in 1000.

(1659) *Legumin*.—The seeds of most leguminous plants, as well as the sweet and the bitter almond, contain a substance which presents a close analogy in properties with the casein of milk. Liebig indeed considers it to be identical with this substance, but the analysis of Dumas and Cahours indicates a difference in composition between the two bodies. There is, however, some doubt whether the chemists last named operated upon a homogeneous substance.

Legumin is usually extracted from peas or from almonds, by digesting the pulp of the crushed seeds in warm water for two or three hours. The undissolved portion is strained off by means of linen, and the turbid liquid is allowed to deposit the starch which it holds in suspension: it is next filtered and mixed with dilute acetic acid. A white flocculent precipitate is thus formed, which must be collected on a filter and washed. It is then dried, powdered, and digested, first in alcohol and afterwards in ether. In

this form it was analysed by Dumas and Cahours. Rochleder however considers that it was not perfectly pure, since the substance so prepared is not entirely soluble in a cold concentrated solution of potash, which leaves a flocculent matter. The alkaline solution may be decanted from the undissolved flocculi, and again precipitated by the addition of acetic acid. The legumin thus obtained was regarded by Rochleder as pure, and yielded on analysis the same results as were furnished by casein.

According to Dumas and Cahours, legumin is precipitated from its concentrated solutions in pearly flocculi by the addition of acetic acid. It is redissolved by acetic acid in excess, and by many other vegetable acids; it is also soluble in ammonia and in dilute solutions of the alkalies. It is insoluble in boiling water, and in cold alcohol and ether. Cold water dissolves it in considerable quantity, and the liquid, when heated to ebullition, deposits it in flocculi resembling those of coagulated albumin. The aqueous solution of legumin obtained by digesting peas in water is not coagulated by heat, according to Liebig, but on evaporation it forms insoluble pellicles resembling those yielded by solutions of casein. Legumin is associated in the seed with considerable quantities of potassic, calcic, and magnesian phosphates. It is coagulated by rennet like the casein of milk, and the Chinese make a kind of cheese from peas and beans. Dried peas contain about one-fourth of their weight of legumin.

§ II. GELATIGENOUS SUBSTANCES.

(1660) The substances contained in the second group of azotised bodies have hitherto been found only in animals. They contain a smaller amount of carbon and a larger quantity of nitrogen than those of the albuminoid group. The proportion of sulphur is also considerably less. The gelatigenous bodies consist of two principal varieties; viz., those which yield *gelatin*, and those which yield *chondrin*: neither gelatin nor chondrin appears to exist in the soluble form in the animal body, but it is in all cases the result of the prolonged action of boiling water upon the gelatigenous or chondrin-producing tissues.

According to the researches of Mulder, of Scherer, of Fremy, and of other chemists, the composition of gelatin is identical with that of the tissue which yields it by boiling. Chevreul found that a given quantity of tendinous matter when converted into gelatin by boiling it with water was not altered in weight. The following

table exhibits the composition of gelatin, chondrin, and some gelatigenous tissues:—

| Components. | Fremy. | Scherer. | Mulder. | | Scherer. |
|----------------|---------|-------------|----------|-----------|------------|
| | Ossein. | Sclerotica. | Gelatin. | Chondrin. | Cartilage. |
| Carbon . . . | 50·4 | 50·1 | 50·40 | 49·97 | 50·5 |
| Hydrogen . . . | 6·5 | 7·1 | 6·64 | 6·63 | 7·0 |
| Nitrogen . . . | 16·9 | 18·7 | 18·34 | 14·44 | 14·9 |
| Sulphur . . . | } 26·2 | 24·1 | 24·62 | 0·38 | } 27·6 |
| Oxygen . . . | | | | 28·58 | |
| | 100·0 | 100·0 | 100·00 | 100·00 | 100·0 |

The quantity of nitrogen given in Fremy's analysis of ossein is probably too low, for the same chemist found in it upon another occasion as much as 17·86 per cent. of nitrogen. Schlieper has shown that gelatin and the gelatigenous tissues contain a small quantity of sulphur, amounting in isinglass to 0·6 per cent. It will be observed that the composition of chondrin differs from that of gelatin in containing more oxygen and less nitrogen; while the per centage of carbon and of hydrogen is the same in both substances.

(1661) GELATIN is an azotised principle which hitherto has been obtained from animal substances only. Certain structures (the principal of which are the white fibrous tissue, the cellular tissue, the skin, the serous membranes, and the organic constituent of bone), when boiled with water, yield a compound, which if the solution contains more than 1 per cent. of it, causes the liquid to gelatinize on cooling; hence its name of *gelatin*. This substance does not appear to exist in a free state, but is developed by the action of boiling water upon the tissues above mentioned; its solution, when evaporated to dryness, leaves a brownish-yellow transparent mass. *Isinglass* which is prepared from the inner membrane of the floating bladder of sturgeons and other fishes, when boiled with water, furnishes gelatin in a state of considerable purity. *Glue* is a variety of gelatin of inferior quality. *Size*, as prepared from parchment, is another form of gelatin which is met with in commerce.

Gelatin softens and swells up in cold water, but is not dissolved until the liquid is warmed; it is insoluble in alcohol and in ether. It may be precipitated from its aqueous solution by the addition of an excess of alcohol, when it falls in white flocculi, which are nearly free from saline compounds. Its solu-

tion is without taste or smell; it is abundantly precipitated by solutions of corrosive sublimate, and of platinic chloride, as well as by the infusion of galls. The compound which gelatin forms with tannic acid is the basis of leather; it is of a buff colour, and is formed even in very dilute solutions. Albumin is also precipitated by the same solutions, but gelatin may be distinguished from albumin, since it is not rendered turbid as albumin is by the addition of potassic ferrocyanide to its solution in acetic acid. Salts of aluminum, of lead, of copper, and of iron, do not produce any precipitates in a solution of gelatin; but if a solution of potash be added to the mixture of gelatin with alum, or with ferric sulphate, the basic aluminic or ferric sulphate which is formed carries down a large proportion of gelatin. In a dissolved condition gelatin soon becomes acid on exposure to air, and then loses its gelatinous character. Gelatin is capable of dissolving a considerable quantity of calcic phosphate. By the frequent boiling of its aqueous solution, gelatin is converted into an isomeric compound which does not possess the faculty of gelatinizing as the liquid cools. Chlorine precipitates gelatin completely, forming with it a peculiar white elastic compound which appears to consist of gelatin in combination with hypochlorous acid; this compound when treated with ammonia yields nitrogen, ammonia hydrochlorate, and unchanged gelatin. Solutions of gelatin are not rendered turbid by the addition of acids. Concentrated sulphuric acid dissolves gelatin without change of colour, and gradually converts it into glycocine, leucine, and some other bodies. Gerhardt found that when isinglass was boiled for some days with dilute sulphuric acid, ammoniac sulphate was formed, and a considerable quantity of a saccharine body which was susceptible of the alcoholic fermentation. Nitric acid produces oxalic acid from it amongst other substances.

A solution of gelatin to which the alkalies have been added in small quantity loses its faculty of gelatinizing, but the liquid on being neutralized gives no protein. Gelatin is decomposed by strong alkaline solutions; at a boiling temperature ammonia is evolved, and leucine and glycocine are among the products.

(1662) CHONDRIN (from *χόνδρος*, cartilage) differs from gelatin in composition: it is also coagulated by the vegetable acids, such as acetic acid, as well as by alum, and by the normal and the basic acetates of lead, none of which yield precipitates with gelatin. Most of these precipitates are soluble in an excess of the precipitant.

Chondrin is obtained by boiling the cornea of the eye, or any of the permanent cartilages, with water for some hours; it may also be obtained from the temporary cartilages prior to ossification. Its solution gelatinizes on cooling. It is remarkable that when a permanent cartilage becomes ossified, it yields not chondrin but gelatin by boiling with water. Recent researches appear to show that by oxidation chondrin becomes converted into gelatin.

Preparation of Glue and Size.

(1663) The preparation of gelatin on a large scale gives rise to a branch of industry of considerable importance, viz., the manufacture of glue and size.

The strongest glue is obtained from the parings of ox-hides, and from the ears and refuse trimmings of thick hides in general, which yield from 45 to 50 per cent. of glue. These clippings are first steeped for some days in lime water, to remove the hair, the blood, and other impurities; they are then washed in cold water, and are placed to drain upon a sloping pavement, in layers of two or three inches thick, and are turned over once or twice a day; the quicklime thus absorbs carbonic acid from the air, and becomes converted into chalk; so that the injurious effects of lime at a boiling heat upon the gelatin are prevented. The washed clippings are next introduced into a copper which is filled to two-thirds of its capacity with rain water, and furnished with a perforated false bottom; frequently the animal matters are put first of all into a coarse rope cloth, and the whole is placed in the cauldron, a precaution which prevents the portions of skin, when they begin to gelatinize, from adhering to the bottom and sides of the boiler, and so becoming burned; fresh portions of clippings are added as the animal matters gradually sink down into the liquid which is kept gently boiling. A still better method consists in boiling the liquid by the injection of steam under moderate pressure, by which means the direct application of fire to the boiler is avoided. As soon as a portion of the liquid sets into a firm jelly on cooling, the fire is checked, and the solution is allowed to run into a deep vessel or *settling-back*, where it is kept warm for some hours to allow the impurities to subside. The undissolved matters contained in the cloth are again boiled with water, and yield an inferior description of glue; if boiled a third time they give a still weaker gelatinous product or size; the refuse, after this treatment, may still be advantageously applied as manure.

From the settling-back, the solution is transferred to long

wooden boxes or coolers, in which it gelatinizes; when sufficiently solid it is removed, cut into blocks, and each block is split by a wire frame into slices. The slices of moist glue are then laid upon nets placed in a wooden frame, and are so arranged in lofts as to allow free circulation of air. These cakes of glue are turned over two or three times daily, and the marks which are seen upon the glue exposed for sale are those left by the threads of the nets. This operation of drying is the most delicate part of the manufacture, since at this stage much of the success of the operation depends upon the state of the weather. A sudden rise of temperature might liquefy the whole; the occurrence of a fog might render it mouldy, or a frost might split all the cakes into fragments. Spring and autumn are found to be the most favourable seasons for the manufacture of glue. After the drying has proceeded to a certain extent in the open air, the process may advantageously be shortened by the use of artificial heat from a stove.

When glue is properly made, it should be of a pale brown colour, hard, brittle, and should break with a smooth, glassy fracture. Cold water does not dissolve glue, but merely softens it, and causes it to swell up.

Size is a less tenacious kind of glue, and is chiefly made from parings of parchment, and of the thinner kind of skins. It is almost entirely used in the gelatinous condition, so that the precarious process of drying is dispensed with. Much of the gelatin at present sold in fine shreds for use in confectionery is obtained from clippings of hides, which are boiled with water till they form a very liquid size, which is allowed to become clear by standing, and is then dried in very thin sheets, and afterwards cut up into shreds.

Gelatin is also extracted from bones, which are first crushed and then digested in strong iron vessels with high pressure steam, at a temperature ranging between 284° and 302° (140° and 150° C.; 1670).

A preparation, known to brewers and wine merchants under the name of *finings*, is employed for clarifying beer or wine from suspended matter. When shreds of gelatin are digested in sour beer or wine, a solution is formed, which when mixed with the liquor to be clarified separates as an insoluble jelly, and this, as it subsides, carries with it mechanically the finely suspended particles; the clear liquor is afterwards drawn off from this sediment.

Preparation of Leather.

(1664) The hides of animals, like the soft parts in general, are prone to putrefaction and decomposition, if kept in a flexible and moist condition, and when allowed to dry, they become too rigid and brittle to allow of their employment for a number of purposes, to which they would otherwise be admirably adapted.

The operations of the tanner have in view the preservation of the hide from decay, and the preparation of a material possessed of the requisite suppleness, tenacity, and power of resisting the action of moisture. These objects are effected by combining the gelatinous tissue of the hide with astringent and mucilaginous matter.

The hides of different animals vary very much in thickness. The hippopotamus is furnished with a hide which is in some parts between one and two inches (from 25 to 50 millimetres) thick, while the leather produced from the skins of the lamb and of the kid does not equal ordinary pasteboard in thickness.

The thicker kinds of leather receive the general name of *hides*: and the strongest parts of these hides, which cover the back of the animal, constitute the *butts*. Ox-hides, the most valuable of which are those imported from the plains of South America, and from the Cape of Good Hope, yield the principal portion of this leather, which is largely consumed for the soles of boots and shoes, for harness, and for articles requiring much strength and durability. The upper-leathers of boots and shoes are chiefly made of calves' and seals' skins; while for book-binding, for aprons, and for ordinary dyed leathers, the leather furnished by sheep-skins constitutes the material principally used.

The skin of most animals is highly elastic; it consists of two portions which are quite distinct in chemical composition; the first is an outer thin superficial layer, the *epidermis*, which dips down and lines the tubes containing the roots of the hair, and which rises in blisters after a scald. The epidermis is composed of a pellicle resembling horny matter in composition; it is stained yellow permanently by the action of concentrated nitric acid: beneath this is the cellular layer, termed the *rete mucosum*, in which the colouring matter resides, but which is now generally regarded as a less compact portion of the epidermis: and below this is the second portion, consisting of the thick sensitive vascular integument, or *dermis*, which constitutes the true skin. When the dermis is boiled with water for some hours, it becomes dissolved, leaving the vascular parts, which can be removed by straining through linen or flannel; the clear liquid is nearly colourless; it gelatinizes on cooling, and consists mainly of gelatin. It gives with tincture of galls the well-known insoluble precipitate by which such solutions are characterized.

Excepting in those cases where it is desired to preserve the hair, as in the different species of furs, the preliminary steps in the preparation of all skins are pretty much the same, whatever the use to which the leather is applied, but greater care is requisite with the thinner kinds. After the hair has been removed, the preservative process according to the nature of the skin to be operated on. Four principal processes are in use for the preparation of leather. They consist of—

1. *Tanning*.—This is employed for the thicker kinds of leather; it is essentially a process for combining the astringent principle of plants with the hide.

2. *Sumaching*.—This operation is similar in its results to tanning, but is less laborious and tedious; it is performed upon the thinner leathers or *skins*, which are often subsequently dyed.

3. *Tawing*.—This process is followed in preparing white and black kid, principally for the glover: in this operation alum and common salt are worked with some oily matter into the skin.

4. *Shamoying*.—This process is used in the preparation of wash-leather. It consists essentially in combining some suitable fatty matter with the texture of the softer part of the hide.

Liming, Unhairing, and Raising the Skin.—In all cases the first thing to be done is to cleanse the skin thoroughly from blood, from the salt used in preserving it, and from other extraneous matters. This is effected, in the case of recent hides, simply by washing, or, in those which have been salted, by soaking them for some days in pits in which the water is occasionally changed. It is frequently found advisable, in order to expedite this cleansing, to place the hides in the fulling-mill, where they are beaten with heavy hammers shod with iron, by which the skin is speedily rendered supple. The ears and projecting useless pieces having been removed, and disposed of to the glue-maker, the hides are generally transferred to pits containing lime-water, with an excess of lime, which gradually dissolves the sheath of the hairs, and combines with the fat; here they remain for three weeks or a month, and are transferred gradually from pits containing a weak lime-water to those in which the proportion of lime is much more considerable. In some of the French tanneries a weak solution of caustic soda has been substituted for lime-water, with decided advantage; the skin is more rapidly prepared for unhairing, and the excess of caustic soda is afterwards much more readily removed than the excess of lime. Sometimes, instead of plunging the hides into lime-water, they are placed in a warm room till a slight degree of putrefaction commences; during this incipient putrescence ammonia is disengaged, and the hair becomes loosened as readily as when lime is used.

In order to remove the loosened hair, the hides are placed upon a sloping semi-cylindrical table, with a rounded end, termed *the beam*, and upon this, with a two-handled knife, the hide is scraped on the hair side to remove the epidermis and hair. By this operation the upper surface of the cuticle marked by the insertions of the hair is exposed; it is of a denser structure than the layers of cuticle below, and it forms what is called the *grain* of the skin; great care is taken not to injure this grain as such injury impairs the quality of the leather, and much reduces its value. The hair having been removed, the hide is once

more rinsed, and scraped upon the beam on the flesh side, to remove any irregularities and adhering loose cellular tissue.

The cleansed hide is then immersed for twelve hours in a bath of weak sulphuric acid and water (1 part of acid and 1000 of water), which *raises* the skin, that is to say, makes it swell, opens its pores, removes adhering lime, and fits it for the actual operation of tanning. Care must be taken to avoid an excess of sulphuric acid, as it is liable to injure the texture of the hide. The removal of lime from the skin is a process of great importance, since, owing to the circumstance of the astringent matter being of an acid character, it would combine with the lime, instead of with the gelatin, and would form a harsh, insoluble compound within the pores of the skin, which would impair the suppleness of the leather.

(1665) 1. *Tanning*.—Up to this point the preparation of the skin is very similar for each kind of leather; when the operation of tanning is to be performed, it is conducted in the manner now to be described.

The process of tanning is a very slow one. A weak infusion of bark, called *ooze*, is first prepared and pumped off into rectangular pits, six or eight feet deep, sunk in the earth, and lined with wooden planking; into these the hides are introduced, one by one, in an extended state. These pits of weak ooze are termed *handlers*, from the circumstance that the hides are for some weeks daily transferred from one pit to another, into oozes of gradually increasing strength: in about six weeks they are ready for the pits termed *layers*. In these pits the partially-tanned hides are placed, each hide being separated from the one above and the one below it by a layer of coarsely-ground oak bark; the pits are then filled up with water. Here the hides remain for about three months, and are afterwards transferred to another pit, and similarly treated; but the hides which before were uppermost, and consequently in the weakest part of the infusion, now are undermost, and in the strongest part. Sometimes the hides require to be passed a third time through the layers. At the end of this time, the skin, if of the thickness of a good ox-hide, will be completely tanned, as may be known by cutting it across with a knife, when the surface of the section will exhibit a uniform brown colour: a white line in the centre shows that this part is imperfectly tanned. About 300lb. of oak bark are required to tan 100lb. of fresh skin: they yield about 150lb. of leather.

From the tanpits the hides are removed to the drying-loft, where they are, in dry weather, exposed to a free current of air, assisted, when the weather is cold or damp, by heat, furnished by steam-pipes. When the leather is sufficiently dry, it is beaten upon a kind of horse, or cylindrical beam, and is subsequently rolled with a brass roller, loaded with a weight of from 10 to 20 cwt.

Many attempts have been made to shorten this tedious process; for example, either by the employment of stronger oozes at first, or by the operation of sewing up the hide, filling it with the tanning infusion, and allowing the liquid to force its own way through the pores of the hide, aided by the influence of gravitation; or by passing the hides between rollers, as they come out of the spent ooze, and then allowing them to be transferred to stronger ooze; but it has been generally found that the leather so prepared is harsher and less durable than that obtained in the old way. This is found to be the case especially in thick hides: the surface gets tanned hard in the strong ooze; the inner portions are by this means protected from the tanning action, and their complete conversion into leather, which is so desirable, is prevented. Moreover, it is found that it is useful that a certain portion of the gummy and mucilaginous matter contained in the bark should be absorbed by the hide; it increases the suppleness of the leather, and therefore renders it more durable: by the process of quick tanning, the quantity of mucilaginous matter which the hide takes up is materially and injuriously reduced.

Currying.—The thinner skins, such as are used for the upper-leather of boots and shoes, as well as the thicker kinds employed in the manufacture of hose, in some parts of harness, &c., have to undergo the further process of currying, the object of which is, by impregnating them with oil, to render them less pervious to water, and make them more supple and pliable, as well as to give them that gloss and finish which, in many cases, is considered essential. In currying, the leather (a calf-skin, for example) is thoroughly soaked in water, and shaved while wet with a peculiar two-handed knife, upon a smooth, heavy, flat beam, faced with lignum vitæ and placed nearly vertically, the object of this operation being to equalize the thickness of the skin in its different parts. The skin is then thrown into water and worked while moist upon a flat stone table with the flesh side downwards. It is thus uniformly thinned out and stretched. Here it is next *stuffed* or *dubbed*, that is to say, it is thoroughly impregnated with a mixture of coarse fish-oil and tallow, after which it is hung up in a loft to dry and allow the oil completely to penetrate the leather and take the place of the water.

When dry, the skin is rendered supple and is 'grained' by rubbing it with a grooved ball of boxwood, first on the flesh side, after folding the grain side inwards; the operation is then repeated on the grain side. In this state, after another scraping on the flesh side, or *whitening*, it is ready to be stored away. Previous to sale, however, another process, technically termed *waxing*, is performed. This consists merely in rubbing in upon the flesh side a mixture of lampblack and oil with a hard brush. A coat of tallow and size is then rubbed over this with a sponge; it is polished with a ball of glass, and a final coat of thin size completes the operations of the currier. For ladies' shoes the skin is blackened on the grain side, which is easily effected by rubbing it over with a solution of ferrous sulphate; the astringent matter of the leather immediately strikes a deep inky black with the iron salt; a weak alkaline liquid is brushed over the whole, the skin is allowed to dry, it is then grained, and finished off with a coat of oil and tallow.

Stenhouse finds that when shreds of thin leather, such as the upper-leather of shoes, are digested, under a pressure of two atmospheres, in a Papin's digester, with lime and a considerable quantity of water, the leather is almost entirely decomposed, the tannic acid combines with the lime, forming an insoluble compound, and a glue is obtained on evaporating the solution, amounting on the average to 25 per cent. of the leather employed. Thick sole-leather does not yield glue or gelatin when similarly treated. Analysis did not indicate any considerable difference in the composition of these different leathers. Even thin leathers, if kept for several years, lose the power of furnishing gelatin when decomposed by the foregoing method of treatment.

(1666) 2. *Morocco Leather.*—The thin kinds of leather which are dyed and used for ornamental purposes, as for coach-linings, chair-covers, book-binding, &c., are tanned differently, but much more expeditiously than hides. The finest kind of this leather is made from the skin of the Barbary goat, and hence the term *Morocco leather* as commonly applied to it. In the preparation of these skins the wool or hair is removed in the usual way, and the lime is then worked out by a process termed *abating*. In this operation the skins are put into a weak solution of an ammoniacal salt (dogs' dung being the material preferred); the lime forms a soluble compound with the acid of the salt, setting ammonia at

liberty; this softens the skin, and at length renders it so porous that when a portion of air is included in a fold of the skin, the air may be squeezed through it. The skin is next cleansed on the beam, and is sewed up in the form of a bag, the grain side outwards, and is ready for the *sumaching*, or tanning, which is accomplished in about twenty-four hours. A weak and warm solution of sumach is prepared in a large tub; a portion of sumach leaves and of a stronger infusion is poured into the bag formed by sewing up the skin, and this, when distended with air, is tied up and thrown into the vat, where the floating bags are kept in constant motion for some hours; after which they are piled up on a sloping shelf on the side of the vat, where, by mutual pressure, a portion of the tanning solution is forced through the pores of the skin. The operation is repeated with a stronger infusion of sumach; after which, the skins are cut open, washed, dried, and subsequently dyed. In the operation of dyeing, the flesh sides of two of the moistened skins are placed in contact, and are made to adhere by striking them out and scraping them on a flat table, and the dye-stuff is then applied to each skin in succession, by which means it is limited to the grain side. A *light blue* colour may be given to the skin by the use of a mixture of potassic ferrocyanide and nitrate of iron; a *green* by a combination of the barberry with indigo; a *maroon* by a mixture of archil and ammonia with indigo; a *scarlet* by the action of cochineal, alum, and potassic carbonate; and a rich *purple*, known as *royal purple*, by means of indigo faced with cochineal. Red morocco is usually dyed before it is tanned with sumach.

(1667) 3. *Tawing*.—The thin and delicate skins which are employed in the manufacture of 'kid gloves' are subjected to a different and more careful process than that above described: they are first washed to free them from blood, and from the salt employed to preserve them from putrefaction, and are then anointed on the flesh side with cream of lime, and left for a few days; after which they are washed, and the hair is plucked off. They are then soaked in lime-water for a fortnight or three weeks, at the expiration of which time they are carefully smoothed with a whetstone upon a bean. The lime is next removed by soaking the skins in a mixture of bran and water which has been allowed to become sour; the lactic acid which it contains forms a soluble salt with the lime, and at the same time swells the skin and opens its pores, reducing it to the form of a thin, white, extensible membrane, technically termed a *pelt*. In this condition it is ready for the operation of tawing, or passing through the *white bath*. Tawing, in fact, consists in preparing the skin with a solution of aluminic chloride, and subsequently working in a quantity of oily and farinaceous matter.

This white bath is composed of a mixture of alum and common salt, dissolved in water in the proportion of 12 gallons of water to every 100 skins, and from 12 to 18lb. of alum and 2½ to 3lb. of salt: after the skins have been introduced into the mixture the temperature is gradually raised nearly to boiling. When the skins have been soaked for some time in the bath, they are thoroughly kneaded together by placing them in a revolving drum, by which means the liquor is well incorporated with them. They are next washed, first with water, then with a mixture of bran and water, and are dried, after which they are worked with the *paste*. In preparing this paste, about 3 gallons of the alum liquor are mixed with 13 or 14lb. of wheat flour and the yolks of 50 eggs, and in this bath the skins are worked separately, and allowed to remain for 24 hours: at the end of that time they are kneaded together by the action of the revolving drum; they are again dried; they are next dipped in water for a few minutes, and *staked* or stretched, and are worked upon the board with a softening iron, by which means they are greatly extended in all directions; after which they are stretched upon frames to prevent them from shrinking during the dry-

ing. When dry they are tinted, if necessary, with a mixture of whitening and ochre, and are finally polished and ironed.

(1668) 4. *Shamoying*.—The operation of shamoying (so called from its having been applied to the skin of the *chamois*) consists in working into the skin a quantity of oil, which supplies the place of the vegetable astringent, or of the aluminic chloride, in the processes of tanning and tawing. In preparing the skin for shamoying, the operations of unhairing, and of raising, are the same as in ordinary tanning. A large proportion of shamoyed leather forms what is known as *wash-leather*. This is made from sheep-skins, which are split for the purpose by means of a machine contrived with this view: the grain side of the skin is used in the preparation of hat-linings, and for other purposes where but little tenacity is requisite, while the flesh side is converted into wash-leather. After the skins have been soaked in bran and water, they are spread out upon a table, and lightly sprinkled with oil; they are then folded into balls, each containing four skins, and are beaten for two or three hours in the fulling stocks, with heavy wooden hammers faced with copper; after this they are opened out, again sprinkled with oil, and a second time passed through the fulling stocks, until they cease to appear greasy. They are next hung up in a warm room, where the oil absorbs oxygen; and this oiling and airing is repeated two or three times: the skins are then scraped, and seoured with a weak alkaline ley, which saponifies the excess of the oil. Afterwards they are washed with water, dried at a gentle heat, and then smoothed and rolled. The thicker leather, known as *buckskin*, is prepared in a similar manner, but the skin used is not split, the grain being removed by means of a knife, which raises a sort of nap upon the surface, but does not cut the leather, whilst it confers upon the skin the desired softness and extensibility.

CHAPTER XII.

CHEMICAL PROPERTIES OF SOME OF THE SOLIDS AND FLUIDS OF ANIMAL ORIGIN.

§ I. *Solid Constituents of Animals.*

(1669) THE solid constituents of the animal body differ very materially from those of vegetables. The bony framework of the animal system contains a large proportion of inorganic insoluble salts; and the different tissues, into the composition of most of which nitrogen enters, vary widely from each other in chemical properties. It must not, however, be supposed that any organ of the body consists of any chemical compound in a state even approaching to purity. The complex structure of these organs, consisting as they do of vascular, nervous, and cellular components, independently of the peculiar and proper substance of the organ itself, forbids the possibility of any such simple character in its chemical constitution, although one or two proximate principles may give to it the distinctive features which it offers to the chemist.

The bones, the ligaments, the muscles, and the nerves thus exhibit unmistakable differences in chemical properties, owing to the predominance in each of certain proximate animal principles.

It will be useful to consider briefly the chief chemical characteristics of some of the most extensively diffused of these tissues.

(1670) *The Bones* present the same general properties throughout the higher classes of vertebrate animals. When dried at 212° till they cease to lose weight, they are found to consist of about one-third of their weight of organic matter; the remaining two-thirds being composed principally of calcic phosphate and carbonate, and magnesian phosphate. These facts may be readily verified:—If a bone, freed from fat and periosteum, be suspended in a vessel containing hydrochloric acid diluted with 6 or 8 parts of water, an effervescence will be seen to occur over the whole surface of the bone, owing to the decomposition of the calcic carbonate; in the course of three or four days the salts will have been dissolved out, and the remainder, which still retains the shape of the bone, will be found, after soaking in distilled water repeatedly renewed, to consist of the animal matter or *ossein* only. Its rigidity will have disappeared, and it will have become perfectly flexible; but if it be dried, it will assume a semi-transparent appearance, resembling that of horn. When boiled for a few hours in water, it will be gradually dissolved, with the exception of a little fat and a few vascular and fibrous shreds, and the solution will gelatinize on cooling, forming a weak glue or size. The solution thus obtained is indeed nearly pure gelatin, and, like this substance, is precipitated copiously by tannic acid and by infusion of galls (1661).

The acid solution when neutralized by ammonia deposits the earthy phosphates, which may be separated by filtration; and on adding to the clear liquid a solution of ammoniac oxalate, the calcium which was contained as carbonate in the bone is precipitated as calcic oxalate.

Bones may be boiled for many hours in water without undergoing any further change than the separation of a quantity of grease, which rises to the surface of the liquid; but if placed with water in a Papin's digester and exposed to a temperature of about 302° (150° C.), the gelatin is dissolved, and the earthy matters are left, and subside in a disintegrated form.

When bones are distilled in closed vessels at a gradually increasing temperature, a large quantity of fœtid, volatile, and tarry matters pass over, accompanied by a considerable proportion of ammoniac carbonate, and some other volatile alkalies formed on

the type of ammonia. The residue in the retort constitutes animal charcoal, and contains the calcic phosphate with a quantity of carbon diffused through it in a very finely divided state. The saline components of the bone may be obtained in an isolated form by calcining bones for some hours in an open fire, when a white ash is left. The composition of bones differs slightly at different ages, and even in different parts of the body of the same animal. The *Teeth* are similar in composition to the bones, but the portion which projects over the gums is eneased with a compact hard crust, known as the *enamel*, and which contains but a very small proportion of animal matter:—

Composition of Bones and Teeth in 100 parts.

| Constituents. | Heintz. | | | Berzelius. | |
|--------------------------|------------|--------|---------------|--------------|---------|
| | Ox. Femur. | Sheep. | Man. Forearm. | Human Tooth. | Enamel. |
| Animal matter | 30·58 | 26·54 | 31·11 | 28·0 | 2·0 |
| Calcic phosphate | 57·67 | 61·99 | 59·14 | } 64·3 | 88·5 |
| Calcic fluoride | 2·69 | 2·79 | 2·23 | | |
| Calcic carbonate | 6·99 | 6·92 | 6·32 | 5·3 | 8·0 |
| Magnetic phosphate . . . | 2·07 | 1·58 | 1·20 | 1·0 | 1·5 |
| Other salts | | | | 1·4 | |

The bones of fishes contain a smaller proportion of calcic phosphate than is found in those of the higher orders of vertebrata. The scales of fishes have a composition somewhat similar to that of bone, but they contain calcic phosphate in small quantity only.

The proportion of earthy matter in the bones in the human species is occasionally deficient in certain forms of disease. In one instance of what the Germans call *cranio-tabes* in children, Schlossberger found the earthy salts to fall in the spongy portion of the bone as low as 28·16 per cent. of the dry bone, and in several cases the proportion of earthy matter was as low as 50 per cent.; similar facts have been noticed by other observers. Numerous analyses of the bones of different parts of the human body, in various conditions of health and of disease, and at different periods of life, have been executed by Von Bibra, who has published a special work on the subject (*Chemische Untersuchungen über die Knochen und Zähne*); and an elaborate paper by Fremy, upon the hard parts of animals, is contained in the *Annales de Chimie*, III. xliii. 47; many other writers might also be quoted. For fuller information on this subject, and on the chemical composition of the various tissues of the animal body generally, the reader is referred to Lehmann's treatise on *Physiological Chemistry*,

a translation of which has been executed for the Cavendish Society by Dr. G. E. Day.

The organic matter contained in the envelope of the *Crustacea* consists of a substance termed *chitin*, which, according to Fremy, contains no nitrogen; both Schmidt and Lehmann, however, find nitrogen in this substance (1672). The animal component of the shells of the *Mollusca* contains nitrogen, and has been termed by Fremy *conchiolin*; it is distinct from albumin, and resembles ossein in composition, but when boiled does not furnish gelatin. The hard covering of the *Crustacea*, and the shells of the *Mollusca* and of the eggs of birds, contain but a very small proportion of calcic phosphate, the principal earthy component in these cases consisting of calcic carbonate. The subjoined analyses show the centesimal composition of some of these substances:—

| Constituents. | Prout. | Bucholz. | Chevreul. | |
|-------------------------------|---------------------|----------------|----------------|------------------|
| | Shell of hens' egg. | Oyster shells. | Shell of crab. | Scales of perch. |
| Animal matter | 2·0 | 0·5 | 28·6 | 57·4 |
| Calcic phosphate | 1·0 | 1·2 | 6·0 | 37·8 |
| Calcic carbonate | 97·0 | 98·3 | 62·8 | 3·0 |
| Magnesian phosphate | | | 1·0 | 0·9 |
| Other salts | | | 1·6 | 0·9 |

(1671) *Horny Matter*, or *keratin* (from κέρας, horn).—The composition of buck-horn and of ivory much resembles that of bone; but horny matter in general, whether in the shape of cow-horn, tortoise-shell, whale-bone, the claws of beasts of prey, or the nails of the fingers and toes, the scales of fishes, the feathers of birds, or the wool and hair of animals generally, is of a different composition; it contains but little saline matter, not exceeding 2 or 3 per cent., and does not furnish gelatin when boiled with water at high temperatures under pressure. It becomes soft on the application of heat, a circumstance which is turned to account in the manufacture of common articles in horn, so that they can thus be moulded in some measure to the desired form. Horn is gradually and with difficulty dissolved by alkaline solutions, to which it yields up a portion of sulphur; and on neutralizing the solution with an acid, a precipitate is formed which resembles that obtained from the albuminoid compounds: this precipitate, however, presents properties which are slightly different according to the nature of the source from which it is derived. Horny tissues are gradually dissolved by boiling with concentrated acetic acid. By prolonged digestion with dilute sulphuric acid, 1 of acid to 4 of water, they are decomposed, and furnish leucine and a considerable proportion of tyrosine (1618). If horny tissue be fused with caustic potash it is decomposed, evolving between 4 and 5 per cent. of amyliæ. Horny matter is intermediate in composition

between the albuminoid and gelatigenous components of the body. It contains less carbon and more nitrogen and sulphur than the albuminoid compounds. The following table gives the composition of some of the different varieties of these bodies.

Scherer's analyses (*Liebig's Annal.*, xl. 54) are calculated with the old equivalent of carbon, 6·115.

| Constituents. | Scherer. | | | | Fremy. | |
|-----------------|----------------------|------------------|-------|---------|------------------|-----------------|
| | Epidermis (foot.) | Hair (human). | Wool. | Quills. | Turtle shell. | Whale- bone. |
| Carbon . . . | 51·04 | 50·62 | 50·65 | 52·42 | 53·6 | 50·8 |
| Hydrogen . . | 6·80 | 6·61 | 7·03 | 7·21 | 7·3 | 7·4 |
| Nitrogen . . . | 17·22 | 17·93 | 17·71 | 17·90 | 16·4 | 16·5 |
| Sulphur . . . | } 24·94 | 24·84 | 24·61 | 22·47 | 2·0 | } 25·3 |
| Oxygen, &c. . . | | | | | 20·7 | |

| Constituents. | Mulder. | | | | Croockewit. | Schmidt. |
|-----------------|-------------------|----------------|------------------|--------------------|-------------|----------|
| | Nails (human). | Horn (cow). | Hoof (horse). | Sericin (silk). | Sponge. | Chitin. |
| Carbon . . . | 50·3 | 50·0 | 50·4 | 48·61 | 46·51 | 46·64 |
| Hydrogen . . . | 6·9 | 6·8 | 7·0 | 6·50 | 6·31 | 6·60 |
| Nitrogen . . . | 17·3 | 16·3 | 16·7 | 17·34 | 16·15 | 6·56 |
| Sulphur . . . | 3·2 | 3·4 | 3·0 | } 27·55 | 0·50 | } 40·20 |
| Oxygen, &c. . . | 22·3 | 23·5 | 22·9 | | 30·53 | |

From the foregoing table it will be seen that horny matter differs but little from gelatin in ultimate composition; though in its reactions it more closely resembles the albuminoid group. Horny tissue is stained yellow by nitric acid. The quantity of sulphur in the hair is very considerable, and has been found to average from 3 to 5 per cent., though in some specimens of red hair Von Bibra found it to amount even to 8 per cent. The cause of the variety of the colour of the hair appears to be due to the variations in colour of the animal oil with which it is impregnated. The tint of the hair may be altered readily by steeping it in a solution of chlorine, as well as by moistening it with various nostrums which act upon the sulphur contained in the hair (897). The inorganic constituents of the feathers of birds vary in quantity in the different species from 1 to 6 or 7 per cent. (Gornp-Besanez.) Silica is always present, and in the largest quantity in the feathers of granivorous birds, in which it forms on the average four-tenths of the entire earthy material. Silica is also found in the ashes of hair when burnt. In human hair the ash amounts to from 0·92 to 1·57 per cent.: and of this the silica constitutes nearly

one-seventh. The hair and wool of animals contain in general rather more ash than human hair.

Silk.—This substance appears to consist of two distinct azotised components, one of which, *silk-gelatin*, is soluble in water, and, according to Cramer, amounts to about one-third of the weight of the silk; this gelatinoid body may be represented by the formula $C_{30}H_{50}N_{10}O_{16}$ according to the analyses of Stædeler and of Cramer, while the inner layer of *sericin* (from *sericum*, silk) contains 4 atoms of hydrogen and 4 of oxygen less, or $C_{30}H_{46}N_{10}O_{12}$. The colour of the silk is due to a small quantity of oily matter. Gossamer threads also contain sericin. Sericin is a white silky-looking substance which is left after successive exhaustion of the silk by water, alcohol, ether, and boiling acetic acid, or simply by boiling the silk in water under pressure. It is insoluble in cold dilute alkaline solutions, but soluble in concentrated sulphuric and hydrochloric acids, and in an ammoniacal solution of oxide of nickel.

The organic constituent of the *common sponge*, according to Mulder, consists of *fibroin*, but it contains 1·9 per cent. of phosphorus, and 1·08 of iodine. It is closely analogous to sericin, but is insoluble in ammoniuret of nickel. When boiled with dilute sulphuric acid, glycocine and leucine are amongst the products.

(1672) *Chitin* ($C_{12}H_{23}N_2O_{11}$ P Schmidt).—The substance mentioned as *chitin* (from $\chi\tau\acute{\omega}\nu$, a mantle) in the foregoing table, constitutes the true skeleton of insects generally. It may be obtained by boiling the outer wing-cases of the cockchafer in water, alcohol, ether, acetic acid, and solution of potash in succession. Pure chitin is a white substance, which retains the form of the texture from which it is obtained. It is soluble in concentrated nitric and hydrochloric acids without colouring them, and these solutions, after neutralization with ammonia, yield a precipitate with infusion of galls. Oil of vitriol gradually dissolves it, and slowly lets fall a black precipitate, whilst acetic acid and aminonic acetate remain in solution, and sugar is also found to be present. When distilled it also yields acetic acid and ammoniac acetate; boiling concentrated solution of potash does not affect it. This substance is one of the simplest forms of the nitrogenised plastic materials. It presents some points of analogy with vegetable fibre, particularly in the production of acetic acid by its decomposition.

The compound to which Fremy assigns a composition isomeric with that of cellulose is distinct from chitin. Berthelot calls it *tunicin* (1106), from its entering into the composition of the envelope of some of the tunicate mollusks. It yields, when treated with acids, products similar to those furnished by chitin.

(1673) *Cartilage*.—The articular extremities of the bones are encrusted with a white elastic opaque horny substance which contains but little saline admixture (from 3 to 6 per cent. of salts); by long boiling it is gradually dissolved, and forms a liquid which on cooling furnishes a tremulous jelly. The transparent cornea, the rings of the trachea, the elastic parts of the ears, nose, and eyelids, and the flexible prolongations of the ribs are also composed of the same material; this substance, however, is not true gelatin, but the modification of it termed chondrin (1662).

White fibrous tissue, and the materials of which the tendons, ligaments, and inelastic tendinous expansions are composed, consists of a substance which by continued boiling is almost completely dissolved, and a solution of gelatin is formed, which gelatinizes on cooling. *Yellow fibrous tissue* has a different com-

position: it is insoluble in boiling water, and in weak acids and alkalis, but is readily soluble in hot concentrated sulphuric acid, and in a strong solution of potash. It resists putrefaction for a long time, and possesses great elasticity. Nitric acid forms a yellow compound with it. The yellow fibrous tissue is an advantageous source of leucine when digested with sulphuric acid which has been diluted with $1\frac{1}{2}$ parts of water.

(1674) *Muscular tissue* consists principally of fibrin in a coagulated form (1656), but being highly vascular, and containing nearly three-fourths of its weight of water, it is permeated with a fluid consisting partly of blood and partly of substances secreted from it, independently of a small proportion of nervous and adipose matter. If lean beef be minced fine, and digested in three-fourths of its weight of cold water and then expressed, this treatment being repeated twice, a solution will be obtained which contains in a concentrated form the soluble constituents of the muscular tissue. These consist chiefly of albumin, and the soluble salts of the blood, of the crystallizable animal principles termed kreatine and inosin, of phosphoric acid and at least three organic acids, viz., the lactic, the inosic, and the butyric; possibly also acetic and formic acids are present in small quantity; the colour of the solution is due to the red colouring matter of the blood. The salts consist chiefly of potassic and magnesian phosphates, and a small quantity of sodic chloride, and of calcic phosphate.

When this expressed liquid is heated nearly to the boiling point, the albumin becomes coagulated, carrying with it a large proportion of the colouring matter; this coagulum generally amounts to between 2 and 3 per cent. of the fresh muscle operated on. The juice of flesh, when carefully freed from fat and concentrated by evaporation, is now prepared in large quantities in countries where cattle are abundant, and is sold as *Liebig's extract of meat*.

(1675) *Inosic Acid* ($H_2C_{10}H_{12}N_4O_{11}$? Liebig).—This compound derives its name from *ινός*, 'of fibre.' According to Gregory, it is found only in the flesh of the common fowl and of the turkey. Inosic acid presents the appearance of a syrupy liquid, which is not soluble in alcohol. It has an agreeable taste of the juice of meat, and becomes readily decomposed, mere boiling of the solution producing its partial decomposition.

Inosic acid may be prepared from the mother liquor obtained from the flesh of the common fowl after the separation of the kreatine (1607): alcohol is to be added to this liquid till it becomes milky, when it is set aside to crystallize, and the baric and potassic inosates are slowly deposited; they are dissolved in water, and baric chloride is added to the hot aqueous solution; on cooling, the baric inosate crystallizes; by a second crystallization this salt is obtained in a state of purity,

and the acid may be obtained from it by the cautious addition of sulphuric acid.

The salts which inosic acid forms with the alkalies may be crystallized. When decomposed by heat, they emit an agreeable smell of roast meat. *Potassic inosate* crystallizes in long delicate four-sided prisms, which are sparingly soluble in alcohol. *Baric inosate* crystallizes in scales of a pearly lustre, which effloresce in a dry air; they are sparingly soluble in cold water, but freely so in boiling water, and are insoluble in alcohol. *Cupric inosate* forms a light blue insoluble powder which is not dissolved by acetic acid.

(1676) *Inosin, Inosite, or Muscle Sugar* ($C_6H_{12}O_6, 2H_2O$).—This interesting body was discovered by Scherer in the juice of flesh: but according to Lehmann it is only found in the involuntary muscles, the heart yielding it most readily; it has been found in the urine in Bright's disease (Cloetta), and in the same secretion in diabetes (Hohl). It may be obtained by the following process:—After separating the kreatine by crystallization, the baryta is removed by the cautious addition of sulphuric acid so long as it occasions a precipitate. The liquid is then filtered, and the free lactic acid separated by repeatedly washing with ether. Alcohol is added to separate the salts; and by gradually increasing the quantity of alcohol, small crystals, resembling those of gypsum, are formed; these crystals consist of inosin. They must be redissolved in water, and recrystallized. Inosin has recently been shown by Vohl to be identical with phaseo-mannite, which is obtained from the seed of the common kidney-bean, *Phaseolus vulgaris*.

Inosin forms colourless efflorescent prisms, which at a temperature somewhat below 212° lose nearly 17 per cent. of water ($2H_2O$). The residue has then the composition of grape-sugar which has been dried at 212° . At 410° ($210^\circ C.$), the dry mass melts to a colourless liquid, which, on cooling, quickly sets into a crystalline mass. It has a sweet taste, and is freely soluble in water, less so in rectified spirit, and is insoluble in absolute alcohol and in ether. Dilute acids and alkalies, even when boiled with it, produce no change. Its solution has no rotatory action upon a ray of polarized light. With concentrated nitric acid it yields a nitro-substitution compound [$C_6H_6(NO_2)_6O_6$], and this may be precipitated in oily drops, which crystallize, by the addition of concentrated sulphuric acid. Nitro-inosin is freely soluble in alcohol, but not in water, and explodes when sharply struck. It may be obtained crystallized in colourless rhombohedra. If inosin be evaporated to dryness with nitric acid and the residue treated with ammonia and calcic chloride, evaporated to dryness and gently warmed, a pink coloration is produced, which is considered to be characteristic. A solution of inosin to which caustic

potash has been added dissolves hydrated cupric oxide with a blue colour, but does not reduce it to cupreous oxide when the liquid is boiled. The solution of inosin gives a white precipitate when mixed with one of basic plumbic acetate. Inosin is not susceptible of the vinous fermentation, but with chalk and cheese it yields lactic and butyric acids.

