ORGANIC CHEMISTRY

W. H. PERKIN

F. STANLEY KIPPING

ORGANIC CHEMISTRY

PART I.

BY

W. H. PERKIN, Jun., Ph.D., F.R.S.
PROFESSOR OF ORGANIC CHEMISTRY IN THE OWENS COLLEGE

AND

F. STANLEY KIPPING, Ph.D., D.Sc. (Lond.)
LECTURER AND ASSISTANT IN THE CHEMICAL RESEARCH LABORATORY, CENTRAL TECHNICAL COLLEGE, CITY AND GUILDS OF LONDON INSTITUTE

J. B. LIPPINCOTT COMPANY
PHILADELPHIA
1894

PREFACE.

Our original intention was to write a small text-book on Organic Chemistry, based on the syllabus drawn up by the Science and Art Department, in the hope that it would be useful to students attending the elementary or advanced classes in the subject, and not without value to teachers as a handy book of reference. As, however, it soon became apparent that, by making comparatively few additions, the subject-matter might be made to include the facts usually dealt with in a course of about sixty lectures, the scope of the work was enlarged to this extent, so as at the same time to make it more useful to general students as an introduction to Organic Chemistry.

Part I., which deals with the fatty compounds, contains, in the first place, a general account of the methods most frequently employed in the separation, purification, and analysis of organic compounds, and in the determination of molecular weight. The preparation and properties of typical compounds are then described, attention being directed to those changes which come under the heading of general reactions rather than to isolated facts regarding particular substances. Questions of constitution are also discussed at some length, and in the case of most of the typical compounds, the facts on which the given constitutional formula is based are specifically mentioned. This course was adopted, not only in order to avoid the introduction of a long chapter on structure at an earlier stage, but also because, in our opinion, a constant use of constitutional formulæ, accompanied by a clear conception of their meaning, is one of the greatest helps, even to a beginner, in committing the facts to memory.

A considerable proportion of the text, dealing as a rule either with matters of less importance or of a more advanced nature, is printed in small type, and should be left out of consideration until the rest of the subject-matter has been mastered, or, at any rate, studied. The consideration of the 'summary and extension' at the conclusion of some of the more important chapters, should also be postponed until the student has acquired some knowledge of the subject, as the method here adopted is not well suited to the requirements of a beginner.

One of the principal objects throughout has been to treat the subject from a practical point of view (as far as this could be done in a text-book on theoretical chemistry), because, unless a thorough course of practical work accompanies the theoretical, no really satisfactory progress can be made. The student should himself perform many of the simple exercises involved in the purification and analysis of organic compounds, and should prepare typical substances in order to become practically acquainted with their properties. Such general operations as oxidation, reduction, hydrolysis, nitration, sulphonation, &c., and the more important general reactions for the identification of the several classes of compounds, should also be included in the practical course.

In many respects we have made free use of the excellent text-books of V. Meyer and Jacobson and von Richter, of Beilstein's *Handbuch*, and of Ost's *Lehrbuch der technischen Chemie*. We are also much indebted to Dr A. Harden for help in revising the proof-sheets and in preparing the index.

CONTENTS.

ORGANIC CHEMISTRY.

PART I.

CHAPTER I.

COMPOSITION, PURIFICATION, AND ANALYSIS OF ORGANIC COMPOUNDS.

Origin and Present Meaning of the Term 'Organic.'—Although spirits of wine, sugar, fats, and other substances obtained directly or indirectly from animals or plants have always claimed a large share of attention from chemists, their investigation met with only slight success until towards the close of the last century, when the composition of many of these natural products was established by the French chemist Lavoisier (1743–94). Lavoisier it was who first showed that vegetable substances are generally composed of carbon, hydrogen, and oxygen, whilst animal substances, although consisting for the most part of the same three elements, frequently contain nitrogen, and sometimes phosphorus and sulphur.

The peculiar composition of these natural products, and the fact that they behaved differently from mineral compounds, led to the belief that all animal and vegetable substances were produced under the influence of some peculiar **vital** force, and that their formation was regulated by laws quite different from those which governed the formation of mineral substances; consequently, it was thought impossible to prepare any animal or vegetable product artificially or synthetically in the laboratory.

For these reasons compounds obtained from animals and plants—that is to say, directly or indirectly from living *organisms*—were called **organic**, and were classed separately from **inorganic** or mineral substances.

This distinction between organic and inorganic compounds appears to have been generally accepted until 1828, when Wöhler succeeded in obtaining urea, an excretion of certain animal organisms, from ammonium cyanate, a substance which was at the time considered to be inorganic or mineral, because it could be produced in the laboratory; this synthesis showed conclusively that the influence of a living organism was not necessary for the production of the 'organic' substance urea.

After this important discovery it was soon found that many other so-called 'organic' substances could be prepared in the laboratory from 'inorganic' materials without the help of a vital force, and ultimately it came to be generally acknowledged that the formation of 'organic' and 'inorganic' substances is governed by precisely the same laws.

The supposed difference between the two classes of compounds having been shown to be purely an imaginary one, the terms 'organic' and 'inorganic' lost their original meaning; they are, nevertheless, still made use of in the classification of chemical compounds. The atoms of carbon are distinguished from those of all other elements by their extraordinary capability of combining with one another and with hydrogen to form compounds, such as CH_4, C_6H_6, $C_{10}H_8$, &c., the molecules of which are often composed of a very large number of atoms; the atoms of other elements, however, rarely combine with hydrogen to form more than one or two compounds, and have only to a very limited extent the power of combining with one another. In consequence of the properties just mentioned, carbon forms a larger number of compounds than any other element, and, speaking generally, these compounds are related to one another, but widely different to those of other elements.

For these reasons it is convenient to consider the carbon compounds separately, and to distinguish them by the term *organic*, which recalls the fact that carbon is a most important constituent of all animal and vegetable substances; organic chemistry, therefore, is the *chemistry of the carbon compounds.*

Some of the simpler compounds of carbon, such as carbon dioxide, carbon monoxide, carbon bisulphide, &c., which are of general importance, are always described in works on inorganic chemistry for the sake of convenience; they are, nevertheless, organic compounds, because they contain carbon.

Composition of Organic Compounds.—In spite of their great number, organic compounds are almost always comparatively simple in composition, being made up, as a rule, of not more than four or five elements.

Organic substances, such as sugar, starch, and tartaric acid, which occur in the vegetable kingdom, almost invariably consist of carbon, hydrogen, and oxygen, although a few—morphine and strychnine, for example—contain nitrogen as well. Those occurring in the animal