(1677) *Chemical Effects of Cooking upon Food.*—A consideration of the chemical constituents of muscular tissue enables us readily to understand the principal changes produced in the cooking of meat. The common processes of cooking have been very clearly explained by Liebig.

The operation of *roasting* consists in the gradual coagulation of the albumin, as the heat penetrates from the surface towards the interior: those parts which are nearest the centre, unless the roasting be continued for a sufficient length of time, do not become hot enough to allow the albumin to coagulate; hence they appear red, juicy, and *underdone* as it is called; the superficial portions become brown, and partially altered in composition, but the greater part of the sapid and saline constituents of the juices contained in the meat are retained, although a certain proportion exudes, or is evaporated; whilst a part of the fat is melted off, and collects below, as *dripping*.

In *boiling* meat the result is somewhat different: when the flesh is placed in cold water, and the heat is gradually raised, the soluble albumin, the soluble salts, and the flavouring portions of the meat (which are contained entirely in the soluble parts), begin to pass out into the water, and the meat gradually becomes impoverished, while the liquid in which it is boiled gains in a corresponding degree in flavour and nutritive qualities—the meat becoming hard, ragged, fibrous, and tasteless at the surface, owing to the loss of its albuminous cement. When the water boils, the heat gradually penetrates the mass of the flesh, and as soon as it has risen high enough to coagulate the albumin which is still left in the central portions, the joint is said to be cooked through.

In order to preserve the full flavour of the meat during the boiling, it is necessary to make the water boil before introducing the joint to be cooked, and then to maintain it gently simmering until every part of the mass has attained a temperature of from 167° to 185° (75° to 85° C.). By this treatment, the albumin contained in the superficial layer of the meat is suddenly coagulated, and thus offers an obstacle to the free escape of the soluble portions from within; the meat therefore is proportionately richer, whilst the broth suffers to the same extent.

Liebig has introduced an improved method of preparing strong meat tea for invalids, founded upon the foregoing considerations. Lean beef or other meat is minced finely when raw, mixed with an equal weight of cold water, and slowly heated to boiling. After boiling for a minute to coagulate the albumin, the liquid is strained through a cloth, and the fibrous portion exposed to pressure; the broth thus obtained is seasoned with the usual condiments, and furnishes a nutritive soup of excellent flavour, which would gain but little by longer boiling, but it has scarcely any colour.

A still more nutritious broth may be obtained in the following manner:—Take one-third of a pound of raw beef or chicken, mince it very finely, and mix it with 14 ounces of cold distilled water, to which four drops of hydrochloric acid and from 10 to 18 grains of salt have been added; digest for an hour, and strain out the meat upon a hair sieve; wash the residue upon the sieve with 5 ounces of distilled water. In this way about a pint of a cold extract of meat is obtained, which may be taken cold, or if warm, it must not be heated above 122° (50° C.). The whole of the uncoagulated albumin, one of the most nutritive constituents of the meat, is thus extracted and administered to the invalid; whereas, if the broth be boiled, the albumin becomes coagulated, and is skimmed off and wasted.

The undissolved fibrin when washed once or twice becomes hard and insipid, and is difficult of digestion. The dark colour of soup contributes scarcely anything to its flavour, but custom leads us to associate the idea of strength and flavour with its appearance. The brown tint which long boiling gives, may, as is well known in the kitchen, be supplied by a little burnt sugar, and thus the eye as well as the palate may be satisfied.

The antiseptic power of common salt in preserving meat has been known from time immemorial, but no satisfactory explanation of its mode of action has been given. The process of salting detracts considerably from the nutritive value of the flesh so preserved. When raw meat is salted, the liquid portion speedily begins to ooze out, and to dissolve the salt, forming what is commonly termed *brine*, which is a saturated solution of salt in the juice of the flesh; the meat thus becomes proportionately impoverished of its albumin and of its sapid and saline components, and at the same time is deprived of its tendency to putrefy. Many other substances besides common salt possess antiseptic properties; such for instance as sodic, ammoniac, boric, and plumbic acetates, acetic acid, calcic, mercuric, and cupric chlorides,

cupric sulphate, and potassic dichromate. Kreasote and carbolic acid are especially powerful as antiseptics. Many other metallic salts, such as zincic chloride and sulphate, might also be mentioned.

(1678) *Components of the Brain.*—The chemical knowledge of the components of the brain and nervous system is less satisfactory than that of many of the foregoing substances. It may be observed that these organs are especially remarkable in a chemical point of view. The brain contains a large proportion of albumin in the uncoagulated form; but it seems to owe its particular properties to the presence of a solid fatty body, formerly in its impure state termed *cerebric acid*. This substance has more recently been obtained in a pure form by Liebreich (*Liebig's Ann.* cxxxiv. 29), who calls it *protagon* (from *πρωτος*, first), as the most important constituent of nervous substance. In addition to this body, cholesterin, and the ordinary fats, stearin and olein, are likewise present.

The human brain contains in 100 parts, about 7 parts of albumin, 5 of the above-mentioned fats, and 80 of water.

Protagon ($C_{116}H_{240}N_4PO_{22}$?) crystallizes from its alcoholic solution in microscopic needles; these when dry appear like a light flocculent powder, which is sparingly soluble in cold alcohol and in ether. In water it swells up to an opaque mass of pasty consistence, which furnishes an opalescent solution when more largely diluted. Normal acetic acid dissolves it when gently warmed, and deposits crystals unaltered on cooling. When mixed with concentrated solutions of calcic or sodic chloride and boiled, its solution becomes coagulated. When heated even below 212° it is decomposed, a change which occurs more quickly when dry than when it is moist. When boiled for twenty-four hours with baryta water, it becomes decomposed into baric glyceri-phosphate, and a new base, *neurine*, which Baeyer has shown to be hydrated trimethyl-ethylum oxide $[(CH_3)_3C_2H_5, NHO]$, and which has been obtained synthetically by Wurtz. Baric salts of other fatty acids are also formed during the decomposition of protagon by baryta water.

Protagon is a very easily alterable substance. Liebreich isolates it in the following manner; in order to obtain a brain free from blood, an animal is killed by opening the carotid arteries, and water is injected until the liquid runs off colourless from the veins. The brain is then removed from the skull, freed from its membranes, and rubbed up into a smooth paste with water,

and the mass agitated in a flask with a mixture of ether and water; the mixture is cooled down to 32° (0° C.) and the ether when clear is decanted, fresh ether being added, and the treatment renewed until the ethereal solution ceases to dissolve any more cholesterin. The undissolved portion is next drained upon a filter, and digested at a temperature not exceeding 113° (45° C.) in alcohol of 85 per cent.: the solution is filtered whilst hot; the filtrate is cooled to 32° (0° C.), and the copious flocculent precipitate thus obtained, after washing with cold ether to remove cholesterin, is dried *in vacuo* over sulphuric acid. The residue is finally dissolved in alcohol at 113° , and if the filtered liquid be allowed to cool slowly, microscopic needles of protagon are deposited.

Protagon has been found in the brain of man, as well as in that of the horse, ox, and dog; also in the blood, and in various organs. Liebreich, indeed, considers that not only cerebrin, but myelin, lecithin, oleo-phosphoric acid, and phosphorized fat, consist either of protagon more or less pure, or of products of its decomposition.

Neurine $C_5H_{15}NO = (CH_3)_3C_2H_5N,HO$ is a powerfully alkaline base, produced by boiling protagon with baryta water as already described. It may be isolated by removing the excess of baryta by means of carbonic acid, concentrating the liquid to a syrupy consistence, and adding absolute alcohol in order to separate the salts. The alcoholic liquid is again evaporated to a syrupy state, dissolved a second time in absolute alcohol, and the neurine is separated as a platinum salt ($2C_5H_{14}NCl, PtCl_4$) by the addition of an alcoholic solution of platonic chloride. The salt is freely soluble in water, and crystallizes in large yellow six-sided rhombic plates. The platinum salt may be decomposed by sulphuretted hydrogen, and on evaporation the hydrochlorate of neurine is obtained in delicate needles ($C_5H_{13}N, HCl$).

§ II. COMPOSITION AND PROPERTIES OF SOME OF THE MOST IMPORTANT ANIMAL FLUIDS.

(1679) The fluids contained in the animal body may be considered in the following order:—

A. *Plastic nutrient liquids*, under which are included the *blood*, and its tributaries, the *chyle* and the *lymph*; in connexion with which it will be convenient to notice *milk*.

B. Liquids more or less necessary to the process of digestion, including the *saliva*, the *gastric juice*, the *pancreatic fluid*, the *secretions of the mucous membranes*, and the *bile*.

C. Excrementitious matter, comprising the *urine*, the *cutaneous*

secretions, and the solid *excrements*; with which may be noticed *pus*, the product of the suppurative process.

A. *Plastic Nutrient Liquids*.—I. *The Blood*.

(1680) THE blood is the most important of the fluids contained in the animal system, since it supplies the material from which the various organs of the body are derived. The remarks which follow refer to the blood of the human species unless otherwise specified.

Since the blood is a fluid which consists of a mixture of a variety of different ingredients, and since it is every moment undergoing changes of the most varied and complicated description, its composition cannot be expected to exhibit the same definite character as that of a crystallized mineral; and yet there is considerable uniformity in the chemical composition of blood during health. In the vertebrate animals the blood is a somewhat viscid fluid of a red colour, which is more or less bright according to the part of the system from which the liquid has been taken; that from the arteries, or *arterial* blood, being of a florid red, while that drawn from the veins, or *venous* blood, is of a dull purple. Blood has a peculiar odour, which differs somewhat in animals of different species. This odour is more strongly developed by the addition of oil of vitriol to the blood. When left to itself, the blood presents the remarkable phenomenon of coagulation, in consequence of which it appears first to become semi-solid, and eventually it separates into two portions, one of which constitutes the solid *cruor*, or *crassamentum*, and the other the liquid or *serous* portion. This coagulation generally commences in from three to five minutes after the blood has been drawn, and the clot continues to contract for ten or twelve hours. Coagulation is retarded by exposure to a low temperature; it occurs most rapidly at about 100° or 110° (37°·8 to 43°·3 C.). The coagulation is due to the presence of fibrin, which exists in the blood in a state of solution whilst it is circulating in the living organism, but solidifies shortly after its removal from it: the cause of this coagulation is still doubtful. It is not due to the escape of ammonia as supposed by Dr. Richardson, because the presence of ammonia in the atmosphere above does not prevent the coagulation. Hoppe-Seyler believes it to be due to the mutual action of two soluble albuminous bodies, one of which he terms the *fibrinoplastic*, the other the *fibrinogenous* substance, the first being abundant in the red globules, the second in lymph

and ehyle (*Erlenmeyer's Zeitschrift f. Chem. u. Pharm.*, 1864, 737). During coagulation the fibrin carries with it all the colouring matter of the blood, so that the clot has a deep red hue, and the serum is left colourless or straw-coloured. The reason of this complete separation of the colouring matter is revealed by the microscope. Blood, when exposed to a high magnifying power, is found not to be a homogeneous fluid, but to contain a multitude of small flattened disks, of a deep red colour, tolerably uniform in size in the same animal, but varying in magnitude and shape in different species of animals. These *blood disks*, or *red corpuscles*, float in a transparent, nearly colourless fluid, termed the *liquor sanguinis*. In human blood these red corpuscles are circular and slightly biconcave: in most other mammalia the blood disks are also circular; in birds they are elongated and oval, with an elevated centre; and in amphibia they are oval and slightly convex. These observations explain the cause of the complete separation of the colouring matter when the blood coagulates; since the fibrin, in the act of solidification, entangles the red corpuscles in its meshes, and separates them mechanically, just as white of egg removes the solid impurities suspended in syrup when it is used to clarify that liquid. If the blood be whipped with a bundle of twigs during the process of coagulation, the fibrin attaches itself in the form of white elastic filaments to the twigs, while the red particles are separated from it by the agitation. The defibrinated blood is of a deep red colour, and does not coagulate. Blood is prevented from coagulating by allowing it to flow from the vein into alkaline solutions, or into a concentrated solution of many salts of the alkalies, such as potassic nitrate and sodic sulphate and acetate. In some cases of sudden death, the blood is also found to have lost its property of spontaneous coagulation. In certain states of the system, owing partly to the slower coagulation of the fibrin, the upper surface of the clot is entirely free from colouring particles, the red corpuscles having subsided, and left a stratum of variable thickness and of yellowish colour; to this coating the name of the *buffy coat* of the blood has been given; it is sometimes spoken of as the *inflammatory crust*, owing to its frequent occurrence during inflammatory diseases.

(1681) *Composition of the Blood*.—The following substances have been found as normal constituents of the blood:—Albumin, fibrin, colouring matter or hæmatin, globulin; oleic, stearic, lactic, phosphoric, sulphuric, and hydrochloric acids, in combination with sodium, potassium, ammonium, calcium, and magnesium; minute portions of cholesterolin, and a small quantity of phosphorized fat,

which is probably protagon. The blood likewise contains in solution oxygen and nitrogen, derived from the atmosphere, and carbonic acid, which is produced by the reaction of the oxygen upon the constituents of the blood. These gases may be displaced by transmitting a current of hydrogen through the liquid. Lehmann, by passing a current of hydrogen through ox-blood till it ceased to expel carbonic anhydride, and then adding acetic acid without admitting air, and again transmitting hydrogen, found that an expulsion of carbonic anhydride ensued, and he inferred that recent blood must contain a free alkaline carbonate, in quantity equal to about 0.1628 per cent. of its weight.

The following table, based upon the observations of Schmidt and the analyses of Lehmann, is given by the latter chemist as representing the average quantitative relation of the principal constituents of normal blood. It will be observed that the blood is here regarded as composed of two portions, one consisting solely of the red particles, and the other of the liquid in which these red corpuscles are suspended, termed the *liquor sanguinis*, which consists of the serum holding fibrin in solution:—

| <i>Sp. gr. of Blood Corpuscles</i> , 1.0885. 1000 parts of blood corpuscles contain:— | <i>Sp. gr. of Liquor Sanguinis</i> , 1.028. 1000 parts of liquor sanguinis contain:— |
|---|--|
| Water 688.00 | Water 902.90 |
| Solid constituents 312.00 (consisting of) | Solid constituents 97.10 (consisting of) |
| Hæmatin (with iron) 16.75 | Fibrin 4.05 |
| Globulin and cell membrane 282.22 | Albumin 78.84 |
| Fat 2.31 | Fat 1.72 |
| Extractive matters 2.60 | Extractive matters 3.94 |
| Mineral substances (without iron) 8.12 | Mineral substances 8.55 |
| Chlorine 1.686 | Chlorine 3.644 |
| Sulphuric anhydride (SO ₃) 0.066 | Sulphuric anhydride (SO ₃) 0.115 |
| Phosphoric anhydride (P ₂ O ₅) 1.134 | Phosphoric anhydride (P ₂ O ₅) 0.191 |
| Potassium 3.328 | Potassium 0.323 |
| Sodium 1.052 | Sodium 3.341 |
| Oxygen 0.667 | Oxygen 0.403 |
| Calcic phosphate 0.114 | Calcic phosphate 0.311 |
| Magnestic phosphate 0.073 | Magnestic phosphate 0.222 |

The ash of ox-blood contains about 6.84 per cent. of ferric oxide (Lehmann).

The following table gives the results of the average composition of human blood in man and in woman, according to the analyses of A. Becquerel and Rodier:—

| | • Male. | Female. | | |
|--|---------|---------|--------|--------|
| Specific gravity of defibrinated blood | 1'0600 | 1'0575 | | |
| Of serum | 1'0280 | 1'0274 | | |
| Water | 779'00 | 791'10 | | |
| Fibrin | 2'20 | 2'20 | | |
| Fatty matters { Serolin | 1'60 { | 1'62 { | | |
| { Phosphorized fat | | | { 0'02 | { 0'02 |
| { Cholesterin | | | { 0'49 | { 0'46 |
| { Saponified fat | | | { 0'09 | { 0'09 |
| Albumin | 69'40 | 70'50 | | |
| Blood corpuscles | 141'10 | 127'20 | | |
| Extractive matters | 6'80 | 7'40 | | |
| | 1000'10 | 1000'02 | | |
| Salts . . . { Sodid chloride | 3'10 | 3'90 | | |
| { Other soluble salts | 2'50 | 2'90 | | |
| { Earthy phosphates | 0'33 | 0'35 | | |
| Metallic iron | 0'57 | 0'54 | | |
| | 6'50 | 7'69 | | |

The average specific gravity of healthy human blood is from 1'052 to 1'057, but it is liable to considerable variation, principally owing to differences in the proportion of the red corpuscles: it is usually more dilute in the female than in the male. The density of the serum is more uniform, and is generally between 1'027 and 1'029. The serum is a somewhat alkaline, straw-coloured, highly albuminous liquid, which becomes coagulated, and forms a semi-transparent jelly when heated to about 170° (76°·7 C.). Its average composition has been already given under the head of liquor sanguinis, in the table quoted from Lehmann; but since the liquor sanguinis consists of serum holding fibrin in solution, fibrin must be deducted from the list of the components of the serum.

(1682) *Hæmoglobin, Cruorin, or Hæmatocrystallin.*—The characteristic component of the red globules of the blood may be obtained in a pure form in crystals; and these have been observed to occur sometimes in old extravasations, and in certain forms of disease. The colouring matter assumes the shape of irregular crystalline fragments, or of perfectly-formed transparent red rhombic prisms, which are very sparingly soluble in water; yielding a solution which becomes coagulated at about 145°·4 (63° C.). Alcohol and nitric acid also produce a precipitate in the liquid. The aqueous solution of hæmoglobin is precipitated by solutions of corrosive sublimate, of mercurous nitrate, and of cupric sulphate. Acetic acid dissolves the crystals readily; ammonia produces a liquid of

the colour of peach-blossoms ; potash does not dissolve them, but changes the colour of the crystals to a dirty yellow, the alkalies decomposing it into hæmatin and globulin. If digested in the presence of chlorides with a great excess of glacial acetic acid, the globulin is separated, and a crystalline body known as *hæmin* (hydrochlorate of hæmatin) is separated ; it amounts to about 3·85 per cent. of the hæmoglobin employed. The hæmin crystals are insoluble in water, alcohol, or ether, but they are decomposed by acids excepting the hydrochloric and the acetic ; alkalies also decompose them, setting hæmatin free ; and if treated with ammonia hæmatin may be procured : from hæmin, by the addition of ammonia, hæmatin (1684) may be obtained.

Lehmann has pointed out a method by which the crystals of hæmoglobin may be readily obtained from the blood of various animals, particularly from that of the guinea-pig, the rat, and the mouse. After the serum has been well drained from the clot, the coagulum is to be placed in a cloth, and the greater part of the colouring matter washed out by means of a small quantity of water. The deep red liquid thus obtained is to be filtered, and a current of oxygen gas transmitted through it for about half an hour : after this, a current of carbonic anhydride is to be transmitted through the solution, for about 15 minutes. During the latter process the liquid gradually becomes filled with small crystals which, if allowed to subside, can be separated from the liquid portion. Lehmann found that the formation of these crystals was favoured by the action of solar light ; and Hoppe-Seyler facilitates crystallization by adding to the aqueous solution about one-fourth of its bulk of alcohol, and cooling to the melting point of ice. The crystals may be purified by redissolving in water, and again precipitating by alcohol and cooling. The crystals obtained from the blood of different animals present differences of form. They are generally prismatic, but those of the rat and the mouse are tetrahedral, those of the squirrel six-sided tables. They are sparingly soluble in cold water, but more so in warm water, and are freely soluble in feebly alkaline solutions such as serum. The ultimate analysis of hæmoglobin furnishes results almost identical with those obtained from albumin. It contains 0·42 per cent. of iron (Schmidt, Hoppe-Seyler) ; phosphates are also present in considerable proportion in the ash.

(1683) The globulin contained in hæmoglobin has already been described (1653) as a compound bearing a strong analogy to albumin ; it is contained in a state approaching to purity in

the crystalline lens, and it constitutes the most abundant ingredient in the blood-globules.

Hæmoglobin is very readily acted upon by oxygen, and by many other gases, and is concerned intimately with the changes produced in the blood during the process of respiration. In the moist state the crystals retain oxygen loosely combined, and absorb it from the air, but part with the gas in the vacuum of the air-pump when boiled. They lose water over sulphuric acid in vacuo, and become of a brick-red colour. By passing hydrogen, carbonic anhydride, or nitrous oxide through their solution the oxygen is expelled; and when the expulsion is effected by hydrogen or carbonic anhydride, the colouring matter furnishes crystals like those from oxidized blood, but differing in colour and in optical properties. Oxygen gas is also absorbed by the red corpuscles when suspended in the serum or when dissolved in water, the liquid assuming a brilliant red colour, whilst a disengagement of carbonic anhydride occurs. It is owing to this action of oxygen that in the coagulum of venous blood, the upper portion, which is the part most exposed to the action of the air, is of a brighter red than the lower portions of the clot. Carbonic anhydride is likewise absorbed by the red corpuscles; their colour then becomes changed to a dull purple, but the brilliancy of the red hue may be restored by further exposure to the action of oxygen: many saline solutions, such as those of potassic nitrate, also restore the red colour, and a similar effect may be obtained if syrup be added to the liquid. The solution of the colouring matter in water also experiences similar modifications in colour. Sulphuretted hydrogen causes the colour to pass into a dull green, and the red hue cannot be afterwards restored. Nitrous oxide colours hæmoglobin purple, and oxygen reproduces the scarlet colour in blood which has been thus acted upon. Carbonic oxide combines with hæmoglobin, producing a brilliant scarlet; and this body may be obtained in crystals. With nitric oxide a similar compound may be obtained, N_2O_2 , taking the place of CO, or of O. Carbonic oxide and nitric oxide cannot be displaced by oxygen from hæmoglobin, while nitrous oxide may be displaced by it. Sulphurous anhydride, and acid gases in general, darken its colour, which is again restored by oxygen. Admixture with saline solutions also restores the red hue to blood which has been darkened by sulphurous acid. From these facts it is obvious that hæmoglobin is a compound extremely prone to change under the influence of many reagents.

When examined by the prism, a solution of the colouring

matter of the blood exhibits a characteristic spectrum, as first noticed by Hoppe-Seyler. That of arterial blood presents two absorption bands, D and E. Under the action of reducing agents on hæmoglobin, such as an alkaline solution of ferrous tartrate, and as it is found in the venous system after death by drowning, these two bands disappear, and a single one less defined at the edges presents itself in the space between the two seen in arterial blood; the general absorption becomes more intense at the same time towards the red, but less so in the blue. If the red solution be treated with acetic or tartaric acid the liquid becomes of a brown red colour, and exhibits a new characteristic series of absorption bands due to the decomposition of the original colouring matter, by the action of the acid. After the addition of an alkali the scarlet or oxidized hæmoglobin solution exhibits, when treated with reducing agents, two absorption bands somewhat more refrangible than those of arterial blood. (Stokes, *Proceed. Roy. Soc.*, xiii. 355.) These changes are best observed in a somewhat dilute solution: the more refrangible parts of the spectrum suffer a considerable but general absorption. It has been proposed to employ these spectrum observations for the identification of blood, very small quantities sufficing for the purpose. The use of the microscope for this purpose has been recommended, but it does not increase the delicacy of the observation materially.

Another very delicate test for the presence of the colouring matter of the blood has been found to be the following, known as the guaiacum test:—Place a portion of the suspected blood-stain in contact with a drop of water; if any colour is produced in the liquid, add to a drop of it, upon a piece of white porcelain, a drop of an alcoholic solution of guaiacum; a reddish-white precipitate of the resin is formed, and on adding to this a drop of solution of hydrogen peroxide, or of ozonised ether, a blue colour speedily appears. Old dry blood-stains may be macerated in a drop or two of water for an hour or two; if no colour is thus extracted, a drop of tincture of guaiacum is allowed to fall upon the moistened spot. It should then be pressed firmly on white blotting-paper; if no blue stain is produced there is nothing present to prevent the proper application of the test. Another drop of the tincture of guaiacum is added to the stain, and then a drop or two of solution of hydrogen peroxide. In a minute or two, if the stain be due to blood, a blue impression of the stain may be procured by firmly pressing the moistened portion upon a piece of white blotting-paper. The change of colour thus produced is due to the oxidation of the guaiacum, by means of the hydrogen peroxide in the presence of blood. The peroxide in the absence of the blood colouring-matter, has not this power. A saturated solution of the inner portion of the guaiacum in alcohol of sp. gr. 0.830 should be made, and it should be preserved from the light in a bottle covered with black paper. Guaiacum resin becomes blue when treated with chlorine, with ozonised air, and with solution of potassic manganate or permanganate; but these reactions do not interfere with its application in the manner above directed (A. Taylor, *Guy's Hosp. Rep.*, 1868).

(1684) *Hæmatin*, or *Hæmatosin* (from *αἷμα*, blood; $C_{44}H_{44}N_6O_6Fe$?

Mulder).—This substance is the result of the decomposition of hæmoglobin, the true colouring principle of the blood. It presents a considerable analogy with the albuminous principles, and may, like them, exist either in a coagulated or an uncoagulated form. Hæmatin is the principal constituent of the body that contains iron, and, according to the analysis of Mulder, it contains 6.6 per cent. of the metal. It appears to be probable that, like the sulphur and the phosphorus in albumin, this iron is not combined with oxygen. The peculiar colour of hæmatin is manifestly not dependent upon the iron which it contains, since nearly the whole of this substance may be removed without affecting the dark brown colour of the hæmatin; for example, if hæmatin be allowed to remain for some time in contact with concentrated sulphuric acid, and the liquid be then diluted, an evolution of hydrogen will take place, and ferrous sulphate will be formed in the liquid. The brown insoluble residue thus obtained contains carbon, hydrogen, nitrogen, and oxygen, in the same proportion as in hæmatin from which the iron has not been removed. If chlorine be passed through a solution of hæmatin in water, ferric chloride is formed, and a white precipitate, termed *chlorhæmatin*, is produced, which Mulder represents as $(C_{44}H_{44}N_6O_{24}Cl_{12}$, or $C_{44}H_{44}N_6O_6, 6Cl_2O_3)$, a compound analogous to that which is formed with protein, when albumin, suspended in water, is similarly treated. Hæmatin constitutes but a small proportion of the red particles of the blood (according to Berzelius, about 1-20th), the remaining portion consisting chiefly of globulin.

It is difficult to obtain hæmatin in a state of purity, and as yet it has only been insulated in its coagulated form. Blood which has been freed from fibrin by agitation with twigs before coagulation, is to be mixed with about 8 times its bulk of a saturated solution of sodic sulphate. After standing for a few hours, the colouring matter subsides; it must be collected on a filter, and washed with a solution of sodic sulphate. If the residue upon the filter be now boiled with alcohol acidulated with sulphuric acid, the colouring matter is dissolved. The liquid must be filtered while hot, and a portion of globulin, which has been dissolved, is to be thrown down by the addition of ammoniac sesquicarbonate. The red liquid thus obtained is again to be filtered, and evaporated to dryness; after which the solid residue must be digested successively with water, alcohol, and ether, and again be dissolved in alcohol containing ammonia, by which the remaining portions of globulin will be separated in the insoluble form; the solution is then to be filtered and evaporated to dryness; after which everything that is soluble is to be removed by digestion with water. The residue is considered to be pure hæmatin.

Coagulated hæmatin as thus obtained forms a dark mass, which assumes a slight lustre on pressure. It is destitute of odour and of taste, and is insoluble in water, alcohol, ether, and the fatty and essential oils. It is, however, readily dissolved by weak alcohol which has been acidulated with sulphuric or hydrochloric acid: the solution is of a deep brown colour, but it becomes blood red on the addition of an alkali. Water precipitates the acidulated alcoholic solution. Strong acids decompose hæmatin, and extract the greater portion of its iron. Aqueous solutions of the alkalies, both caustic and carbonated, dissolve it freely; when these solutions are boiled, the colour, which is at first bright red, passes through dull red into green. Hæmatin is precipitated completely from its ammoniacal solution in alcohol, by salts of silver, of lead, and of copper. According to Denis, 1000 parts of blood contain 0.56 of metallic iron; so that reckoning the quantity of blood in a man of average stature at 30lb., it would amount to 120 grains, or 7.8 grms., of iron in the blood of the entire human body.

(1685) 2. CHYLE.—The term *chyle* is applied to the liquid derived from the nutritive portions of the food, which are absorbed

from the inner surface of the intestines by a set of vessels, termed the *lacteals*; these pour their contents into one large absorbent trunk, called the *thoracic duct*, by which the chyle, as fast as it is supplied, is emptied into the general current of the circulation. The chyle differs in its qualities according to the nature of the food which has been taken, and according to the situation in which it is collected for examination. When removed from the body, it, in the course of a few minutes, undergoes a spontaneous coagulation, owing to the presence of fibrin. In this respect chyle differs from all the other animal fluids, except blood and lymph.

Chyle is an opalescent fluid, of a yellowish-white, or pale reddish colour. It has a somewhat saline mawkish taste, and a very feebly alkaline reaction; it is generally more or less milky, from its holding in suspension minute granules, and globules of fatty matter; this milkiness is particularly observable when the food has contained much fat. Chyle, when boiled, generally deposits a few albuminous flocculi. Few satisfactory opportunities have occurred for examining the composition of human chyle. The proportion of fibrin contained in the chyle of the lower animals is subject to considerable fluctuations. In the chyle of a horse it was found by Simon to amount to 0.44 parts per cent.; in that of a cat Nasse found 0.13 parts of fibrin; and Rees found 0.37 parts of fibrin per cent. in that of the ass. When collected from the lacteals, before passing through the mesenteric glands, chyle frequently does not coagulate spontaneously, and the coagulation only occurs fully in that taken from the thoracic duct.

It has been observed that the quantity of fibrin is greater in animals from which the chyle has been collected while fasting. The quantity of fibrin in the chyle is also increased after passing through the mesenteric glands, as though a considerable portion of fibrin were added during its transmission through these organs. It appears not to be improbable that the albuminous matters are gradually converted into fibrin during their passage through the vessels, in the same way that albumin is formed while the aliments are passing from the stomach through the small intestines; since the quantity of fibrin increases the nearer it approaches to the point where the chyle empties itself into the general mass of the circulating fluid. Hoppe-Seyler considers that lymph and chyle contain a soluble albuminoid matter, *fibrinogen*, possibly the same as Prout's *incipient albumin*, which, when mixed with one of the soluble constituents of the blood-globules *fibrinoplastin*, produces by combination true coagulable fibrin, which he states he has thus obtained synthetically. A few blood corpuscles are found

floating in the chyle when it has reached the thoracic duct; and, when viewed by the microscope, multitudes of minute granules are seen in suspension, in addition to which there are other corpuscles, resembling those of pus in appearance; besides which, floating globules of fat are discernible in considerable numbers: in fact, chyle resembles blood in composition, but it is far more dilute; the proportion of solid matters in the chyle of the horse varies from 4 to 9 per cent., whilst in the blood it rises as high as 22 per cent.

The chyle, on exposure to the air, assumes more or less of a red colour, and thus approximates in another remarkable particular to the blood. This colour becomes increased in intensity after the liquid has passed through the mesenteric glands.

(1686) 3. LYMPH.—This is a colourless, or yellowish fluid, which has usually a faintly alkaline reaction. It is procured from the *lymphatic* vessels, and, owing to the difficulty of obtaining it in sufficient quantity, it has been but imperfectly examined. It is distinguished from all other animal fluids, except the blood and the chyle, by the presence of fibrin in solution: in consequence of which it coagulates in a few minutes after it has been withdrawn from the body, and forms a scanty colourless coagulum. The quantity of fibrin in lymph from the human body, obtained in cases of injury, has been found to be between 0·3 and 0·5 per cent.; in the horse it varied from 0·04 to 0·33 per cent. The quantity of albumin in human lymph is stated to vary from 0·4 to 6·0 per cent., but in the latter case it is not improbable that the lymph was mixed with effused serum.

(1687) 4. MILK.—This important secretion is produced by the mammary gland of the female animal of the order *Mammalia*, after giving birth to young: from the circumstance that the milk constitutes the entire food of the young animal for many months, it presents a high degree of physiological interest in relation to the supply of food, and to the processes of nutrition and of growth.

Milk is a liquid of a well-known yellowish, or bluish-white appearance, which is produced by the presence of a large quantity of oily matter in suspension. It has a sweet taste, a slight but agreeable odour, and in woman and the herbivora it has a feebly alkaline reaction: in the carnivora it is said to be slightly acid. When allowed to stand undisturbed for a few hours, the greater part of the fatty matter rises to the surface, and forms the layer which constitutes cream. When viewed by the microscope in a

very thin layer, milk appears to be transparent: it contains a large number of highly refracting, transparent, oily globules floating in a transparent liquid; these globules are contained in a very thin investing membrane, which is not visible till the milk is treated with dilute acetic acid. Agitation of the milk with ether does not dissolve the fat, but if a small quantity of potash be added to milk, and it be then shaken up with ether, the fat is completely dissolved, the pellicle which envelopes the globules having been removed by the action of the potash.

The object of churning, in the preparation of butter from cream, is to break up mechanically the little sacculi which enclose the oily matter, and thus to facilitate the agglomeration of the fatty particles into masses, and to favour the separation of the liquid constituents which enter into the formation of the *butter-milk*. The more completely the albuminous and caseous matters are washed away, and the more compactly the butter is pressed, the longer may it be preserved without becoming rancid, since the caseous matter acts as a ferment, which speedily effects a partial decomposition of the fat. The addition of salt to the butter preserves the fats unaltered for a considerable period, by retarding the decomposition of the azotised matter.

In addition to oily matter, milk contains two other characteristic ingredients, viz., milk-sugar and casein, both of which are held in solution. Albumin is absent from this solution in its usual condition, but it is abundant in the *colostrum*, or milk which is first produced after the birth of the young animal. The quantity of albumin in the *colostrum* of the cow is so considerable, that it coagulates when heated. The *colostrum* is denser than normal milk; it has a yellowish colour, and approaches serum in quality. It is worthy of observation that the sugar contained in milk is of a kind which does not undergo alcoholic fermentation, and consequently is not likely to produce an evolution of carbonic anhydride during digestion, so that distension of the tender stomach and intestines of the young animal from this cause is guarded against.

The salts contained in milk consist of the chlorides of sodium and potassium, of phosphates of the alkalies, and of a certain proportion of soda and potash, which are combined with the casein and confer solubility upon it; in addition to which, phosphates of calcium and magnesium are also found in considerable quantity. These phosphates are essential to the development of the bones of the young animal. A minute quantity of ferric oxide, amounting, according to Haidlen, to 0.47 per cent. of the entire quantity of the ash, is also found in milk. No sulphates, lactates, or salts of

ammonium, are present in fresh milk. The quantity of salts found in cow's milk usually amounts to about 0·7 per cent. In woman's milk it is about 0·2 per cent. The composition of milk varies, not only in the different species of animals, but also in the same animal at different periods of lactation, the proportion of butter being especially liable to fluctuation, and being greatly under the influence of diet: it also appears that the milk last yielded during the act of milking is the richest. The following table comprises the results of the analysis of 100 parts of milk in various species of animals, and will give an idea of the general nature of this liquid:—

| Constituents of Milk. | Woman. | Cow. | Goat. | Ass. | Sheep. | Bitch. |
|----------------------------|--------------------------|------------------|---------|------------------|------------------|------------------|
| Water | 88·6 | 87·4 | 82·0 | 90·5 | 85·6 | 66·3 |
| Butter | 2·6 | 4·0 | 4·5 | 1·4 | 4·5 | 14·8 |
| Sugar and soluble salts . | 4·9 | 5·0 | 4·5 | 6·4 | 4·2 | 2·9 |
| Casein and insoluble salts | 3·9 | 3·6 | 9·0 | 1·7 | 5·7 | 16·0 |
| Sp. gr. varies | { from 1·030 to 1·034 | { 1·030 1·035 | { 1·036 | { 1·023 1·035 | { 1·035 1·041 | { 1·033 1·036 |

The spontaneous acidification of milk when kept, and the consequent curdling of the milk, as well as the action of acids generally, in coagulating milk, and the effect of various neutral salts of the earths upon this liquid, have already been mentioned (1119, 1657).

B. *Liquids concerned in Digestion.*

(1688) 1. THE SALIVA.—This secretion is poured out by the parotid and other glands, the ducts of which empty themselves into the cavity of the mouth. Its chief use appears to be to lubricate and moisten the food, and to facilitate the act of deglutition. The saliva varies in composition considerably in different animals. In man it is an opalescent, somewhat viscid liquid, which froths remarkably on agitation. The quantity of fixed solids which it contains in solution was found by Lehmann to lie between 0·388, and 0·841 per cent., but it has been observed as high as 1·6 per cent. In the dog the solids amount to about 1·03, and in the horse to 1 per cent. In addition to epithelial particles, and to the mucus derived from the mouth itself, the saliva contains a peculiar organic principle, termed *ptyalin* (from *πτύελον*, spittle), which resembles sodic albuminate, and which is very prone to putrefaction. Ptyalin constitutes about one-third of the soluble solids of the saliva. It is characterized by its power of converting starch, even in the granular form, into dextrin and into sugar.

The saliva in health has a feebly alkaline reaction; its alkalinity is increased during mastication, and diminishes after the process of digestion is completed. In inflammatory affections of the *primæ viæ* the saliva is, however, generally acid, and the same fact has been observed in various other forms of inflammatory disease. The inorganic constituents of the saliva consist of salts of potassium and sodium, with a considerable quantity of the salts of calcium, which last is deposited from the saliva of many animals (the horse, for example) in the form of crystallized carbonate, when the secretion is exposed to the air and allowed to absorb carbonic acid. It likewise occasionally contains lactates of the alkali-metals. Saliva also always contains a small quantity of calcic phosphate. This calcic phosphate, mingled with a variable proportion of calcic carbonate and of salivary mucus, constitutes those calculous concretions which sometimes form upon the teeth, and are known as *tartar*. Minute quantities of potassic sulphocyanide are also present in the saliva, as may be proved by the red colour which it yields on the addition of a dilute solution of ferric chloride. When sulphur has been taken medicinally, Wright found the quantity of the sulphocyanide to be considerably increased. The sulphates are almost entirely absent from the ash of saliva.

(1689) 2. THE GASTRIC JUICE.—This important secretion is the principal agent in effecting the digestion of the albuminoid portions of the food, but it exerts scarcely any action upon the starchy and fatty constituents. The gastric juice, as its name (from *γαστήρ*, the stomach) implies, is poured out from the lining membrane of the stomach. Its composition varies at different times, in consequence of which, when obtained from an empty stomach, its reaction upon litmus paper is either neutral or slightly alkaline; but after the ingestion of food into the stomach, it is always acid. In this, which may be considered its normal state, the gastric juice is a clear colourless liquid, which has a peculiar odour, and a slightly saline and acid taste. It does not become turbid when boiled, and it is remarkable for its antiseptic powers. It may be kept for many days at $100^{\circ}\cdot4$ (38° C.) without exhibiting any tendency to become putrid. The nature of the acid contained in the gastric juice has been much disputed, some chemists maintaining with Prout that it is the hydrochloric, others with Blondlot, that it consists of phosphoric acid in the form of calcic superphosphate, and others that it is composed of lactic acid. In truth it appears generally to consist of a mixture of hydrochloric

and lactic, with traces of butyric and propionic acids. The principal saline matters present are common salt, with small quantities of calcic and magnesic chlorides, sodic lactate, and traces of calcic and ferric phosphates. The quantity of calcic phosphate is very small, and the sulphates and phosphates of the alkali-metals are almost entirely wanting. In addition to these bodies, however, the gastric juice contains a small quantity of a peculiar organic compound, which has been termed *pepsin* (from $\pi\acute{\epsilon}\psi\iota\varsigma$, cooking), to which, in conjunction with the free acid, the remarkable solvent and digestive powers of the gastric juice are owing.

Pepsin is an albuminoid body, soluble in water, but insoluble in alcohol or in ether. Its aqueous solutions are precipitated by corrosive sublimate, by salts of lead, and by solutions of tannic acid, but not by potassic ferrocyanide in acetic solutions. When boiled it loses its peculiar power of effecting digestion. An artificial gastric juice, which acts as a solvent upon muscular fibre, boiled eggs, and albuminoid substances generally, may be obtained by digesting the mucous membrane of the stomach with a warm but very dilute solution of hydrochloric acid. Dried pepsin, mixed with from 20 to 50 per cent. of starch, is now an article prepared for medicinal use. The quality of this artificial pepsin may easily be tested by putting a dose of the preparation into half an ounce of water, adding 20 drops of hydrochloric acid, and then letting it stand, at a temperature of 100° ($37^{\circ}\cdot 8$ C.), upon 2 grammes, or about 30 grains of hard-boiled egg minced small. The whole should be dissolved in a couple of hours; a similar quantity of lean beef chopped fine should be also readily dissolved in the same time. The solutions thus obtained do not coagulate on the application of heat. They contain what Prout terms *incipient albumin* (the *peptones* of more recent writers), which do not acquire the ordinary properties of albumin until after it has been subjected to the action of the pancreatic and biliary secretions. In preparing pepsin for medicinal use the mucous membrane of the stomach of the pig is generally employed as the source of the pepsin, the most active portion being the glandular layer, extending chiefly along the greater curvature towards the cardia.

In the appendix to Lehmann's work (vol. iii. p. 503), it is stated on the authority of Gruenewaldt, who had an opportunity of making experiments upon a woman suffering from a gastric fistula, that the weight of the gastric juice secreted in twenty-four hours amounted to the enormous quantity of 31 lb.; but the greater portion of this liquid was, of course, re-absorbed by the mucous surface. In this case the gastric juice was carefully

analysed by Schmidt. The following are his results. It had a sp. gr. of 1·020. When heated, it emitted an odour of butyric and propionic acids, and was found to contain in 1000 parts:—

| | |
|--|--------|
| Water | 954·13 |
| Pepsin | 0·78 |
| Sugar, albuminates, lactic and butyric acids, and ammonia | 38·43 |
| Potassic chloride | 0·70 |
| Sodic chloride | 4·26 |
| Potash | 0·17 |
| Calcic phosphate | 1·03 |
| Magnesian phosphate | 0·47 |
| Ferric phosphate | 0·01 |

No free hydrochloric acid was found in this analysis; but when the stomach of this patient was irritated by introducing peas instead of masticated food, free hydrochloric acid was obtained from the gastric juice, which was secreted unmixed with saliva.

Schmidt found the quantity of free hydrochloric acid in the gastric juice of dogs, when unmixed with saliva, to amount to from 0·245 to 0·423 per cent. Small quantities of ammoniac chloride were also present in it.

The inner surface of the intestines also pours out a large quantity of fluid, which is actively concerned in the process of digestion; it aids indifferently to bring into solution amylaceous, oleaginous, and albuminoid matters (Bidder and Schmidt).

(1690) 3. THE PANCREATIC FLUID.—The secretion from the pancreas resembles the saliva in some respects. It has an alkaline reaction, and putrefies rapidly. It possesses the power of saccharifying starch in an eminent degree, so that it assists in an important manner in the assimilation of the amylaceous portion of the food, which is not rendered soluble by the action of the gastric juice. Bernard considers that one of its chief functions is to aid in the assimilation of fatty substances, but it does not saponify the fats, as he at first imagined. It is, however, certain that the pancreatic fluid furnishes a very perfect emulsion when agitated with oil, and it has been found that such an emulsion continues to exhibit the same milky appearance if left at rest for fifteen or twenty hours. Under these circumstances the emulsion, which at first has an alkaline reaction, generally becomes acid, and butyric and other volatile acids are found in the liquid. The liquid from the pancreas has a specific gravity of 1008 or 1009, and contains about 10 per cent. of solids

in solution; among which are leucine, xanthine, guanine, and inosin. It generally becomes coagulated when heated, and is one of the few secretions which contains albumin in the soluble form, the proportion of albumin having been found by Tiedemann and Gmelin, in some cases, to amount to 4 per cent. of the entire liquid. They also ascertained the presence of albumin in this secretion in the horse, the sheep, and the dog.

(1691) 4. MUCUS.—Those cavities of the body which communicate with the external surface are lined with a peculiar kind of membrane, distinguished as the mucous membrane. The material of which these membranes consist appears closely to resemble albumin in its coagulated state, but it is covered with a pavement of nucleated epithelium cells, which are continually undergoing gradual disintegration and solution. A tough viscid secretion, termed *mucus*, constantly bathes the surface of these membranes. In this secretion the epithelial particles can be traced in different stages of disintegration. The characters of mucus differ greatly according to the surface from which it is obtained; but it usually assumes the appearance of a tough glairy semi-transparent mass, which swells up in water, but is not dissolved by this liquid. To the substance which gives it this glairy consistence the name of *mucin* has been applied. Mucin is turned yellow by nitric acid; but it differs from albumin, since its solutions are not precipitated by corrosive sublimate: it is also not precipitated from its acid solutions by potassic ferrocyanide until after the acid solution has been boiled. The mucus from the surface of the alimentary canal and its appendages is coagulated by acetic acid and weak acids in general, but it is soluble in alkaline solutions. The mucus from the surface of the urinary organs is dissolved to a certain extent both by acids and by alkalies. Both forms of mucus are immediately coagulated by alcohol, and the secretion presents many characters resembling those of a solution of albumin. Alkaline chlorides are abundant in mucus from the nose; and the phosphates of the alkalies and small quantities of the phosphates of the earths are also present.

(1692) 5. THE BILE.—This important secretion is produced from venous blood by the liver, and in most animals provision is made for its accumulation in a sac connected with the gland, termed the *gall-bladder*. When taken from this receptacle it constitutes *gall*, or *cystic bile*.

Human bile is a ropy liquid of a yellowish-green colour

when concentrated, but of a bright yellow when diluted. It has a peculiar musky odour and a bitter taste. When poured into water it sinks to the bottom, and does not mingle readily with it, but it may be mixed with it by agitation, and it then forms a liquid which froths strongly, like a solution of soap. The viscosity of the bile is owing to the presence of a quantity of mucus from the gall-bladder, which it holds in solution. Owing to the presence of this mucus the bile is very prone to putrefaction; but if the mucus be got rid of by coagulation with acetic acid and filtration, or otherwise, the bile may be preserved without decomposition for some time. When freed from mucus, bile is soluble readily in water and in alcohol, but insoluble in ether. The vegetable acids do not coagulate it; but hydrochloric, sulphuric, and nitric acids occasion precipitates immediately if concentrated, or more slowly if diluted. Aqueous solutions of bile are precipitated copiously by solutions of basic plumbic acetate; the solution is soluble in excess of lead acetate to some extent, and is freely soluble in an excess of acetic acid.

Ox bile, owing to the facility with which it may be procured, is the variety which has been chiefly examined. It has usually a sp. gr. of about 1.026, and, according to Berzelius, it contains the following ingredients in 100 parts:—

| | |
|--|-------|
| Water | 90.44 |
| Biliary and fatty bodies | 8.00 |
| Mucus | 0.30 |
| Watery extract, chlorides, phosphates, and lactates | 0.85 |
| Soda | 0.41 |

Human bile, according to Goup-Besanez, contains the following constituents in 1000 parts:—

| | |
|--------------------------------------|----------------|
| Solids | from 177 to 92 |
| Water | „ 823 „ 908 |
| <hr/> | |
| Biliary acids with alkali | from 108 to 56 |
| Fat and cholesterin | „ 47 „ 40 |
| Mucus and colouring matter | „ 24 „ 15 |
| Ash | „ 11 „ 6 |

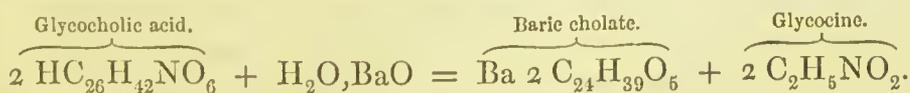
No albumin is present in the bile, but its organic constituents contain a small percentage of nitrogen. It also contains sulphur in notable quantity. It is remarkable that the salts found in the bile of salt-water fishes consist almost exclusively of those of potassium, while the salts of the bile of fresh-water fishes, and of

the herbivora, consist chiefly of those of sodium, although, from the circumstances in which the two classes of animals are placed, the opposite results might have been anticipated.

Owing to the facility with which bile undergoes decomposition, the statements of the earlier chemists who examined this liquid were contradictory; but the masterly researches of Strecker have at length removed all doubt respecting the true nature of the biliary secretion. The result of these investigations has been to show that ox bile may be regarded as a species of soap formed by the combination of two peculiar resinoid acids with sodium. Both of these resinous acids (the *glycocholic* and the *taurocholic*) contain nitrogen. The *taurocholic* acid also contains sulphur, but the *glycocholic* acid is free from this element. Ox bile likewise contains, in addition to the mucus of the gall bladder, minute quantities of cholesterin, and a small amount of stearic, oleic, and lactic acids, united with potassium and ammonium. Besides these substances, a peculiar colouring matter is found in combination with an alkaline base (*Lieb. Ann.*, lxx., lxxvii., and lxx.).

(1693) *Glycocholic Acid* [*Cholic Acid* of Strecker (from $\chi\omicron\lambda\eta$, bile); $\text{HC}_{26}\text{H}_{42}\text{NO}_6$].—This acid constitutes the principal portion of the resinous matter of ox bile; it forms white, voluminous, silky, acicular crystals, which shrink much in drying; it is sparingly soluble in cold water, more freely so in hot water; the solution on cooling deposits crystals, which have a bitterish-sweet taste. Alcohol dissolves it freely, but leaves it as a resinous mass on evaporation: it is very sparingly soluble in ether. The salts which it forms with the metals of the alkalies and of the earths may be crystallized; they are soluble in alcohol.

Glycocholic acid, when boiled with excess of an alkaline liquid, such as solution of baryta, undergoes a remarkable decomposition: the whole of the nitrogen is separated in the form of glycocine, which remains in the solution, and a new resinoid acid, the *cholic acid* of Demarçay (*cholalic acid* of Strecker), is found in combination with barium:—



The elements of 1 molecule of glycocholic acid, with those of 1 of water, contain the elements of 1 molecule of cholic acid and 1 of glycocine; so that the decomposition of glycocholic acid by alkalies is analogous to that of hippuric acid, by acids. If glycocholic acid be boiled with acids it gradually loses water, and

becomes converted first into *cholonic acid* ($C_{26}H_{41}NO_5$), and then into glycocine and *choloidic acid* ($C_{45}H_{78}O_9$; 1695), and the latter, by a further loss of water, is ultimately changed into *dyslysin* ($C_{48}H_{72}O_6$).

Solutions of the normal plumbic acetate, of corrosive sublimate, and of argentic nitrate, produce no precipitates in an aqueous solution of glycocholic acid. The salts which it forms with the alkalis are also unaffected by solution of baric chloride; but they are precipitated when mixed with solutions of the salts of copper, of lead, of iron, and of silver. The silver precipitate is somewhat soluble in boiling water, and crystallizes as the solution cools. Acetic and other acids, when added to the solutions of the glycocholates, decompose them, and throw down the acid in the form of a resin. *Sodic glycocholate* ($NaC_{26}H_{42}NO_6$) may be obtained in crystals by the addition of three or four times its bulk of ether to its alcoholic solution, but it does not crystallize either from water or from alcohol: it fuses easily to a resinous mass. The crystals have a very characteristic form; they consist of six-sided prisms, with the ends obliquely truncated. The *crystallized bile* of Platner consists of a mixture of potassic and sodic glycocholates.

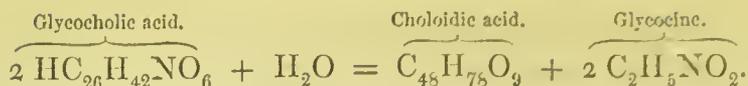
Preparation.—Glycocholic acid is not obtained pure without considerable difficulty. Recent ox bile is evaporated, and the residue is dried at a temperature of 248° (120° C.); after which it is digested with cold absolute alcohol. The solution thus obtained is filtered, and anhydrous ether is added gradually, by which means a brown resinous mass is separated. As soon as the liquid has thus deposited most of the colouring matter, it is decanted, and the potassic and sodic glycocholates, which are still retained in solution, are precipitated by the further addition of ether. The liquid becomes milky, and a further separation of a resinoid substance occurs, after which the glycocholates are gradually deposited in the form of stellate tufts of needles. These crystals must be washed with anhydrous alcohol, containing one-tenth of its weight of ether, and then dried rapidly *in vacuo*. In order to obtain the acid, the crystals must be dissolved in water, and precipitated by dilute sulphuric acid; crystals of glycocholic acid are slowly deposited. This substance, however, is not pure even yet, for a part only of these crystals is soluble in water, scales of a body isomeric with glycocholic acid being left; this insoluble portion has been termed *paracholic acid* by Strecker. If paracholic acid be dissolved in alcohol, the addition of water precipitates it in the form of crystals of glycocholic acid.

(1694) *Cholic Acid* of Demarçay, *Cholalic Acid* of Streeker; ($\text{HC}_{24}\text{H}_{39}\text{O}_5, \text{H}_2\text{O}$, and $2\frac{1}{2}\text{H}_2\text{O}$); *Fusing pt.* 383° (195° C.).—By adding hydrochloric acid drop by drop to the solution of boric cholate obtained by boiling glycocholic acid with baryta, the cholic acid is separated as a resinous mass; and this, on adding a small quantity of ether, is converted into colourless tetrahedra or octahedra, which are brittle and efflorescent. Cholic acid is very slightly soluble in water, forming with it a solution which distinctly reddens litmus. It is however freely soluble in alcohol, but less soluble in ether. The ethereal solution deposits the acid in rhombic tabular crystals which contain H_2O ; this water of crystallization may be expelled by a gentle heat, after which the acid fuses at 383° , and a little beyond this it loses its basic water, and becomes converted into choloidic acid, and by a still further heat, into dyslysin (1695).

The cholates of the alkali-metals and of barium are soluble in water and in alcohol; most of them may be crystallized from their alcoholic solution. The most characteristic test for cholic acid is furnished by treating it with sugar and sulphuric acid; an intense red colour, passing into a violet, is thus developed. Pettenkofer, to whom this observation is due, has founded upon it an excellent test for the presence of bile in organic fluids; cholic acid is formed by the action of the sulphuric acid upon the resinoid acids of the bile, and then furnishes the reaction in question. In order to apply this test, an alcoholic extract of the substance for examination is prepared, and dissolved in water; a drop of syrup consisting of 1 part of sugar to 4 of water is then added, and pure sulphuric acid free from sulphurous acid is cautiously poured in; the liquid at first becomes turbid, but it clears as more acid is added, and passes in succession through cherry red, carmine, and purple, into violet. The temperature must not be allowed to rise beyond 122° or 131° (50° or 55° C.), and care must be taken not to use too much sugar, as it would be liable to become charred by the sulphuric acid. Acetic acid may be substituted for the syrup in applying this test.

Cholic acid approaches the fatty acids in character, and its salts are somewhat analogous to ordinary soaps.

(1695) *Choloidic Acid* ($\text{C}_{48}\text{H}_{78}\text{O}_9$).—Glycocholic acid is soluble in cold concentrated acetic, sulphuric, and hydrochloric acids without alteration, but it is decomposed when heated with them. If glycocholic acid be boiled with hydrochloric acid, glycocine is separated, and a new resinous acid, the *choloidic* of Demarçay, is produced:—



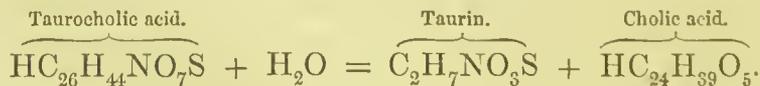
Two molecules of cholic acid, by the abstraction of the elements of one molecule of water, furnish one of choloidic acid.

Choloidic acid is a resinous, white, friable substance, freely soluble in alcohol, scarcely soluble in ether, and insoluble in water. It reddens litmus, and when treated with sulphuric acid and sugar produces the same reactions as cholic acid. The alkaline choloidates are soluble in alcohol and in water, but they do not crystallize: baric choloidate is insoluble in water. These salts are isomeric with the cholates, but do not at all resemble them. Choloidic acid is stated to contain no basylous hydrogen, but this is not probable.

Both cholic and choloidic acids, like oleic acid, when distilled with nitric acid yield, by oxidation, the volatile fatty acids of the group $\text{C}_n\text{H}_{2n}\text{O}_2$; acetic, butyric, caproic, cœnanthylic, caprylic, pelargonic, and capric acids having been discovered in the results of the distillation by Redtenbacher. Various other oxidized products remain in the retort, among which are oxalic and cholesteric acids (1700), and a crystallizable body termed *choloidanic acid* ($\text{C}_{16}\text{H}_{24}\text{O}_7$).

By long boiling with hydrochloric acid, the choloidic acid in turn is decomposed; each molecule loses 3 molecules of water, and becomes converted into neutral resin ($\text{C}_{43}\text{H}_{72}\text{O}_6$) fusible at 284° (140° C.), and which, from the difficulty of bringing it into solution by ordinary solvents, Berzelius called *dyslysin* (from δύσ, difficult, λύσις, solution).

(1696) *Taurocholic Acid; Choleic Acid* of Strecker ($\text{HC}_{26}\text{H}_{44}\text{NO}_7\text{S}$).—The sulphuretted acid of ox bile is the less abundant of its two components; though it is the principal ingredient in the bile of serpents, of fishes, and of some other animals; it does not appear to have been isolated in a perfectly pure state. It has however been ascertained that it gives rise, by treatment with acids, to cholic or to choloidic acid, and to dyslysin, but instead of glycocine it furnishes a remarkable crystallizable body, which contains all the sulphur of the acid; this substance has been named taurin ($\text{C}_2\text{H}_7\text{NO}_3\text{S}$):—



Preparation.—In order to obtain taurocholic acid of tolerable purity, the following method recommended by Heintz may be employed:—To an aqueous solution of ox bile, normal plumbic acetate is added so long as it occasions a precipitate; the mucus, the oily acids, and the principal part of the glycocholic acid are thus thrown down, and must be separated by filtration. To the clear liquid a solution of basic plumbic acetate must next be added in small quantities at a time, until the successive precipitates become quite white, and assume a plaster-like consistence, when the liquid must be again filtered and precipitated by the addition of an excess of basic plumbic acetate mixed with free ammonia. This precipitate, which consists almost entirely of plumbic tauro-

cholate, must be purified by solution in alcohol, and reprecipitation by water, after which it must be decomposed by the action of sulphuretted hydrogen, and the taurocholic acid may then be obtained by evaporating the solution, after filtering it to remove the plumbic sulphide.

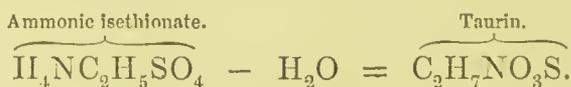
The taurocholates of the alkali-metals are very soluble in water and in alcohol. They give no precipitate with normal salts of lead, but with basic salts of this metal slowly deposit a plaster-like compound, which is soluble in boiling water. They yield with sulphuric acid and sugar a violet colour similar to that produced by the cholates.

(1697) The bile of most animals yields taurin when treated with the concentrated mineral acids, since the occurrence of taurocholic acid is almost universal in this secretion, but the other resinoid acid varies in different classes of animals; that obtained from the bile of the pig, for example, is termed (from $\upsilon\varsigma$, $\upsilon\delta\varsigma$, a pig), *hyocholic acid*, and contains $(\text{HC}_{27}\text{H}_{12}\text{NO}_5)$. Hyocholic acid yields glycocine when boiled with acids, whilst a new resinoid acid, the *hyocholalic* $(\text{HC}_{25}\text{H}_{29}\text{O}_4)$, is separated. The compound which hyocholic acid forms with lead does not possess the fusible plaster-like character which distinguishes the lead salts of glycocholic and taurocholic acids.

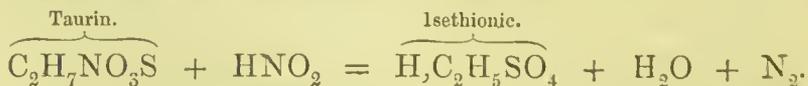
By long boiling with acids hyocholic acid is converted into glycocine, and *hydyslysin* $(\text{C}_{50}\text{H}_{76}\text{O}_6)$, which is homologous with dyslysin, but contains 2 (CH_2) more than the latter compound. Hyocholic acid itself is homologous with cholic acid $(\text{HC}_{26}\text{H}_{40}\text{NO}_6)$, the resinous acid produced by boiling glycocholic acid with water, which under these circumstances loses the elements of one atom of water. *Hyocholeic acid* $(\text{HC}_{27}\text{H}_{44}\text{NO}_6\text{S})$, the sulphuretted acid of pigs' bile, bears a similar relation in its composition to taurocholic acid that the hyocholic does to glycocholic acid; that is to say, it contains 1 atom of oxygen less, and 1 atom of carbon more, than taurocholic acid. Strecker has also discovered in the pig's bile a small quantity of a new base, which he terms *choline* $(\text{C}_8\text{H}_{13}\text{NO})$.

(1698) *Taurin* $(\text{C}_2\text{H}_7\text{NO}_3\text{S})$.—This remarkable substance was first procured from ox bile, and hence its name, from *taurus*, a bull. It may be prepared by freeing fresh bile from mucus by the addition of an acid, and filtering it; the clarified bile is then boiled for some hours with hydrochloric acid; the liquid decanted from the resinous acids is evaporated on the water-bath nearly to dryness, and decanted from the crystals of sodic chloride which have separated: the mother-liquor is then mixed with 5 or 6 times its bulk of alcohol, and the liquid on cooling yields crystals of taurin, which must be purified by recrystallization from water. The crystals of taurin assume the form of a six-sided prism terminated by four and six-sided pyramids resembling those of quartz. Taurin has a cooling taste; it is soluble in about 16 parts of cold

water, but it is not soluble in absolute alcohol or in ether. The mineral acids dissolve taurin without alteration, but do not combine with it, and even when heated with it they do not decompose it. Taurin contains more than 25 per cent. of sulphur, but is a compound of remarkable stability. When burned in the open air it emits abundance of sulphurous anhydride. A solution of caustic potash dissolves it, and if boiled down with it nearly to dryness, decomposes it, ammonia being evolved abundantly, while potassic sulphite and acetate are formed. Hence it appears that the sulphur is already in an oxidized condition. Taurin is isomeric with sulphite of aldehyd-ammonia, a compound which may be prepared artificially, but which differs in properties from taurin; $C_2H_4O, H_3N, SO_2 = C_2H_7NO_3S$. Streeker (*Chem. Gaz.*, 1854, 388) has however succeeded in procuring taurin artificially from ammoniac isethionate. Isethionic acid is prepared by absorbing olefiant gas by means of sulphuric anhydride, and the product thus obtained is dissolved in water; on neutralizing the liquid with ammonia, and evaporating it until crystals are formed on cooling, the ammoniac isethionate ($H_4NC_2H_5SO_4$) is obtained. Now this salt contains the elements of 1 molecule of taurin and 1 of water:—



On heating the isethionate gradually to 446° (230° C.), it loses 11 per cent. of its weight, and the residue, when dissolved in water, yields by spontaneous evaporation crystals which have the form and properties of taurin from bile. By the action of nitrous acid taurin may be reconverted into isethionic acid:—



Cloetta has found taurin in small quantity ready formed in the lungs of the ox.

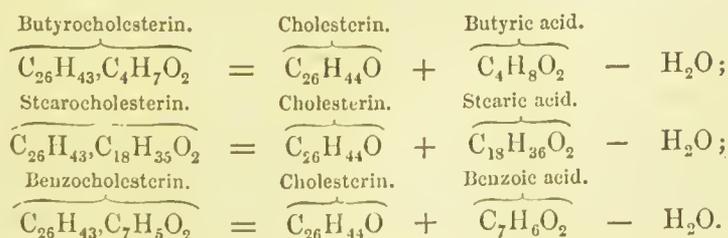
(1699) *Cholesterin* (from $\chiολή$, bile, $\sigmaτέαρ$, suet; $C_{26}H_{44}O$, H_2O); *Fusing pt.* 293° (145° C.).—This crystallizable fatty body constitutes a never-failing ingredient of healthy bile, though, according to Berzelius, it does not exceed in quantity one part in 10,000 of the bile. It is probably held in solution by the agency of taurocholic acid, which possesses a certain solvent power over cholesterin. It acquires its chief interest and importance from the circumstance that, owing to its extreme insolubility, it cannot be reabsorbed when once deposited, and hence it frequently accumulates in the gall-bladder, and forms the principal ingredient

in the most common variety of *gall-stone*, or biliary calculus. Cholesterin is found also as a normal constituent of the blood; it is present in the brain in considerable quantity; it is moreover a constituent of the yolk of the egg, and in small proportion is a very frequent component of serous and fibrous exudations. It appears likewise to be always present in pus, and is commonly met with in the residue of the putrefaction of muscular tissue. It also occurs in the vegetable kingdom, having been found in small quantity in almond oil and olive oil, as well as in wheat, peas, and other seeds.

Preparation.—Gall-stones which contain cholesterin have a crystalline structure; they fuse on the application of heat, and they often have a specific gravity less than that of water. Such calculi furnish the best source of cholesterin. In order to obtain it from them, the powdered gall-stones should be boiled in alcohol; the solution as it cools deposits characteristic rhombic plates of cholesterin, which, after one or two recrystallizations, is obtained in a pure state.

Cholesterin is nearly insoluble in water, but it is readily soluble in ether. When the ethereal solution is mixed with half its volume of alcohol and left to spontaneous evaporation, regular crystals are deposited; they contain about 5 per cent. of water: when heated to 212° , the crystals become opaque, and the water is expelled. Cholesterin fuses at 293° , and becomes crystalline on cooling; it may be distilled at a temperature of 662° (350° C.) without decomposition; but at a somewhat higher temperature it is partially decomposed. In the open air it burns with a smoky flame. The alkalies do not act upon it.

Berthelot finds that by heating cholesterin for some hours in a sealed tube with various acids in excess, compounds may be obtained corresponding to the ethers of cholesterin, thus verifying the suggestion of Gerhardt, that cholesterin is a monobasic alcohol ($C_{26}H_{43}HO$). In this manner the following compounds have been formed:—



These cholesteric ethers are white fusible compounds, sparingly soluble in boiling alcohol, which may be employed to purify them from unaltered cholesterin or acid. They are freely soluble in ether, and are readily decomposed by heating them with an alcoholic solution of potash.

(1700) Concentrated sulphuric acid decomposes cholesterin, by removing water and forming a mixture of three isomeric resinoid hydrocarbons ($C_{26}H_{42}$).

termed *cholesterilin*, which are distinguished by the letters *a*, *b*, and *c*. These hydrocarbons bear the same relation to cholesterin that olefiant gas does to ethyl alcohol. Long boiling of cholesterin with nitric acid converts it first into a resinous mass and then decomposes it, producing, amongst other bodies, *cholesteric acid* ($H_2C_8H_8O_8$), which assumes the form of a light-yellow deliquescent substance, of an acid and bitter taste; it is readily soluble in alcohol. According to Redtenbacher, the production of acetic, butyric, caproic, and oxalic acids, also accompanies the formation of cholesteric acid.

(1701) *Biliary calculi* are often found in the gall-bladder in large numbers; they vary a good deal in appearance and shape: in some cases they are nearly semi-transparent, and crystallized throughout, at other times they are strongly tinged with the colouring matter of the bile. Occasionally the cholesterin is deposited upon a nucleus of calcic phosphate, or of biliary colouring matter in combination with lime.

In some species of oriental goats, waxy-looking concretions, called *bezoars*, of a brownish-green colour, are occasionally found in the stomach and intestines; they contain a substance termed *lithofellic acid* (from *λίθος*, a stone, *fel*, gall; $HC_{20}H_{25}O_4$). This body a good deal resembles cholesterin in appearance; it crystallizes in six-sided prisms, or in small rhombic prisms, with an oblique terminal face. It is insoluble in water, sparingly soluble in ether, but largely soluble in hot alcohol and in acetic acid. Concentrated sulphuric acid also dissolves it freely, the solution becoming milky when diluted with water. Lithofellic acid fuses at 401° (205° C.), and if heated to a little beyond this, it is converted into a resinous mass, the fusing point of which is reduced to about 230° (110° C.). If this resin be redissolved in alcohol it is again converted into the crystallizable acid. Lithofellic acid burns with an agreeable odour and a white smoky flame. It forms soluble salts with the alkali-metals; the salts of lead and of silver are insoluble, and soften in hot water. Lithofellic acid is distinguished from cholesterin by its higher melting point, and by its ready solubility in solutions of the caustic and carbonated alkalies, and in acetic acid. When treated with sulphuric acid and sugar, it gives a violet colour resembling that produced by glycocholic acid.

(1702) The following table will assist in indicating the relations which subsist between the most important of the numerous compounds obtainable from the bile:—

| | | | |
|------------------------|-------------------------|------------------------|---------------------|
| Glycocholic acid . . . | $C_{26}H_{43}NO_6$ | Hyochohic acid . . . | $C_{27}H_{43}NO_5$ |
| Cholonic acid . . . | $C_{26}H_{41}NO_5$ | Hyocholalic acid . . . | $C_{25}H_{40}O_4$ |
| Cholic acid . . . | $C_{24}H_{40}O_5, H_2O$ | Hydodyslysin . . . | $C_{50}H_{76}O_6$ |
| Choloidic acid . . . | $C_{48}H_{78}O_9$ | Hyocholeic acid . . . | $C_{27}H_{45}NO_6S$ |
| Dyslysin . . . | $C_{48}H_{72}O_6$ | Lithofellic acid . . . | $C_{20}H_{36}O_4$ |
| Taurocholic acid . . . | $C_{26}H_{45}NO_7S$ | Glycocine | $C_2H_5NO_2$ |
| Cholesterin . . . | $C_{26}H_{44}O, H_2O$ | | |
| Taurin | $C_2H_7NO_3S$ | | |

(1703) *Colouring Matters of the Bile*.—If an alcoholic solution of bile be filtered through a column of animal charcoal, it runs off nearly deprived of colour. The colouring matter of the bile appears to exist in three modifications; one of them is brown, a

second red, and the third green: the latter is abundant in the herbivora; it forms the *biliverdin* of Berzelius, who considered this green pigment to be identical with chlorophyll, or the green colouring matter of vegetables, an opinion since found to be erroneous. The exact composition of all these colouring bodies is yet a matter of dispute. They have lately been elaborately examined by Thudichum, but his numerous analyses still leave the subject undecided. Stædeler's analysis of biliverdin (*Liebig's Annal.*, cxxxii. 323) leads to the formula $(C_{16}H_{20}N_2O_5)$. It is insoluble in water, but is taken up by alcohol and by ether. The *cholepyrrhin*, or *biliphæin*, obtained by Brücke crystallized from its solution in chloroform, according to Maly, is an amide of biliverdin. In human bile the brown pigment preponderates; it has been termed *bilifuscin*. This bilifuscin is soluble in absolute alcohol, but insoluble in chloroform and in absolute ether, and nearly insoluble in water. Stædeler gives its formula as $C_{16}H_{20}N_2O_4$, or as containing H_2O more than bilirubin, and an atom of oxygen less than biliverdin. The red colouring matter is of an acid character; it is insoluble in water, sparingly soluble in alcohol and in ether, but soluble in chloroform, from which it may be obtained in crystals of a dark red colour ($C_{16}H_{18}N_2O_3$; Stædeler), and is by this chemist called *bilirubin*. It combines with the alkalies, forming solutions which are of a deep orange-yellow, and when largely diluted, of a yellow colour, like that of a jaundiced person; with the earths it forms compounds which are insoluble in water and in alcohol. This brownish-red colouring matter of the bile is very rapidly altered by reagents. The changes of colour produced in it by the action of nitric acid have been proposed as one means of detecting the presence of bile in certain cases, as, for instance, when it occurs in urine: when a solution containing this colouring matter is mixed with nitric acid, the colour becomes at first green, then blue, passing rapidly into violet; it then changes to red, and finally the red passes slowly into yellow.

Many biliary calculi contain a large quantity of the colouring material in combination with lime, with which it forms a brown compound insoluble in water. Calculi are also frequently found in the ox composed of a pure intense yellow colouring substance, much prized by artists for its durability and for the brilliancy of its tint.

The greater part of the colouring matter of the bile, with a small portion of bile itself, passes off with the fæces, but by far the larger proportion of this secretion is reabsorbed into the

system, where it has been conjectured to supply a portion of the material consumed by the oxygen in respiration for the maintenance of animal heat. This theory, however, seems to be questionable, since the constituents of the bile have not been satisfactorily discovered in normal blood.

The resinous acids of the bile, which constitute the characteristic components of this secretion, appear to be truly formed by the liver itself. The mode of action of the liver differs therefore in an important manner from that of the kidneys, since these glands do not produce the compounds excreted by them.

(1704) Sugar is not an ingredient in normal bile, but it is remarkable that this substance is formed rapidly from glycogen (1095) one of the constituents of the liver itself, in which organ sugar is found in considerable quantity after death (Bernard). The full significance of this fact, in its physiological bearings, cannot be said to be at present understood.

In cases of metallic poisoning, the liver has generally been found to contain traces of the metal that has been swallowed, but it is important to bear in mind that iron, copper, and manganese are always present in minute quantity in the ashes of healthy human bile. Lead, arsenic, and antimony have been detected in the liver, in cases where they had been taken in poisonous doses; and there is no reason to suppose that traces of these substances will not be found in the liver, if duly sought for after death during the exhibition of these metals in medicinal doses.

C. *Excrementitious Products.*

(1705) THE URINE.—This fluid is separated by the kidneys from arterial blood. Healthy human urine, to which the following remarks are applicable, unless otherwise specified, is a clear liquid, usually of a light amber colour, and, if passed when fasting, is feebly acid to litmus; but, according to Benec Jones, the acidity diminishes during digestion, and while this process is most active, the urine is often found to be slightly alkaline. Urine has a peculiar odour, and a saline bitter taste; as it cools, it frequently becomes more or less turbid, from deposition of urates. Its specific gravity varies with the diet and state of health of the individual, but it usually averages about 1.020. The quantity passed during the twenty-four hours also varies with the quantity of liquids taken, but on an average it may be estimated in the adult at from 40 to 50 ounces. Urine, when left to itself, speedily begins to undergo change. In most cases it

first exhibits an increase of acidity, as Scherer has shown; but after standing for a few days it begins to putrefy, and then acquires a powerfully alkaline reaction and an ammoniacal odour, owing to the conversion of the urea into ammonic carbonate. This alkaline decomposition of the urine sometimes takes place within the bladder, particularly after injuries to the spinal cord attended with paralysis of the lower part of the body. The mucus of the bladder appears to act as a ferment upon the urine, and has a large share in producing this decomposition of the urea.

Composition.—Urine contains among its components, urea, a small quantity of kreatine and kreatinine, uric acid, traces of hippuric acid, and of glucose, besides hydrochloric, sulphuric, and phosphoric acids, in combination with potassium, sodium, calcium, magnesium, and traces of ammonium. It also always contains a little vesical mucus, together with a peculiar colouring matter, and some other ill-defined azotised principles. In addition to these bodies, Stædeler has noticed the presence of minute quantities of certain acids homologous with the carbonic and with oleic acid. The bodies contained in the urine are mainly the products of oxidation, occasioned by the action of respired air upon the blood and nitrogenised tissues, and upon the sulphur and phosphorus which they contain. The following table represents the composition of an average sample of healthy human urine:—

| | | | |
|---------------------|----------------------------|--------------------------------|-------------------------------------|
| | Specific gravity | 1·020 | |
| | Water | 956·80 | In 100 parts of solid matter. |
| Solid matters, 43·2 | Organic matters, 29·79. | Urea | 14·23 . 33·00 |
| | | Uric acid | 0·37 . 0·86 |
| | | Alcoholic extract | 12·53 . 29·03 |
| | | Watery extract | 2·50 . 5·80 |
| | | Vesical mucus | 0·16 . 0·37 |
| | Fixed salts, 13·35. | Sodic chloride | 7·22 . 16·73 |
| | | Phosphoric anhydride | 2·12 . 4·91 |
| | | Sulphuric anhydride | 1·70 . 3·94 |
| | | Lime | 0·21 . 0·49 |
| | | Magnesia | 0·12 . 0·28 |
| | Potash | 1·93 . 4·47 | |
| | Soda | 0·05 . 0·12 | |
| | | <hr/> 999·94 | <hr/> 100·00 |

The quantities of the various components of the urine are, however, subject to material variation, even in the same individual at different times, although he may be in perfect health. The

quantity of solid matters, and especially of urea, is proportionately somewhat increased with the increased amount of exercise taken, as the direct experiments of Lehmann have shown. Indeed, it has been found to be a general rule that the waste and reparation of the body are in direct proportion to the amount of exercise taken: during active exercise the number of inspirations in a given space of time is increased, a larger quantity of oxygen is brought into contact with the blood and the tissues, and a more rapid waste of the components ensues, and consequently a greater supply of food is demanded after exercise than after the individual has been in a state of repose for an equal interval.

In all animals the urine appears to form the principal outlet for the nitrogen of the effete azotised tissues of the system, though the compounds in which it is excreted vary with the kind of animal.* Carnivorous animals, such as the lion, the tiger, and the leopard, excrete the greater part of the nitrogen in the form of urea; and produce but a small quantity of uric acid. The urine of these animals is clear, and nearly colourless, with an offensive odour and a strongly acid reaction; but it putrefies rapidly, and quickly becomes alkaline, owing to the decomposition of the urea. The herbivora likewise excrete a large quantity of urea; but hippuric acid in considerable quantity is contained in their urine, whilst uric acid is nearly wanting. Many of these animals, such as the rhinoceros and elephant, excrete a urine containing a large quantity of the bicarbonates of calcium and magnesium, in consequence of which their urine is either turbid when voided, or it speedily becomes so. The phosphates are almost entirely absent from the urine of the herbivora, but they occur abundantly in the fæces of these animals. Carnivorous birds excrete uric acid in abundance in the form of a superurate of ammonium, and they also appear to excrete small quantities of urea: but urea is completely absent in granivorous birds, which excrete abundance of uric acid combined with a variable amount of ammonia. In those carnivorous reptiles which live out of water, such as the serpent tribe, the excretions are semi-solid, and consist almost entirely of uric acid; whilst in the amphibia, such as the frog and the toad, urea appears, with very little uric acid. Uric acid has also been found in the excrements of insects. From these facts,

* Ranke estimates the quantity of nitrogen which passes off by the alvine evacuations in man at $\frac{1}{2}$ of that excreted by the kidneys, but nearly the whole of this is derived from undigested portions of the food; it must vary with the nature of the food, and but a very small proportion, if any, has any connexion with the waste of the tissues.

it is clear that in those animals which drink freely, the nitrogen is excreted principally in the form of urea, whilst in those which take very little fluid nutriment it is separated chiefly in the form of uric acid.

In diseases attended with fever the quantity of uric acid in human urine is greatly increased. The question of the source whence uric acid is derived is full of interest, especially to the practical physician, since its morbid prevalence is intimately connected with some of the most distressing maladies which afflict the human frame, such, for example, as gout, rheumatism, and certain forms of calculous conerctions from the urine. In some kinds of gout, uric acid is developed and retained in the system, chiefly in the form of sodic urate, in the neighbourhood of the smaller joints, such as those of the fingers and toes and the wrists, forming deposits commonly known as chalk-stones. The system is in these cases loaded with lactic and acetic acids, the latter of which is thrown off abundantly in acid sweatings. Dr. Garrod, in cases of gout, has invariably found uric acid to be present in the blood, and he has also frequently detected it in the blood in Bright's disease: it has been found occasionally in healthy blood. Uric acid is likewise discovered without difficulty in the blood of animals from which the kidneys have been extirpated.

The composition of the urine is found to vary at different times of the day. That voided in the morning, for example, after abstinence from food for some hours, is the result chiefly of chemical actions going on within the body itself, and is furnished by the decomposition of the tissues. Such urine has a very different composition from that passed in the evening, into which various bodies have been absorbed directly from the stomach. These bodies necessarily vary with the food, and variation in the quality of the food is also the principal cause of variation in the quantity both of uric acid and of urea. In proportion to the quantity of nitrogen contained in the food, the proportion of urea excreted increases. This was distinctly proved by C. G. Lehmann, and his results have been confirmed by all subsequent observers. With reference to this point, it was found by Lehmann in a series of experiments upon his own person, that after restricting himself to an animal diet for twelve days, he excreted daily 821 grains (53·2 grms.) of urea, and 21·6 grains, or 1·4 grms. of uric acid. After an exclusively vegetable diet for a similar period, the quantity of urea in twenty-four hours amounted to 348 grains, or 22·5 grammes, and the uric acid to 15·4 grains, or 1 gm.; and after subjecting himself for three days to a diet from which

nitrogen was as far as possible excluded, the quantity of urea fell to 237 grains (15·4 grms.). When a highly azotised diet was taken, the same observer found that five-sixths of the entire quantity of nitrogen taken in the food were eliminated from the system in the form of urea. With an ordinary mixed diet, according to observations extended over 15 days, the urine amounted to 37·3 ounces daily, and it contained 501 grains (32·5 grms.) of urea, and 18·2 grs. or 1·183 grms. of uric acid. This quantity of urea thus obtained during the use of an ordinary mixed diet agrees very closely with the average results collected by Dr. Parkes, and with the average of a long series of experiments by Dr. E. Smith upon himself (*Phil. Trans.*, 1861, 765). The last-named observer found that with an average hourly excretion in the twenty-four hours of 21·7 grains of urea, the average at night per hour was only 16·5 grains. He likewise ascertained that the excretion of urea does not take place at any fixed period after its formation, and that the influence of agents upon the production of urea must be watched for several days. The elimination of urea was often suddenly and considerably increased within less than an hour after taking a draught of water. This was particularly manifest during a period of prolonged fasting. The quantity of sulphates in the urine is also mainly influenced by the proportion of azotised food taken; these salts, indeed, appear to be derived principally from the oxidation of the sulphur contained in the albuminoid compounds assimilated from the food. When a mixed diet was used, Lehmann found the quantity of sulphates excreted daily to represent 108 grains of SO_3 ; with an animal diet it rose as high as 165 grains, and when a purely vegetable diet was consumed, the quantity of SO_3 excreted in the twenty-four hours fell to 90 grains. Many substances when taken into the stomach pass off unchanged by the kidneys, especially those which are of a saline nature, such, for instance, as potassic iodide and ferrocyanide: these salts may be detected in the urine in less than half an hour after they have been swallowed.

Sehunek has made an elaborate, though as yet incomplete, investigation of the colouring matters of the urine (*Proceed. Roy. Soc.*, xvi. 130). The most important is *urian* ($\text{C}_{43}\text{H}_{51}\text{NO}_{26}$), a dark yellow deliquescent amorphous body of peculiar odour. It is soluble in alcohol and in ether, and becomes decomposed on boiling, into an organic acid and a resin.

(1706) *Urinary Concretions*.—Although the urine in a healthy individual usually remains clear and transparent, even after it has cooled, it not unfrequently, under the influence of disturbed

health, deposits more or less abundantly some of its less soluble constituents: these deposits in certain cases assume the form of a light flocculent powder; at other times they appear in more compact grains, which constitute the different forms of gravel, and in other instances they collect into larger masses, and give rise to urinary calculi.

The most common urinary sediments are those which contain uric acid. When the uric acid is uncombined with bases, it often appears in small crystalline masses, resembling grains of coarse sand, constituting the ordinary variety of *red gravel*, which consists of uric acid tinged with the yellow colouring matter of the urine: this sediment, if examined under the microscope, is usually seen to possess the form of rhomboidal crystalline plates, the edges of which are frequently rounded. In other cases the acid is found in the form of a light-brown amorphous sediment consisting of urates of sodium and ammonium. Both these sediments, and especially the latter, are materially influenced by diet: excess of any kind, particularly in animal diet, drinking too much of aceseent fermented liquors, over-anxiety, exposure to cold, damp weather, and want of exercise, very frequently produce an increased excretion of uric acid, and cause a deposit of the urates of sodium and ammonium even from persons in health. In those suffering from an habitual deposit of red gravel, an animal diet frequently aggravates the disease in a remarkable manner. On the other hand, it has been observed that uric acid is less abundant in the urine in summer, and is generally diminished after copious sweats. Lehmann states that the formation of uric acid calculi is unknown in tropical climates.

When *phosphoric acid* is present in the urine in excess, it sometimes shows itself in the form of a white sand, which is usually crystallized, and consists of ammonio-magnesian phosphate: but occasionally the deposit is amorphous. These two varieties of sediment constitute *white gravel*; they are attended almost constantly by an alkaline state of the urine.

The principal varieties of urinary *calculi* as distinguished from *sediments* are the following:—1. Uric acid; 2. Ammonio urate; 3. Calcic oxalate; 4. Calcic phosphate; 5. Ammonio magnesian phosphate; 6. Fusible calculus (a mixture of the two preceding forms); 7. Xanthic oxide, or Xanthine; and 8. Cystic oxide, or cystin. Urinary calculi are in many cases formed upon some foreign body as a nucleus, such as a clot of blood or a crystal of any kind, and are usually deposited in concentric layers.

1. *Uric acid* calculi are usually of a brownish-red or fawn colour: they have a smooth or finely-tuberculated surface; when

sawn through they are generally found to be composed of concentric laminae, and are somewhat crystalline. If a fragment of such a calculus be heated before the blowpipe, it is consumed, emitting a peculiar animal odour, and leaving only a minute white ash. This variety of calculus is soluble in a solution of potash, and uric acid is precipitated in white silky crystals on supersaturating the solution with an acid. If a fragment be heated on a slip of glass with nitric acid, it is dissolved with effervescence, leaving an orange-coloured residue, which is rendered of a beautiful pink or crimson colour by the addition of a drop of ammonia, after which the addition of a solution of potash develops a magnificent purple (1638).

2. The *ammonic urate* calculus is very rare: it is usually clay-coloured, and smooth; and is deposited in fine concentric layers of an earthy appearance. It is more soluble in water than the preceding variety, and is dissolved with extrication of ammonia when heated with a solution of potash; in other characters it resembles uric acid.

3. *Calcic oxalate* often occurs as a morbid ingredient of urine. The *mulberry calculus* consists of this substance: this form of concretion has usually a deep brown colour; it is deeply tuberculated and rough, and is very dense and hard. When heated before the blowpipe, it first blackens, and then, if exposed to a moderate red heat, it burns to a white ash consisting of calcic carbonate, which is dissolved by acids with effervescence; but if it has been more strongly heated, the ash is alkaline to test-paper, and consists of pure lime. The finely-powdered calculus is soluble in nitric and hydrochloric acids, but it is insoluble in acetic acid. Concretions of calcic oxalate have been found in some of the lower animals, as well as in man. Prout considered its occurrence in the urine to be due to faulty assimilation of saccharine matters, but the conditions under which it is produced are not well ascertained.

4. Calcic phosphate forms a rare species of calculus, the *bone-earth calculus* ($\text{Ca}_3, 2\text{PO}_4$), which is usually of a pale brown colour, with a very smooth surface, and is regularly laminated in its texture; these laminae are often deposited in crystals radiating from the nucleus. The bone-earth calculus is infusible before the blowpipe; it is readily dissolved by hydrochloric acid, and the calcic phosphate may be precipitated from this solution in a gelatinous state by the addition of ammonia.

5. Another form of phosphatic calculus consists of ammonio-magnesian phosphate (H_4NMgPO_4). It is not unfrequent, and is

spoken of by the older writers as *triple phosphate*. It is white, brittle, and more or less crystalline in structure; it is seldom laminated, and its surface is uneven. It fuses with difficulty before the blowpipe, emitting an odour of ammonia: dilute acids dissolve it readily, and the solution when neutralized with ammonia deposits it again in a crystalline form.

6. A third species of phosphatic concretion is the *fusible calculus*, which consists of a mixture of the two preceding varieties. It is of frequent occurrence, and forms white friable masses which are rarely laminated, and often acquire a large size. This form of calculus fuses readily before the blowpipe; it is soluble in dilute acids, from which ammoniac oxalate separates calcic oxalate, and pure ammonia throws down the magnesium as ammoniac-magnesian phosphate. When the occurrence of phosphatic deposits is habitual, it always indicates a state of constitution severely disordered. Occasionally these phosphates are secreted from the lining membrane of the bladder in large quantity, forming a mortar-like mass of concretions. The earthy phosphates are introduced into the system in considerable quantity in the seeds of the cerealia: beer contains so much magnesian phosphate, that, on adding ammonia, the ammoniac-magnesian phosphate is precipitated in abundance.

The phosphates are also common ingredients of calculi in herbivorous animals: in many instances they appear to be deposited from the urine simply from the development of free alkali, either owing to the decomposition of the urea, or to excess of alkaline matter introduced from without.

Compound calculi are not unfrequent; they are formed of a succession of laminæ, composed of one or other of the foregoing varieties. For instance, uric acid, calcic oxalate, and fusible calculus sometimes occur in successive layers in the same concretion.

7 and 8. The characters of the rare calculi containing the compounds known as *xanthic* and as *cystic oxide* have been already described (1612, 1643).

The further prosecution of this subject belongs more properly to a work devoted to pathology than to one treating of general chemistry. For the microscopic appearances of the various substances deposited from the urine, the reader is referred to Golding Bird's treatise *On Urinary Deposits*, and to Beale's treatises *On the Microscope*, and *On Urine, Urinary Deposits, and Calculi*.

(1707) The urine in disease undergoes other important modifications in its constitution: two only of these will be adverted to on the present occasion.

Diabetic Urine.—In the disease termed *diabetes* the urine is found to contain a large quantity of grape-sugar, which is almost entirely wanting in the healthy state of the secretion. The source of this sugar lies in the faulty digestion of the food. The sugar appears to be absorbed directly from the alimentary canal into the blood, and is thence separated unchanged by the kidney. Percy has found that cane-sugar when injected into the blood is separated in an unaltered form in the urine. The quantity of sugar which is excreted in twenty-four hours by patients suffering from diabetes is frequently enormous, amounting in some cases to upwards of $1\frac{1}{4}$ lb. of solid glucose. The proportion of sugar excreted in this disease is greatly under the control of the diet; substances which contain much amylaceous or saccharine matters, such as bread and potatoes, always occasion the excretion of a larger quantity of sugar: under the use of opium, and an animal diet, the saccharine matter is very considerably diminished.

If sugar be suspected in the urine, its presence may be indicated by the employment of Trommer's test, in which the reducing action of glucose upon the salts of copper is taken advantage of. The urine is first rendered strongly alkaline by the addition of a solution of potash, and a few drops of cupric sulphate in solution are added; on agitation, the hydrated cupric oxide, which is at first precipitated, is redissolved, forming a blue solution; and upon boiling the liquid, the yellow hydrated cupreous oxide, which is speedily converted into the red anhydrous cupreous oxide, is thrown down. If this reaction does not occur, no sugar is present. Since, however, other bodies besides sugar exercise a similar reducing influence on the cupric salts, the presence of sugar should be further confirmed by the test of fermentation. In order to apply this test, a small quantity of yeast is added to a portion of the urine, which is placed in an inverted tube over mercury, and exposed to a temperature of from 77° to 86° (25° to 30° C.); if sugar be present, gaseous carbonic anhydride is liberated in the course of a few hours. Bence Jones, however, in confirmation of Brücke's statement, finds minute quantities of sugar even in healthy urine (*Q. J. Chem. Soc.*, xiv. 40) in quantity varying from 1.1 to 1.9 grs. per 10,000 grs. of urine.

(1708) *Albuminous Urine.*—The other important alteration of the urine here to be noticed consists in the excretion of a large quantity of albumin. When this occurs it may be recognized by slightly acidulating the urine, and applying heat. Coagulation follows if albumin be present; and a similar effect is produced on the addition of nitric acid. In this disease the seat of mischief

is the kidney itself, and its powers of secretion are modified in an important manner. In a state of health, this organ does not allow the albuminous portion of the blood to escape, but in particular forms of disease it permits albumin to pass, and retains the urea, which may then be detected in dropsical effusions, and in various fluids contained in the body.

(1709) 2. CUTANEOUS EXCRETIONS.—Notwithstanding the great importance to health of the due performance of the functions of the skin as an excretory organ, the chemical nature of the products which it throws off has been but imperfectly studied, since the collection of these compounds is attended with considerable difficulty, owing partly to the great extent of surface from which the excretion takes place, and partly to the variation in composition which it presents in different parts of the body.

The solid not volatile constituents of the sweat have been found to range between about 0.5 and 1.25 per cent.; the proportion of water varying with the temperature and hygroscopic condition of the atmosphere, with the amount of liquids swallowed, with the kind of exercise taken by the individual, and with the rapidity of the circulation. Among the solid constituents, sodic chloride is the most abundant. Lactates, butyrates, and acetates of ammonium and sodium are also present, besides small quantities of calcic phosphate; phosphates of the alkali-metals are absent, and the sulphates are found only in very small amount. Carbonic anhydride and nitrogen are likewise exhaled from the surface of the body in considerable quantity, particularly the former. The sweat contains, moreover, a quantity of a peculiar azotised matter very prone to decomposition, as well as an odorous principle. The cutaneous excretion from the general surface of the body has almost invariably an acid reaction, owing to the presence of free formic and lactic acids; but the excretion from the axillæ and the feet is sometimes found to be alkaline. With regard to the quantity, all that can be stated is that it usually exceeds in bulk that of the urine during the summer; but that in winter the urine preponderates in amount, while the quantity of cutaneous transpiration is greatly and proportionately diminished. In fact, processes occur upon the surface of the skin, which resemble those both of the kidney and of the lungs: thus, like the kidneys, the skin excretes nitrogen and acid substances as well as the chlorides; and, like the lungs, it separates large quantities of carbonic anhydride and aqueous vapour. The actions

of the skin, and of the kidneys and lungs, are, therefore, though to a very limited extent, vicarious; and when the functions of the skin are seriously interfered with, it usually happens that derangements more or less serious, either of the kidneys or of the lungs, occur.

(1710) 3. SOLID EXCREMENTS.—After the chyle has been absorbed into the system during the gradual passage of the mixed constituents of the food through the intestinal canal, those parts which are destined to become excrementitious gradually acquire a fæcal odour, and are at length ejected from the body. The composition of these excrementitious matters necessarily exhibits great variations, which depend mainly upon the nature of the food taken. Berzelius found a specimen of human excrement which he examined, after the use of an ordinary mixed diet, to contain three-fourths of its weight of water, the rest consisting of biliary matter and alimentary débris. A large quantity of phosphates of calcium and of magnesium, and other insoluble salts of the food, is obtained on incinerating the dried residue. Playfair found in a sample which he examined, about 15 per cent. of nitrogen in the dry residue, and 45 per cent. of carbon; but these proportions will necessarily be subject to variation with the kind of food taken. The ratio which these numbers bear to each other does not differ much from that which represents the proportion of the same elements in fresh muscle, which likewise contains three-fourths its weight of water. According to Liebig, the total average weight of fæculent matter in its recent state excreted by a healthy adult in twenty-four hours amounts to $5\frac{1}{2}$ ounces: Lawes states the average in healthy male adults to be 4.2 oz., and in adult females 1.3 oz. The offensive odour of fæcal matter is due to some intermediate products of oxidation. These odorous substances have not been accurately examined, but they may be produced artificially by fusing casein with caustic potash, as in the preparation of tyrosine (1618). This odour is of a different nature and of a more putrid character when the quantity of bile secreted is below the usual amount.

Dr. W. Marcet has obtained from healthy human excrement a peculiar crystallizable principle which, from its origin, he terms *excretine*; he attributes to it a composition expressed by the formula $C_{75}H_{156}SO_2$: it has a feebly alkaline reaction; it fuses at about $201^{\circ}.4$ (94° C.), and is insoluble in water and in a solution of potash, but is readily soluble in ether. He has also extracted from the excrements a fusible olive-coloured fatty body, which he has named *excretolic acid*; but he has not recorded any attempt to determine its composition.

(1711) 4. PUS.—This is a liquid which is never met with excepting as a product resulting from actions excited by injury, or by disease. When the suppurative process is going on favourably, pus forms a thick, opaque, yellowish fluid, which, when examined by the microscope, is found to consist of a transparent liquid, in which a large number of corpuscles are seen to be floating. These corpuscles are larger than the red corpuscles in human blood; they consist of a granular cell membrane enclosing a viscid granular matter, and a nucleus which adheres to the membrane. Pus generally has a feebly alkaline reaction. The fluid portion holds a considerable quantity of albumin in solution, and closely resembles ordinary serum: leucine is also commonly present (Bödeker). The pus globules contain a large proportion of fat, and of cholesterin. *Pyin* is the name which has been given to an albuminoid substance sometimes found in pus; it is soluble in water, but is precipitated by acetic acid and by a solution of alum. The dried residue of pus yields a large amount of salts; in the experiments of Lehmann the saline constituents exceeded 12 per cent. of the total dry matter: the proportion of phosphates and of salts of potassium was very considerable.

CHAPTER XIII.

ON THE NUTRITION OF PLANTS AND ANIMALS.

§ I. *On the Nutrition of Vegetables.*

(1712) ORGANIZED beings have been arranged under the two great divisions of *plants* and *animals*; and although the lowest genera in each division approximate so closely that it is difficult to decide where one division begins and the other ends, yet in their general relations they are not only widely different, but even opposed to each other in the functions which they discharge in the economy of creation, the operations of the plant being complementary to those of the animal in the nicely-adjusted balance of organic life, each affording support and nutriment to the other. The principal functions of the plant and animal may be contrasted thus:—

| <i>Plants</i> | <i>Animals</i> |
|--|--|
| Decompose water and carbonic anhydride. | { Produce and evolve water and carbonic anhydride. |
| They evolve oxygen. | |
| They absorb and assimilate nitric acid and ammonia. | { They produce and emit urea, and other azotised compounds which yield ammonia. |
| They are fixed in the soil. | |
| They have no power of voluntary action. | { They possess the power of locomotion. |
| Their growth is continuous, and there is no absorption of matter once deposited. | |
| | { Their actions are under the control of the will. |
| | { Their growth, and the absorption of deposited matter in the adult, go on <i>pari passu</i> . |

Two important functions have been allotted to the vegetable creation, one of which consists in the elaboration from inorganic matter of the various materials necessary to the support of animal life; the other consists in the removal of carbonic anhydride from the atmosphere, the plant retaining the carbon and fixing it in its tissues, while the oxygen is restored to the air. During these changes, which require the action of the solar rays, the plant stores up for the future use of man, or of the animal creation, a portion of energy derived from the sun's rays, to be again given out when necessary in the form of heat during combustion, or of muscular force when the vegetable serves as food to the animal. These wonderful changes are produced by the operations of the vegetable cell; each cell possessing a separate and independent power, by means of which it is enabled to assimilate new matter; from this assimilated matter it produces new cells, and these in like manner multiply and produce innumerable other cells. These successive developments of vegetable cells may be readily watched under the microscope in the case of the growth of the globules of yeast (11114). The compounds produced in the yeast globules are cellulose, which forms the cell membrane, and the internal substance, which contains a body allied to albumin. The plant-cell in the case of yeast does not elaborate the azotised product, but assimilates it from the solution in which it grows; there is, however, no doubt that albumin is elaborated in other instances by the vegetable cell:—in the wheat plant, for example, the azotised gluten is stored up in the seed, and in this case it can only be derived from the inorganic materials of the soil and of the atmosphere.

But the mere existence of an organized structure, even when animated by vitality, is not sufficient to produce these results of vital activity. It is necessary, in addition, that the plant be

exposed to a temperature ranging between 41° and 86° (5° and 30° C.), and to a certain degree of moisture. In the higher manifestations of plant life, solar light is also essential. If at any time the temperature fall so low that the plant is frozen, its vitality is destroyed, and the delicate structures of the tissues are impaired by the solidification and forcible expansion of the juices which they contain. Life is also destroyed not less completely by exposure of the organism to a temperature of 212° , or even to one considerably below that point. The higher orders of plants require for their full development that they shall be rooted in a congenial soil, and be supplied freely with air and moisture.

A plant in a state of health is continually undergoing increase; this increase, however, may either be checked or facilitated by modifying the circumstances under which it is placed. In order that the method of regulating this development may be more fully understood, it is necessary to examine what the materials are of which this increase consists, and whence they are supplied. In all plants there are two distinct sets of substances present; one of these is organic in its nature, and is represented by sugar, starch, wood, albumin, and so on; the other is inorganic, and is represented by the various salts found in the ashes of plants. The materials from which these compounds are formed must, therefore, be supplied in some shape or other to the growing plant; in fact, they constitute its food. Experiment has, moreover, proved that the form in which these matters are presented to the plant is by no means unimportant, for the elementary bodies, with the exception of oxygen, are never directly assimilated; they must previously have entered into combination in some form or other. The compound constituents of the food of plants are supplied from two sources, the atmosphere and the soil. Those furnished by the atmosphere consist chiefly of carbonic anhydride, water, ammonia, and nitric acid; while the saline compounds, which vary with the nature of the plant, are derived from the soil. Without these different articles of food—viz., carbonic anhydride, water, ammonia, and the salts of the soil—plants could no more continue to exist than animals could do if deprived of their natural nutriment.

The root of a plant may be considered as its mouth, and the leaves as its lungs. When a shower of rain descends through the air, it carries with it all the soluble matters which that portion of the air contains; these soluble matters consist chiefly of carbonic anhydride, with minute quantities of carbonate and nitrate of ammonium. The carbonic anhydride, as we have already stated,

is abundantly furnished by the processes of respiration in animals, by combustion, and by a variety of other sources. The ammonia is furnished mainly by the putrefaction and partial oxidation of animal and vegetable matters, and is present in the air, in a quantity far more minute than carbonic anhydride, but still in appreciable amount (369). Nitric acid is produced whenever a flash of lightning passes through the moist air, and this compound is generated even when silent discharges of electricity take place. Every shower of rain which falls to the earth, thus dissolves and carries with it food for vegetation: charged with these nutritive materials, the water percolates through the soil, from which it takes up small quantities of soluble salts. It thus arrives at the spongioles of the roots, where it is absorbed and carried up by the ascending current of sap to the leaves, and to the remotest extremities of the branches, where, under the influence of some azotised matter, and of the solar light, the carbonic acid undergoes a remarkable change: a portion of the water likewise experiences decomposition, in consequence of which, oxygen gas, mingled with a quantity of nitrogen varying from one-half to one-tenth of the bulk of the oxygen, is given out. Supposing that this decomposition be effected upon carbonic anhydride and water, in the proportion of an equal number of molecules of each of these compounds, a substance would be formed, having the same ultimate composition as fruit-sugar; $6(\text{CO}_2 + \text{H}_2\text{O} - \text{O}_2) = \text{C}_6\text{H}_{12}\text{O}_6$.

Although it has been stated that the principal supply of carbonic anhydride is furnished to the plant as a solution in water which is absorbed from the soil by the roots, it must not be forgotten that the leaves also present powerfully absorbent surfaces, and, like the lungs in animals, not only minister to the respiration of the organism, but are frequently the inlet of a variety of substances which are capable of assimilation, as well as of those that are not so. Carbonic anhydride, in particular, is absorbed by the leaves with great rapidity, as has been shown by the experiments of Pepys and others.

Sugar appears to be the basis or foundation of organic matter in general, and from it all the varieties of organized products might be obtained, by the addition or subtraction of oxygen and of the elements of water and of ammonia. If it be supposed that each molecule of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) is deprived in the plant of the elements of 1 molecule of water, a body having the composition of starch or cellulose would be the result, and starch may again be brought into solution when necessary for the plant, by the action of diastase, or of some principle which acts as a ferment,

and enables it to resume the water which it had lost. The latter change actually takes place during the germination of seeds, which, when moistened, swell and absorb oxygen, while carbonic anhydride is emitted, and the starch, under the influence of diastase, is converted into dextrin or sugar, in one of which forms it serves as food for the young plant. If the growth of the seed be checked at a particular stage by suddenly raising the temperature, a large portion of the starch will be found to have disappeared from the seed, and its place will have been taken by sugar; these being in fact the changes which occur in the process of malting (1098). But, if germination be allowed to proceed, the starch and the sugar gradually disappear, and ligneous fibre is formed, which contains the elements of fruit-sugar minus those of 1 molecule of water. During the ripening of fruits the pulp slowly assimilates the elements of water, and becomes sweet; the fibrous portions of the fruit being greatly diminished, while the saccharine and mucilaginous constituents are increased.

According to the observations of Fremy and Decaisne, many unripe fruits contain starch (but this appears to be incorrect as a general rule), ligneous fibre, pectose (1102), and a peculiar substance capable of furnishing gum, which they have termed *gumose*: in addition to these ingredients, tannin and some of the vegetable acids are present. During the period of the growth of the fruit, whilst it retains its green colour, it decomposes carbonic anhydride, and emits oxygen like the leaves of a tree: but when the fruit begins to ripen, it gradually becomes softer and more transparent, and oxygen is absorbed, while carbonic anhydride is evolved. During this evolution of carbonic anhydride, a succession of slow oxidations is taking place within the cellules of the fruit; the tannin first disappears, and the vegetable acids are then gradually consumed; when this point has been reached, the fruit is generally in the proper condition to be eaten. If it be kept longer, the sugar in its turn experiences oxidation, and the fruit becomes flat and tasteless, and by prolonged keeping it undergoes decay.

The correctness of most of the foregoing statements is easily verified. The process of ripening generally takes place best while the fruit hangs upon the tree; but in many cases, as in the apple, the pear, and the orange, the fruit continues to ripen after it has been gathered. In each case oxygen gas is absorbed, and carbonic anhydride evolved. The proportion of acid contained both in growing and in detached fruits is less in the ripe than in the unripe fruit. The disappearance of the acidity in fruits during the process of maturation depends upon this absorption of oxygen, as is well exemplified in the case of the common cider-apple. This fruit, when whole, has an austere sour taste, but, by crushing and exposing it to air for a short time, the flavour becomes sweet and agreeable; the vegetable acid having undergone a slow oxidation, in consequence of which it has become converted into water and carbonic anhydride. The increase in the quantity of sugar during ripening is in some cases very great, as for instance in the apricot, which while green contains scarcely any sugar, though in the ripe fruit as much as 10 or 11 per cent. has been found.

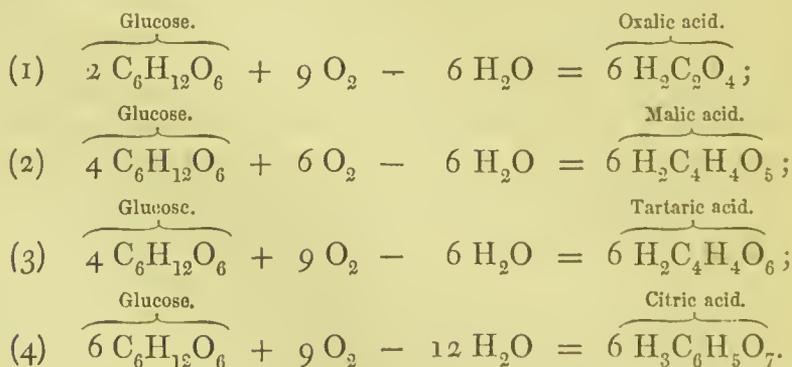
Buignet (*Ann. de Chimie*, III. lxi. 233) has submitted a large number of fruits to a careful examination during the process of ripening. He finds that in acid fruits the sugar either consists of inverted sugar, as in the grape, the cherry,

the gooseberry, and the fig, or it consists of a mixture of this sugar with pure cane-sugar, as is the case in the apricot, the peach, the apple, the pine-apple, the citron, the orange, the plum, and the raspberry. This inverted sugar appears to have been derived from cane-sugar, as no other variety of sugar seems to be convertible into it. The banana is not an acid fruit; it contains a good deal of starch during ripening, and yields sucrose.

The cane-sugar of acidulous fruits does not appear to be derived from starch—indeed, no starch is to be found in any of these acid fruits; but instead of starch they contain an astringent compound which furnishes a colourless combination with iodine, and which has a still stronger tendency to unite with iodine than is possessed by starch itself. This circumstance may be taken advantage of in determining the relative quantity of this substance present in a given fruit, or in the same fruit at different periods of maturity; for by employing a standard solution of iodine and adding starch paste to the liquid, it is easy to ascertain the number of divisions of the iodine liquor added from the burette before the starch begins to show its characteristic coloration; the colourless compound formed contains from 16 to 17 per cent. of iodine. When this astringent substance is boiled with diluted sulphuric acid (1 of acid to 100 of water) it yields a saccharine solution.

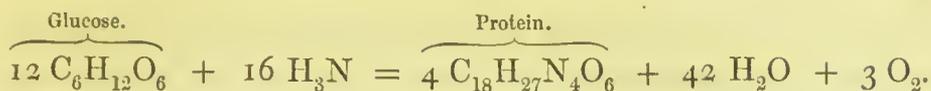
Buignet considers that the conversion of the cane-sugar into inverted sugar in the fruit is due to a special ferment, not to the action of the acid: the following experiment supports this view:—He took two portions of peach juice, diluted one with twice its bulk of alcohol, by which the ferment was coagulated and rendered inert; the other portion he mixed with twice its bulk of water containing calcic carbonate in suspension; in half an hour he filtered both liquids; the rotatory power of each was alike; in twenty-four hours the neutralized liquid, containing unaltered ferment, had become ropy, and the whole of the cane-sugar had become inverted, while the portion to which the alcohol had been added remained unaltered.

It may be instructive to observe how readily, by absorption of oxygen and separation of water from sugar, the principal vegetable acids may be supposed to be generated:—



Again, if instead of forming sugar, 10 molecules of carbonic anhydride and 8 of water were to give up the whole of their oxygen, a compound would be furnished, corresponding to oil of turpentine, and forming the basis of many of the resins; $10 \text{ CO}_2 + 8 \text{ H}_2\text{O} - 14 \text{ O}_2 = \text{C}_{10}\text{H}_{16}$.

The complicated azotised principles may be also traced in theory to grape-sugar; for example:—



These equations have been given with the view of pointing out the simple relations of sugar to the various organic acids, and not with any intention of asserting that the changes which they indicate actually take place in the form thus represented, though it is obvious that some such changes must occur. Sugar or gum, and starch or ligneous fibre, are among the most abundant and generally diffused vegetable products, and it is very probable that these bodies may furnish the materials from which the various vegetable acids and other simpler compounds of vegetable origin are obtained: but if this hypothesis be doubted, there is no difficulty in tracing these acids and the other bodies to the carbonic anhydride and water upon which the plant operates. For instance, oxalic acid might be produced from carbonic anhydride and water by the following changes; $4\text{CO}_2 + 2\text{H}_2\text{O} - \text{O}_2 = 2\text{H}_2\text{C}_2\text{O}_4$. In the case of malic acid, the changes might be the following: $4\text{CO}_2 + 3\text{H}_2\text{O} - 3\text{O}_2 = \text{H}_2\text{C}_4\text{H}_4\text{O}_5$; and so on with the others.

It is impossible, in the existing state of our knowledge, to trace the cause, or even the exact nature, of the changes produced in the various fluids which circulate in the plant or in the animal. The theory which has the strongest apparent analogies in its favour is, that, by the presence of some albuminous ferment analogous to diastase or synaptase, an elimination of various compounds takes place in particular organs, just at those points where these ferments are deposited. It is further supposed that the same complex organic fluid is capable of undergoing changes differing according to the nature of the substance which excites fermentation, and that hence it happens, that the same fluid may deposit in different tissues secretions possessed of very different qualities (1097). The substances thus produced must necessarily be complementary to each other: that is to say, the product of secretion and the altered fluid which furnishes it, taken together, must contain the same elements as the original substance from which they were produced. The foregoing hypothesis affords no explanation of the manner in which compounds previously existing in the circulating fluid, as urica is known to do in the blood, are separated from it by the ordinary operation of secretion; but the processes of diffusion, dialysis, and osmosis are probably concerned importantly in these cases.

(1713) *Food of Plants.*—As has been already stated, plants are the grand reducing instruments in the great laboratory of

Nature, and by renewing to man fresh materials suitable for fuel, they are restoring to him the power which he has exhausted in combustion under the boilers of the steam-engine, or in muscular energy, either in his own person or in that of the beasts subservient to his will. This energy can only be again renewed by a fresh supply of food, which must be drawn ultimately from the vegetable creation. Owing to their reducing action upon water and carbonic anhydride, plants are continually exhaling oxygen during the day-time, but at night they emit carbonic anhydride. This emission of carbonic anhydride appears to be in most instances a mere transudation; the gas is absorbed by the roots by night as well as by day, but in the absence of solar light, neither carbonic anhydride nor water is decomposed, and both escape unchanged into the air; hence it was at one time supposed that plants during the night actually produce carbonic anhydride. A real generation of carbonic anhydride does, however, take place during the germination of the seed, during flowering, and during the maturation of the fruit; that is to say, at such times as the saccharine or acid compounds are undergoing oxidation. It is worthy of remark, that at this time sugar disappears rapidly from the plant, so that if the sugar-cane or beet-root be gathered after flowering, the produce of sugar is greatly diminished.

The functions of ammonia in vegetation are almost as essential as those of carbonic anhydride, inasmuch as the juices of all plants contain a portion of azotised matters which are necessary to their well-being, and which form an important item in their composition, particularly when considered in relation to the nutritive qualities of the plant as an article of food. One of the principal circumstances which give to animal manure its high value, is the large proportion of ammoniacal compounds which it is capable of supplying.

All plants, in addition to their chief constituents, carbon, hydrogen, oxygen, and nitrogen, contain minute quantities of certain salts, which are no less essential to their growth and development, than those elements which occur in larger quantities. Some idea of the probable use of these inorganic matters may be formed from a consideration of the effects producible in the laboratory, upon the various products of vegetation, by the acids and by the alkalis. Starch and cane-sugar, for example, are converted into grape-sugar by the action of dilute sulphuric acid aided by heat; and if starch be mixed with dilute sulphuric acid, and with a material which, like manganese dioxide, furnishes oxygen, formic acid is one of the products. In like manner, under

the influence of potash, the natural fats and oils are decomposed into fatty acids and glycerin. Analogous changes may be supposed to occur under the influence of acids and of alkalis, in the yet more subtle chemical operations which are constantly taking place in the organs of living plants and animals, by which the arrangement of their components is modified and altered. In other cases, the obvious use of the saline matters is to furnish a skeleton or support for the plant. This is clearly one use of silica in the stem of the grass tribe, and of calcic oxalate in many of the lichens.

It has already been remarked that the food of plants is derived from two sources, viz., the atmosphere and the soil. From the atmosphere, carbonic and nitric acids, ammonia, and water are supplied; while from the soil are furnished the various saline materials necessary to the healthy growth of the plant. Now, in certain cases, all these materials, with the exception generally of carbonic anhydride and water, may be present in quantity too scanty to produce a luxuriant crop; and the great practical problem submitted to the farmer for solution is the discovery of the nature of the missing materials in any given case; and of the means by which these missing materials may be most cheaply and effectually supplied.

When a crop is carried off from the land, it necessarily takes with it a certain amount of mineral matters. If these mineral bodies be present in the soil in small quantity, and if fresh crops be continually carried off without provision for the return of the matters so removed, the land will in process of time become exhausted of one or more of these necessary ingredients, and sterility will be the inevitable result. One great object of the farmer in manuring his land is to restore these sparingly distributed but essential saline bodies in proportion as they are removed from the farm in the form of corn, of straw, of hay, or of stock which has been reared upon the produce of the land.

It is manifest that a fertile soil should retain its fertility if the manure supplied restores exactly those substances which previous crops had removed. There are few substances which more nearly fulfil this purpose than farm-yard manure, because the salts and mineral ingredients present in the food pass off almost wholly into the excretions of the animal; and thus the ingredients restored, so far as the supply extends, are nearly identical with those which have been removed: since, if the ash obtained from a given weight of any specific crop be compared with the ash obtained by burning the excreta of animals fed upon an equal

quantity of the same crop, the composition of the ash in the two cases will be nearly identical.

It is, however, well known that the recent droppings of cattle are far more effectual as manure than the ashes of such manure when burned; partly, because the recent manure contains carbon in a form which, during its decay within the soil, gradually supplies carbonic anhydride to the roots of the plant; but chiefly, as it appears, because it contains a large proportion of nitrogen, which, during its putrefaction, furnishes ammonia, or some other azotised compound, in a form suited to the wants of the growing crop.

It is owing to similar causes that night-soil and urine possess so high a value as manure. They are much richer in nitrogenised compounds, and in phosphates, than farm-yard manure; and, indeed, they contain all the saline constituents of the corn and animal food, as well as almost all the nitrogen of the azotised constituents of the food which had been conveyed into the stomach, whether those azotised constituents had been assimilated or not. The Chinese have long been aware of the importance of these materials as manure, and they collect and carefully restore to their fields that which we in the pride of superior civilization discharge into sewers, and wastefully consign to the ocean, after allowing it to accumulate in offensive mud-banks within our tidal rivers, upon the shores of which, by the ebb and flow of the tide, it is alternately exposed to the heat of the sun and to the action of the water, under circumstances the most favourable to its decomposition; in consequence of which it is constantly contaminating the atmosphere of our large towns with sickening effluvia.

(1714) *Varieties of Soil.*—In order to render the chemical action of manures intelligible, it will be necessary to take a rapid survey of the principal kinds of soil, and of the nature of the saline ingredients required by ordinary farm crops during their growth.

Soils vary greatly in physical characters, as well as in chemical composition. A soil may, for example, be described as *clayey*, *sandy*, *marly*, or *calcareous*, according as alumina, silica, or lime is the prevailing ingredient. The land will also be *stiff* or *porous*, *moist* or *dry*, owing partly to these peculiarities, and partly to its geological position, according as it rests upon clay, upon sand, upon chalk, or upon gravel; its character will also vary, in part, with its site, according as it lies high or low, and as its surface is inclined or horizontal. But these considerations, though of high importance to the agriculturist, lie beyond the province of the chemist, whose principal attention must be directed

primarily to the *chemical* peculiarities of the soil. In order that a soil may be fertile it must not only be well drained and sufficiently watered, but it must possess a certain quantity both of organic and of saline ingredients.

Seeds, it is true, in some cases may be made to germinate and develop plants upon flannel, or in well-washed siliceous sand, if duly moistened from time to time with distilled water. The plants thus obtained may even sometimes flower; but they never produce fertile seed; and, if these plants be burned, the weight of the ash which they yield never exceeds that of the ash yielded by a quantity of seed equal to that from which the plants were raised. By adding suitable saline mixtures to washed siliceous sand, Wiegmann and Polstorf, however, obtained tobacco, oats, barley, and other plants, in healthy growth, which furnished perfect seed. In these cases the plants had been supplied with those materials, the absence of which had in the previous experiments prevented their mature development. But it must not be hastily concluded from these results, that organic manures can advantageously be dispensed with in agriculture; experience has fully proved that a judicious combination both of organic and of saline manures is essential, and it is owing to ignorance of this fact that many of the patent mineral manures, when used alone, have so signally failed.

Different classes of plants, in order to the production of a luxuriant growth, require a soil possessed of physical qualities which must vary according to the kind of crop; and, in addition to this, each species of plant requires a variation in the chemical composition of the soil, suited to its peculiar habits. The prevailing and most abundant components of the soil, whether they be siliceous, aluminous, or calcareous, are not those which exert the greatest influence upon the development of the plant. They simply constitute the matrix in which the plant grows; and this matrix is more or less favourable to its growth according as its physical character is more or less conformed to the wants of the plant; but the chemically active constituents of the soil consist of certain soluble saline compounds which are generally found in it in comparatively small quantities. In natural and fertile soils these salts are already present, either in an active or soluble form, or else in the passive or insoluble condition, stored up in rocks which have not as yet become disintegrated by exposure to the weather.

(1715) *Liebig's Classification of Crops by their Ashes.*—In order to ascertain the nature of the salts which are essential to

the growth of any plant, Liebig insisted on the importance of an analysis of the ashes obtained by burning such plants, grown upon a soil which is known to suit them; and in accordance with this suggestion, a great number of careful analyses of the ashes of the more important varieties of cultivated plants have been made both on the Continent and in this country. From the results thus obtained it appears, 1. that the number of the mineral constituents of plants is comparatively small; 2. that the nature of the mineral constituents varies in different tribes of plants; and 3. that it varies even in different parts of the same plant.

Potash, soda, lime, magnesia, with now and then small quantities of alumina, oxide of iron, and oxide of manganese, are the bases found in vegetable tissues; and they occur in combination with sulphuric, silicic, and phosphoric acids, as well as with hydrochloric, and with various organic acids; the carbonates of these bases, which are so frequently found in the ashes of plants, are derived from the compounds of the organic acids with the alkalis which the plant contains, and which organic acids are destroyed when it is burned.

Liebig has proposed to class vegetables for agricultural purposes according to the composition of their ashes, and the following table will give an idea of the general principle which he has adopted. It will be observed that the same plant may appear in two different columns, as though it belonged to two different classes. The ash of the tubers of the potato, for example, is rich in alkaline salts, while the haulm abounds in salts of calcium; hence, as is shown in the second subdivision of the table, the potato should be regarded as belonging to the alkalino-calcareous class:—

| Alkaline. | Calcareous. | Siliceous. |
|--|--|---|
| Maize (straw) Turnips (roots) Beet Potatoes (tubers) Jerusalem artichokes (tubers) | Tobacco Peas (straw) Potatoes (haulm) Clover Jer. artichokes Turnips (tops) | Wheat Barley Oats Rye } (stem) |
| Alkalino-calcareous. | Calcareo-siliceous. | Alkalino-siliceous. |
| Peas Jer. artichokes Potatoes Turnips | Barley | Wheat Oats Rye } (corn) |

The results of such analyses suggest a probable reason why plants of different species do not all thrive equally well in a soil which may be highly productive of a particular crop; since a soil which abounds in the saline matters required by one crop may be deficient in the ingredients necessary for the full development of plants of a different species. Root crops, and succulent plants generally, require abundance of alkaline and calcareous salts; and experience has shown that the green shoots of all plants are those which contain these constituents in the largest proportion; the grasses, and plants with stiff but not woody stems, are rich in silica; while the grain crops, and seeds in general, as well as those plants which are richest in azotised nutritive materials, abound in phosphates of the metals of the alkalies and of the earths.

Not only does the composition of the ash vary in different plants, but its quantity varies also within wide limits. According to the estimate of Johnston, a ton of each of the following substances, in its undried condition, contains upon the average the under-mentioned proportion of ash:—

| One ton of | lb. of ash. | One ton of | lb. of ash. |
|-----------------------------|-------------|----------------------|-------------|
| Potato tops contain . | 26 | Wheat straw contains | 220 |
| Turnip tops „ . | 48 | Oat straw „ | 140 |
| Hay contains from 90 to 180 | | Barley straw „ | 110 |
| Pea haulm contains . | 100 | Rye straw „ | 60 |
| Bean straw „ . | 70 | Rape dust „ | 120 |

It is evident that all plants must, to a certain extent, deprive the soil of its *saline* components; since no plant adds anything to these materials which already exist in the soil, but on the contrary, every crop that is carried off removes with it a corresponding amount of mineral material. Owing, however, to this important and undeniable fact, to which public attention was first strongly directed by Liebig, many persons have been tempted to overlook the necessity of organic materials in the manure; and considerable disappointment has often been experienced in finding that the restoration of mineral matters to the soil was not the only condition required to renew, or to preserve its fertility. Messrs. Lawes and Gilbert have rendered essential service to agriculture by their admirable researches upon this point, which have recalled public attention to a circumstance of cardinal importance to the agriculturist.

(1716) *Modes of Action of Manures.*—It would be a serious mistake to suppose that a supply of the proper manure can always be predicated from a knowledge of the composition of the ashes

of a plant, or from the analysis of the soil to be manured. Manures may act in one of three principal ways:—1. as direct food for the plant; 2. as what, for want of a better term, may be viewed as stimulants to its growth at a particular stage; and 3. as chemical agents which modify the constitution of other substances already present in the soil. Liebig has specially called attention to the first of these modes of the action of manures. The second of these methods has been particularly elucidated by Lawes, who showed that in the early stage of the growth of turnips, no manure is to be compared in efficacy with superphosphate of lime; although the plant itself contains so small a proportion of phosphates that it was precisely the plant fixed upon by Liebig, on theoretical grounds, as the one which, from its non-requirement of phosphates, was particularly well calculated to be grown upon land which might have been supposed to have been exhausted of its phosphates by a previous wheat crop. It is now well known to the practical farmer, that the superphosphate, when drilled in judiciously with the turnip seed, stimulates the growth of the plant in the earliest and most critical stage of its existence, and thus secures a far more abundant return than when the supply of superphosphate is omitted. It is, however, probable that no manure acts simply as a stimulant, but that all such manures enter into the composition of the plant itself. These stimulating manures appear to supply through certain stages of the plant's growth a constituent or constituents, which, though present in the soil, may not be so in a sufficiently concentrated form, or which, owing to the imperfect development of the root, may not be sufficiently within the reach of the plant at the particular time when they are most needed.

The experiments of the same patient and indefatigable agriculturist, which have been carried on in conjunction with Dr. Gilbert, in a systematic manner, and upon a large scale for a quarter of a century, have shown to the satisfaction of unprejudiced observers that the direct supply of phosphates to wheat crops frequently does not materially increase the produce, because ordinary wheat land already contains a far larger proportion of phosphates distributed through it than is necessary to the growth of many successive crops of wheat. This circumstance appears to be in great measure dependent upon a peculiarity in the mode of growth of the wheat plant; it strikes down the fibres of its roots to a great depth into the earth, by which means it is enabled to appropriate the phosphates of a much larger extent of soil than can come within the reach of the short tuft of fibres which con-

stitutes the root of a crop like the turnip. An interesting illustration of the influence of the development of the root upon the nature of the manure required is afforded by a comparison of wheat and barley, which contain similar mineral constituents in nearly the same proportions:—Wheat sown in autumn makes root all the winter, and is enabled to extract saline matters from the soil to a great depth; consequently it is seldom benefited by mineral manures directly applied, though it is greatly affected by the general mineral riches of the soil. Barley, on the other hand, is sown in spring; it throws out and depends upon root fibres nearer the surface, and is frequently much benefited by the use of manures containing phosphates. It is also found, and apparently for similar reasons, that the addition of potassic silicate as a manure does not materially strengthen the stem in wheat, but that the employment of ammoniacal manures, including the best varieties of guano, enables large crops of wheat to be raised for several consecutive years on the same piece of land; the ammonia appearing to supply nitrogen to the gluten of the wheat, and acting also as a general stimulant to the growth of the plant. But although this has been established as a scientific fact, it is not recommended that this practice be substituted for the system of rotation at present in use; though it appears that with the aid of nitrogenous manures wheat may be grown in larger quantities, and more frequently in the rotation, without injury to the fertility of the soil.

It is a matter of experience that land which will not grow two remunerative crops of the same kind in succession (wheat for instance) without intermediate manuring, will yet, after a succession of turnips, barley, and clover, again be fit for wheat with comparatively light manuring; and that this system of rotation produces effects similar to those obtained by *fallowing*, or allowing the land to lie uncropped for a year. Lawes and Gilbert consider that clover and some other leguminous crops are especially valuable to the land, by supplying a quantity of nitrogenous organic matter to the soil, in a form particularly well calculated for assimilation by the succeeding wheat crop.

It is generally supposed that all the nitrogen found in combination in plants, has been obtained by the plant either from nitric acid or from ammonia, or from some azotised compound present in the soil in the form of manure; and that plants have not the power of directly assimilating nitrogen from the atmosphere. It appears to be probable, however, that the leguminous plants generally introduced by the farmer in rotation have a particular apti-

tude for condensing and retaining the nitrogen which is presented to them during their growth, and that they store it up, so that by the *débris* of their roots, and still more abundantly if ploughed into the land, they furnish a valuable source of nitrogen to succeeding crops. Wheat, on the contrary, accumulates but a comparatively small amount of nitrogen, and consequently thrives best when aided by the stimulus of manures containing that element. Lawes and Gilbert found that the addition of 5 lb. of ammonia per acre in the form of manure, produced an increase of about a bushel of wheat; from which it would appear, calculating from the known composition of the corn and the straw, that not more than about two-fifths of the quantity of nitrogen supplied in the manure is retained in the gluten of the seed, in the straw, and in other parts of the plant.

Liebig accounts for the beneficial effects of the rotation of crops by supposing that each plant in succession avails itself of saline matters which were unnecessary to the preceding crop. The process of fallowing appears to owe a certain portion of its efficacy to the gradual disintegration of the rocks, under the united influence of air, moisture, and alternations of temperature; in consequence of which, various substances, which were previously insoluble, are reduced to the soluble condition, and thus rendered available for the wants of the succeeding crop. It appears, however, to be probable, that the accumulation of compounds containing nitrogen within the soil during the period of fallow, has a material influence upon the following grain crop; but further experiments are still needed to elucidate the theory of fallowing.

The third mode in which manures act, viz., by the influence which they exert upon the components of the soil, is well exemplified in the application of lime, the most important uses of which are of an indirect character, although undoubtedly it is in some cases beneficial by supplying one of the mineral constituents essential to the healthy development of the plant.

Lime is applied to the land in the form either of slaked lime or of chalk. In the condition of slaked lime its chemical effects are exerted upon both the inorganic and the organic constituents of the soil. By its action upon the inorganic constituents, the insoluble silicates and the clays are decomposed: and potash, soda, alumina, and magnesia are set at liberty. Lime also decomposes salts of iron, rendering its oxide insoluble; it likewise partially decomposes common salt, forming sodic carbonate and calcic chloride. The effects upon the organic constituents of the soil are even more important; for it is upon rich peaty soils, which

abound in organic matter, that the beneficial influence of lime is most evident. In such cases it occasions the decomposition of the organic matter, and gives rise to the formation of carbonic and nitric acids, as well as of ammonia; all of which bodies are important ingredients in the nutriment of the young plant; and at the same time the lime also liberates the saline constituents of a former vegetation, leaving them in a state well fitted for assimilation by the growing crop. This decay in the organic matter is produced by the simultaneous action of lime, atmospheric air, and moisture: it therefore takes place most rapidly near the surface, and is attended with the formation of nitric acid and ammonia, at the expense, in part probably, of the nitrogen of the atmosphere, just as occurs in the artificial nitre beds of Sweden, France, and other countries of the Continent. Similar effects are produced, though much more slowly, by the action of chalk or calcic carbonate; and the beneficial results occasioned by the application of chalk are consequently less immediately perceived, and are diffused over a longer period of time.

In connexion with this indirect action of manures, it may be mentioned, that the beneficial effects of carbonic acid on the growth of plants are not limited to its direct action in supplying carbon to the crop; it performs a function not less important, owing to its solvent power. The carbonates and phosphates of calcium and of magnesium, and the oxide of iron are insoluble in pure water, but they are all dissolved to a small extent by water charged with carbonic acid, particularly in presence of ammoniacal salts, and they are thus rendered available to the nutrition of the plant (R. Warrington, *Journ. Chem. Soc.*, 1866, p. 296).

(1717) *Varieties of Manures.*—It has already been stated that the most important manures are those which are furnished by the excreta of animals; *guano* is one variety of this kind of manure; it consists of the decomposing excreta of sea-fowl which have fed upon fish; from its origin it abounds in phosphates and in ammoniacal salts; *farm-yard manure*, both solid and liquid, and night-soil and urine are also manures of a similar kind. Phosphates are abundantly supplied by *bone dust*, which also contains a considerable amount of gelatin. In burnt bones the gelatin is destroyed. The so-called *coprolites*, which consist principally of calcic phosphate, are probably *débris* of extinct animals, found in the tertiary beds of the Norfolk ‘Crag,’ and when reduced to powder and mixed with about half their weight of sulphuric acid, they furnish one source of the manure which is known as *superphosphate of lime*. In this compound, the sulphuric acid liberates a

portion of phosphoric acid, under the influence of which part of the bone earth is rendered soluble.

In the foregoing facts we see strikingly displayed the mutual dependence of the vegetable and the animal creation. If the plant be necessary to supply organized food for the animal, the animal in his turn ministers in a manner not less important to the support of the plant. The animal, with every breath that he draws, sends forth carbonic anhydride into the atmosphere, and supplies carbon, which may ere long form an integral portion of the growing plant; the excreta which he rejects as useless and noisome are greedily absorbed by the rootlets of countless tribes of vegetables; and when life no longer animates his frame, the muscular, the gelatinous, and the nervous tissues, during putrefaction, are returned to the atmosphere in the form of water, carbonic anhydride, ammonia, and sulphuretted hydrogen; while the hard and compact bony portions of his body gradually moulder into dust. These various compounds supply, it may be, future crops of wheat, of turnips, or of potatoes, with their necessary carbon, ammonia, or phosphates; and the crops thus raised in time furnish sustenance to other generations of living beings: so that the very molecules of carbon, of nitrogen, or of hydrogen, which once formed part of the body of the beasts of the forest in former ages, may again become portions of living, breathing animals, or may at this moment constitute a portion of our own corporeal system.

The ashes of wood, of peat, and of coal are also valuable as manures, since they return to the soil the mineral ingredients which were removed from it by the vegetation of which they formed a part. Hence the burning of heath or of turf upon waste land commonly renders it more fertile; for it not only furnishes a considerable amount of mineral manure in an available form, but it also assists materially in disintegrating the felspathic constituents of the soil, which are much more readily acted upon by air and moisture after having been thus exposed to a moderate ignition, than when present in their natural condition. It is in the same way that the burning of stiff clay, and subsequently distributing it upon the land, is sometimes beneficial.

Specific manures are in some cases required for particular crops upon certain soils. *Gypsum*, or calcic sulphate, is a highly important manure for leguminous crops, such as clover, in cases where lime or sulphates are deficient. *Sodic nitrate* in other cases forms a useful top-dressing to barley. *Common salt*, when applied judiciously to land where this ingredient is wanting, has

been known to produce excellent results; and the importance of *liming* under various circumstances has been already alluded to.

For the further prosecution of this subject the reader is referred to works on agricultural chemistry, particularly to Liebig's *Agricultural Chemistry*, Johnston's *Lectures on Agricultural Chemistry*, and to the papers of Boussingault, in the *Annales de Chimie*, of Lawes and Gilbert, of Way, and of Voelcker, in the *Journal of the Royal Agricultural Society*.

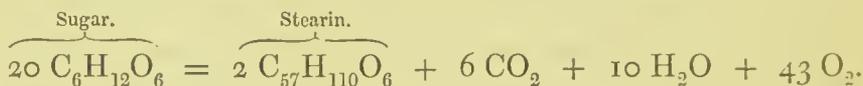
§ II. NUTRITION OF ANIMALS.

(1718) *Chemical Nature of the Food of Animals*.—The food of animals is considerably less simple than that of plants. Even plants have no power of directly assimilating any elementary bodies with the exception of oxygen, though few compounds are less complicated in their constitution than water, carbonic anhydride, and ammonia. Animals, on the other hand, appear to require substances which have been elaborated by the organism of plants, and thus brought nearer to their own more complicated structure.

The best instance of an aliment fully capable of supporting life and expressly elaborated for that purpose, is furnished in the case of milk. Upon this the infant or young animal lives for some time exclusively, thrives, and grows rapidly; and as Prout has remarked, it contains four distinct principles, which may be taken as the types of the four chief varieties of alimentary substances. These types are, 1. the *aqueous*; 2. the *albuminous* or azotised, represented by casein; 3. the *saccharine*, supplied by sugar of milk; and 4. the *oleaginous*; to these ought to be added, 5. the *saline*, which is equally essential. It might, therefore, be anticipated that a suitable diet should contain a certain proportion of each of these principles; for, although the body possesses the power of altering and assimilating food to an extent varying greatly with the circumstances under which it is placed, yet experience has amply demonstrated that no one of these principles can be wholly withheld from any animal of the higher orders for a lengthened period without producing fatal results. It has been shown, for example, when animals are fed exclusively upon sugar, upon gelatin, or upon albumin, that they die of starvation; although, when these different materials are given in mixture, the animal lives and thrives. It has also been observed that those aliments which are admitted to be the most nutritious, and which are most largely used as articles of food, are those which contain all these principles in due proportion. A good example

of this kind is afforded in bread made from wheaten flour: its starch and sugar represent the saccharine principle, its gluten furnishes the azotised or albuminous material; water it of course contains; and it also furnishes the phosphates and other salts of the alkalies and earths, including sodic chloride. It likewise contains small quantities of fatty or oily matter, though the amount of this constituent is hardly adequate to the wants of the system; this deficiency is, however, supplied by the common habit of eating it with butter, milk, fat bacon, or some other oleaginous substance.

Animals appear to possess to some extent the power of deoxidizing saccharine matter and converting it into fat. The removal of a certain number of atoms of carbonic anhydride, of water, and of oxygen, from glucose would furnish the elements of the ordinary forms of fat; for example:—



An interesting illustration of the artificial conversion of sugar into a body belonging to the series of the fats, is afforded in the production of butyric acid by the fermentation of a solution of sugar under the influence of casein (1285); and a striking proof of the convertibility of sugar in the animal economy into a fatty substance, is given by the experiments of Guudlach and others upon the feeding of bees. In these experiments it was found that the insects, when supplied with pure sugar only, secreted wax in abundance; about 20lb. of sugar being consumed by the bees whilst they were producing 1lb. of wax.

The exact relative value of the saccharine and oleaginous principles of the food is not clearly understood, but one important difference between their functions is made evident, in the mode in which fat admits of being stored up in the economy in a form which allows of its being subsequently absorbed when needed: fat thus appears to serve as a sort of fly-wheel in the nutritive economy.

(1719) *Liebig's Classification of the Components of Food.*—The great objects of the supply of food were regarded by Liebig as twofold, viz., 1. the renewal of the tissues after they have become effete; and 2. the maintenance of animal heat. The constituents of the food were chiefly considered by him in their relation to these two great functions, and were subdivided into *plastic nutritive materials*, which consist exclusively of the albuminoid principles, and into *respiratory food*, including the saccha-

rine and oleaginous principles of Prout. Liebig estimates that some of the more important materials used as food contain these two principal modifications in the following proportions; what he termed the respiratory materials being all calculated, for the convenience of comparison, in the quantities of starch to which they would be equivalent:—

| | Plastic azotised matter. | Respiratory materials reckoned as starch. | |
|---------------------|-----------------------------|--|--------------------------|
| Veal contains . . . | 10 | 1 | |
| Hare's flesh . . . | 10 | 2 | |
| Beef | 10 | 17 | |
| Horse beans . . . | 10 | 22 | |
| Peas | 10 | 23 | |
| Fat mutton. . . . | 10 | 27 = | 11'23 fat |
| Fat pork | 10 | 30 = | 12'5 fat |
| Cow's milk | 10 | 30 = | { 8'8 fat 10'4 sugar. |
| Woman's milk . . . | 10 | 40 | |
| Wheat flour | 10 | 46 | |
| Oatmeal | 10 | 50 | |
| Rye flour | 10 | 57 | |
| Barley | 10 | 57 | |
| Potatoes. | 10 | 86 to | 115 |
| Rice | 10 | 123 | |

There is, however, a third great purpose to be attained by the assimilation of food, viz., the maintenance of the supply of energy, which by the actions of the living body becomes transformed into nervous or muscular power. The share which each of the principal constituents of the food of animals has in contributing to muscular force has within the last few years excited the close scrutiny of the physiologist and the chemist, and has not hitherto been decided (1726).

Liebig, and those who adopt his views, regard fat, sugar, starch, and alcohol, as articles which supply respiratory materials only; and he remarks that when from external circumstances, such as exposure to cold, there is a greater demand upon the respiratory function, there is an instinctive craving for additional quantities of food which furnish those substances by which the temperature of the body is maintained above that of the surrounding air: the Laplander and the Greenlander, for instance, drink train-oil, and are more prone to excess in spirits than the dweller in a more temperate climate. Alcohol, it must be observed, is not simply food: it acts as a powerful stimulant upon the nervous system, and hence its effects are complicated. The non-azotised ingredients of the food which find their way into the blood do not

leave the body until they have, by conversion into water and carbonic anhydride, experienced complete oxidation, so as to yield up in the body all their potential energy as actual energy.

The azotised ingredients of the food likewise evolve heat in the act of oxidation; but since these materials constitute the more highly elaborated, and less abundant, yet indispensable components of the food of animals, their consumption merely in the supply of heat must be considered as extremely wasteful; whilst at the same time these bodies are less perfectly adapted than the non-azotised constituents of the food for the maintenance of animal heat. Moreover, the azotised matters are chiefly excreted in the form of urea, a substance which is still combustible, and carries off a heat-producing power, amounting, according to Frankland's experiments, to about one-third of that of an equal weight of dry muscle.

From the table above quoted it appears that in milk and in the different varieties of corn (which are the most perfect forms of nutritive matter), the proportion which the plastic bear to the respiratory materials is, for 1 of the former, from 3 to 6 of the latter. The proportions of these components, however, vary considerably in the food of different classes of animals, and their organs of digestion are modified to meet these differences. The carnivora, for example, live on the flesh and blood of other animals, which in chemical and physiological properties are identical with their own, and which after digestion in the stomach are reduced to a soluble condition; in this form they are absorbed, and enter into the composition of the animal. In the herbivora the organs of digestion are more complicated, since their food contains only small quantities of nitrogenized constituents. It is found, on the whole, that animals of equal weight require more or less food, in proportion as the compounds which contain nitrogen are less or more abundant in it. The nitrogen occurs in the food principally in the form of compounds which have the same composition as the albumin and fibrin of animals. Vegetable albumin and fibrin are the principles which furnish plastic nutriment to the herbivora, and if they be withheld for any protracted period, starvation ensues. Hence it appears that one essential condition to the maintenance of animal life is the assimilation of certain materials, which are identical in constitution with the principal constituents of the blood. Animals do not possess the power of forming these principles, yet they produce a multitude of others from them by their decomposition; for example, plants cannot produce the gelatinous principles, neither do they furnish

the constituents of the brain, both of which are elaborated in the animal frame from the components of the food. The azotised compounds, when taken alone, are insufficient to support life; saccharine and oleaginous matters are absolutely necessary, and in the young, even of carnivora, they form, in the shape of milk, a most important part of their nutriment. Even the flesh diet of the carnivora contains a large proportion of fat, which supplies the necessary material of this kind.

In our estimate of the importance of the different materials which enter into the composition of food, we must not overlook the various salts; particularly common salt, calcic phosphate, and the sulphates and phosphates of the alkali-metals. Common salt is essential for the supply of the hydrochloric acid of the gastric juice, and the sodium of the bile. Calcic phosphate is necessary to the building up of the bones; and not a cell or a fibre of the body can be formed without the presence of the soluble phosphates.

Liebig has pointed out the singular manner in which these different salts are associated in the different parts of the body; sodic chloride, for instance, abounds in liquids which, like the blood and the serous exudations, have an alkaline reaction, and it is commonly accompanied by trisodic phosphate. Potassic phosphate, on the other hand, occurs in liquids which, like the juice of the flesh, have an acid reaction.

(1720) *Process of Digestion.*—The preliminary cooking to which much of our food is submitted is not essential to the process of digestion, but is generally resorted to in order to please the palate; but where a mixture of many kinds of food is to be assimilated by the stomach, the process of cooking may be made to assist the operations of digestion. The principal steps by which the food, after its reception into the mouth, is converted into a part of the living organism, are the following:—The food is first masticated and thoroughly mixed with the saliva. Animals which are carnivorous chew their food less completely, and are supplied less abundantly with saliva, than those that are herbivorous. The reason is obvious, since in the carnivora, the fleshy nature of their aliments enables the latter to be more readily assimilated than is the case in the herbivora, many of which, by ruminating, subject their food a second time to a thorough trituration and intermixture with the saliva. Birds that are granivorous are furnished with a strong hollow muscle, the gizzard, which is especially designed for the purpose of triturating the seed, to aid which, the birds swallow pebbles and gravel. The food, having been masticated and reduced to a pulp by intermixture with the saliva, is next

transferred to the stomach, where it becomes mingled with the acid secretion of the gastric juice (1689). After remaining for a few hours in this organ, the principal proportion of the albuminous and fibrinous constituents of the food is brought into the liquid form; but the fatty matters remain unaffected, and the starchy components are but imperfectly converted into the soluble condition of dextrin, or of sugar. From the stomach, the food, now reduced to a pulsatious mass termed *chyme*, passes to the duodenum, or commencement of the intestinal canal, where it is mixed, first with the secretion from the liver, and then with that from the pancreas.

Physiologists are not agreed upon the share which the bile takes in the function of digestion, but both the bile and the pancreatic secretion are alkaline, and the chyme, immediately after admixture with these liquids, assumes the appearance of an emulsion; in its further passage along the intestinal canal, it is mixed with a secretion from the inner surface of the jejunum and of the ileum, which still further modifies the food, completing the conversion of starch into a soluble compound, and rendering the fatty matters capable of assimilation. In the small intestines a separation of the aliment into two portions is effected; the larger of these portions is absorbed into the system, the smaller portion, consisting of vegetable fibre and insoluble and undigested matters, becomes excrementitious, acquiring a peculiar odour, and is ultimately rejected. The absorbed portion is taken up partially as a thin, milky liquid (the chyle), which is absorbed from the inner surface of the intestines by the lacteals, and these vessels empty themselves through the thoracic duct, into the subclavian vein: a still larger portion is absorbed by the mesenteric veins, which transmit their contents to the liver, to be there further elaborated before they are transferred by the hepatic veins to the right auricle of the heart.

One principal change wrought in the food, during its conversion into chyme, consists in its being rendered soluble, and combined with water; but it is evident that the mere fact of the conversion of the food into the liquid form is by no means the only essential condition, since soluble matters, such as the casein of milk, are frequently first converted into a solid form in the stomach, and are then gradually redissolved; the elements of the food are thus re-arranged, and if casein be the substance acted on, it is converted into albumin; but the change which fits dead organized matter for again becoming a portion of the living frame is not understood. The solid form in which azotised matters are gene-

rally presented to the stomach, may be designed (by demanding a longer stay in this organ) to facilitate and allow time for the completion of this change; while the amylaceous and oleaginous principles of the food, which simply supply the respiratory fuel, do not require so long a stay in the stomach. It is worthy of remark that albumin, even after it has been given as the sole constituent of the food, when it has once been dissolved, cannot be detected as such in the fluid of the stomach, either by boiling or by the action of nitric acid; it is not till after it has passed through the duodenum, and become mixed with the secretions of the liver and the pancreas, that albumin manifests itself by the ordinary reagents.

When digestion is duly performed, no gaseous products are set free; but when it is faulty, we often have a train of symptoms more or less distressing, owing to the evolution of carbonic anhydride, nitrogen, and hydrogen gases, which produce painful flatulence and distension.

There is a very great difference in the digestibility of the different articles used as food; some being completely chymified in two hours, and others requiring as much as six before this effect is produced. Very slight circumstances frequently interfere with the digestive process. Fats are apt to disagree, and so are all substances into the composition of which they enter largely; such as pastry, rich stews, and fried dishes; owing partly to the production of the peculiar volatile acids of fat during the processes of cooking or digestion, and partly owing to the difficulty with which such food is penetrated by the gastric juice. Where such food has been taken, the assimilating powers of the stomach are often interfered with, and the injurious effects thus occasioned are frequently manifested in the form of a sick-headache. Fermented liquors, if taken in small quantity, often afford a healthy stimulus to the stomach, but if taken in excess they arrest digestion and produce serious disturbance, independently of their enervating effects.

(1721) *Nutrition and Disintegration*.—Having thus traced the food into the blood, we may pass on to consider the course by which it becomes incorporated with the tissues of the living body. The offices of the blood may be considered under three principal heads:—1. that of *nutrition*, or reparation of the effete parts of the corporeal frame; 2. that of *respiration*, or the maintenance of animal heat and muscular and mental action; and 3. that of *secretion*.

1. *Nutrition*.—There is abundant evidence to show that the various tissues of the body are undergoing a constant succession

of changes which are essential to the maintenance of life, and that the more actively the vital powers are exerted, the more rapidly do these various changes occur, necessitating the supply of food more frequently and abundantly. Sooner or later after the deposition of any particle has taken place in any particular tissue, it is in its turn removed to make room for a new and equally fleeting successor. The principal organs of the body, with the exception of its solid frame-work, consist of albuminous and muscular tissue, and of those peculiar compounds which constitute the mass of the brain and of the nerves. Albumin and fibrin, the basis of these tissues, are contained ready formed in the blood, and they appear to be deposited at those points where they are needed, by a process somewhat analogous to that of simple coagulation. No advantage, however, would be gained, if the portions which they displace were to be re-absorbed in the form of albumin or of fibrin into the mass of blood. The change which attends the absorption of matter once deposited is deep-seated, and is essentially connected with the manifestations of vital activity. No portion of albumin or of fibrin seems to be removed, as such, into the system; consequently the fibrin and albumin contained in the blood in a healthy state must be considered as freshly elaborated, and as existing in it as a preliminary to its constituting an integral part of the body; and, therefore, as being in a form ready for assimilation. The effete tissues are decomposed at the moment of their removal, and are converted previously to absorption into new and distinct compounds; thus furnishing the second source whence the blood derives its component parts. This removal is effected by the agency of oxygen, supplied during respiration, and carried by the blood to every part of the system: the organic particles thus removed are therefore in a more oxidized form than that in which they were deposited, and they are absorbed at first into the blood itself, from which they are quickly eliminated in some of the excretions from it. The nitrogen, for example, is removed partly in the form of urea, or of uric acid, and partly in that of ammonia: the carbon is chiefly got rid of as carbonic anhydride; and the phosphorus and sulphur, as phosphates and sulphates. These different matters are eliminated through four principal channels, viz., 1. the excreta of the alimentary canal; 2. the urine; 3. the entaneous excretions; and 4. the pulmonary exhalation.

Having already considered the principal chemical relations of the first three excrementitious products, we shall now confine our attention to the nature of the pulmonary exhalation.

(1722) 2. *Respiration*.—The important function discharged by the lungs consists in the admission of atmospheric air into the body, in such a manner as shall enable it to act upon and oxidize the blood; the most obvious chemical change which is produced in the respired air consisting in the abstraction of oxygen from it, and the substitution of a bulk of carbonic anhydride nearly equal to that of the oxygen removed. The lungs act as an immense filter, through which, in the higher classes of animals, the whole mass of the blood is made to circulate as often as it passes through the heart. The venous blood as it arrives in the lungs is of a deep purple colour. It leaves them of a florid arterial red. The general structure of the lungs is such that these organs may be regarded as consisting of two sets of tubes, the larger of which is for the admission of air. The air-tubes are subdivided into a countless multitude of small ramifications, around which the blood-vessels are distributed in an extremely fine net-work: by this arrangement an immense surface is exposed to the air, with a comparatively small expenditure of space. The lining membrane of the air-tubes is kept continually moist by the secretion from their surface. Through this delicate membrane air passes readily by endosmosis into the blood-vessels beneath, and in consequence of this action the venous blood exchanges a portion of its carbonic anhydride with the oxygen held in solution by the liquid which bathes the surface of the air-tubes. The oxygen in this form obtains admission into the current of the circulation. The mere displacement of carbonic anhydride from the blood, although unattended with any perceptible chemical change, produces an alteration of colour from purple to scarlet. During the circulation of the aerated blood through the minute capillary vessels of the body, the absorbed oxygen effects those chemical changes which are essential to the maintenance of animal life. The tissues are broken up; urea, carbonic, lactic, uric, sulphuric, phosphoric, and perhaps other acids are formed; these are removed by the kidneys, the skin, and the lungs. While these decompositions are being effected, fresh particles, of constitution similar to the tissues undergoing decomposition, are being deposited from the blood, which receives the acid products, and is thus materially altered in colour and composition. When the blood again passes through the lungs, the carbonic anhydride is mechanically displaced from it by oxygen, and the scarlet colour is restored, while the other principles are in great part eliminated by the kidneys.

During the process of respiration a small quantity of nitrogen as well as of oxygen is absorbed, and this must be regarded as the

chief, if not the sole, source of the nitrogen which is undoubtedly exhaled by the skin. It is probable that this nitrogen is not the result of any chemical change, but that it has been merely absorbed into the system owing to its solubility; the quantity in the respired air does not vary materially from the original amount; indeed, if the blood be saturated with nitrogen, the amount of this gas which is absorbed will be equal to that which is evolved. By making animals respire in an atmosphere of oxygen and hydrogen, nitrogen is always found to be given out, since it is displaced from the blood by the hydrogen. According to the experiments of Regnault and Reiset (*Ann. de Chimie*, III. xxvi. 511), warm-blooded animals, if made to respire in a confined space, always exhale an appreciable quantity of nitrogen; the amount, however, of this is so small, as not to exceed $\frac{1}{100}$ part of the quantity of oxygen consumed. When the animals were in a state of exhaustion from want of food, an absorption of nitrogen commonly occurred to a similar extent. Traces of hydrogen, of marsh gas (Pettenkofer), and of ammonia are also present in respired air.

From the experiments of Magnus, which have since been amply confirmed by the careful researches of subsequent observers, it seems that a portion at least of the oxygen absorbed by the arterial blood is in a state different from that of ordinary solution. Water at 100° ($37^{\circ}8$ C.) is not capable of dissolving more than about one-fortieth of its bulk of oxygen, and the solvent power of serum is not materially different. Consequently, each pound of blood could not dissolve more than about three-fourths of a cubic inch (12 c. c.) of oxygen; but direct experiments have proved (supposing 10 lb., or about 4.5 kilogr. of blood to pass through the lungs per minute) that the average quantity of oxygen absorbed is not less than three times that amount.

The red particles are intimately concerned in this process of conveying the oxygen; and a portion of the oxygen which they thus absorb is given off unaltered when the solution is placed in the vacuum of the air pump. Carbonic oxide also displaces its own volume of oxygen from the arterial blood. There is no doubt that the greater part of the chemical change is effected by the oxygen after it reaches the capillary vessels which constitute the great laboratory of the body; for until it reaches these minute branches, the blood retains its florid hue, but on its exit from them it has the dark tint of venous blood.

(1723) *Proportion of Carbonic Anhydride exhaled during Respiration.*—The earliest trustworthy observations upon the chemical changes produced during respiration are due to Lavoisier

and to Seguin, and since their time numerous eminent chemists have made this process an object of study; particularly in relation to the quantity of oxygen consumed, and of carbonic anhydride produced. Much discrepancy, however, exists among the earlier statements regarding the proportion of carbonic anhydride contained in the respired air. We are indebted to Prout for a satisfactory explanation of these differences, which he proved to arise mainly from the fact that the quantity varies in the same individual at different times; and the numerous careful experiments published subsequently to those of Prout have fully established the correctness of these observations. It is now well known that the proportion of carbonic anhydride exhaled in a given time by the same animal, varies according to the rapidity of the circulation: the more vigorous the circulation, the larger is the quantity of this gas evolved: thus, *cæteris paribus*, a larger quantity is formed after a meal than when the animal is fasting; the proportion is also higher when the animal is awake than when sleeping, and a much larger quantity is exhaled during active exertion than during a similar period of repose. Indeed, the number of respirations may be more than doubled by exercise, and an immediate and even more than proportionate increase of the quantity of carbonic anhydride exhaled occurs (p. 905).

An important series of direct experiments upon respiration in man was undertaken by Scharling (*Liebig's Annal.* xlv. 214, and lvii. 1). Other experiments upon the same subject by Andral and Gavarret will be found in the *Annales de Chimie*, III. viii. 129. More recently, Regnault and Reiset have published an extensive and elaborate series of researches upon the respiration of various classes of animals, from which several new and important conclusions have been deduced (*Ann. de Chimie*, III. xxvi.); and Pettenkofer and Voit have pursued the same subject with an elaborate apparatus contrived to render the observations still more precise (*Liebig's Annal.*, Suppl. bd. ii. 1. and cxli. 295); whilst in our own country Dr. E. Smith has published a very extensive and laborious series of researches, many of which were performed upon himself (*Phil. Trans.*, 1859, 681).

Scharling's experiments were made upon persons of different ages who were placed in an air-tight chest, freely supplied with atmospheric air, which was deprived of carbonic anhydride by causing it to pass through a solution of potash. The respired air was transmitted through a succession of vessels, filled with sulphuric acid in order to retain moisture, with solution of potash to retain carbonic anhydride, and with sulphuric acid to retain

moisture which the current of air might mechanically carry over from the solution of potash. The increase in weight of the last two vessels indicated the amount of carbonic anhydride. A continuous current of air through the apparatus was maintained by means of the regulated action of an air pump, and the quantity of carbonic anhydride contained in the air of the chest at the close of the experiment was determined by direct analysis. By means of experiments conducted with this apparatus, it was ascertained that, on an average, the production of carbonic anhydride during sleep amounted only to three-fourths of that given out by the same individual for an equal interval of time during the period that he was awake. It was also found that the production of carbonic anhydride was proportionately greater in children than in adults, as was to have been anticipated from the greater activity of the vital functions during the period of growth and development. The average production of carbonic anhydride was also greater in male than in female adults, as might be expected from the smaller size of the latter; but in adult individuals of both sexes, if of equal weight, *cæteris paribus*, the consumption of carbon appeared to be nearly equal. The same observer has also shown that the quantity of carbon exhaled in the form of carbonic anhydride from the surface of the skin, in the adult, does not on the average exceed one-third of an ounce in the twenty-four hours. In cold-blooded animals, however, the respiration effected through the skin is much more extensive; frogs and salamanders will continue to live for several days after the lungs have been removed, owing to this entaneous respiration (Regnault).

Dr. E. Smith's experiments were made by measuring the quantity of air admitted to the lungs by means of a portable dry gas meter, adjusted to the mouth and nose by means of tubes with valves, and a suitable mask. The expired air was passed through weighed vessels; one filled with pumice, moistened with sulphuric acid; a second consisting of a box with numerous partitions, filled with solution of caustic potash; a third, was a drying apparatus with sulphuric acid; finally, the air was passed through baryta water, as a test of complete removal of the carbonic anhydride.

The average quantity of carbon which passes off during the day from the lungs and skin of an adult man is estimated by Dumas at about $8\frac{1}{2}$ ounces avoirdupois. These results have been almost exactly confirmed by the more recent experiments of Scharling. E. Smith estimates the average amount of a person at rest, 7.144 oz.; of one in the non-laborious class, 8.68 oz.;

of one in the laborious class, 11·7 oz. Andral and Gavarret found in their experiments that the quantity of exhaled carbonic anhydride was nearly the same as that given by Scharling. Pettenkofer and Voit found that a man who weighed 60 kilogr. or 132½ lb. emitted when at rest, in 24 hours, 911·5 grms. CO₂, or 341 grms. (12·02 oz.) of carbon, and during exertion as much as 1284·2 grms. CO₂, which is equal to 481·5 grms., or 16·98 oz. of carbon, a proportion much higher than that noted by other observers.

It is, however, obvious that the amount of carbonic anhydride, and the proportion which it bears to the respired oxygen, must vary with the nature of the food. When carbon is converted into carbonic anhydride, the volume of this gas which is formed is exactly equal (under similar circumstances of temperature and pressure) to that of the oxygen which has entered into its composition; but when hydrogen is oxidized, the whole of the oxygen with which the hydrogen has combined disappears from the gases exhaled; and a similar remark applies to that portion of oxygen which enters into combination so as to form solid or liquid azotised compounds. It can therefore only happen that the volume of carbonic anhydride exhaled and of oxygen consumed shall be equal, when the whole of the inhaled oxygen is employed in the oxidation of carbon. The direct experiments of Regnault and Reiset have, however, shown that the proportions of carbonic anhydride, and of respired oxygen, vary within very wide limits. From similar causes, when much fat is taken with the food, a large portion of oxygen disappears. Thus it may be proved by calculation that when butter supplies the respiratory food, for every 31 volumes of oxygen absorbed, 21 only of carbonic anhydride can be produced; and a similar, but smaller, disappearance of oxygen occurs when alcoholic liquors have formed part of the food consumed. Regnault and Reiset found in their experiments that dogs, when fed on meal, exhaled about 74 volumes of carbonic anhydride for 100 volumes of oxygen absorbed; but when fed on amylaceous substances the quantity of carbonic anhydride rose to 93 per cent.* A dog which had been fed upon mutton suet, emitted only 69·4 per cent. of carbonic anhydride; the deficiency being in this case consumed in converting the excess of hydrogen in the fat into water. Pettenkofer and Voit have since obtained analogous results. These observations, however,

* When dogs are fed upon a diet containing flesh with an extreme quantity of amylaceous matters, or sugar, the percentage vol. of oxygen to that of the carbonic anhydride may rise as high as 140 to 100, and hydrogen, or marsh-gas, is among the products of respiration (Pettenkofer and Voit).

are only true if the entire results of the 24 hours are taken. The proportions are very different if the comparisons are made during rest or sleep, and waking or active exertion, the proportion of oxygen consumed during sleep being invariably higher than during the hours of wakefulness. When animals which had been long kept without food were subjected to experiment, the percentage of carbonic anhydride was about the same as when they were confined to an animal diet; because the tissues of the animal constituted the source whence the carbonic anhydride was supplied; the animal was, in fact, feeding upon its own flesh. During a fast of 24 hours, Dr. E. Smith found the quantity of carbon exhaled by himself was reduced from 7.85 oz., the average when he was taking no exertion, to 5.923 oz. Rabbits fed upon vegetables emitted from 85 to 95 per cent. of carbonic anhydride, compared with the volume of oxygen absorbed; and granivorous birds yielded from 90 to 103 per cent., the volume of carbonic anhydride frequently exceeding that of the oxygen consumed. When these birds were confined to a flesh diet, the quantity of carbonic anhydride fell to about 67 per cent. of the oxygen consumed (Regnault and Reiset).

In the course of these experiments, it was ascertained that, provided the quantity of oxygen be proportionately increased, an animal may continue to breathe without injury in an atmosphere containing a considerable amount of carbonic anhydride; the injurious effects of carbonic anhydride in the air appearing to depend rather upon the mechanical obstacle which it offers to the escape of the gas already in the blood, than to any directly poisonous action of the anhydride itself. By increasing the facility for its diffusion by the addition of oxygen, or even of hydrogen, to air already containing a considerable quantity of carbonic anhydride, the animals continued to breathe such air without injury. Regnault found that the proportion borne by the carbonic anhydride exhaled, to that of oxygen consumed, is not altered when pure oxygen is substituted for atmospheric air, and the same relations were observed when the animals were caused to respire in an atmosphere consisting of a mixture of oxygen and hydrogen.

Pettenkofer and Voit, by comparing together the quantity of oxygen consumed during the day and during the night by the same individual, have ascertained that a considerable quantity of oxygen is absorbed during sleep, and that the oxygen thus stored up in the body is again during waking hours expended in the production of carbonic anhydride, and they consider that a part

of the refreshment produced by sleep is connected with this absorption of oxygen. In support of this view, they cite comparative experiments upon a diabetic patient and upon one suffering from leukaemia, where no sensible refreshment was afforded by sleep, and in which cases no accumulation of oxygen took place in the system.

In the table which follows, these results are compared with each other. The men were weighed at 6 o'clock in the morning and again at 6 o'clock in the evening, and a third time at 6 o'clock the following morning. The numbers give the quantities in grammes, of carbonic anhydride, water, urea, and absorbed oxygen. The numbers in the last column express the proportion between the oxygen contained in the carbonic anhydride exhaled, taking the oxygen in the air inspired at 100:—

*Absorption of Oxygen and Exhalation of Carbonic Anhydride,
in grammes.*

| Conditions. | Period. | Excreted. | | | | Absorbed. | Volume. |
|-------------------------------|-------------------|-------------------|-------------------|-------|--------|-----------|-----------------------|
| | | CO ₂ . | H ₂ O. | Urea. | Sugar. | Oxygen. | O : CO ₂ . |
| 1. Healthy man at rest. | Day | 532·9 | 344·4 | 21·7 | ... | 234·6 | 100 : 175 |
| | Night | 378·6 | 483·6 | 15·5 | ... | 474·3 | 58 |
| | Total in 24 hours | 911·5 | 828·0 | 37·2 | ... | 708·9 | 94 |
| 2. Healthy man at work. | Day | 884·6 | 1094·8 | 20·1 | ... | 294·8 | 100 : 218 |
| | Night | 399·6 | 947·3 | 16·9 | ... | 659·7 | 44 |
| | Total in 24 hours | 1284·2 | 2042·1 | 37·0 | ... | 954·5 | 98 |
| 3. Diabetic patient. | Day | 359·3 | 308·6 | 26·9 | 246·4 | 278·0 | 100 : 94 |
| | Night | 300·0 | 302·7 | 20·2 | 148·1 | 294·2 | 74 |
| | Total in 24 hours | 659·3 | 611·3 | 49·2 | 394·5 | 572·2 | 84 |
| 4. Leukæmic patient. | Day | 480·9 | 322·1 | 15·2 | .. | 346·2 | 100 : 101 |
| | Night | 499·0 | 759·2 | 21·7 | ... | 329·2 | 110 |
| | Total in 24 hours | 979·9 | 1081·3 | 36·9 | ... | 675·4 | 105 |

In the healthy man, the quantities of carbonic anhydride and oxygen consumed may also be compared in the following manner :

| | Of 100 parts of CO ₂ were exhaled | | | Of 100 parts of Oxygen were absorbed | |
|-----------------|---|-----------|--|---|-----------|
| | By day. | By night. | | By day. | By night. |
| At rest | 58 | 42 | | 33 | 67 |
| At work | 69 | 31 | | 31 | 69 |

Hence it appears that the absorption of oxygen by the body during waking and sleeping, during rest and exertion, is more

uniform than the evolution of oxygen in the formation of carbonic anhydride.

The increase of carbonic anhydride caused by muscular effort, it is to be noted, is exhaled chiefly during the day, whilst muscular exertion is going on; whereas the increase in the absorption of oxygen is most marked during the night. The deeper and more frequent respiration which occurs during bodily exercise depends therefore, primarily, not so much upon the demand for more oxygen by the system as upon the necessity of getting rid of the carbonic acid which has been generated, and of reducing the temperature of the blood. Comparatively little variation in the quantity of oxygen absorbed occurs during the daytime whether the person be at rest or in action, and comparatively little variation occurs in the quantity of carbonic anhydride exhaled during the night, whether the previous day has been one spent tranquilly or in active exertion, the amount of carbonic anhydride exhaled during the night being dependent upon the quantity of oxygen absorbed during the day.

A remarkable result also may here be noted in respect to the excretion of urea, which is found not to be increased by increased muscular effort, but to depend upon the amount of nitrogen in the food, a circumstance which has a very important bearing upon the question of the origin of muscular force, to which reference will hereafter be made (1726).

The general conclusion drawn by Pettenkofer and Voit from these experiments is this:—That during the night oxygen is accumulated in the body in proportion to the albuminoid food consumed, and that this store of oxygen is preserved for the wants of the following day. If this be true, it is obvious that no accurate estimate of the balance of consumption and assimilation can be arrived at unless the experiment extends over at least 24 hours; and it seems also to be probable that the chemical changes due to bodily exertion occur much more gradually than has hitherto been supposed.

An interesting illustration of the great differences in the mode of respiration which may occur even in the same animal under altered circumstances, is also afforded by the observations upon hibernating animals. Marmots were found during their torpid condition to consume not more than one-thirtieth of the amount of oxygen which they required in their active state. These animals at the commencement of their hibernation are fat, but they lose weight considerably before they resume their active condition. A remarkable observation upon these animals was

made by Sæe, and confirmed by Regnault and Reiset. The marmot whilst in a torpid condition increases in weight, owing to an absorption of oxygen, which amounts to nearly one-half of that inhaled; this oxygen becomes converted into water, the greater portion of which is retained in the system for a while, but the animal at intervals evacuates it from the bladder, so that in the long run its weight becomes diminished. In fact, during its sleep its temperature is really maintained by the slow combustion of the store of fat which it had accumulated preparatory to its winter's repose.

Ed. Smith found in his own case that the quantity of carbonic anhydride evolved might be increased tenfold by strong exertion. The quantity of carbonic anhydride, according to these experiments, evolved per hour was as follows:—

| | | | |
|--------------------------|------------|-------------------------------------|------------|
| During sleep . . . | 19·0 grms. | Walking 2 miles an hour . . . | 70·5 grms. |
| Lying down to sleep | 23·0 „ | Walking 3 miles | 100·6 „ |
| In sitting posture . . . | 29·0 „ | Ascending treadmill 28·65 } 189·6 „ | |
| | | feet per minute | |

During exercise upon the treadmill the pulse rose to from about 70 to 150 per minute, and the number of inspirations from 11 to 22.

The air which has passed through the lungs in the ordinary process of respiration, is by no means deprived of its oxygen; it usually contains about 4 per cent. only of carbonic anhydride; the greater portion of the air which is expelled during expiration has not proceeded further than the larger ramifications of the bronchi. In ordinary respiration 30 cubic inches, or about one-tenth, of the quantity of the air in the lungs is changed with each act of respiration, the total capacity of the lungs being about 300 or 330 cubic inches. The number of respirations in a healthy adult averages per minute from 14 to 15, but the bulk, as well as the frequency, of the inspiration varies with each individual, according to the circumstances in which he is placed, and the necessity of a larger or smaller supply of oxygen to the system. Assuming that the volume of air inspired each time is 30 cubic inches, and that 15 inspirations occur per minute, not less than 375 cubic feet of air would pass through the lungs of each individual in 24 hours.

If we assume that the average evolution of carbon by the lungs of an adult man of the weight of 154 lb. or 69·85 kilo. amounts to 8·5 ounces avoirdupois (241 grms.) in twenty-four hours, it is easy to calculate the quantity of oxygen which is required during respiration for that period:—8·5 oz. of carbon would require about 22·66 oz. (401 grms.), or 16·73 cubic feet of oxygen for its

conversion into carbonic anhydride, and would yield 28,912 cub. in. of this gas at 60°, bar. at 30 inches,—or 21 cub. in. per minute: consequently, if 10 lb. of blood pass through the lungs per minute, every pound of blood in its passage through these organs must emit about 2 cub. in. of carbonic anhydride. Now, since for the oxidation of 8½ oz. of carbon, 22·66 oz. of oxygen are required, and since it is found that an adult emits on the average a volume of carbonic anhydride equal to 85 per cent. of the oxygen inhaled, it may be inferred (allowing 15 per cent. for the amount of oxygen fixed by hydrogen, &c.), that not less than 26·7 oz. (757 grms.), or upwards of 1½ lb. of oxygen, are daily consumed by every adult; and allowing for 1·4 oz. (39·75 grms.) of dry solid matter evacuated by the intestinal canal, and 2·2 oz. (62·37 grms.) of solids by the urine, the whole of the remaining portion of the food (exclusive of about 4½ lb. of water, which is eliminated by the kidneys and the skin), must pass off in the gaseous form by the lungs.

The results obtained by Barral upon the average assimilation and consumption of food in twenty-four hours during summer and winter, conducted upon his own person, may here be cited (*Annales de Chimie*, III. xxv. 129).

Quantities in oz. avoirdupois of Food and Excreta in twenty-four hours.

| Period of the Year. | Consumed. | | | Evolved. | | | | |
|---------------------|------------------|---------|------------------|--------------------------|---------------------|----------------|--------|-------------------|
| | Food taken. | | Oxygen absorbed. | Water by skin and lungs. | Carbonic anhydride. | Total excreta. | | |
| | Solid not dried. | Liquid. | | | | Urine. | Fæces. | Nasal secretions. |
| | | | Not dried. | | | | | |
| In July . . . | 24·4 | 59·7 | 27·42 | 40·27 | 31·34 | 36·14 | 2·66 | 1·19 |
| In December . . | 39·2 | 57·9 | 37·44 | 45·43 | 43·32 | 39·97 | 5·00 | 1·15 |
| Or in 100 parts. | | | | | | | | |
| In July . . . | 75·4 | | 24·6 | 36·1 | 28·8 | 34·7 | | 0·4 |
| In December . . | 72·2 | | 27·8 | 33·8 | 32·3 | 33·2 | | 0·7 |
| | 100 | | | 100 | | | | |

Although these results are not free from objection, they possess considerable interest. The amounts of carbonic anhydride emitted and of oxygen absorbed are inferred from the difference between the quantity of carbon, hydrogen, and nitrogen found by analysis in the food taken, and that furnished by the solid and liquid excretions. This mode of calculation necessarily involves these numbers in some uncertainty, since all the errors of experiment fall upon them. It was found that the total quantity of oxygen absorbed amounted to fully one-third of the entire weight of the solid and liquid constituents of the food. The proportion of nitrogen to that of carbon contained in the food taken was as 1 : 12·8. The excess of nitrogen in the food over that of the solid and liquid excretions varied from one-third to one-half; and this excess must have passed off through the skin and lungs; but this estimate is probably too high, although it does not

attain to much more than 1 per cent. upon the volume of the carbonic anhydride. The proportion of nitrogen found in the solid excreta did not amount to one-fifth of that contained in the urine.

The proportion of carbonic anhydride exhaled in winter is much greater than in summer, and the quantity of water is also a little greater in winter. The latter circumstance is explained by the fact, that more air passes through the lungs in winter than in summer, and it is less loaded with moisture on entering them; but in both cases the air quits them nearly saturated with aqueous vapour at the temperature of the body, consequently it will carry off more moisture in the winter than in summer.

According to the observations of E. Smith, the respiratory process, *cæteris paribus*, is most active in spring, and least so in autumn; but the proportion of carbonic acid decreases as the summer advances, and the frequency of respiration and the amount of air inspired are about one-third less in August than in April.

The exact form in which the compounds which are destined to produce animal heat exist in the blood is unknown, but there can be no doubt that the permanently alkaline condition of the blood (which Liebig attributes to trisodic phosphate in the carnivora, and Lehmann to sodic carbonate in the herbivora), is concerned in a very important manner in this oxidating process: for it is uniformly observed that compounds of organic origin are much more readily oxidized in the presence of alkalies than they are when in a neutral or in an acid condition; doubtless because the products of oxidation being commonly acid, the presence of a base with which those acids can combine facilitates the formation of the acid, whether it be carbonic or any other acid compound.

(1724) *Animal Heat*.—The temperature of the human body, whatever may be the temperature of the atmosphere, is uniformly maintained at 98° or 100° ($36^{\circ}\cdot6$ or $37^{\circ}\cdot7$ C.), that of birds at from 106° to 108° ($41^{\circ}\cdot1$ to $42^{\circ}\cdot2$ C.), and that of warm-blooded reptiles at about 85° ($29^{\circ}\cdot4$ C.). But as the temperature of the air is many degrees, in this climate often 45° (25° C.) or more, below that of the human body, it is clear, since the animal frame is subject to cooling at the same rate as other natural objects, that a constant supply of heat is necessary to the maintenance of this steady temperature. In order to diminish the quantity of heat required to be generated, animals are furnished with coats of hair, of feathers, of wool, and of other light, porous, non-conducting materials, which greatly retard their rate of cooling; and the thickness of these coats varies in the same animal with the season of the year, and the average temperature to which the animal is exposed. Man supplies himself with clothing, which experience teaches him to adapt to the varying circumstances under which he is placed.

This constant evolution of heat in the living body is occasioned

by the gradual combustion of the carbon and of the hydrogen supplied in the food ; the combustion being effected by the agency of the respired oxygen. All bodies, when they enter into combination with others, whether quickly or slowly, evolve heat, and when the products resulting from combination are the same, the amount of heat which is developed for the same weight of the compound products is also identical (199). Carbon and hydrogen are already combined with each other in the body, and in the act of their combination have already evolved a certain amount of heat ; the combustion of a hydrocarbon, therefore, does not produce the same amount of heat as the combustion of an equal quantity of carbon and hydrogen not previously in a state of combination ; still a very large quantity of heat is developed during their oxidation, and if this oxidation be effected within the body, the heat thus liberated will necessarily contribute towards maintaining the temperature of the body. According to the experiments of Despretz, 1 gramme of pure carbon during combustion evolves heat enough to raise the temperature of 14,200 times its weight of water through 1° of F., or enough heat to convert into vapour 12.63 times its weight of water at 100° ($37^{\circ}.8$ C.), or the temperature of the body ; the heat developed by the combustion of 241 grms. or 8.5 ounces of carbon should, therefore, suffice to evaporate 3.043 kilog. of water daily, or nearly 6.61 lb. This quantity of water is more than double the average amount of that which is actually exhaled from the entire body in the twenty-four hours, the average not exceeding, if the air from the lungs be assumed to be saturated, 1 lb. from the lungs and $1\frac{1}{2}$ lb. from the skin.* The surplus heat from the carbon, as well as that from the hydrogen, the amount of which is not so easily estimated, is expended in keeping up the temperature of the body, and in generating the muscular force which is exerted by the individual. Upon the principle of the conservation of energy, it follows of necessity that in climbing, the calculated quantity of heat expended is greater than that which is really evolved, part being actually consumed in the effort of lifting ; while in the descent from an elevation the reverse must hold good. Experiments have shown that animals exhale more carbonic anhydride in proportion to their weight, as their temperature is higher. It

* Dr. E. Smith, however, in his experiments, found that the air which passed from the lungs was never fully charged with moisture. During a working day the average amount of water exhaled by him from the lungs was 5 oz. whilst fasting ; under ordinary circumstances it varied from 7.4 to 8.4 oz. in the same time.

has been estimated that birds evolve of carbonic anhydride half as much again as the mammalia do; but Regnault finds that, in some cases, the disproportion is much more considerable. The smaller the animal, the larger is the proportionate extent of its cooling surface, and consequently the larger is the quantity of carbon which must be oxidized within it in order to maintain a temperature equal to that of the larger animal; linnets, for instance, evolve 10 times as much carbonic anhydride in proportion to their weight, as the domestic fowl. Small animals consequently consume a much larger quantity of food in proportion to their weight than large animals, and this may account for the greater proportionate activity of many small animals when compared with larger ones.

Since the diffusion of animal heat over different parts of the body is tolerably uniform, the source of heat should be diffused likewise. Provision appears to have been made for this essential condition, in the circumstance that the principal action of oxygen upon the constituents of the body takes place in the capillary vessels, which are distributed throughout the whole organized structure; and therefore the heat resulting from this action is also equally distributed through the different parts of the body. A certain amount of chemical action doubtless takes place in the lungs, where the blood first comes into contact with the air, and this increased chemical action would be needed to supply the heat carried off by the vapour which passes off at each expiration; but the main oxidizing actions occur deep in the structures of the body itself.

(1725) *Demand for Food varies with the Temperature.*—Since, then, the combustion of the hydrocarbonous portions of the blood are those best adapted to the production of animal heat, it might be expected that, as the demand for heat varies at different seasons and in different climates, the quantity and quality of the food demanded should also vary accordingly. Experience proves that such is the case; the appetite is keener in winter than in summer, and the aliments which we are then in the habit of consuming partake more of a fatty and carbonaceous character: the inhabitants of the polar regions maintain the necessary supply of heat by an abundant consumption of blubber and train-oil,* while those who live in tropical climates content themselves with a lighter and more succulent vegetable diet. The liver secretes

* It is, however, difficult to say whence the whale and the seal in their icy climate derive the means of accumulating their stores of blubber and oil.

a fluid rich in carbon, and in certain cases may act as one outlet of hydrocarbonous matters to the system. Respiration in a hot climate takes place with diminished frequency. It must also be remembered, that equal volumes of air admitted to the lungs by respiration at high and at low temperatures contain very different weights of oxygen; air at 40° ($4^{\circ}\cdot4$ C.) contains one-tenth more by weight of oxygen than an equal bulk of air at 90° ($32^{\circ}\cdot2$ C.). Less carbon, therefore, is thrown off by the lungs in equal intervals of time in a hot climate than in a cold one, by which means the too rapid production of animal heat is avoided; but the excess of carbon carried into the system must, nevertheless, be got rid of, and this must be effected in a manner that shall not produce heat. Owing to the beautiful compensating system upon which our bodies are constructed, one organ, if necessary, can relieve another from its burden, and the liver carries off this excess of carbon in an unburned form; provided the quantity be only moderate, this vicarious action may be effected without inconvenience, but if it be excessive, enlargement and congestion of the gland ensue, and disease, more or less serious, is the result. In a dry state of the atmosphere, however, less duty falls upon the liver, inasmuch as free evaporation goes on from the surface both of the lungs and of the skin, and thus the temperature of the body is reduced. In dry weather, therefore, carbon may be emitted by the lungs in larger quantity without inconvenience; but when the temperature of the air is high, and at the same time loaded with moisture, this source of relief is cut off, and an oppressive sensation of languor is experienced.

There is still a great want of accurate direct experiments on the production of carbonic anhydride under great differences of atmospheric temperature and moisture, and a correct series of observations on this subject, in arctic and in tropical regions, would be highly valuable both to the physician and the physiologist. Upon this point the experiments of Lehmann (*Physiological Chemistry, Transl. Car. Soc.*, vol. iii. page 347) may be cited. He found that 1000 grammes weight of pigeons yielded in *dry* air 6.055 grammes of carbonic anhydride per hour at 75° , and 4.69 grammes at 100° ; the same animals in *moist* air yielded 6.769 grammes at 73° , and 7.76 grammes at 100° . And 1000 gramme weight of rabbits exhaled in *dry* air 0.451 gramme of carbonic anhydride per hour at 160° , and as much as 0.677 gramme in a *moist* atmosphere at the same temperature.

When the saccharine and oleaginous portions of our food are given in excess, they are thrown off by the liver and the kidneys;

Tiedemann and Gmelin found, when they fed animals on butter and starch, that the urine was loaded with fatty matter, and bilious diarrhœa was an almost constant attendant. The azotised principles of the food go to form the azotised principles of the blood, and are necessary for the reproduction of the muscular and other tissues; and hence the importance of a mixed diet for the due support of the vital functions. The nutritive value of different articles of food is, therefore, entirely relative; and is dependent upon the proportion in which each is mingled with other bodies in which the four staminal principles are combined together in due proportion.

It must not be overlooked, however, that the most advantageous mixture of nutritive materials will vary with the circumstances under which the animal is placed. In the human species, the milk is adapted to the wants of the new-born infant, which will be wrapped in clothes, and shielded from the weather; and the materials consist of about 10 parts of plastic matter, 10 of fat, 20 of sugar, and 0.6 of salts. In the case of the cow, where the young animal is more exposed to the vicissitudes of the weather, the proportion of these constituents is altered, the milk containing to every 10 parts of plastic material, 11.11 of fat, and 14 of sugar. The composition of the milk at different periods of lactation also varies in an important manner, in order to meet the altering wants of the young animal in the successive stages of its growth.

A few animals are entirely carnivorous: but it must be remembered that all flesh, even that which is usually considered to be lean, contains, in addition to azotised matter, a certain quantity of the oleaginous or fatty principle. The herbivora consume with their food large quantities of saccharine and amylaceous compounds, which, by the abstraction of oxygen, are converted into fat; such animals are capable of being fattened in a remarkable manner, whereas the carnivora seldom acquire any great store of fat, in consequence of a deficient supply of the material best adapted for conversion into that substance.

It has been already remarked, that when increased demands are made upon the strength of animals, as in taking exercise, the number of respirations is increased, and the circulation quickened, and more carbonic anhydride evolved; and there can be no doubt that this increased demand upon the muscular effort is, for the time, supported by the increased stimulus resulting from the more rapid chemical action upon the blood and tissues of the body. If the views advocated by Traube, Haidenheim, and Frankland be correct, the development of animal heat is, however,

to be regarded as a residual and secondary, though by no means an unimportant physiological result, the development of muscular energy being first provided for, while the animal heat developed is the necessary residuum of the transformation of energy into muscular power, even when the muscular power is exerted externally.

(1726) *On the Origin of Muscular Power.*—It is now admitted by both physiologists and chemists, that muscular power is derived from the action of the oxygen supplied during respiration upon the digested portions of the food, either in their circulating condition as constituents of the blood, or after they have become part of the tissues of the living body. But it is still a matter of dispute whether these constituents must be first converted into actual muscle before their oxidation can give rise to mechanical force; or whether it be not possible that muscular work may also be derived from the oxidation of the constituents of the blood, in their passage through the muscle, and though they may be unfit for conversion into muscular fibre.

Liebig distinctly maintains that the non-azotised portions of the food are mere heat givers, and that the transformation of the azotised tissues is the source of the dynamical power of the animal.

This view has been largely accepted; it is still supported by Ranke, by Playfair (see his lecture "On the Food of Man in Relation to his Useful Work," published in 1865), and by many men of eminence. On the other hand, it has been opposed by J. R. Mayer, who distinctly stated in 1845, that "a muscle is only an apparatus by means of which the transformation of force is effected, but it is not the material by the change of which the mechanical work is produced;" and he regards "the blood, a slowly-burning liquid, as the oil in the flame of life." Lawes and Gilbert were led to similar conclusions from their observations on the feeding of cattle, and Mayer's view has recently received experimental confirmation from Pettenkofer and Voit, from Ed. Smith, and particularly from Fick and Wislicenus, *Phil. Mag.*, 1866, and from Frankland (*Ibid.*).

For the satisfactory solution of this important problem, the following data are requisite:—

1st. The amount of force which can be generated by the oxidation of a given weight of muscle in the body.

2nd. The amount of force actually *exerted* by the muscles in the body during a given time, and

3rd. The quantity of muscle actually *oxidized* in the body during the same time.

If the total amount of work performed in the given time be greater than could possibly be generated by the oxidation of the muscle consumed during the same time, it necessarily follows that the power of the muscles is not derived *exclusively* from their own substance.

1st Datum. To determine the amount of force generated, it is necessary to agree upon a unit; and the unit which is now generally adopted for the measurement of mechanical force is that which is represented by the lifting of a kilogramme to the height of a metre, or, as it is commonly termed, a metre-kilogramme (mkg.). The connexion between this unit and the amount of heat which is represented is supplied by the experiments of Joule, who has shown that an expenditure of heat sufficient to raise 1 kilog. of water 1° C. would suffice to raise 1 kilog. to the height of 423 metres, or 423 kilogs. to the height of 1 metre; and conversely, that the fall of 1 kilog. from the height of 423 metres, or of 423 kilogs. from the height of 1 metre, would develop an amount of heat, when the weight is suddenly brought to rest, sufficient to raise 1 kilog. of water 1° C. Consequently 423 metre-kilogs. of force are required to raise 1 kilog. of water 1° C. (129).

The first datum has been given by Frankland; for he finds that if 1 gramme of dry muscle be burned in oxygen, it will give out a quantity of heat which will raise 2161 kilogs. to a height of 1 metre. Consequently it is impossible that the consumption of a gramme of muscle in the ordinary wear and tear of the body can produce a force greater than this. If, in climbing, for example, 2161 kilogs. be lifted to a height greater than 1 metre by the waste of 1 gramme of muscle, it is certain that the oxidation of something besides muscular tissue must have taken place. In reality, however, the muscle never leaves the body in a completely oxidized form; it passes off mainly in the shape of urea, which when burned still gives out heat equivalent for each gramme to 934 mks. Now as muscle and albumen would furnish almost exactly one-third of their weight of urea, the quantity of heat emitted by 1 grm. of muscle during its conversion into urea would amount to 1848 mks. instead of the full 2161 mks. (Frankland).

2nd Datum, the amount of muscular force actually exerted in lifting a known weight in a given time to a known height. Fick and Wislicenus have attempted to furnish this by climbing a steep mountain, the weight lifted being their own bodies, the altitude of the mountain being known. At the same time they endeavoured to obtain the

3rd Datum—viz., the quantity of muscular tissue expended in

producing this amount of exertion, by determining the quantity of nitrogen excreted by the kidneys during the effort, and comparing it with that which escaped by the same channel before and after the exertion. They assume that the whole of the nitrogen of the metamorphosed tissues passes off in the urine, and of course the accuracy of their result depends on the truth of this assumption, which is pretty generally adopted by physiologists.

It would occupy too much space to go in detail into the precautions adopted, or into the objections which may fairly be raised against the manner in which this ingenious method of attempting to solve the problem was carried into effect.

Instead of allowing themselves their ordinary diet during and after their experiment, the Swiss professors placed themselves for the day before upon a diet free from nitrogen, and ate a plentiful meal after their exertion was concluded. The precaution thus adopted produced a paradoxical result; for during the effort of climbing, which lasted $5\frac{1}{2}$ hours, *less* nitrogen was excreted in the urine than escaped through this channel during the same period of repose before the exertion commenced.

Imperfect, however, as the results are at present, they yet possess a high degree of interest, as will be seen from the considerations which follow.

The height of the Faulhorn from the lake of Brienz at the point selected was 1956 metres; the weight of one of those who made the experiment was 66 kilogs., and the time occupied was $5\frac{1}{2}$ hours. But the effort required to raise the body to a given height is by no means a complete measure of the muscular exertion made in the time. The heart is in perpetual action, the ribs are in alternate rise and fall, the peristaltic and other movements are constantly going forward; and last, not least, the state of tension into which the various muscles are thrown during the whole time, in order to preserve the body in the erect position, is continually exhausting muscular energy within the body. In this ascent the average number of pulsations per minute was in Fick's case 120; and it has been calculated that each beat of the heart of a man of ordinary stature and strength is equivalent to 0.64 metre kilogrammes, whilst, according to data furnished by Donders, an ordinary inspiration of 36.6 cub. inches (600 cub. centim.) represents 0.63 mkg., and Fick's inspirations averaged 25 per minute during the ascent.

No satisfactory measures of the amount of exertion expended in maintaining the muscular tension have been made, but from the incomplete data we possess it cannot be less than equal in amount to the effort manifested by the weight raised in climbing.

The amount of force expended by one of these gentlemen (Professor Fick) in climbing was therefore:—

| Metre. | Kilo. | Min. | Hrs. | Mkg. | Metre kilogrammes. |
|--------|-------|------|------|-----------------------------------|------------------------|
| 1956 | × | 96 | . | . | weight raised = 129096 |
| | | | | 120 × 60 × 5.5 × 0.64 pulsations | = 25344 |
| | | | | 25 × 60 × 5.2 × 0.63 respirations | = 5197 |
| | | | | Muscular tension not calculated. | <hr/> |
| | | | | | <u>159637</u> |

This would require a consumption, according to Frankland's estimate, of $\frac{159637}{1848} = 86.3$ grammes, if the whole of the nitrogen of the muscle were converted into urea. Now, the nitrogen found in the urine during the ascent amounted to—

| | Grms. | = | Dry muscle. Grms. |
|---|-------|---|----------------------|
| In the $5\frac{1}{2}$ hours during the ascent | 2.255 | = | 14.85 |
| In the 6 hours after the ascent | 2.400 | = | 15.78 |
| Together | 4.655 | = | 30.63 |

So that the total quantity of muscular fibre which was oxidized in the ascent, if measured by the urine, and if the whole of the urea excreted during the following 6 hours be included, scarcely amounts to more than one-third of the quantity necessary to occasion the effect, without taking into account the quantity expended in producing the muscular tension, which probably would require at least an equal consumption of material to maintain it. So far, therefore, as these experiments go, it appears to be clear that something besides azotised material was expended in maintaining the energy manifested in the ascent. It must be added that the results furnished in the case of Wislicenus likewise confirm these conclusions most completely.

No doubt it will be urged, and with justice, that in order to enable us to draw rigorous conclusions, experiments of this kind should be prolonged for several days in succession, that the food taken should be such as the observer is habitually accustomed to take, and that careful analyses of the urine should be made for several days before and several days after those devoted to the ascent. There is also no doubt that experiments on the tread-wheel, as practised by Dr. Ed. Smith, admit of far greater precision than these of the Swiss professors, though it requires rare steadiness of purpose to carry them through.

(1727) 3. *Secretion*.—Having now considered the functions of the blood in regard to nutrition, and to respiration, we have lastly to offer a few remarks upon the process of secretion. It is worthy of remark that in every instance where a purely excrementitious matter is formed, the substances excreted are produced in the mass of the blood, at a distance from the point at which they are separated. The bile furnishes an exception, but, as it has been already stated, the great proportion of this fluid is re-absorbed into the system; it therefore cannot be considered as purely excrementitious. In experiments in which the kidneys have been removed from animals, uric, phosphoric, and sulphuric acids, as well as urea, are found to accumulate in the blood; the kidney is, therefore, not to be looked upon as an oxidizing or acidifying organ, but as an organ through the agency of which acids are separated from the system, combined with, and nearly neutralized by, alkaline matters. A similar principle holds good in the case of the lungs, which may be viewed as a gland by which carbonic anhydride is excreted; in this case also the carbonic anhydride is not formed by the lungs, but is simply eliminated by their action. It appears, therefore, that those organs which are destined for

the separation of excretions from the body do not form the various substances, but simply eliminate them. But the case is otherwise with the glands which furnish substances destined to be consumed subsequently by the economy: these glands in such instances seem to effect a true transformation of the blood, one part of which forms the peculiar matter of the secretion (as for example, sugar of milk in the mammary gland), the other, or complementary portion, is returned into the mass of circulating fluid. The true mechanism of secretion is at present unknown. It has been imagined that secretion may present a certain analogy with the case of vinous fermentation, in which, little as we know of the cause, we understand the conditions requisite to produce it; for it appears that the main point consists in the presence of certain organic molecules, since it is found by the experiment of placing yeast in a tube closed with filtering paper, and dipping it into a solution of syrup (p. 150), that actual contact with those organisms is necessary to produce the decomposition, the liquid in the tube being the only part which ferments: hence we may conceive why blood out of the gland does not undergo the same changes as when circulating through it. No satisfactory attempt has hitherto been made to explain why one substance should produce one kind of decomposition, and a different substance a totally different decomposition, although the compound operated on be the same in both cases.

CHAPTER XIV.

ATOMIC VOLUMES—LAW OF BOILING POINTS.

(1728) HAVING now completed our survey of the different classes of organic compounds, we may proceed in the last place to review briefly some points connected with the theory of the atomic constitution of matter which could not conveniently be discussed until the chemical properties of the various compounds, both organic and inorganic, had been described.

Two theories of the composition of material bodies have been maintained with varying degrees of credit from the earliest ages of the Grecian philosophy to the present time: the one founded on metaphysical views; the other, and now the generally received opinion, based on physical considerations.

Upon the first view of the constitution of matter, it is sup-

posed that the particles of which bodies consist are capable of subdivision without limit. Every particle of matter must possess an upper and a lower surface, and therefore it is conceivable that these surfaces may be separated from each other.

The second view, which was upheld, amongst other illustrious men, by Newton, maintains that though matter is susceptible of subdivision into molecules of inconceivable minuteness, there is a point beyond which no power within the reach of man, whether mechanical or chemical, can carry this reduction, and these particles are hence appropriately termed *atoms* (or indivisibles). This view has acquired great additional probability since the phenomena of chemical combination have been better understood and more accurately examined. Upon this *atomic* hypothesis, as now generally admitted, it is supposed that the particles of which each element consists have a definite and uniform size, the atom being the smallest quantity of any substance which is capable of existing in combination with other particles (1061).

The phenomena of chemical combination, and the laws of definite, multiple, and equivalent proportion, as well as the existence of polymeric and metameric compounds, indeed admit of a simple explanation by the aid of this hypothesis, which, as developed by Dalton, has received the name of the *atomic theory*.

Dalton assumed that the ultimate particles of any given element are of uniform size, and possess the same relative weight; but that the particles of different elements differ from each other in weight, and possibly also in size. When chemical combination takes place between any two elementary bodies, combination is supposed to occur between them atom to atom. Hence the proportions in which bodies unite must of necessity be definite and invariable. In like manner the law of multiple proportion becomes a physical necessity, since compounds must be formed by the union of 1 atom of one of the elements with 1, 2, 3, 4, or more atoms of the other element; or 2 atoms of one element with 1, 3, 5, or 7 atoms of the other (1064).

The combining numbers of the different elements were supposed by Dalton simply to express the relative weights of their atoms, and hence the term *atomic weight* was by many writers used as synonymous with that of *chemical equivalent* (13), or *combining proportion*, though there is really a fundamental distinction between the ideas of the atom and the equivalent, as we have already fully shown.

Nothing is known of the absolute size or weight of these ultimate particles of matter, but it appears to be certain that the

amount of heat, of electricity, and of chemical force associated with each chemical atom, is perfectly definite. We are also in ignorance of the form of these atoms, for it is clearly proved that the minutest particle of matter which the eye, assisted by the most powerful microscope, is able to perceive, yet consists of an indefinite multitude of atoms: the configuration of such minute visible particles cannot therefore furnish any clue to the shape of the ultimate particles of which the body is composed. It is, however, not improbable that the atoms of the elementary bodies are either spherical or spheroidal; the simplicity of such forms being most in harmony with the equality of attraction in different directions.

§ I. ATOMIC VOLUMES.

(1729) VARIOUS attempts have been made to determine the relative sizes of the atoms of different elements, some of which will be briefly noticed almost immediately. It is probable that, even in solids, the distances between the component particles are much greater than the diameters of the particles themselves; and in gaseous bodies these intervals of course will be very much greater than in liquids or in solids. The observations of Dalton and of Gay-Lussac upon the effects of temperature upon gases led these philosophers to the conclusion that the expansion or contraction which æriform bodies undergo when subjected to equal increments or decrements of temperature, *cæteris paribus*, is uniform; and it has hence been argued, that in æriform substances equal numbers of the constituent molecules are contained in equal volumes, and that the relative distances between the molecules of all gases must be uniform. More accurate researches have, however, shown that, although for general purposes the law of the uniformity of expansion of gases by heat may be admitted, yet it is not mathematically true, but that it is a *limited* law, and that the departure from this law is particularly evident in the case of those vapours and gases which are readily liquefied by pressure (*note*, p. 252, Part I.) The equivalent quantities of many of these bodies are proportionate to their densities, as shown in the table on the following page, and their specific gravities are consequently represented by numbers which exhibit the ratio of their combining proportions.

In compound gases it might be supposed that the increased bulk occupied by the compound atom or molecule would interfere with the regularity of their expansion; but the bulk of solid matter in any gas is so small compared with the entire space

which it occupies, that no sensible irregularity due to this cause is perceptible.

The only elementary bodies of which the specific gravity has been ascertained in the aëriform state are those included in the following table, and of these only four are gaseous at ordinary temperatures:—

| Atomic weight. | Weight of equal vols. vapour. | Name of element. | No. of atoms in mol. | Specific gravity. | | Name of observer. |
|----------------|-------------------------------|------------------|----------------------|-------------------|-----------|-------------------|
| | | | | Calculated. | Observed. | |
| 1 | 1 | Hydrogen . . | 2 | 0·0691 | 0·0692 | Regnault |
| 14 | 14 | Nitrogen . . | 2 | 0·9674 | 0·9713 | Regnault |
| 35·5 | 35·5 | Chlorine . . | 2 | 2·4531 | 2·4700 | Gay-Lussac |
| 80 | 80 | Bromine . . | 2 | 5·5281 | 5·5400 | Mitscherlich |
| 127 | 127 | Iodine . . . | 2 | 8·7560 | 8·7160 | Dumas |
| 16 | 16 | Oxygen . . . | 2 | 1·10563 | 1·10563 | Regnault |
| 32 | 32 | Sulphur . . . | 2 | 2·2168 | 2·2300 | Deville & Troost |
| 79·5 | 79·5 | Selenium . . | 2 | 5·4860 | 5·6800 | Deville & Troost |
| 129 | 129 | Tellurium . . | 2 | 8·9130 | 9·0000 | Deville & Troost |
| 31 | 62 | Phosphorus . | 4 | 4·2840 | 4·4200 | Dumas |
| 75 | 150 | Arsenicum . . | 4 | 10·1670 | 10·6000 | Mitscherlich |
| 112 | 56 | Cadmium . . . | 1 | 3·8690 | 3·9400 | Deville & Troost |
| 200 | 100 | Mercury . . . | 1 | 6·9101 | 6·9760 | Dumas |

In the second column of this table the figures represent the number of grammes of each element which would furnish equal volumes of vapour under equal pressures at the highest temperature at which such observations have hitherto been made, viz., at 2552° (1400° C.; Deville and Troost, *Comptes Rendus*, lvi. 891).

It will be observed that in the case of the first nine on the list, these numbers coincide with those which represent the atomic weights of these particular elements: phosphorus and arsenicum are represented by numbers which are equal to twice those of their atomic weights, while cadmium and mercury are represented by numbers equal to the half of their atomic weights.

The vapour of the three elements of the sulphur group exhibits, at temperatures not far removed from the boiling point of these bodies, a very much greater density than when the temperature is raised to 2000°, or upwards. Sulphur itself at 932° (500° C.), yields a vapour which is 3 times as dense as its calculated amount; but as the temperature is raised the vapour gradually becomes less dense, until at about 2012° (1100° C.), it is reduced to the normal density. Analogous results were obtained by Deville and Troost in the case of selenium and tellurium (*Comptes Rendus*, lvi. 891).

It has been supposed, in order to explain these anomalies, which have their counterpart in the case of the vapours of certain organic acids, such as the formic, acetic, and butyric, that the

repulsive power of heat may be insufficient at low temperatures to cause the complete resolution of a body into its separate molecules, but that as the temperature is raised the repulsive power of heat effects the separation. Such a supposition is not in contradiction to known analogies.

In the cases of phosphorus and arsenium, the highest temperature to which they have been submitted fails, however, to cause any such resolution, the vapour density of these two elements being both at low and at very elevated temperatures, subject to uniform expansion, so that the ultimate molecule, instead of containing 2 atoms, as in the case of the elements previously considered, must contain 4 atoms.

Cadmium and mercury belong to a group in which the vapour density shows that the molecule contains a single atom only.

(1730) *Atomic Volume of Compound Gases.*—Allusion has been already made (14) to the important law of combination—viz., that when two gaseous substances unite, the bulk of the resulting compound, if gaseous or vaporous, when it does not coincide with the united bulk of its components, yet always bears a simple relation to it. The two gases after combination never occupy a larger volume than they did when separate. No fixed rule, however, can be laid down by which it can be predicted whether condensation will occur; or, if it occur, what will be the amount of condensation that will accompany the act of combination. In the majority of instances, where equal volumes of the component gases unite, as in the acids containing hydrogen, no change of volume takes place. Numerous cases, nevertheless, exist where, as in the compounds of mercury, equal volumes of different gases or vapours in uniting become condensed to one-half of their former bulk. When two volumes of one gas unite with one of a second, the condensation is generally found to be in such a proportion that the three volumes after combination occupy the space of two. This is exemplified by nitrous oxide, hypochlorous anhydride, and steam, and the probability that such is also the case with carbon led Mitscherlich to adopt two volumes of vapour as the representative of the atom of carbon. Such a mode of condensation, however, is not uniform. In some cases the three volumes are condensed into one, as in cyanogen, and in light carburetted hydrogen gas; whilst in the complex molecules of organic chemistry the condensation is much greater. The following table comprises the determination of the vapour density of the principal substances described in the Second Part of this work, and it exhibits the degree of condensation in each case:—

Table showing the Density of several Compound Gases and Vapours.

| 1. Gases united without Condensation. | | | | | | | |
|--|--------------------|---------------|----------------------------------|----------------------|------------------------|----------------------|---------------------|
| Name. | Constituents. | | Formulae. | Density. | | | Authority. |
| | | | | Calculated H = 1. | Calculated Air = 1. | Observed Air = 1. | |
| Hydrochloric acid . . . | vols. 1 H | vols. 1 Cl | $\frac{\text{HCl}}{2}$ | 18.2 | 1.2611 | 1.2474 | } Biot and Arago |
| Hydrobromic acid . . . | 1 H | 1 Br | $\frac{\text{HBr}}{2}$ | 40.5 | 2.7986 | 2.731 | |
| Hydriodic acid . . . | 1 H | 1 I | $\frac{\text{HI}}{2}$ | 64.0 | 4.4125 | 4.443 | Gay-Lussac |
| Hydrocyanic acid . . . | 1 H | 1 Cy | $\frac{\text{HCy}}{2}$ | 13.5 | 0.934 | 0.9476 | Gay-Lussac |
| Nitric oxide . . . | 1 N | 1 O | $\frac{\text{NO}}{2}$ | 15 | 1.038 | 1.0389 | Bérard |
| Sal-ammoniac . . . | 2 H ₃ N | 2 HCl | $\frac{\text{H}_4\text{NCl}}{4}$ | 13.4 | 0.9259 | 0.89 | Bineau |
| Hydriodate of phosphuretted hydrogen . . . | 2 H ₃ P | 2 HI | $\frac{\text{H}_4\text{PI}}{4}$ | 40.5 | 2.798 | 2.77 | ditto |
| Hydrobromate ditto . . . | 2 H ₃ P | 2 HBr | $\frac{\text{H}_4\text{PBr}}{4}$ | 28.7 | 1.983 | 1.906 | ditto |
| Mercuric sulphide . . . | 1 S | 2 Hg | $\frac{\text{HgS}}{3}$ | 77.3 | 5.34 | 5.510 | Mitscherlich |
| 11 Volumes condensed into 8. | | | | | | | |
| Phosphoric chloride . . . | $\frac{1}{2}$ P | 5 Cl | $\frac{\text{PCl}_5}{4}$ | 52.1 | 3.601 | 3.654 | Cahours |
| 3 Volumes condensed into 2. | | | | | | | |
| Steam | 2 H | 1 O | $\frac{\text{H}_2\text{O}}{2}$ | 9 | 0.6220 | 0.6235 | Gay-Lussac |
| Nitrous oxide . . . | 2 N | 1 O | $\frac{\text{N}_2\text{O}}{2}$ | 22 | 1.5241 | 1.5200 | Colin |
| Hypochlorous anhydride . . . | 2 Cl | 1 O | $\frac{\text{Cl}_2\text{O}}{2}$ | 43.5 | 3.005 | | |
| (Chloric peroxide) | 1 Cl | 2 O | $\frac{\text{ClO}_2}{2}$ | 33.8 | 2.331 | 2.322 | Gay-Lussac |
| (Nitric peroxide). | 1 N | 2 O | $\frac{\text{NO}_2}{2}$ | 23 | 1.592 | 1.720 | Mitscherlich |
| Do. below 82° F. | 2 N | 4 O | $\frac{\text{N}_2\text{O}_4}{2}$ | 46 | 3.184 | 2.70 | Müller |
| Calomel | 2 Hg | 1 Cl | $\frac{\text{HgCl}}{2}$ | 117.7 | 8.136 | 8.350 | Mitscherlich |
| Mercurous bromide | 2 Hg | 1 Br | $\frac{\text{HgBr}}{2}$ | 140 | 9.674 | 10.140 | ditto |
| *Carbonic oxide . . . | 2 C? | 1 O | $\frac{\text{CO}}{2}$ | 14 | 0.9674 | 0.967 | Wrede |
| †Sulphuretted hydrogen . . . | 2 H | 1 S | $\frac{\text{H}_2\text{S}}{2}$ | 17 | 1.174 | 1.1912 | Gay-Lussac |

* Here it is assumed that 1 atom of carbon yields 2 volumes of vapour. Many chemists consider that it yields only 1 volume, but no data exist for proving either hypothesis.

† Sulphur, in accordance with Bineau's researches upon it at high temperatures, is found to have an atomic volume equal to that of oxygen; and selenium and tellurium have been shown by Deville and Troost to be analogous to it.

Table showing the Density of several Compound Gases and Vapours.

[Continued.]

| Name. | Constituents. | | Formulae. | Density. | | | Authority. |
|------------------------------|---------------------------------|------------------|----------------------------|----------------------|------------------------|-----------------------|-------------------------|
| | | | | Calculated H = 1. | Calculated Air = 1. | Observed. Air = 1. | |
| Seleninretted hydrogen . . . | vols. 2 H | vols. 1 Se | $\frac{H_2Se}{2}$ | 40.7 | 2.8213 | 2.795 | Bineau Calculated |
| Telluretted hydrogen . . . | 2 H | 1 Te | $\frac{H_2Te}{2}$ | 65.5 | 4.526 | 4.489 | |
| Sulphurous anhydride . . . | 1 S | 2 O | $\frac{SO_2}{2}$ | 32 | 2.2112 | 2.247 | Berzelius |
| Selenious anhydride . . . | 1 Se | 2 O | $\frac{SeO_2}{2}$ | 55.7 | 3.8419 | 4.03 | Mitscherlich |
| Carbonic anhydride . . . | 2 CO | 1 O | $\frac{CO_2}{2}$ | 22 | 1.5203 | 1.529 | Regnault |
| Sulphuric anhydride . . . | 2 SO ₂ | 1 O | $\frac{SO_3}{2}$ | 40 | 2.764 | 3.01 | Mitscherlich |
| 4 Volumes condensed into 2. | | | | | | | |
| Corrosive sublimate . . . | 2 Hg | 2 Cl | $\frac{HgCl_2}{2}$ | 135.5 | 9.363 | 9.800 | ditto |
| Mercuric bromide | 2 Hg | 2 Br | $\frac{HgBr_2}{2}$ | 180 | 12.438 | 12.160 | ditto |
| Mercuric iodide . . . | 2 Hg | 2 I | $\frac{HgI_2}{2}$ | 227 | 15.666 | 15.600 | ditto |
| Mercuric & ammoniac iodide | 2 Hg 4 I, 8 H 2 N | | $\frac{HgI_2(H_4NI)_2}{8}$ | 93 | 6.43 | 6.49 | { Deville & { Troost |
| Phosgene gas . . . | 2 CO | 2 Cl | $\frac{COCl_2}{2}$ | 49.5 | 3.420 | 3.6808 | J. Davy |
| Ammonia . . . | 3 H | 1 N | $\frac{H_3N}{2}$ | 8.5 | 0.5896 | 0.590 | H. Davy |
| Carbon disulphide | 2 S | 2 C ? | $\frac{CS_2}{2}$ | 38 | 2.6260 | 2.6447 | Gay-Lussac |
| Sulphuryl chloride . . . | 2 SO ₂ | 2 Cl | $\frac{SO_2Cl_2}{2}$ | 67.5 | 4.664 | 4.703 | Regnault |
| Ethylene dibromide . . . | 2 C ₂ H ₄ | 2 Br | $\frac{C_2H_4Br_2}{2}$ | 94.0 | 6.157 | 6.485 | ditto |
| Dutch liquid . . . | 2 C ₂ H ₄ | 2 Cl | $\frac{C_2H_4Cl_2}{2}$ | 49.5 | 3.420 | 3.478 | ditto |
| Monochlorinated Dutch liquid | | | $\frac{C_2H_3Cl_3}{2}$ | 66.7 | 4.613 | | |
| Dichlorinated Dutch liquid | | | $\frac{C_2H_2Cl_4}{2}$ | 84.0 | 5.804 | | |
| Trichlorinated Dutch liquid | | | $\frac{C_2HCl_5}{2}$ | 101.25 | 6.996 | | |
| Solid carbon chloride . . . | | | $\frac{C_2Cl_6}{2}$ | 118.5 | 8.188 | 8.157 | ditto |
| Sulphur chloride . . . | 2 S ? | 2 Cl | $\frac{S_2Cl_2}{2}$ | 67.5 | 4.644 | 4.700 | Dumas |
| 7 Volumes condensed into 4. | | | | | | | |
| Phosphuretted hydrogen . . . | 3 H | $\frac{1}{2}$ P | $\frac{H_3P}{2}$ | 17 | 1.175 | 1.185 | Dumas |
| Arseniuretted hydrogen . . . | 3 H | $\frac{1}{2}$ As | $\frac{H_3As}{2}$ | 39 | 2.748 | 2.695 | ditto |

Table showing the Density of several Compound Gases and Vapours.

[Continued.]

| Name. | Constituents. | | Formulae. | Density. | | | Authority. |
|--|---------------------------|--------------|------------------------------------|----------------------|------------------------|----------------------|-----------------------|
| | | | | Calculated H = 1. | Calculated Air = 1. | Observed Air = 1. | |
| Arsenious iodide | vols. $\frac{1}{2}$ As | vols. 3 I | $\frac{\text{AsI}_3}{2}$ | 228 | 15.67 | 16.100 | Mitscherlich |
| Phosphorus tri- chloride . . } | $\frac{1}{2}$ P | 3 Cl | $\frac{\text{PCl}_3}{2}$ | 68.7 | 4.713 | 4.875 | Dumas |
| Arsenious chloride | $\frac{1}{2}$ As | 3 Cl | $\frac{\text{AsCl}_3}{2}$ | 90.7 | 6.184 | 6.300 | ditto |
| Antimony tri- chloride . . } | $\frac{1}{2}$ Sb | 3 Cl | $\frac{\text{SbCl}_3}{2}$ | 114.2 | 7.894 | 7.800 | Mitscherlich |
| Bismuth tri- chloride . . } | $\frac{1}{2}$ Bi | 3 Cl | $\frac{\text{BiCl}_3}{2}$ | 158.5 | 10.934 | 11.160 | Jacquelain |
| <i>5 Volumes condensed into 3.</i> | | | | | | | |
| Chlorous anhy- dride . . . } | 2 Cl | 3 O | $\frac{\text{Cl}_2\text{O}_3}{3}$ | 39.7 | 2.740 | 2.6461 | Millon |
| <i>9 Volumes condensed into 4.</i> | | | | | | | |
| Phosphorus oxy- trichloride . } | $\frac{1}{2}$ P | 1 O 3 Cl | $\frac{\text{POCl}_3}{2}$ | 76.8 | 5.32 | 5.400 | Wurtz |
| Phosphorus sulphotri- chloride . . } | $\frac{1}{2}$ P | 1 S 3 Cl | $\frac{\text{PSCl}_3}{2}$ | 84.8 | 5.86 | 5.878 | Cahours |
| <i>5 Volumes condensed into 2.</i> | | | | | | | |
| Carbon trichlo- ride (liquid) } | 2 C? | 3 Cl | $\frac{\text{CCl}_3}{2}$ | 59.25 | 4.094 | 4.082 | Regnault |
| Vanadic oxytri- chloride . } | 1 V | 1 O 3 Cl | $\frac{\text{VOCl}_3}{2}$ | 86.9 | 6.005 | 6.108 | Roscoe |
| Ferric chloride* . | 4 Fe? | 6 Cl | $\frac{\text{Fe}_2\text{Cl}_6}{2}$ | 162.5 | 11.223 | 11.39 | } Deville & Troost |
| Aluminic chloride | 4 Al? | 6 Cl | $\frac{\text{Al}_2\text{Cl}_6}{2}$ | 133.9 | 9.252 | 9.34 | |
| Aluminic bromide | 4 Al? | 6 Br | $\frac{\text{Al}_2\text{Br}_6}{2}$ | 267.5 | 18.483 | 18.6 | ditto |
| Aluminic iodide . | 4 Al? | 6 I | $\frac{\text{Al}_2\text{I}_6}{2}$ | 408.5 | 28.227 | 27.0 | ditto |
| Boric fluoride . | 2 B? | 3 F? | $\frac{\text{BF}_3}{2}$ | 33.9 | 2.345 | 2.312 | Dumas |
| Boric chloride . | 2 B? | 3 Cl | $\frac{\text{BCl}_3}{2}$ | 58.7 | 4.055 | 3.942 | ditto |
| <i>6 Volumes condensed into 2.</i> | | | | | | | |
| Cyanogen . . . | 4 C? | 2 N | $\frac{\text{C}_2\text{N}_2}{2}$ | 26 | 1.800 | 1.8064 | Gay-Lussac |
| Carbon tetra- chloride . . } | 2 C? | 4 Cl | $\frac{\text{CCl}_4}{2}$ | 77 | 5.320 | 5.3 | Regnault |

* The vapour volume of one atom of each of the different metals is assumed to correspond with that of 1 atom of carbon, and consequently to be double that of the atom of hydrogen; and the same assumption is made in the case of silicon and of boron.

Table showing the Density of several Compound Gases and Vapours.

[Continued.]

| Name. | Constituents. | | Formulae. | Density. | | | Authority. |
|------------------------------------|---------------|--------------|---------------------------------------|----------------------|------------------------|-----------------------|-----------------------|
| | | | | Calculated H = 1. | Calculated Air = 1. | Observed. Air = 1. | |
| Marsh gas . . . | vols. 2 C? | vols. 4 H | $\frac{\text{CH}_4}{2}$ | 8 | 0.552 | 0.557 | Thomson |
| Titanic chloride . | 2 Ti? | 4 Cl | $\frac{\text{TiCl}_4}{2}$ | 96 | 6.633 | 6.836 | Dumas |
| Zirconic chloride . | 2 Zr? 4 | 4 Cl | $\frac{\text{ZrCl}_4}{2}$ | 115.8 | 8.002 | 8.15 | { Deville & Troost |
| Stannic chloride | 2 Sn? | 4 Cl | $\frac{\text{SnCl}_4}{2}$ | 130 | 8.98 | 9.199 | Dumas |
| Silicic fluoride . | 2 Si? | 4 F? | $\frac{\text{SiF}_4}{2}$ | 52 | 3.587 | 3.600 | ditto |
| Silicic chloride . | 2 Si? | 4 Cl | $\frac{\text{SiCl}_4}{2}$ | 85 | 5.873 | 5.939 | ditto |
| Chromium oxy- chloride . . } | 2 Cr? 2 O, | 2 Cl | $\frac{\text{CrO}_2\text{Cl}_2}{2}$ | 77.8 | 5.376 | 5.52 | ditto |
| <i>7 Volumes condensed into 2.</i> | | | | | | | |
| Niobic chloride . | 2 Nb? | 5 Cl | $\frac{\text{NbCl}_5}{2}$ | 137.5 | 9.84 | 9.6 | { Deville & Troost |
| Tantalalic chloride | 2 Ta? | 5 Cl | $\frac{\text{TaCl}_5}{2}$ | 179.27 | 13.00 | 12.9 | |
| Tungstic oxy- chloride } | 2 W? O | 4 Cl | $\frac{\text{WOCl}_4}{2}$ | 171 | 11.86 | 10.74 | Debray |
| <i>8 Volumes condensed into 2.</i> | | | | | | | |
| Arsenious anhy- dride . . . } | 2 As | 6 O | $\frac{(\text{As}_2\text{O}_3)_2}{2}$ | 198 | 13.483 | 13.85 | Mitscherlich |
| Tungstic chloride | 2 W? | 6 Cl | $\frac{\text{WCl}_6}{2}$ | 198.5 | 13.75 | 11.86 | Debray |
| Olefiant gas . . | 4 C? | 4 H | $\frac{\text{C}_2\text{H}_4}{2}$ | 14 | 0.971 | 0.978 | Saussure |
| Ethylene carbon chloride . . } | 4 C? | 4 Cl | $\frac{\text{C}_2\text{Cl}_4}{2}$ | 83 | 5.72 | 5.82 | Regnault. |

In the foregoing table all compounds into the composition of which carbon and hydrogen both enter are represented by a molecular weight equal to 2 volumes of vapour (H = 1 being taken as unity); and in the majority of other cases the formulæ given are also 2-volume formulæ. This, indeed, is the normal volume of bodies in the aëriform state.

Exceptions, however, occur in the case of the salts of ammonia; the hydrochlorate, hydrobromate, hydrocyanate, and the hydrosulphate of the sulphide (H_4NHS) furnish 4 volumes of vapour. Caunizzaro and Kopp have each endeavoured to explain this anomaly on the supposition that at the high temperature necessary to volatilize these bodies decomposition takes place, and the salt

is resolved into its two constituents, ammonia and the gaseous acid; and as the temperature falls they enter again into combination.* This view is ingenious, and it is also applicable to a case such as that of the ammonia hydrosulphate $(\text{H}_3\text{N})_2\text{H}_2\text{S}$, which yields a 6-volume vapour such as would be produced by the separation of the compound into its constituents, ammonia (4 vols.) and sulphuretted hydrogen (2 vols.).

Similar explanations have been suggested in the case of hydriodate and hydrobromate of phosphuretted hydrogen, the molecule of each of which yields 4 volumes of vapour. Anhydrous ammonium carbamate $\text{H}_4\text{NH}_2\text{NCO}_2$, according to the observation of Bineau, yields 6 volumes of vapour; and this would be the result if it broke up into 2 $\text{H}_3\text{N}=4$ vols., and $\text{CO}_2=2$ vols.

In like manner Regnault observed that the compound $\text{C}_2\text{Cl}_6\text{O}$, obtained by acting with chlorine upon methylic ether, yields 4 vols. of vapour, which may be explained on the supposition that when heated it splits into phosgene $\text{COCl}_2=2$ vols., and carbon tetrachloride CCl_4 , also $=2$ vols.

Phosphorus pentachloride, PCl_5 , is also a body which yields 4 vols. of vapour, and which, at high temperatures, it has been suggested may be resolved into phosphorous chloride, $\text{PCl}_3=2$ vols., and free chlorine Cl_2 , also $=2$ vols.; an hypothesis which has been confirmed by the direct experiments of Deville upon the pentachloride, and upon phosphorus pentabromide, PBr_5 , which exhibits a similar anomaly.

There are, however, cases in which such an explanation is inadmissible. The double iodide of mercury and ammonium ($\text{HgI}_2, 2 \text{H}_4\text{NI}$) when heated yields 8 volumes of vapour; but each atom of iodide of ammonium yields 4 volumes, and of mercuric iodide 2 volumes, so that the compound salt yields only 8 volumes, instead of the 10 that it should do if dissociation had occurred. Chlorous anhydride, Cl_2O_3 , is a 3-volume gas at ordinary temperatures; but it is clear that it is a true combination, and not a mixture of chlorine and oxygen, and chloric peroxide, Cl_2O_4 , furnishes 4 volumes of vapour instead of 2 volumes. Nitric oxide, N_2O_2 , is also a 4-volume gas, while nitrous oxide, N_2O , exhibits the normal condensation of 2 volumes.

Some remarkable irregularities have been observed in the volume occupied by the vapours of many volatile compounds. Many of these vapours at a low temperature have a density much

* Deville, however, finds that ammonia hydrochlorate may be heated to 1900° (1038°C.), and on cooling is still found in combination; whilst ammonia, if in a free state, would at that temperature be decomposed into its constituent gases.

greater than that which they possess when more strongly heated. The vapours of the volatile acids, such as the formic and the acetic acids in particular, exhibit this anomaly in a marked degree (1274).

(1731) *Atomic Volumes of Solids.*—I. *Simple Bodies.*—It has been supposed that if the atoms of all the elementary bodies were of the same size, the specific gravities of the bodies in their solid form would be in the same proportion as their atomic weights. In such a case, however, either the particles composing the solid must be in actual contact, or the intervals between the particles must be equal. Dumas showed many years ago that the specific gravity of certain isomorphous metals is nearly in the direct ratio of their atomic weights. Since then both Schröder and Kopp have pointed out a number of remarkable relations between the density of different bodies and their atomic weights. Kopp has shown that many of the elementary bodies may be arranged in groups, each group consisting of members in which the solid atomic volume is identical. If such weights of the different elementary bodies as represent the atomic weights of each be compared together, the bulk occupied by each body will be such as is indicated in the column headed *atomic volume* in the table on the opposite page.

The atomic volume (or specific volume) of any substance, simple or compound, may be calculated by dividing its atomic weight by its specific gravity. For example, if d = the density or specific gravity, q = the atomic weight, and v = the atomic volume, $\frac{q}{d} = v$.

A simple mode of determining experimentally the atomic volume of a body was employed by Playfair and Joule. Their apparatus or *volumenometer* consists of a globular flask provided with a long narrow neck, about twelve inches in length, graduated from below upwards, to indicate grains of water. The flask is provided with a tubulure (accurately fitted with a ground stopper) for the admission of the solid body for experiment. When the instrument is to be used it is to be filled up to the mark 0° on the stem with water, with oil of turpentine, or with some liquid which exerts no solvent action on the body. It is then inclined to one side, the stopper removed, and a weighed quantity of the solid under experiment is carefully introduced: the stopper is then replaced, and the number of divisions which the liquid is raised in the stem indicates in grains the quantity of water which has been displaced. Thus, if 56 grains of iron (the number of grains corresponding to the atomic weight of the metal) be

Table of the Atomic Volumes of Elementary Bodies.

| Name of element. | Atomic wt. | | Atomic vol. | | Calculated sp. gr.* | Observed specific gravity. |
|------------------|------------|-------|-------------|-------|---------------------|---|
| | O=100. | H=1. | O=100. | H=1. | | |
| Carbon . . . | 75 | 12 | 22 | 3.52 | 3.41 | 3.55, 3.336, (diamond) Jacquelin |
| Boron . . . | 68.1 | 11 | 25.4 | 4.10 | 2.68 | 2.68, Deville |
| Glucinum . . | 58.3 | 9.3 | 26.8 | 4.44 | 2.10 | 2.1, Debray |
| Chromium . . | 328 | 52.5 | 44 | 7.00 | 7.45 | 6.81, Wöhler |
| Cobalt . . . | 369 | 59 | 44 | 7.00 | 8.38 | 8.49, Brunner; 8.51, Berzelius; 8.95, Rammelsberg |
| Copper . . . | 395 | 63.5 | 44 | 7.00 | 8.97 | 8.96, Berzelius; 8.72, Karsten; 8.92, Marchand and Scheerer |
| Iron | 350 | 56 | 44 | 7.00 | 7.95 | 7.84, Broling; 7.79, Karsten |
| Manganese . . | 345 | 55 | 44 | 7.00 | 7.94 | 8.03, Bachmann; 8.01, John |
| Nickel . . . | 369 | 59 | 44 | 7.00 | 8.38 | 8.40, Tourte; 8.82, Tuppiti; 8.60, Brunner; 8.90, Schröder |
| Iridium . . . | 1232 | 197 | 57 | 9.12 | 21.6 | 21.15, Deville and Debray |
| Osmium . . . | 1244 | 198.4 | 57 | 9.12 | 21.8 | 21.4, Deville and Debray |
| Palladium . . | 666 | 106.4 | 57 | 9.12 | 11.7 | 11.3—11.8, Wollaston, Deville |
| Platinum . . | 1232 | 197 | 57 | 9.12 | 21.6 | 21.0, Borda; 21.5, Berzelius, Wollaston |
| Rhodium . . . | 652 | 104.4 | 57 | 9.12 | 11.4 | 11.0, Wollaston; 11.2, Cloud; 12.1, Deville and Debray |
| Ruthenium . . | 651 | 104.2 | 57 | 9.12 | 11.4 | 11.1—11.4, Deville and Debray |
| Zinc | 406 | 65 | 57 | 9.12 | 7.14 | 7.14, Wertheim; 6.86—7.21, Berzelius |
| Gold | 1229 | 197 | 64 | 10.04 | 19.20 | 19.34, G. Rose; 19.26, Brisson |
| Silver | 675 | 108 | 64 | 10.04 | 10.53 | 10.53, G. Rose; 10.4, Karsten |
| Aluminum . . | 171 | 27.5 | 66 | 10.56 | 2.59 | 2.56—2.67, Deville |
| Molybdenum . | 600 | 96 | 66 | 10.56 | 9.09 | 8.62—8.64, Bucholz [D'Elhuyart |
| Tungsten . . . | 1150 | 184 | 66 | 10.56 | 17.40 | 17.2, Allen; 17.4, Bucholz; 17.6, Allen |
| Uranium . . . | 750 | 120 | 66 | 10.56 | 18.28 | 18.4, Péligot |
| Silicon . . . | 175 | 28 | 70 | 11.24 | 2.49 | 2.49, Deville; 2.33, W. A. Miller |
| Lithium . . . | 43.5 | 7 | 73.5 | 11.80 | 0.593 | 0.593, Bunsen [path |
| Arsenicum . . | 468 | 75 | 81.0 | 12.96 | 5.7 | 5.7—5.969, Guibourt; 5.67, Hera- |
| Cadmium . . . | 700 | 112 | 81.0 | 12.96 | 8.6 | 8.60, Stromeyer; 8.63, Karsten, Kopp; 8.54—8.667, Schröder |
| Magnesium . . | 150 | 24 | 86.0 | 13.76 | 1.743 | 1.743, Bunsen [raday |
| Mercury . . . | 1250 | 200 | 91 | 14.56 | 13.6 | 13.6, Kupffer, Karsten; 13.56, Fa- |
| Selenium . . . | 495 | 79.5 | 103 | 16.28 | 4.8 | 4.8, Schaffgotsch; 4.30—4.32, Berzelius [haupt |
| Sulphur . . . | 200 | 32 | 101 | 16.16 | 1.99 | 1.99—2.05, Karsten; 1.99, Breit- |
| Tin | 742 | 118 | 101 | 16.20 | 7.28 | 7.28, Herapath; 7.29, Kupffer, Karsten |
| Indium | 472.5 | 75.6 | 636 | 10.2 | 7.42 | 7.421, Winkler |
| Phosphorus . . | 193.5 | 31 | 105.5 | 16.88 | 1.83 | 1.83, Schrötter; 1.77, Berzelius |
| Thallium . . . | 1275 | 204 | 107.1 | 17.1 | 11.9 | 11.91—11.81, Crookes; 11.862, Lamy |
| Antimony . . . | 762 | 122 | 113.5 | 18.16 | 6.7 | 6.71, Marchand and Scheerer; 6.7, Karsten; 6.697, Schröder |
| Lead | 1294 | 207 | 114 | 18.24 | 11.35 | 11.44, Berzelius; 11.35, Herapath; 11.33, Kupffer; 11.36, Reich |
| Tellurium . . . | 800 | 129 | 128 | 20.08 | 6.25 | 6.25, Berzelius |
| Bismuth . . . | 1312 | 210 | 133 | 21.34 | 9.84 | 9.88, Thénard; 9.83, Herapath; 9.8, Marchand and Scheerer |
| Calcium | 250 | 40 | 158 | 25.32 | 1.58 | 1.578, Bunsen |
| Bromine | 500 | 80 | 160 | 25.6 | 3.12 | (liquid) 2.99, Löwig; 2.97, Balard |
| Chlorine . . . | 221.5 | 35.5 | 160 | 25.6 | 1.38 | (liquid, about 1.33), Faraday |
| Iodine | 793.7 | 127 | 160 | 25.6 | 4.95 | 4.95, Gay-Lussac |
| Strontium . . . | 547 | 87.5 | 215 | 34.56 | 2.54 | 2.54, Bunsen [0.985, Schröder |
| Sodium | 143.7 | 23 | 147.5 | 23.60 | 0.972 | 0.972, Gay-Lussac and Thénard; |
| Potassium . . . | 243.7 | 39 | 281 | 44.96 | 0.865 | 0.865, Gay-Lussac and Thénard |
| Rubidium . . . | 533 | 85.4 | 350 | 56.1 | 1.52 | 1.52, Bunsen |

* The column headed *calculated sp. gr.* indicates the numbers which, if used as divisors of the atomic weights, yield the numbers adopted as the atomic volumes of the elements.

introduced, the liquid will rise 7·1 divisions in the stem of the instrument, indicating the atomic volume by simple inspection. If the quantity of the substance employed be greater, say three or four times the atomic weight in grains, the rise in the stem, when divided by 3 or by 4, as the case may be, indicates the atomic volume of the body under observation. The same experiment also furnishes the data for determining approximately the specific gravity of the body, since the weight of the substance used, when divided by the number of divisions which the liquid has risen (corresponding to the weight of the bulk of water equal to the solid), will, of course, give the specific gravity.

Schröder, Kopp, and many of the chemists who have worked upon this subject, have made their calculations upon the oxygen scale of atomic weights; but recently Kopp and others have adopted calculations from the hydrogen unit; both sets of numbers are therefore given in the table to facilitate reference.

From the foregoing table, it is apparent that several groups of *isometric* elementary bodies (that is to say, bodies possessed of equal atomic volume), exist; and that between many of these groups, multiple relations of a simple kind occur; for example:—

1. The atomic volume of the group containing cobalt, copper, iron, manganese, and nickel, is double that of carbon, as found in the diamond.

2. The atomic volume of the group containing aluminum, molybdenum, and tungsten, is to that of the iron group as 3 : 2.

3. The atomic volume of lead is double that of platinum and its congeners.

4. There are indications of an equality in the atomic volume of the halogens—chlorine, bromine, and iodine; but the specific gravities of these bodies are not known with sufficient accuracy to admit of a satisfactory comparison. That of chlorine is only an approximation, and it was in the liquid form, whereas, iodine, with which it is compared, was in the solid state.

5. It has been supposed that the atomic volume of potassium is double that of sodium; but if this be so, the specific gravities of the two metals obtained by experiment must be inaccurate. If that of sodium were 0·99, and that of potassium 0·84, the ratio of their atomic volumes would be as 290 : 580, or as 23·2 : 46·4.

(1732) *Influence of Isomorphism and of Dimorphism on Atomic Volume.*—Kopp has further shown that the coincidence in atomic volume first observed by Dumas in the case of certain isomorphous metals, holds good very generally with isomorphous bodies; so that, when the volumes occupied by equivalent weights of such

bodies are compared together, the volumes, allowing for errors of observation, are identical. This law is found to hold good both with elementary and with compound bodies.

A close approach to isomorphism in compound bodies does not, however, necessarily indicate the isomorphism of all their corresponding constituents. Zincic sulphate, for example, is isomorphous with ferrous sulphate, but metallic zinc and metallic iron are not isomorphous, nor do they possess the same atomic volume; and indeed, strictly speaking, the salts are not identical in form, for though the crystals resemble each other in their geometrical figure, yet when their angles are accurately measured, considerable differences are detected. The solid volume of the crystallized sulphate of zinc, and of iron differs but little; the atomic volume of zincic sulphate, according to Filhol's experiments, being 72.4, and that of ferrous sulphate 73.6, and since so large a proportion of the mass of the salt is in each case made up by substances which are identical, the same general form is preserved in both salts.

In the case of dimorphous substances, the specific gravity of the body in one of its forms is greater than it is in the other form; consequently, such substances possess two different atomic volumes. The following table contains the specific gravity and atomic volume of a few dimorphous substances:—

| Dimorphous bodies. | Specific gravity. | Atomic volume. | |
|--------------------------------|-------------------|----------------|--------|
| | | O = 100. | H = 1. |
| { Diamond | 3.41 | 22 | 3.5 |
| { Graphite | 2.09 | 36 | 5.7 |
| { Native sulphur (octahedral). | 2.05 | 97.5 | 15.6 |
| { Prismatic sulphur | 1.98 | 101 | 16.2 |
| { Viscous sulphur | 1.957 | 102 | 16.2 |
| { Iceland spar | 2.72 | 229 | 36.6 |
| { Aragonite | 3.00 | 211 | 33.7 |

(1733) *Disturbing Influence of Temperature.*—There can be no doubt that the atomic volume of a body is a character as definite as is its specific gravity, or its atomic weight; but the determination of its precise amount is opposed by some peculiar and considerable obstacles. One of these arises from the difficulty of accurately determining the specific gravity of a solid, under circumstances which shall be properly comparable. Since the bulk of all bodies varies with the temperature, and increases as the temperature rises, the specific gravity, as taken in the ordinary

method, will be liable to variation according to the temperature. This would be of little consequence, however, if the amounts of expansion produced by equal increments of heat were alike in all bodies; but experiment distinctly proves that this is not the case, and the great extent of this variation among many of the simple bodies may be seen by the subjoined table:—

*Cubic Expansion of some of the Metals from 32° to 212°
(0° to 100° C.).*

| Metal. | Equal vols. | | Atomic volumes. | | Approximative ratio of expansion for at. vols. | | Authority. |
|-----------|---------------|---------------|-----------------|---------------|--|-------|------------------------------------|
| | parts at 32°. | gain at 212°. | parts at 32°. | gain at 212°. | | | |
| Iron . . | 100 | 0'354 | 44 | 0'147 | } 1'0 | 0'150 | Dulong and Petit. |
| Platinum | 100 | 0'264 | 57 | 0'150 | | | |
| Copper . | 100 | 0'515 | 44 | 0'226 | } 1'5 | 0'225 | Lavoisier and Laplace. Smeaton. |
| Zinc . . | 100 | 0'882 | 57 | 0'332 | | | |
| Gold . . | 100 | 0'440 | 64 | 0'291 | } 2'0 | 0'300 | Lavoisier and Laplace. Smeaton. |
| Silver . | 100 | 0'573 | 64 | 0'366 | | | |
| Antimony | 100 | 0'325 | 113'5 | 0'368 | } 2'5 | 0'350 | Lavoisier and Laplace. Smeaton. |
| Bismuth. | 100 | 0'417 | 133 | 0'563 | | | |
| Tin . . | 100 | 0'581 | 101 | 0'586 | } 3'75 | 0'562 | Smeaton. Lavoisier and Laplace. |
| Lead . . | 100 | 0'854 | 114 | 0'974 | | | |
| Mercury . | 100 | 1'802 | 91 | 1'640 | 11'0 | 1'650 | Dulong and Petit. |

Supposing that the expansion quantity of each of the metals taken in proportion to its atomic weight (as represented by its atomic volume), were in the multiple ratio represented in the sixth column of the table, the cubic expansion should be such as is indicated in the seventh column. The cubic expansion has been calculated by multiplying by 3 the linear expansion of the different metals.

(1734) 2. *Atomic Volume of Compounds.*—In a few instances, when solid bodies unite, the resulting compound possesses an atomic volume equal to the united volumes of its components: *e.g.*, in the case of sulphide of copper, 16'16 being the atomic volume of sulphur, 7'1 that of copper, 23'26 is that of the sulphide; for it is found by experiment, that the specific gravity of this sulphide is 4'1, and its atomic weight is 95'5: now $95'5 \div 4'1 = 23'29$. But this simple relation between the bulk of the compound, and that of its components, is of rare occurrence. Condensation, however, appears to occur according to certain laws, though they are by no means so simple as those which regulate the act of combination amongst gases.

Schröder observed that when from the atomic volume of a

series of analogous combinations, such as the oxides, the volume of the metal which each compound contains is deducted, the same number is frequently obtained as a representative of the volume of those constituents which are common to all the members of the class. When from the analogous sulphates, for instance, the atomic volume of the metallic oxide contained in each is deducted, the residue for sulphuric anhydride remains the same. Kopp extended these views, and supposed that he had deduced from them additional arguments in support of the binary theory of salts; but the results of observation, as Filhol has shown (*Ann. de Chimie*, III. xxi. 429), may be equally well explained upon the older view, and, indeed, even better; for I have found, by a very slight modification of one of the values for sulphuric anhydride, that numbers are obtained with which the results of experiment accord quite as well as with the numbers assumed by Kopp, as will be seen almost immediately.

The oxides may be subdivided into four classes, in each of which the oxygen must be supposed to undergo a different amount of condensation. In the first class, the atomic volume of oxygen is assumed by Kopp to be 16, the metal retaining its original volume; in the second and more numerous class, the metal retains its original volume, but that of oxygen is 32; in the third class the volume of oxygen is 64. In the fourth class, assuming the volume of oxygen to be 32, the metals undergo condensation in the act of combining: I find, for example, that aluminum, calcium, and strontium are condensed into exactly half their volume. The specific gravity of barium is not known with certainty, but it is probable that this metal likewise belongs to the same class. The condensation experienced by sodium and by potassium is such, that they occupy very nearly one-third of the volume which they possess in the uncombined form; *e.g.*, if the atomic volume of these two metals be divided by 3, we have for sodium $293 \div 3 = 98$; by observation of the density of soda, it is $= 102$, when combined with oxygen of an atomic volume of 32; and for potassium, $562 \div 3 = 187$; while by observation of the density of potash it is 184.

The tables which follow are based upon those given by Kopp, but they include many new data, and several of the results have been re-calculated from the values more recently assigned to the atomic weights of iron, antimony, calcium, chromium, mercury, molybdenum, tungsten, and zinc. The atomic volumes for the various salts are all calculated, not on the binary theory, but on the hypothesis that the salts consist of an oxide united with an anhydride.

Atomic Volumes of certain Oxides.

| CLASS I. Volume of O = 16. | | | | | | |
|---|--------------------------------|-------------------|------------------------------|--|--------------------|---|
| Oxide. | Formula. | At. wt. O=100. | Calculated Atomic Volume. | | Calcul. Sp. gr. | Observed Specific gravity. |
| Antimony . . . | Sb ₂ O ₄ | 1925 | 227 + 64 = 291 | | 6.61 | 6.53, Boullay; 6.70, Karsten. |
| Tin | SnO ₂ | 935 | 101 + 32 = 133 | | 7.03 | 6.96, Mohs; 6.90, Boullay; 6.64, Herapath. |
| CLASS II. Volume of O = 32. | | | | | | |
| Cadmium . . . | CdO | 797 | 81 + 32 = 113 | | 7.05 | 6.95, Karsten. |
| Copper | CuO | 496 | 44 + 32 = 76 | | 6.53 | 6.43, Karsten; 6.15, Boullay; 6.4, Herapath; 6.322, Filhol. |
| Lead | PbO | 1394 | 114 + 32 = 146 | | 9.55 | 9.50, Boullay; 9.361, Filhol. |
| Mercury | HgO | 1350 | 91 + 32 = 123 | | 10.97 | 11.0, Boullay; 11.1, Herapath; 11.19, Karsten. |
| Tin | SnO | 835 | 101 + 32 = 133 | | 6.28 | 6.67, Herapath. |
| Zinc | ZnO | 506 | 57 + 32 = 89 | | 5.68 | 5.43, Mohs; 5.60, Boullay; 5.73, Karsten. |
| Cobalt | Co ₂ O ₃ | 1037 | 88 + 96 = 184 | | 5.63 | 5.60, Boullay; 5.32, Herapath. |
| Iron | Fe ₂ O ₃ | 1000 | 88 + 96 = 184 | | 5.43 | 5.23, Boullay; 5.25, Mohs. |
| Chromium | Cr ₂ O ₃ | 956 | 88 + 96 = 184 | | 5.19 | 5.21, Wöhler. |
| Antimony | Sb ₂ O ₃ | 1825 | 227 + 96 = 323 | | 5.65 | 5.78, Boullay; 5.57, Mohs. |
| Bismuth | Bi ₂ O ₃ | 2960 | 270 + 96 = 366 | | 8.09 | 8.17, Karsten; 8.21, Herapath; 8.45, Dumas. |
| CLASS III. Volume of O = 64. | | | | | | |
| Silver | Ag ₂ O | 1450 | 128 + 64 = 192 | | 7.55 | 8.26, Karsten; 7.25, Boullay. |
| Copper | Cu ₂ O | 892 | 88 + 64 = 152 | | 5.87 | 5.75, Karsten, Dumas; 6.05, Herapath. |
| Mercury | Hg ₂ O | 2600 | 182 + 64 = 246 | | 10.56 | 10.69, Herapath; 8.95, Karsten. |
| Molybdic anhyd. | MoO ₃ | 900 | 66 + 192 = 258 | | 3.48 | 3.46, Bergmann; 3.49, Berzelius. |
| Tungstic anhyd. | WO ₃ | 1450 | 66 + 192 = 258 | | 5.62 | 5.27, Herapath; 6.12, Berzelius. |
| CLASS IV., in which the metal undergoes condensation. O = 32. | | | | | | |
| Alumina | Al ₂ O ₃ | 642 | 66 + 96 = 162 | | 3.96 | 4.154, Filhol; 3.95 (ruby). |
| Baryta | BaO | 958 | 143 + 32 = 175 | | 5.47 | 5.456, Filhol. |
| Strontia | SrO | 650 | 108 + 32 = 140 | | 4.64 | 4.611, Filhol. |
| Lime | CaO | 350 | 79 + 32 = 111 | | 3.15 | 3.18, Filhol, Boullay; 3.08, Leroyer and Dumas. |
| Potash | K ₂ O | 587 | 184 + 32 = 216 | | 2.71 | 2.66, Karsten. |
| Soda | Na ₂ O | 387 | 102 + 32 = 134 | | 2.88 | 2.87, Karsten. |

Kopp divides the chlorides into two classes, in one of which he supposes the volume of the chlorine to be 196, and the other 245, the ratio of these volumes in the two classes being as 4 : 5. The accordance between the observed and the calculated results in these salts is less satisfactory than in the case of the oxides, and it becomes necessary to assume new volumes for those metals which, like potassium, sodium, calcium, and magnesium, undergo condensation in the act of combining: but the volumes thus assumed for them exhibit no simple relation to the volume of these metals in an uncombined state:—

| CHLORIDES, CLASS I. Volume of Cl=196. | | | | | |
|--|--------------------|--------------------|---------------------|-------------------|---|
| Chloride. | Formula. | At. Wt. Cl=443. | Atomic Volume. | Calcul. Sp.gr. | Observed Specific Gravity. |
| Silver . . | AgCl | 1793 | 128 + 196 = 324 | 5.53 | 5.5—5.57, Karsten; 5.55, Boullay. |
| Lead . . | PbCl ₂ | 3472 | 228 + 392 = 620 | 5.60 | 5.68—5.80, Karsten. |
| Barium . . | BaCl ₂ | 2602 | 286 + 392 = 678 | 3.83 | 3.86, Boullay; 3.75, Filhol; 3.7, Karsten. |
| Sodium . . | NaCl | 731 | 147.5 + 196 = 343.5 | 2.13 | 2.26, Mohs; 2.15, Kopp; 2.24, Filhol; 2.08, Karsten; 2.011, Playfair and Joule. |
| Potassium . | KCl | 932 | 281 + 196 = 477 | 1.94 | 1.994, Filhol; 1.94, Kopp; 1.92, Karsten; 1.90, Playfair and Joule. |
| Ammonium | H ₄ NCl | 668 | 218 + 196 = 414 | 1.61 | 1.50, Kopp; 1.53, Mohs; 1.578, Playfair and Joule. |
| CHLORIDES, CLASS II. Volume of Cl=245. | | | | | |
| Cobalt . . | CoCl ₂ | 1624 | 88 + 490 = 578 | 2.81 | 2.937; Playfair and Joule. |
| Copper . . | CuCl | 1237 | 88 + 245 = 333 | 3.71 | 3.68, Karsten; 3.376, Playfair and Joule. |
| Copper . . | CuCl ₂ | 1680 | 88 + 490 = 578 | 2.90 | 3.054, Playfair and Joule. |
| Iron . . . | FeCl ₂ | 1486 | 88 + 490 = 578 | 2.74 | 2.528, Filhol. |
| Mercury | HgCl ₂ | 3386 | 182 + 490 = 672 | 5.04 | 5.14, Gmelin; 5.42, Boullay; 5.40, Karsten. |
| | HgCl | 2943 | 182 + 245 = 427 | 6.90 | 6.99, Karsten; 6.71, Herapath; 7.14, Boullay. |
| Strontium . | SrCl ₂ | 1978 | 215 + 490 = 705 | 2.80 | 2.80, Karsten; 2.96, Filhol. |
| Calcium . . | CaCl ₂ | 1386 | 120 + 490 = 610 | 2.27 | 2.21—2.27, Boullay; 2.24, Filhol; 2.485, Playfair and Joule. |
| Magnesium | MgCl ₂ | 1186 | 86 + 490 = 576 | 2.05 | 2.177, Playfair and Joule. |

Similar relations have been observed with the various sulphides, but the accordance of theory with observation is still less perfect in these cases, owing partly, perhaps to the dimorphism of sulphur, and to the impossibility of ascertaining which modification of this element may be present in the compound.

The sulphates are regarded by Kopp as consisting of $M''SO_4$. They are subdivided by him into two classes: in the first class, SO_4 is assumed to possess a volume = 186; in the second, a volume = 236. There is no simple relation between these two numbers; but if we view the sulphates as formed upon the plan M'_2O, SO_3 , or $N''O, SO_3$, and deduct from the numbers assigned by Kopp for SO_4 , 32 as the atomic volume of one atom of oxygen (adding it in all cases to the numbers which represent the atomic volume of the metal in the salt), the numbers which represent SO_3 in the two classes will be 154 and 204. Now by substituting 153 for 154, we may represent the two volumes of SO_3 by numbers which are in the ratio of 3 : 4, and if this slight alteration be adopted, the atomic volumes obtained by calculation agree as well with those furnished by experiment as those which have been calculated by Kopp.

In the chromates, the tungstates, the carbonates, and the nitrates, but a single class has been recognized for each acid:—

| SULPHATES, CLASS I. $\text{SO}_2 = 153.$ | | | | |
|---|-------------------|---------------------------------|--------------------|--|
| Name of Salt. (Formula $\text{M}'_2\text{O}, \text{SO}_3$) | At. Wt. 0=100. | Calculated Atomic Volume. | Calcul. Sp. gr. | Observed Specific Gravity. |
| Lead . . . | 1895 | $146 + 153 = 299$ | 6'32 | 6'30, Mohs, Filhol; 6'17, Karsten. |
| Baryta . . . | 1458 | $175 + 153 = 328$ | 4'44 | 4'45, Mohs; 4'20, Karsten. |
| Potash . . . | 1087 | $266 + 153 = 419$ | 2'59 | 2'62, Karsten, Filhol; 2'66, Kopp; 2'64, Playfair and Joule. |
| Strontia . . . | 1148 | $140 + 153 = 293$ | 3'92 | 3'59, Karsten; 3'77, Filhol; 3'95, Breithaupt. |
| SULPHATES, CLASS II. $\text{SO}_3 = 204.$ | | | | |
| Copper . . . | 997 | $76 + 204 = 280$ | 3'56 | 3'53, Karsten, Filhol; 3'631, Play- fair and Joule. |
| Silver . . . | 1950 | $160 + 204 = 364$ | 5'35 | 5'34, Karsten; 5'41, Filhol; 5'322, Playfair and Joule. |
| Zinc . . . | 1006 | $89 + 204 = 293$ | 3'43 | 3'40, Karsten, Filhol; 3'681, Play- fair and Joule. |
| Lime . . . | 850 | $92 + 204 = 296$ | 2'89 | 2'93, Karsten; 3'102, Filhol; 2'96, Naumann. |
| Magnesia . . . | 750 | $72 + 204 = 276$ | 2'71 | 2'61, Karsten; 2'628, Filhol; 2'706, Playfair and Joule. |
| Soda . . . | 888 | $162 + 204 = 366$ | 2'42 | 2'63, Kopp; 2'629, Filhol; 2'597, Playfair and Joule. |
| CHROMATES, $\text{CrO}_2 = 196.$ | | | | |
| $\text{M}''_2\text{O}, \text{CrO}_3.$ | | | | |
| Lead . . . | 2022 | $146 + 196 = 342$ | 5'91 | 5'95, Breithaupt; 6'00, Mohs; 5'653, Playfair and Joule. |
| Potash . . . | 1215 | $266 + 196 = 462$ | 2'63 | 2'64, Karsten; 2'74, Kopp; 2'682, Playfair and Joule. |
| Silver . . . | 2078 | $160 + 196 = 356$ | 5'83 | 5'77, Playfair and Joule. |
| TUNGSTATES, $\text{WO}_2 = 212.$ | | | | |
| $\text{M}_2\text{O}, \text{WO}_3.$ | | | | |
| Lead . . . | 2844 | $146 + 212 = 358$ | 7'94 | 8'0, Gmelin; 8'1, Leonhard. |
| Lime . . . | 1800 | $92 + 212 = 304$ | 5'92 | 6'04, Karsten; 6'03, Meissner. |
| CARBONATES, $\text{CO}_2 = 119.$ | | | | |
| $\text{M}_2\text{O}, \text{CO}_2.$ | | | | |
| Cadmium . . . | 1073 | $113 + 119 = 232$ | 4'63 | 4'42, Herapath; 4'49, Kopp. |
| Iron . . . | 725 | $76 + 119 = 195$ | 3'72 | 3'829, Mohs; 3'872, Naumann. |
| Lead . . . | 1670 | $146 + 119 = 265$ | 6'30 | 6'43, Karsten; 6'47, Breithaupt. |
| Manganese . . . | 722 | $76 + 119 = 195$ | 3'70 | 3'55—3'59, Mohs. |
| Silver . . . | 1725 | $160 + 119 = 279$ | 6'18 | 6'08, Karsten. |
| Zinc . . . | 781 | $89 + 119 = 208$ | 3'75 | 4'44, Mohs; 4'4—4'5, Naumann. |
| Baryta . . . | 1233 | $175 + 119 = 294$ | 4'19 | 4'30, Karsten, Mohs; 4'24, Breit- haupt; 4'565, Filhol. |
| Lime . . . | 625 | $92 + 119 = 211$ | 2'96 | 3'00 (Aragonite), Breithaupt; 2'93, Mohs; 2'70 (Iceland spar), Kar- sten; 2'72, Beudant. |
| Magnesia . . . | 525 | $72 + 119 = 191$ | 2'75 | 2'81, Breithaupt; 3'0—3'11, Mohs. |
| Potash . . . | 862 | $266 + 119 = 385$ | 2'24 | 2'26, Karsten; 2'267, Filhol; 2'103, Playfair and Joule. |
| Soda . . . | 662 | $162 + 119 = 281$ | 2'38 | 2'47, Karsten; 2'509, Filhol; 2'427, Playfair and Joule. |
| Strontia . . . | 923 | $140 + 119 = 259$ | 3'56 | 3'60, Mohs; 3'62, Karsten. |

| NITRATES, $N_2O_5 = 326$. | | | | |
|--|---------------------|------------------------------|----------------------------|--|
| Name of Salt. (Formula M_2O, N_2O_5 .) | At. Wt. O = 100. | Calculated Atomic Volume. | Calcu- lated Sp. gr. | Observed Specific Gravity. |
| Lead . . . | 2069 | $146 + 326 = 472$ | 4.32 | 4.581, Filhol; 4.40, Karsten; 4.34, Kopp; 4.316, Playfair and Joule. |
| Silver . . . | 2125 | $160 + 326 = 486$ | 4.37 | 4.36, Karsten; 4.336, Playfair and Joule. |
| Ammonia . . | 1000 | $250 + 326 = 576$ | 1.71 | 1.74, Kopp; 1.635, Playfair & Joule. |
| Baryta . . . | 1634 | $175 + 326 = 501$ | 3.26 | 3.200, Filhol; 3.19, Karsten; 3.284, Playfair and Joule. |
| Lime . . . | 1025 | $92 + 326 = 418$ | 2.45 | 2.240, Filhol. |
| Potash . . . | 1263 | $266 + 326 = 592$ | 2.12 | 2.10, Karsten; 2.06, Kopp; 2.07, Playfair and Joule. |
| Soda . . . | 1063 | $162 + 326 = 488$ | 2.19 | 2.260, Filhol, Karsten; 2.19, Marx; 2.20, Kopp; 2.182, Playfair and Joule. |
| Strontia . . | 1324 | $140 + 326 = 466$ | 2.84 | 2.857, Filhol; 2.84, Karsten; 2.704, Playfair and Joule. |

(1735) 3. *Volumes of Compounds in Solution.*—A series of interesting researches was made a few years ago by Playfair and Joule upon the bulk occupied by the equivalent quantities of different compounds in the solid state, compared with that which they occupy when in solution (*Phil. Mag.*, 1845, vol. xxvii.). Some of these results are included in the table (page 937), in which they are all referred to the quantity of water in grains which an *equivalent* (not the *atom*) in grains of each substance ($H=1$) would displace when immersed in water.

The quantity of water displaced is easily calculated by dividing the equivalent number of the substance by its specific gravity. It was in these cases determined experimentally by taking a given weight, say an equivalent in grains, of the substance under trial, and introducing it into the volumometer, described at page 926.

When known quantities of different salts were brought into solution, and the increase of bulk in the liquid thus produced was ascertained, it was found—1. That a salt when in solution always occupies less space than it did when in the solid state. 2. That equivalent quantities of different salts when in solution occupy either the same volume, or volumes which are simple multiples or submultiples of each other.* If 9 (the equivalent volume of water)

* The atomic volume of a salt in solution, however, varies considerably with the temperature, and increases rapidly as the temperature rises, so that it is only at a particular temperature for each salt that this statement is true. For example, the solution volume of an equivalent of each of the following salts is for—

| | | | |
|---------------------|---------------|----------------------|----------------------|
| Zincic sulphate . . | $ZnSO_4, 7HO$ | at $32^\circ = 56.1$ | at $90^\circ = 63$ |
| Magnesian ,, . . | $MgSO_4, 7HO$ | at ,, = 60.8 | at $85^\circ = 63$ |
| Ferrous ,, . . | $FeSO_4, 7HO$ | at ,, = 61.0 | at $80^\circ = 63$. |

be assumed as the standard of comparison, an equivalent of the different salts, when dissolved in water, increases the volume of the liquid by 9, or by some multiple of 9. For instance, 87 grains or 1 equivalent of potassic sulphate in its dry state, displaces 33 grains of water, but it increases the bulk of the liquid by only 18 grain measures when in solution; 101 grains of potassic nitrate in the solid form displace 48 grains of water, but when in solution they displace 36 grains. In the case of potassic carbonate the condensation is still greater; for 69 grains of the solid salt occupy a space of 39 water grains, and of 9 only when in solution. It is, however, necessary to remark that the volume occupied by the salt when in solution is somewhat influenced by the degree of saturation of the liquid, the increase of volume being slightly greater when the solution approaches the point of saturation. For example, it was found in the case of cane sugar, that when an equivalent of sugar (171 grains) was dissolved in different amounts of water, the increase in volume of the solution was as follows:—

| Sugar. | Water. | Temperature. ° F. | Atomic volume in grain measures of water. |
|--------|--------|----------------------|---|
| 1 | : 120 | 60 | 99'00 |
| 1 | : 10 | 52 | 105'09 |
| 1 | : 1 | 52 | 107'01 |
| 3 | : 1 | 52 | 108'06 |

3. That when a salt usually crystallizes with a large proportion of water of crystallization, such salt, when reduced to the anhydrous state, may be dissolved in water without increasing its bulk.* For example, anhydrous sodic carbonate, and the anhydrous sodic and magnesic sulphates, may be brought into solution without adding to the bulk of the liquid. If the salts be dissolved in their hydrated form, they increase the bulk of the liquid solely by the number of grains of water of crystallization which they contain: so that 143 grains, or one equivalent in grains of crystallized sodic carbonate, or 161 grains of the crystallized sodic sulphate, each of which contains 90 grains or 10 equivalents of water of crystallization, causes an increase of 90 grain measures in the bulk of the water in which it is dissolved; 123 grains, or an equivalent of magnesic sulphate, which contains 7 equivalents

* This observation was originally made by Dalton, but he supposed that in *all* cases when a salt was dissolved in water, the bulk of the liquid was unaltered, except by the bulk of water which the salt might contain.

or 63 grains of water, occasions an increase of 63 grain measures of water when brought into solution.

Volumes in grains of water of an equivalent in grains of several anhydrous salts, both when dry and when in solution (H=1).

| Name of the Metal. | Chloride. | | Bromide. | | Iodide. | | Sulphate. | | Nitrate. | | Carbonate. | |
|--------------------|-----------|----------------|----------|----------------|---------|----------------|-------------------|----------------|----------|----------------|------------|----------------|
| | Dry. | Solu- tion. | Dry. | Solu- tion. | Dry. | Solu- tion. | Dry. | Solu- tion. | Dry. | Solu- tion. | Dry. | Solu- tion. |
| Potassium | 39'3 | 26'8 | 44'0 | 28'8 | 54'2 | 44'0 | 33'0 | 18'0 | 48'9 | 36'1 | 33'0 | 9'2 |
| Sodium . | 29'2 | 18'3 | ... | 19'0 | ... | ... | 27'5 | 1'6 | 39'1 | 26'5 | 22'0 | 0'0 |
| Ammonium | 34'0 | 35'7 | ... | ... | ... | ... | ... | 27'0 | 49'1 | 45'5 | ... | ... |
| Calcium . | 22'5 | 1'6 | ... | ... | ... | ... | 23'4 | ... | ... | ... | ... | ... |
| Strontium . | ... | 0'0 | ... | ... | ... | ... | ... | ... | 39'2 | 26'5 | ... | ... |
| Barium . | ... | 9'8 | ... | ... | ... | ... | 23'9 | ... | 39'8 | 27'0 | ... | ... |
| Magnesium | 22'1 | 2'0 | ... | ... | ... | ... | 22'5 | 0'0 | ... | 18'8 | ... | ... |
| Zinc . . | ... | ... | ... | ... | ... | ... | 21'8 ₅ | 0'0 | ... | ... | ... | ... |
| Iron . . | ... | ... | ... | ... | ... | ... | 24'0 | 0'0 | ... | ... | ... | ... |
| Cobalt . . | 22'1 | ... | ... | ... | ... | ... | 22'0 | ... | ... | ... | ... | ... |
| Copper . . | 22'0 | 8'1 | ... | ... | ... | ... | 22'0 | 0'0 | ... | 18'2 | ... | ... |
| Lead . . | 24'5 | ... | ... | ... | ... | ... | 24'1 | ... | 38'4 | 25'4 | ... | ... |
| Mercury . | 22'0 | 18'4 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| Silver . . | 25'9 | ... | ... | ... | ... | ... | 29'4 | ... | 39'2 | 27'2 | ... | ... |

(1736) 4. *Atomic Volumes of Liquids of Analogous Composition.*

—In the year 1842 an important paper was published by Kopp (*Liebig's Annal.*, xli. 79, 169), in which he showed that when liquids belonging to one homologous series are compared with corresponding terms of other collateral homologous series (*vide* table, p. 38), like differences are observed in their atomic volumes. When, for instance, the atomic volume of a normal acid ($\text{H}\bar{\text{A}}$) ($\bar{\text{A}}$ representing an atom of the salt radicle of any monobasic acid) is compared with its corresponding vinic ether ($\text{C}_2\text{H}_5\bar{\text{A}}$), the atomic volume of the acid, at ordinary temperatures, is about 42.7 less than that of the corresponding compound ether. The atomic volume of the acid ($\text{H}\bar{\text{A}}$) is about 24 less than that of its corresponding methylic compound ($\text{CH}_3\bar{\text{A}}$); and as a necessary consequence, the atomic volume of an ethylic compound is about 18.7 greater than that of the corresponding methylic compound. A more careful examination of the subject has shown that the somewhat considerable divergences observed between the atomic volumes calculated according to these laws, and those actually found by observation, are materially reduced if the liquids be compared, not at *equal* temperatures, but at *corresponding* temperatures. Corresponding temperatures are those at which the cohesion of the liquids compared is equal; or

temperatures at which the liquids emit vapours of equal tension. The tension of the vapours of different liquids through the required range of the thermometric scale is, however, only known in a few instances; but it may be assumed without any very serious error, that corresponding temperatures in liquids are those situated at equal distances below the boiling points of the liquids under comparison. For instance, if the boiling point of alcohol be 173° , and if that of ether be 94° , the temperature of 60° F. would not be a corresponding temperature for these liquids; but if the alcohol be at 60° , which is 113° below its boiling point, the corresponding temperature for ether would be 113° below its boiling point, or -19° .

The atomic volume v of a compound increases as the temperature rises. This, indeed, must be evident from the consideration that the specific gravity d diminishes as the temperature rises, whilst the atomic weight q remains constant; and since $\frac{q}{d} = v$, the atomic volume must necessarily vary inversely as the density of the body, and consequently must increase as the temperature rises. In making comparisons of atomic volumes of compounds it is found advantageous in practice always to calculate them for the boiling point of the respective liquids under a pressure equal to that of 29.92 inches, or 760 m.m., of mercury.

At the time when Kopp first called attention to the atomic volume of liquids, few really exact data existed, by means of which his conclusions could be rigidly tested. Since that period both Pierre (*Ann. de Chimie*, III. xv. 325; xix. 193, and xx. 5), and Kopp himself (*Poggendorff's Annal.*, lxxii. 1 and 223; *Liebig's Annal.*, xciv. 257, xcv. 307), with others, have published a series of important and elaborate researches upon the specific gravity, the expansion, and the boiling points of a considerable number of liquids, by means of which the atomic volume of these liquids at the boiling point may be calculated. The table on the opposite page contains the principal results of Kopp's inquiries arranged for the convenience of comparison.

(1737) *Discussion of Kopp's Conclusions.*—The atomic volumes contained in the foregoing table are those calculated by Kopp for the *boiling point* of their respective liquids given in the fifth column of the table. These boiling points are not in all cases the actual numbers obtained by experiment, but are in some instances modified according to considerations explained in (1738), since the boiling point of many substances is only approximatively known, the estimates of different observers sometimes varying

| Name of Compound. | Formula. | At. wt. H=1. | Sp. gr. at 32°. | Calc. boiling point. ° F. | Atomic volume at boiling H=1. | Diff. in at. vol. for CH ₂ . |
|--|--|-----------------|--------------------|------------------------------------|--|---|
| Water | H ₂ O | 18 | 1'000 | 212°0 | 18'8 | |
| Wood spirit | C H ₃ HO | 32 | 0'8147 | 138°2 | 42'2 | 23'6 |
| Alcohol | C ₂ H ₅ HO | 46 | 0'8095 | 172°4 | 62'5 | 20'3 |
| Fousel oil | C ₅ H ₁₁ HO | 88 | 0'8253 | 275°0 | 124'4 | 3 × 20'6 |
| Carbolic acid . . . | C ₆ H ₅ HO | 94 | 1'0808 | 381°2 | 104'0 | |
| Benzyl-alcohol . . . | C ₇ H ₇ HO | 108 | 1'0628 | 415°4 | 123'7 | 19'7 |
| Formic acid | H C H O ₂ | 46 | 1'2227 | 210°2 | 41'8 | |
| Acetic acid | H C ₂ H ₃ O ₂ | 60 | 1'0620* | 244°4 | 63'8 | 22'0 |
| Propionic acid . . . | H C ₃ H ₅ O ₂ | 74 | 1'0161 | 278°6 | 85'4 | 21'6 |
| Butyric acid | H C ₄ H ₇ O ₂ | 88 | 0'9886 | 312°8 | 107'8 | 22'4 |
| Valeric acid | H C ₅ H ₉ O ₂ | 102 | 0'9555 | 347°0 | 131'2 | 23'4 |
| Benzoic acid | H C ₇ H ₅ O ₂ | 122 | 1'0838† | 487°4 | 126'9 | |
| Acetic anhydride . . | C ₂ H ₃ O ₂ , C ₂ H ₃ O | 102 | 1'0969 | 280°4 | 110'1 | |
| Ether | C ₄ H ₁₀ O | 74 | 0'7366 | 93°2 | 106'4 | |
| Methyl formiate . . | C H ₃ C H O ₂ | 60 | 0'9984 | 96°8 | 63'4 | |
| Methyl acetate . . . | C H ₃ C ₂ H ₃ O ₂ | 74 | 0'9562 | 131°0 | 85'8 | 22'4 & |
| Ethyl formiate . . . | C ₂ H ₅ C H O ₂ | 74 | 0'9394 | 131°0 | 85'7 | 22'3 |
| Ethyl acetate | C ₂ H ₅ C ₂ H ₃ O ₂ | 88 | 0'9105 | 165°2 | 107'8 | 22'1 & |
| Methyl butyrate . . . | C H ₃ C ₄ H ₇ O ₂ | 102 | 0'9210 | 199°4 | 127'3 | 19'5 |
| Ethyl propionate . . | C ₂ H ₅ C ₃ H ₅ O ₂ | 102 | 0'9231 | 199°4 | 125'8 | 18'0 |
| Methyl valerate . . . | C H ₃ C ₅ H ₉ O ₂ | 116 | 0'9015 | 233°6 | 149'6 | |
| Ethyl butyrate . . . | C ₂ H ₅ C ₄ H ₇ O ₂ | 116 | 0'9041 | 233°6 | 149'4 | |
| Tetryl acetate | C ₄ H ₉ C ₂ H ₃ O ₂ | 116 | 0'9004 | 233°6 | 149'3 | |
| Amyl formiate | C ₅ H ₁₁ C H O ₂ | 116 | 0'8945 | 233°6 | 150'2 | |
| Ethyl valerate | C ₂ H ₅ C ₅ H ₉ O ₂ | 130 | 0'8829 | 267°8 | 173'6 | |
| Amyl acetate | C ₅ H ₁₁ C ₂ H ₃ O ₂ | 130 | 0'8837 | 267°8 | 175'5 | |
| Amyl valerate | C ₅ H ₁₁ C ₅ H ₉ O ₂ | 172 | 0'8793 | 370°4 | 244'1 | |
| Methyl benzoate . . . | C H ₃ C ₇ H ₅ O ₂ | 136 | 1'1026 | 374°0 | 150'3 | 24'5 |
| Ethyl benzoate | C ₂ H ₅ C ₇ H ₅ O ₂ | 150 | 1'0657 | 408°2 | 174'8 | 3 × 24'3 |
| Amyl benzoate | C ₅ H ₁₁ C ₇ H ₅ O ₂ | 192 | 1'0039 | 510°8 | 247'7 | |
| Ethyl cinnamate . . . | C ₂ H ₅ C ₉ H ₇ O ₂ | 176 | 1'0656 | 500°0 | 211'3 | |
| Methyl salicylate . . | C H ₃ C ₇ H ₅ O ₃ | 152 | 1'1969 | 433°4 | 157°0 | |
| Ethyl carbonate . . . | C ₄ H ₁₀ C O ₃ | 118 | 0'9998 | 258°8 | 139°4 | |
| Methyl oxalate | C ₂ H ₆ C ₂ O ₄ | 118 | 1'1566‡ | 323°6 | 116'3 | 2 × 25'4 |
| Ethyl oxalate | C ₄ H ₁₀ C ₂ O ₄ | 146 | 1'1016 | 366°8 | 167'1 | |
| Ethyl succinate . . . | C ₄ H ₁₀ C ₄ H ₄ O ₄ | 174 | 1'0718 | 422°6 | 209°0 | |
| Acetone | C ₃ H ₆ O | 58 | 0'8144 | 132°8 | 77'6 | 20'7 |
| Aldehyd | C ₂ H ₄ O | 44 | 0'8009 | 69°8 | 56'9 | 3 × 21'2 |
| Valeraldehyd | C ₅ H ₁₀ O | 86 | 0'8224 | 213°8 | 120'3 | |
| Benzoyl hydride . . . | C ₇ H ₆ O | 106 | 1'0636 | 354°2 | 118'4 | 3 × 23'6 |
| Cumyl hydride | C ₁₀ H ₁₂ O | 148 | 0'9832 | 456°8 | 189°2 | |
| Benzol | C ₆ H ₆ | 78 | 0'8991 | 176°0 | 99'7 | 4 × 21'4 |
| Cymol | C ₁₀ H ₁₄ | 134 | 0'8778 | 347°0 | 185°2 | |
| Naphthalin | C ₁₀ H ₈ | 128 | 0'9774§ | 424°4 | 149°2 | |
| Tetryl (Dibutyl) . . | C ₈ H ₁₈ | 114 | 0'7135 | 226°4 | 186°8 | |
| <i>Atomic Volumes of Liquid Sulphur Compounds.</i> | | | | | | |
| Mercaptan | C ₂ H ₅ HS | 62 | 0'8335 | 96°8 | 76'1 | 3 × 21'5 |
| Amyl mercaptan . . . | C ₅ H ₁₁ HS | 104 | 0'8548 | 248°0 | 140'5 | |
| Methyl sulphide . . . | C ₂ H ₆ S | 62 | 0'8435 | 105°8 | 75'7 | 2 × 22'9 |
| Ethyl sulphide | C ₄ H ₁₀ S | 90 | 0'844 | 195°8 | 121'5 | |
| Methyl disulphide . . | C ₂ H ₆ S ₂ | 94 | 1'064 | 237°2 | 100'7 | |
| Sulphurous anhydr. | SO ₂ | 64 | 1'4911 | 17°6 | 43'9 | |
| Sulphurous ether . . . | C ₄ H ₁₀ SO ₃ | 138 | 1'1063 | 320°0 | 149'5 | |
| Carbon disulphide . . | CS ₂ | 76 | 1'2931 | 116°6 | 62'4 | |

* At 63°. † At 250°. ‡ At 122°. § At 175°. || At 4°.

several degrees. The atomic volumes contained in this table, therefore, differ from the earlier calculations already referred to, which were all made at ordinary temperatures. Now if we compare the hydrated acids contained in Division II. of the table, with the ethers in Division III., it appears that the atomic volume of the hydrated acid is about 43 less than that of the corresponding ether; for instance:—

| | | |
|-----------------------|----------------------|---------------------|
| Butyric ether = 149·4 | Acetic ether = 107·8 | Formic ether = 85·7 |
| Butyric acid = 107·8 | Acetic acid = 63·8 | Formic acid = 41·8 |
| Difference | 41·6 | 43·9 |

The difference between the atomic volume of the normal acid and that of the corresponding methylic compound is about 20·8:—

| | | |
|-----------------------|-----------------------|------------------------|
| Methyl butyr. = 127·3 | Methyl acetate = 85·8 | Methyl formiate = 63·4 |
| Butyric acid = 107·8 | Acetic acid = 63·8 | Formic acid = 41·8 |
| 19·5 | 22·0 | 21·6 |

and, as may be seen by inspection of the table, the mean difference between the atomic volume of the corresponding compounds in the ethyl and the methyl series is about 22·2:—

| | | |
|------------------------|------------------------|-----------------------|
| Ethyl valerate = 173·6 | Ethyl butyrate = 149·4 | Ethyl acetate = 107·8 |
| Methyl valer. = 149·6 | Methyl butyr. = 127·3 | Methyl acetate = 85·8 |
| 24·0 | 22·1 | 22·0 |

Now, since the corresponding compounds of the ethylic and the methylic series differ by (CH_2) , this mean difference in the atomic volume of such corresponding compounds has been assumed by Kopp to represent the volume occupied by each group of (CH_2) when in combination. This difference, it will be seen from the foregoing table, ranges in a large number of compounds between 20 and 24. Kopp fixes 22 as its average value at the boiling point of each compound.

Isomeric liquids of analogous composition, such, for instance, as the different metameric compound ethers, possess atomic volumes which are sensibly equal to each other, and they consequently *at their boiling points* have the same specific gravities; such, for example, as:—

| | | | |
|----------------|--|-----------------|--|
| Butyric acid . | $\text{HC}_4\text{H}_7\text{O}_2 = 107·8$ | Methyl valerate | $\text{CH}_3\text{C}_5\text{H}_9\text{O}_2 = 149·6$ |
| Acetic ether . | $\text{C}_2\text{H}_5\text{C}_2\text{H}_3\text{O}_2 = 107·8$ | Ethyl butyrate | $\text{C}_2\text{H}_5\text{C}_4\text{H}_7\text{O}_2 = 149·4$ |

Numerous other cases may also be seen by comparing the volumes of the ethers which are bracketed together in the table, p. 939. But if the isomeric compounds belong to different and dissimilar

series having a dissimilar typical constitution, the same correspondence is not observed; for example:—

| | |
|--|--|
| Acetone 2 (C ₃ H ₆ O) = 155·2 Methyl valerate CH ₃ C ₅ H ₉ O ₂ = 149·6 <hr style="width: 80%; margin-left: auto; margin-right: 0;"/> 5·6 | Aldehyd 2 (C ₂ H ₄ O) = 113·8 Butyric acid . . HC ₄ H ₇ O ₂ = 107·8 <hr style="width: 80%; margin-left: auto; margin-right: 0;"/> 6·0 |
|--|--|

By comparing together liquids which contain the same number of elementary equivalents, but in which a certain number of atoms of oxygen have been substituted for a corresponding number of atoms of hydrogen, it is found that the atomic volume of oxygen is somewhat greater than double that of hydrogen; as for example:—

| | |
|---|--|
| Acetic anhydride . C ₄ H ₆ O ₃ = 110·1 Butyric acid . . . C ₄ H ₈ O ₂ = 107·8 <hr style="width: 80%; margin-left: auto; margin-right: 0;"/> 2·3 | Acetic acid C ₂ H ₄ O ₂ = 63·8 Alcohol C ₂ H ₆ O = 62·5 <hr style="width: 80%; margin-left: auto; margin-right: 0;"/> 1·3 |
|---|--|

From a similar comparison of compounds in which a certain number of atoms of carbon have taken the place of a corresponding number of atoms of hydrogen, it has been concluded that the volumes of 1 atom of carbon and 2 of hydrogen are equal. This is exemplified, according to Kopp, in the corresponding compounds of the valeric (C₅H₁₀O₂), and the benzoic (C₇H₆O₂) acids; for instance:—

| | | |
|---|---|---|
| Methyl benzoate = 150·3 Methyl valerate = 149·6 <hr style="width: 80%; margin-left: auto; margin-right: 0;"/> 0·7 | Benzoic ether = 174·8 Valeric ether = 173·6 <hr style="width: 80%; margin-left: auto; margin-right: 0;"/> 1·2 | Amyl benzoate = 247·7 Amyl valerate = 244·1 <hr style="width: 80%; margin-left: auto; margin-right: 0;"/> 3·6 |
|---|---|---|

The difference is so slight, that in computing atomic volumes from the composition of a body, each atom of carbon may be considered to occupy a volume equal to two of hydrogen. Kopp concludes that the atom of each element, in entering into combination, does so with its own specific volume; and he further assumes that the same element may have *different* specific volumes according to the position which it occupies in the compound. Oxygen, for example, has a value when it forms a part of the radicle, different from that which it possesses when external to the radicle:—Thus, if O = 16 and H = 1 at the boiling point of the different compounds,

| | |
|--|--------|
| The volume of an atom of carbon | = 11·0 |
| " " of hydrogen | = 5·5 |
| " " of oxygen within the radicle. | = 12·0 |
| " " " external to the radicle | = 7·8 |
| Sulphur within the radicle | = 28·6 |

| | |
|--|--------|
| Sulphur external to the radicle | = 22.9 |
| Chlorine " | = 22.8 |
| Bromine " | = 27.9 |
| Iodine " | = 37.5 |

Kopp, by the employment of these numbers for each atom of the above-mentioned elements present in the molecule of any compound, has arrived by calculation, in a large number of cases, at a close approximation to the observed atomic volume. For example:—Calculating the atomic volumes of alcohol $\left. \begin{array}{l} \text{C}_2\text{H}_5 \\ \text{H} \end{array} \right\} \text{O}$ and of acetic acid $\left. \begin{array}{l} \text{C}_2\text{H}_3\text{O} \\ \text{H} \end{array} \right\} \text{O}$ from the numbers given above, the results would be as follows:—

| For alcohol. | For acetic acid. |
|-------------------------------------|-------------------------------------|
| $\text{C}_2 = 11.0 \times 2 = 22.0$ | $\text{C}_2 = 11.0 \times 2 = 22.0$ |
| $\text{H}_6 = 5.5 \times 6 = 33.0$ | $\text{H}_4 = 5.5 \times 4 = 22.0$ |
| $\text{O} = 7.8 \times 1 = 7.8$ | $\text{O} = 12.0 \times 1 = 12.0$ |
| | $\text{O} = 7.8 \times 1 = 7.8$ |
| Calculated <u>62.8</u> | Calculated <u>63.8</u> |
| Observed 62.5 | Observed 63.8 |

It sometimes happens that equal volumes of two different liquids will contain an equal number of molecules of their constituent compounds; but this, which is the rule with bodies in the condition of gas or vapour, is the exception in the case of liquids.

For the further prosecution of this subject the reader is referred to Kopp's interesting papers in *Liebig's Annalen*, Bde. xev., xevii., and xeviii.

(1738) *Kopp's Law of the Boiling Points*.—At the same time that Kopp pointed out the regular increase in atomic volume which the successive terms of the same homologous series exhibit, he called attention to a not less remarkable regularity in the increase of the temperature required to produce ebullition, as the number of atoms of (CH_2) increases in the compound. By inspecting the table at p. 939, Div. III., it will be seen, on comparing the boiling points of the compounds of ethyl and of methyl, that for every addition of CH_2 in the empirical formula, a rise in the boiling point of about 36° (20° C.) takes place.

It may be stated as a general result of observation, that the boiling point of a normal acid is 113.4° (63° C.) higher than that of its methylic ether, 79.2° (44° C.) higher than that of its ethylic ether, and 23.4° (13° C.) lower than that of its amyllic ether: the boiling point of an alcohol of the form $\text{C}_n\text{H}_{2n+2}\text{O}$ is about 72°

(40° C.) lower than that of its corresponding acid $C_nH_{2n}O_2$; a compound ether of the form $(C_nH_{2n+1}C_nH_{2n-1}O_2)$ boils at about 147°·6 (82° C.) below the acid $(C_nH_{2n}O_2)$ which is isomeric with it.

The rise of temperature for each addition of CH_2 differs, however, in different classes of homologous compounds, as may be seen by an examination of the following table, from which it appears that in the *alcohols* the mean elevation of the boiling point for CH_2 is 31°·4 (17°·4 C.). In the *aldehyds* it is 47° (26° C.), though in this class the divergences from the mean are so considerable that it is probable that several of the assigned boiling points are inaccurate. In the *radicles of the alcohols* the mean rise is 42° (23°·3 C.) and in the *homologues of benzol* it is 41° (22°·8 C.). In the *acids* of the acetic series it is 38°·9 (21°·6 C.), and in the *aniline bases* it is 30°·5 (16°·9 C.)

| Ethers. | Formula. | Observed Boiling Point. ° F. |
|---|-----------------|--|
| Methyl ether . . . | C_2H_6O | -5°·8, Berthelot. |
| Methyl ethyl ether | C_3H_8O | +51°·8, Williamson. |
| Ethyl ether . . . | $C_4H_{10}O$ | 93°·2, Dumas; 93°·5, Kopp; 94°·8, Andrews; 95°, Delffs; 95°·9, Pierre; 96°·3, Gay-Lussac. |
| Methyl amyl ether | $C_6H_{14}O$ | 161°·6, Williamson. |
| Ethyl tetryl ether | $C_6H_{14}O$ | 172°·4—176°, Wurtz. |
| Ethyl amyl ether . | $C_7H_{16}O$ | 233°·6, Williamson. |
| Tetryl ether . . . | $C_8H_{18}O$ | 212°—219°·2? Wurtz. |
| Amyl ether . . . | $C_{10}H_{22}O$ | 338°·0, Gaultier; 338°—347°, Wurtz; 347° to 361°, Rieckher. |
| Mean difference for $CH_2=44°$ F. (24°·4 C.). | | |
| Alcohols. | | |
| Wood spirit . . . | C_2H_4O | 148°—149°·2, Kopp; 149°, Kane; 140°·9— 141°·8, Delffs. |
| Ethyl alcohol . . . | C_2H_6O | 172°·4—173°·8, Kopp; 172°·2, Andrews; 173°, Pierre; 173°·1, Gay-Lussac. |
| Propyl do. . . . | C_3H_8O | 204°·8, Chancel. |
| Butyl do. . . . | $C_4H_{10}O$ | 228°·2, Wurtz. |
| Amyl do. . . . | $C_5H_{12}O$ | 266°·7—271°·4, Kopp; 269°·4, Pierre; 269°·6, Delffs, Cahours. |
| Hexyl do. . . . | $C_6H_{14}O$ | 298°—309°, Faget. |
| Heptyl do. . . . | $C_7H_{16}O$ | 350°·6—351°·5, Stædeler. |
| Octyl do. . . . | $C_8H_{18}O$ | 360°, Bouis; 352°·4, Moschnin. |
| Mean difference for $CH_2=31°·4$ F. (17°·4 C.). | | |
| Aldehyds. | | |
| Acetic | C_2H_4O | 71°·4, Liebig; 71°·6, Pierre; 67°·8, Kopp. |
| Propionic | C_3H_6O | 131°—149°, Guckelberger. |
| Butyric | C_4H_8O | 154°—167°, Guckelberger. |
| Valeric | $C_5H_{10}O$ | 199°·2, Kopp; 204°·8—206°·6, Parkinson; 206°·6, Limpricht. |
| Cinnanthylic . . . | $C_7H_{14}O$ | 311°—316°·4, Bussy. |
| Caprylic | $C_8H_{16}O$ | 340°. |
| Rutic | $C_{10}H_{20}O$ | 446°, Gerhardt. |
| Mean difference for $CH_2=47°$ F. (26° C.). | | |

| Acids. | Formula. | Observed Boiling Point. °F. |
|---|--------------------------|---|
| Formic | $C H_2 O_2$ | 209°·3, Liebig; 212°, Wurtz; 221°·7, Kopp. |
| Acetic | $C_2 H_4 O_2$ | 240°·8, Delffs; 242°·4, Kopp. |
| Propionic | $C_3 H_6 O_2$ | 286°·9, Kopp; about 284°, Dumas and others. |
| Butyric | $C_4 H_8 O_2$ | 312°·8, Kopp, Delffs; 325°·4, Pierre; 327°·2, Pelouze. |
| Valeric | $C_5 H_{10} O_2$ | 346°·1, Delffs; 347°, Dumas and Stas; 348°·4, Kopp. |
| Caproic | $C_6 H_{12} O_2$ | 388°·4, Brazier and Gossleth; 395°·6—405°, Fehling. |
| Enanthylic | $C_7 H_{14} O_2$ | 424°·4, Stædeler. |
| Caprylic | $C_8 H_{16} O_2$ | 456°·8, Fehling. |
| Pelargonic | $C_9 H_{18} O_2$ | 500°·0, Cahours. |
| Mean difference for $CH_2=36^\circ$ (20° C.). | | |
| Anhydrides. | | |
| Acetic | $C_4 H_6 O_3$ | 280°·4, Gerhardt, Kopp; 278°·6, Wurtz. |
| Propionic | $C_6 H_{10} O_3$ | 336°·2, Limpricht and Uslar. |
| Butyric | $C_8 H_{14} O_3$ | About 374°, Gerhardt. |
| Valeric | $C_{10} H_{18} O_3$ | About 419°, Gerhardt. |
| Caprylic | $C_{16} H_{30} O_3$ | About 554°, Chiozza. |
| Mean difference for $CH_2=22^\circ\cdot7$ (12°·6 C.). | | |
| Methylic Ethers. | | |
| Methyl formiate . . | $CH_3 C H O_2$ | 90°·8, Kopp; 91°·2, Andrews. |
| „ acetate . . | $CH_3 C_2 H_3 O_2$ | 131°, Andrews; 132°·3 — 132°·6, Kopp; 139°·1, Pierre. |
| „ propionate . . | $CH_3 C_3 H_5 O_2$ | ? |
| „ butyrate . . | $CH_3 C_4 H_7 O_2$ | 199°·4, Delffs; 203°—203°·2, Kopp; 215°·8, Pierre. |
| „ valerate . . | $CH_3 C_5 H_9 O_2$ | 237°·2—240°·0, Kopp. |
| Mean difference for $CH_2=37^\circ\cdot2$ (20°·7 C.). | | |
| Ethylic ethers. | | |
| Ethyl formiate . . | $C_2 H_5 C H O_2$ | 127°·2, Pierre; 127°·4, Delffs; 128°, Liebig; 130°·5—131°·5, Kopp. |
| „ acetate . . | $C_2 H_5 C_2 H_3 O_2$ | 164°·7, Kopp; 165°·2, Dumas, Delffs, Pierre. |
| „ propionate . . | $C_2 H_5 C_3 H_5 O_2$ | 204°·5—208°·4, Kopp; 213°·8, Limpricht and Uslar. |
| „ butyrate . . | $C_2 H_5 C_4 H_7 O_2$ | 230°, Lerch; 235°·4, Delffs; 237°·7, Kopp; 246°·2, Pierre. |
| „ valerate . . | $C_2 H_5 C_5 H_9 O_2$ | 268°·7, Delffs; 271°·8, Kopp; 272°·3, Otto; 271°·4—273°·2, Berthelot. |
| „ caproate . . | $C_2 H_5 C_6 H_{11} O_2$ | 248°? Lerch; 323°·6, Fehling. |
| „ pelargonate . . | $C_2 H_5 C_9 H_{17} O_2$ | 420°·8 — 424°·4, Cahours; 435°·2, Delffs. |
| Mean difference for $CH_2=38^\circ\cdot8$ (21°·5 C.). | | |
| Other Ethers. | | |
| Propyl acetate . . | $C_3 H_7 C_2 H_3 O_2$ | 2 × 36 About 194°, Berthelot. About 266°, do. |
| „ butyrate . . | $C_3 H_7 C_4 H_7 O_2$ | |
| Butyl formiate . . | $C_4 H_9 C H O_2$ | 25·2 About 212°, Wurtz. 237°·2, do. |
| „ acetate . . | $C_4 H_9 C_2 H_3 O_2$ | |

| Compound Ethers. | Formula. | Observed Boiling Point. ° F. |
|--|--------------------------|--|
| Amyl formiate . . . | $C_5H_{11}C H O_2$ | 237°·2, Delffs; about 240°·8, Kopp. |
| „ acetate . . . | $C_5H_{11}C_2 H_3 O_2$ | 271°·4, Delffs; 272°—279°·1, Kopp. |
| „ propionate . . . | $C_5H_{11}C_3 H_5 O_2$ | About 311°, Wrightson. |
| „ valerate . . . | $C_5H_{11}C_5 H_9 O_2$ | 372°—372°·9, Kopp. |
| „ caproate . . . | $C_5H_{11}C_6 H_{11}O_2$ | 411°·8, Brazier and Gossleth. |
| Mean difference for $CH_2 = 34°·9$ (19°·4 C.). | | |
| Octyl acetate . . . | $C_8H_{17}C_2 H_3 O_2$ | 379°·4, Bouis. |
| Ethyl laurate . . . | $C_2H_5 C_{12}H_{23}O_2$ | 507°, Georgey; 516°, Delffs. |
| Alcohol Radicles. | | |
| Ethyl tetryl . . . | $C_6 H_{14}$ | 143°·6, Wurtz. |
| Tetryl (dipropyl) . . . | $C_6 H_{14}$ | 154°·4, Williams. |
| Methyl hexyl . . . | $C_7 H_{16}$ | 179°·6, Wurtz. |
| Ethyl amyl . . . | $C_7 H_{16}$ | 190°·4, Wurtz. |
| Tetryl (dibutyl) . . . | $C_8 H_{18}$ | 222°·8, Wurtz; 226°·4, Kolbe; 227°·3, Kopp. |
| Butyl amyl . . . | $C_9 H_{20}$ | 269°·6, Wurtz. |
| Amyl (diamyl) . . . | $C_{10}H_{22}$ | 311°, Frankland; 316°·4, Wurtz. |
| Butyl hexyl . . . | $C_{10}H_{22}$ | 311°, Wurtz. |
| Hexyl (dihexyl) . . . | $C_{12}H_{26}$ | 395°·6, Brazier and Gossleth, Williams. |
| Mean difference for $CH_2 = 42°$ (23°·3 C.). | | |
| Hydrocarbons. | | |
| Benzol | $C_6 H_6$ | 176°·7, Kopp; 176°·9, Mansfield; 177°·6, Church. |
| Toluol | $C_7 H_8$ | 218°·7, Church; 222°·8, Glenard and Boudault; 226°·4, Deville, Pelletier, and Walter; 229°·1, Noad; 235°·4, Mansfield. |
| Xylol | $C_8 H_{10}$ | 259°·1, Church; 264°·2, Cahours. |
| Cumol | $C_9 H_{12}$ | 298°·4, Abel; 299°·1, Church; 304°·5, Gerhardt. |
| Cymol | $C_{10}H_{14}$ | 339°·2, Church; 339°·8, Mansfield; 340°·7, Noad; 351°·5, Kopp. |
| Mean difference for $CH_2 = 41°$ (22°·7 C.). | | |

In the homologous ethers which contain chlorine, bromine, iodine, and sulphur, the difference in the boiling point produced by each successive addition of CH_2 is considerably higher than in the compound ethers. For example:—

| Compounds. | Formula. | Difference. | Observed Boiling Point. ° F. |
|--|----------------|------------------|------------------------------|
| Methyl chloride . . . | $C H_3 Cl$ | | -4°, Berthelot. |
| Ethyl chloride . . . | $C_2 H_5 Cl$ | 55°·8 | +51°·8, Pierre. |
| Butyl chloride . . . | $C_4 H_9 Cl$ | $2 \times 52°·5$ | 158°—167°, Wurtz. |
| Amyl chloride . . . | $C_5 H_{11}Cl$ | 48 | 215°·6, Pierre, Cahours. |
| Octyl chloride . . . | $C_8 H_{17}Cl$ | 43 | 347°, Bouis. |
| Mean difference for $CH_2 = 50°$ (27°·7 C.). | | | |
| Methyl bromide . . . | $C H_3 Br$ | | 55°·4, Pierre. |
| Ethyl bromide . . . | $C_2 H_5 Br$ | 50 | 105°·8, do. |
| Butyl bromide . . . | $C_4 H_9 Br$ | $2 \times 43°·2$ | 192°·2, Wurtz. |
| Amyl bromide . . . | $C_5 H_{11}Br$ | 54 | 246°·2, Pierre. |
| Octyl bromide . . . | $C_8 H_{17}Br$ | 43 | 374°, Bouis. |
| Mean difference for $CH_2 = 45°·5$ (25°·3 C.). | | | |

| Compounds. | Formula. | Difference. | Observed Boiling Point. °F. |
|---|--|-------------|---|
| Methyl iodide . . . | C H ₃ I | | 107°·6, Andrews; 111°·2, Pierre. |
| Ethyl iodide . . . | C ₂ H ₅ I | | 158°·0 Pierre; 159°·8, Andrews; 161°·6, Frankland. |
| Butyl iodide . . . | C ₄ H ₉ I | | 249°·8, Wurtz. |
| Amyl iodide . . . | C ₅ H ₁₁ I | | 294°·8, Frankland; 298°·4, Kopp; 300°, Grimm. |
| Octyl iodide . . . | C ₈ H ₁₇ I | | 410°, Bouis. |
| Mean difference for CH ₂ = 43° (23°·9 C.). | | | |
| Methyl sulphide . . | (C H ₃) ₂ S | 2 × 45 | 105°·8, Regnault. |
| Ethyl sulphide . . | (C ₂ H ₅) ₂ S | 6 × 37 | 195°·8, Pierre. |
| Amyl sulphide . . | (C ₄ H ₁₁) ₂ S | | 420°·8, Balard. |
| Mean difference for CH ₂ = 40° (22°·2 C.). | | | |
| Methyl mercaptan . | C H ₃ HS | 27°? | 69°·8, Gregory. |
| Ethyl mercaptan . | C ₂ H ₅ HS | 2 × 46°·8 | 96°·8, Liebig. |
| Butyl mercaptan . | C ₄ H ₉ HS | | 190°·4, Huinann. |
| Amyl mercaptan . | C ₅ H ₁₁ HS | 57°·6 | 242°·6, Krutsch; 248°, Kopp. |
| Mean difference for CH ₂ = 50° (27°·7 C.). | | | |

| Bases. | Formula. | Observed Boiling Point. °F. |
|---|-----------------------------------|-------------------------------|
| Aniline | C ₆ H ₇ N | 359°·6, Hofmann. |
| Toluylia | C ₇ H ₉ N | 388°·4, Muspratt and Hofmann. |
| Xylylia | C ₈ H ₁₁ N | 415°·4—417°·2, Church. |
| Cuminylia | C ₉ H ₁₃ N | 437°, Nicholson. |
| Cyminylia | C ₁₀ H ₁₅ N | 482°, Barlow. |
| Mean difference for CH ₂ = 30°·6 (17° C.). | | |
| Pyridine | C ₅ H ₅ N | 240°, Anderson. |
| Picoline | C ₆ H ₇ N | 271°·4, do. |
| Lutidine | C ₇ H ₉ N | 310°, do. |
| Collidine | C ₈ H ₁₁ N | 356°, do. |
| Mean difference for CH ₂ = 38°·7 (21°·5 C.). | | |

The following series exhibits a curious departure from the usual regularity exhibited by homologous compounds:—

| Nitriles. | Formula. | Observed Boiling Point. °F. |
|--------------------|-------------------------------------|--|
| Methyl cyanide . . | C H ₃ , CN | Kopp, 161°·6; Dumas, 170°·6; Hofmann and Buckton, 170°·6—172°·4. |
| Ethyl cyanide . . | C ₂ H ₅ , CN | Kolbe, Meyer, 190°·4; Grimm, 208°·4. |
| Propyl cyanide . . | C ₃ H ₇ , CN | Dumas and others, 245°. |
| Butyl cyanide . . | C ₄ H ₉ , CN | Schlieper, 257°; Guckelberger, 257°—262° |
| Amyl cyanide . . | C ₅ H ₁₁ , CN | Frankland & Kolbe, 294°·8; Wurtz, 311° |

Considerable irregularities are also observed in the boiling points of many of the derivatives of the diatomic alcohols; for

example, in the alcohols themselves, as the proportion of multiples of CH_2 increases the boiling point falls.

| Glycol Derivatives. | Formula. | Observed Boiling Point. °F. |
|--|--------------------------------------|---|
| Glycol | $\text{C}_2\text{H}_6\text{O}_2$ | 383°, Wurtz. |
| Propylglycol | $\text{C}_3\text{H}_8\text{O}_2$ | 370°—372°, do. |
| Butyl glycol | $\text{C}_4\text{H}_{10}\text{O}_2$ | 361°.4—363°, do. |
| Amyl glycol | $\text{C}_5\text{H}_{12}\text{O}_2$ | 350°.6, do. |
| Mean difference for $\text{CH}_2=11°.2$. (6°.2 C.). | | |
| Ethylene dichloride . . . | $\text{C}_2\text{H}_4\text{Cl}_2$ | 185°—186°.8, Dumas; 185°, Pierre. |
| Propylene dichloride . . . | $\text{C}_3\text{H}_6\text{Cl}_2$ | 212°—217°.4, Reynolds; 219°.2, Cahours. |
| Butylene dichloride . . . | $\text{C}_4\text{H}_8\text{Cl}_2$ | 251°.6, Kopp; 253°.4, Kolbe. |
| Enanthyene dichloride . . . | $\text{C}_7\text{H}_{14}\text{Cl}_2$ | 368°.6, Limpricht. |
| Ethylene dibromide . . . | $\text{C}_2\text{H}_4\text{Br}_2$ | 266°. |
| Propylene dibromide . . . | $\text{C}_3\text{H}_6\text{Br}_2$ | 293°. |
| Amylene dibromide . . . | $\text{C}_5\text{H}_{10}\text{Br}_2$ | 320°. |
| Mean difference for $\text{CH}_2=27°$ (15°.C.). | | |

The ethers of acids homologous with oxalic acid, $\text{C}_n\text{H}_{2n-2}\text{O}_4$, are isomeric with certain ethers of the diatomic alcohols, which affords an opportunity of contrasting these bodies; but it must be admitted that the accuracy of the numbers given for some of the glycolic ethers is questionable.

| Compound ethers. | Formula. | Observed Boiling Point. °F. |
|----------------------------------|--|---|
| Methyl oxalate | $\text{C}_4\text{H}_6\text{O}_4$ | 321°.8, Dumas and Péligré; 327°.2, Delffs. |
| Ethyl oxalate | $\text{C}_6\text{H}_{10}\text{O}_4$ | { 365°, Kopp; 366°.8, Delffs. 388°.4, Fehling. |
| Methyl succinate | | |
| Glycol diacetate | $\text{C}_7\text{H}_{12}\text{O}_4$ | { 366°.8—368°.6, Wurtz. 366°.8, Wurtz. |
| Propylglycol diacetate | | |
| Ethyl succinate | $\text{C}_8\text{H}_{14}\text{O}_4$ | { 417°.2, D'Arcet, Fehling; 422°.6, Kopp; about 392°, Wurtz. |
| Butylglycol diacetate | | |
| Glycol butyro-acetate | $\text{C}_9\text{H}_{16}\text{O}_4$ | { 406°—419°, Simpson. above 392°, Wurtz. |
| Amylglycol diacetate | | |
| Glycol valero-acetate | $\text{C}_{10}\text{H}_{18}\text{O}_4$ | { about 446°, Lourenço. 462°—466°, Wurtz. |
| Glycol dibutyrate | | |
| Ethyl suberate | $\text{C}_{12}\text{H}_{22}\text{O}_4$ | { 500°, Laurent. 500°, Cahours; 503°.6, Balard. |
| Amyl oxalate | | |
| Methyl sebate | $\text{C}_{14}\text{H}_{26}\text{O}_4$ | { 545°, Carlet. about 491°, Lourenço. |
| Glycol divalerate | | |
| Ethyl sebate | | 586°, Carlet. |

A comparison of metameric bodies of analogous composition shows that the boiling points of such compounds coincide very nearly, whereas if they belong to series which differ in their composition, the boiling points may vary widely. The differences between the hydrated acids and the compound ethers metameric

with them, given in the table, p. 944, show the latter point very clearly.

Many of the differences observed between the boiling points obtained by experiment, and the theoretical numbers (calculated according to Kopp's law of a constant difference) may possibly disappear when the boiling points shall have been more accurately determined: but Kopp observes, that it must not be assumed that the boiling points of liquids, when compared at *any* given pressure, will always exhibit the same differences as they do when compared at the average pressure of 30 inches (760 m.m.) of mercury. It does not follow, for instance, though the boiling point of ether is $79^{\circ}5$ below that of alcohol, under a pressure of 30 inches, that under a pressure of 15 inches the difference between these boiling points should still be $79^{\circ}5$: since it is well known that what is called Dalton's law (190), viz., 'that all liquids at equal distances from their boiling point emit vapours of equal tension,' is not correct.

The accurate determination of the boiling point of a liquid is by no means easy, as might be inferred from an inspection of the foregoing tables, where many experimentalists of great skill and experience give for the same well-known substances, numbers which differ by several degrees from each other. Indeed, it has been found, independently of the irregular manner in which many liquids boil in glass vessels (180), that in several cases impurities so slight as not materially to affect the result of ultimate analysis of the substance, may yet produce a considerable effect upon its boiling point.

Numerous attempts have been made to determine the effect which the addition or the removal of a certain number of atoms of each of the elements, carbon, hydrogen, and oxygen, exerts upon the boiling point of the resulting compound. These attempts, however, have not led to any satisfactory result, since the compounds thus compared belong generally to different series. The aldehyds, for example, cannot satisfactorily be compared with the alcohols, and it is only in the same homologous series that an equal rise in the boiling point can be expected for equal increments in the number of the constituent elements.

In the case of the alcohols, the volatile acids, and the compound ethers,—Kopp, assuming a constant difference of $34^{\circ}2$ F. (19° C.) for CH_2 , has calculated a table of boiling points which approximate pretty closely to the observed numbers, the mean of the best observations of which are contrasted with Kopp's calculated numbers.

If the calculated results given in the ensuing table be assumed to be accurate, it follows, if one of the bodies contained in this table be compared with others analogous to it in composition, that the boiling point will be raised by about $52^{\circ}\cdot 2$ (29° C.) for each additional atom of carbon; and that it will be reduced by about $52^{\circ}\cdot 2$ for a diminution of each atom of carbon: but the effect produced by hydrogen is the reverse of that produced by carbon; since for every additional atom of hydrogen, the boiling point is lowered 9° (5° C.); and for every atom of hydrogen which is removed, it is raised 9° :—

| Alcohols. | | | Acids. | | | Compound Ethers. | | |
|-------------------|----------------------------------|---------------------|-----------------------|---------------------|---------------------|------------------|----------------------------------|---------------------|
| $C_nH_{2n+1}HO$. | Observed. ° F. | Calculated. ° F. | H $C_nH_{2n-1}O_2$ | Observed. ° F. | Calculated. ° F. | $C_nH_{2n+1}O_2$ | Observed. ° F. | Calculated. ° F. |
| C_1H_4O | 149 ⁰ ·5 | 138 ⁰ ·2 | $C_2H_2O_2$ | 210 ⁰ ·6 | 210 ⁰ ·2 | $C_2H_4O_2$ | 91 ⁰ ·0 | 96 ⁰ ·8 |
| C_2H_6O | 173 ⁰ ·0 | 172 ⁰ ·4 | $C_3H_4O_2$ | 241 ⁰ ·6 | 244 ⁰ ·4 | $C_3H_6O_2$ | 131 ⁰ ·8 | 131 ⁰ ·0 |
| C_3H_8O | 204 ⁰ ·8 | 206 ⁰ ·6 | $C_3H_6O_2$ | 285 ⁰ ·5 | 278 ⁰ ·6 | $C_4H_8O_2$ | 165 ⁰ ·0 | 165 ⁰ ·2 |
| $C_4H_{10}O$ | 228 ⁰ ·2 ⁹ | 240 ⁰ ·8 | $C_4H_8O_2$ | 312 ⁰ ·8 | 312 ⁰ ·8 | $C_5H_{10}O_2$ | 201 ⁰ ·3 | 199 ⁰ ·4 |
| $C_5H_{12}O$ | 269 ⁰ ·5 | 275 ⁰ ·0 | $C_5H_{10}O_2$ | 347 ⁰ ·2 | 347 ⁰ ·0 | $C_6H_{12}O_2$ | 236 ⁰ ·5 | 233 ⁰ ·6 |
| $C_6H_{14}O$ | 309 ⁰ ·0 | 309 ⁰ ·2 | $C_6H_{12}O_2$ | 388 ⁰ ·4 | 381 ⁰ ·2 | $C_7H_{14}O_2$ | 270 ⁰ ·9 | 267 ⁰ ·8 |
| $C_7H_{16}O$ | ? | 343 ⁰ ·4 | $C_7H_{14}O_2$ | ? | 415 ⁰ ·4 | $C_8H_{16}O_2$ | 311 ⁰ ·0 ⁹ | 302 ⁰ ·0 |
| $C_8H_{18}O$ | 360 ⁰ ·0 | 377 ⁰ ·6 | $C_8H_{16}O_2$ | 456 ⁰ ·8 | 449 ⁰ ·6 | | | |

The following compounds are adduced by Kopp as affording an illustration of this alteration of the boiling point by the addition of carbon and hydrogen in isologous compounds; but the experimental numbers often differ very considerably from the calculated values:—

| Alcohols ($C_nH_{2n}pO_2$). | | Calculated. ° F. | Observed Boiling Point. ° F. |
|------------------------------------|-----------------|---------------------|--|
| Allylic | C_3H_6O | 224 ⁰ ·6 | 217 ⁰ ·4, Hofmann & Cahours. |
| Phenylic | C_6H_6O | 381 ⁰ ·2 | 368 ⁰ ·6 — 370 ⁰ ·4, Laurent; 370 ⁰ ·4, Kopp. |
| Benzyl | C_7H_8O | 415 ⁰ ·4 | 399 ⁰ ·2, Cannizzaro; 404 ⁰ ·6, Kopp. |
| Cinnyl | $C_9H_{10}O$ | 501 ⁰ ·8 | 482 ⁰ , Wolff; 489 ⁰ ·2, E. Kopp. |
| Cuminic | $C_{10}H_{14}O$ | 518 ⁰ ·0 | 469 ⁰ ·4, Kraut. |
| Compound Ethers, $C_nH_{2n}pO_2$. | | Calculated. ° F. | Observed Boiling Point. ° F. |
| Allyl acetate | $C_5H_8O_2$ | 217 ⁰ ·4 | 208 ⁰ ·4 — 212 ⁰ , Hofmann and Cahours; 221 ⁰ , Zinin. |
| Allyl butyrate | $C_7H_{12}O_2$ | 285 ⁰ ·8 | 284 ⁰ , Hofmann and Cahours; about 293 ⁰ , Berthelot. |
| Allyl valerate | $C_8H_{14}O_2$ | 320 ⁰ ·0 | 323 ⁰ ·6, Hofmann & Cahours. |

| Compound Ethers, $C_nH_{2p}O_2$. | | Calculated. °F. | Observed Boiling Point. °F. |
|-----------------------------------|---------------------|--------------------|--|
| Phenyl acetate . . . | } $C_8H_8O_2$ | 374°·0 | { 370°·4, Scrugham. 390°·2, Dumas and Péligot, Kopp. |
| Methyl benzoate . . . | | | |
| Ethyl benzoate . . . | } $C_9H_{10}O_2$ | 408°·2 | { 404°·6, Delffs; 408°·2, Du- mas; 415°·4, Kopp. 410°, Cannizzaro. |
| Benzyl acetate . . . | | | |
| Ethyl toluate | $C_{10}H_{12}O_2$ | 442°·4 | 442°·4, Noad. |
| Ethyl cuminate . . . | } $C_{12}H_{16}O_2$ | 510°·8 | { 464°, Gerhardt & Cahours. 486° — 489°, Rieckher; 501°·8, Kopp. |
| Amyl benzoate . . . | | | |
| Phenyl œnanthylate . . | $C_{13}H_{18}O_2$ | 545°·0 | 527° — 536°, Cahours. |
| Allyl benzoate . . . | } $C_{10}H_{10}O_2$ | 460°·4 | { 446°, Berthelot and De Luca; 467°·6, Zinin. 465°·8, E. Kopp. |
| Methyl cinnamate . . . | | | |
| Ethyl cinnamate . . . | $C_{11}H_{12}O_2$ | 494°·6 | 500°, Marchand; 503°·6, E. Kopp; 510°·8, H. Kopp. |
| Benzyl benzoate . . . | $C_{14}H_{12}O_2$ | 651°·2 | 653°, Cannizzaro. |
| Phenyl caprylate . . . | $C_{14}H_{20}O_2$ | 579°·2 | about 572°, Cahours. |

The reader will find an admirable digest of this subject by Kopp, in Liebig's *Annalen*, vol. xevi. and *Phil. Trans.* 1860.

APPENDIX.

Quantities of Absolute Alcohol by Weight, in Mixtures of Alcohol and Water of the following Specific Gravities (Drinkwater) :—

| Specific Gravity at 60° F. (15°·5 C.) | Alcohol by weight in 100 parts. | Specific Gravity at 60° F. (15°·5 C.) | Alcohol by weight in 100 parts. | Specific Gravity at 60° F. (15°·5 C.) | Alcohol by weight in 100 parts. | Specific Gravity at 60° F. (15°·5 C.) | Alcohol by weight in 100 parts. | Specific Gravity at 60° F. (15°·5 C.) | Alcohol by weight in 100 parts. |
|---------------------------------------|---------------------------------|---------------------------------------|---------------------------------|---------------------------------------|---------------------------------|---------------------------------------|---------------------------------|---------------------------------------|---------------------------------|
| 1·0000 | 0·00 | 0·9967 | 1·78 | ·9934 | 3·67 | ·9901 | 5·70 | ·9869 | 7·85 |
| ·9999 | 0·05 | ·9966 | 1·83 | ·9933 | 3·73 | ·9900 | 5·77 | ·9868 | 7·92 |
| ·9998 | 0·11 | ·9965 | 1·89 | ·9932 | 3·78 | ·9899 | 5·83 | ·9867 | 7·99 |
| ·9997 | 0·16 | ·9964 | 1·94 | ·9931 | 3·84 | ·9898 | 5·89 | ·9866 | 8·06 |
| ·9996 | 0·21 | ·9963 | 1·99 | ·9930 | 3·90 | ·9897 | 5·96 | ·9865 | 8·13 |
| ·9995 | 0·26 | ·9962 | 2·05 | ·9929 | 3·96 | ·9896 | 6·02 | ·9864 | 8·20 |
| ·9994 | 0·32 | ·9961 | 2·11 | ·9928 | 4·02 | ·9895 | 6·09 | ·9863 | 8·27 |
| ·9993 | 0·37 | ·9960 | 2·17 | ·9927 | 4·08 | ·9894 | 6·15 | ·9862 | 8·34 |
| ·9992 | 0·42 | ·9959 | 2·22 | ·9926 | 4·14 | ·9893 | 6·22 | ·9861 | 8·41 |
| ·9991 | 0·47 | ·9958 | 2·28 | ·9925 | 4·20 | ·9892 | 6·29 | ·9860 | 8·48 |
| ·9990 | 0·53 | ·9957 | 2·34 | ·9924 | 4·27 | ·9891 | 6·35 | ·9859 | 8·55 |
| ·9989 | 0·58 | ·9956 | 2·39 | ·9923 | 4·33 | ·9890 | 6·42 | ·9858 | 8·62 |
| ·9988 | 0·64 | ·9955 | 2·45 | ·9922 | 4·39 | ·9889 | 6·49 | ·9857 | 8·70 |
| ·9987 | 0·69 | ·9954 | 2·51 | ·9921 | 4·45 | ·9888 | 6·55 | ·9856 | 8·77 |
| ·9986 | 0·74 | ·9953 | 2·57 | ·9920 | 4·51 | ·9887 | 6·62 | ·9855 | 8·84 |
| ·9985 | 0·80 | ·9952 | 2·62 | ·9919 | 4·57 | ·9886 | 6·69 | ·9854 | 8·91 |
| ·9984 | 0·85 | ·9951 | 2·68 | ·9918 | 4·64 | ·9885 | 6·75 | ·9853 | 8·98 |
| ·9983 | 0·91 | ·9950 | 2·74 | ·9917 | 4·70 | ·9884 | 6·82 | ·9852 | 9·05 |
| ·9982 | 0·96 | ·9949 | 2·79 | ·9916 | 4·76 | ·9883 | 6·89 | ·9851 | 9·12 |
| ·9981 | 1·02 | ·9948 | 2·85 | ·9915 | 4·82 | ·9882 | 6·95 | ·9850 | 9·20 |
| ·9980 | 1·07 | ·9947 | 2·91 | ·9914 | 4·88 | ·9881 | 7·02 | ·9849 | 9·27 |
| ·9979 | 1·12 | ·9946 | 2·97 | ·9913 | 4·94 | ·9880 | 7·09 | ·9848 | 9·34 |
| ·9978 | 1·18 | ·9945 | 3·02 | ·9912 | 5·01 | ·9879 | 7·16 | ·9847 | 9·41 |
| ·9977 | 1·23 | ·9944 | 3·08 | ·9911 | 5·07 | ·9878 | 7·23 | ·9846 | 9·49 |
| ·9976 | 1·29 | ·9943 | 3·14 | ·9910 | 5·13 | ·9877 | 7·30 | ·9845 | 9·56 |
| ·9975 | 1·34 | ·9942 | 3·20 | ·9909 | 5·20 | ·9876 | 7·37 | ·9844 | 9·63 |
| ·9974 | 1·40 | ·9941 | 3·26 | ·9908 | 5·26 | ·9875 | 7·43 | ·9843 | 9·70 |
| ·9973 | 1·45 | ·9940 | 3·32 | ·9907 | 5·32 | ·9874 | 7·50 | ·9842 | 9·78 |
| ·9972 | 1·51 | ·9939 | 3·37 | ·9906 | 5·39 | ·9873 | 7·57 | ·9841 | 9·85 |
| ·9971 | 1·56 | ·9938 | 3·43 | ·9905 | 5·45 | ·9872 | 7·64 | ·9840 | 9·92 |
| ·9970 | 1·61 | ·9937 | 3·49 | ·9904 | 5·51 | ·9871 | 7·71 | ·9839 | 9·99 |
| ·9969 | 1·67 | ·9936 | 3·55 | ·9903 | 5·58 | ·9870 | 7·78 | ·9838 | 10·07 |
| ·9968 | 1·73 | ·9935 | 3·61 | ·9902 | 5·64 | | | | |

This table is founded on synthetic experiments, in which eleven different mixtures of alcohol and water were made, containing respectively 0·5, 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 per cent. of alcohol by weight: the alcohol employed had a specific gravity of 0·7938 at 60° (15°·5 C.).

Proportion of Absolute Alcohol by Weight in 100 parts of Spirit, of different Specific Gravities at 60° (15°·5 C.).

(Fownes. *Phil. Trans.*, 1847.)

| Alcohol per cent. | Specific Gravity. |
|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| 0 | 1·0000 | 25 | ·9652 | 51 | ·9160 | 76 | ·8581 |
| 0·5 | ·9991 | 26 | ·9638 | 52 | ·9135 | 77 | ·8557 |
| 1 | ·9981 | 27 | ·9623 | 53 | ·9113 | 78 | ·8533 |
| 2 | ·9965 | 28 | ·9609 | 54 | ·9090 | 79 | ·8508 |
| 3 | ·9947 | 29 | ·9593 | 55 | ·9069 | 80 | ·8483 |
| 4 | ·9930 | 30 | ·9578 | 56 | ·9047 | 81 | ·8459 |
| 5 | ·9914 | 31 | ·9560 | 57 | ·9025 | 82 | ·8434 |
| 6 | ·9898 | 32 | ·9544 | 58 | ·9001 | 83 | ·8408 |
| 7 | ·9884 | 33 | ·9528 | 59 | ·8979 | 84 | ·8382 |
| 8 | ·9869 | 34 | ·9511 | 60 | ·8956 | 85 | ·8357 |
| 9 | ·9855 | 35 | ·9490 | 61 | ·8932 | 86 | ·8331 |
| 10 | ·9841 | 36 | ·9470 | 62 | ·8908 | 87 | ·8305 |
| 11 | ·9828 | 37 | ·9452 | 63 | ·8886 | 88 | ·8279 |
| 12 | ·9815 | 38 | ·9434 | 64 | ·8863 | 89 | ·8254 |
| 13 | ·9802 | 39 | ·9416 | 65 | ·8840 | 90 | ·8228 |
| 14 | ·9789 | 40 | ·9396 | 66 | ·8816 | 91 | ·8199 |
| 15 | ·9778 | 41 | ·9376 | 67 | ·8793 | 92 | ·8172 |
| 16 | ·9766 | 42 | ·9356 | 68 | ·8769 | 93 | ·8145 |
| 17 | ·9753 | 43 | ·9335 | 69 | ·8745 | 94 | ·8118 |
| 18 | ·9741 | 44 | ·9314 | 70 | ·8721 | 95 | ·8089 |
| 19 | ·9728 | 45 | ·9292 | 71 | ·8696 | 96 | ·8061 |
| 20 | ·9716 | 46 | ·9270 | 72 | ·8672 | 97 | ·8031 |
| 21 | ·9704 | 47 | ·9249 | 73 | ·8649 | 98 | ·8001 |
| 22 | ·9691 | 48 | ·9228 | 74 | ·8625 | 99 | ·7969 |
| 23 | ·9678 | 49 | ·9206 | 75 | ·8603 | 100 | ·7938 |
| 24 | ·9665 | 50 | ·9184 | | | | |

In this table every alternate number is the result of a direct synthetical experiment; absolute alcohol and distilled water being weighed out in the proper proportions, and mixed by agitation in stoppered bottles; after a lapse of three or four days, each specimen was brought exactly to 60° F., and the specific gravity determined with great care.

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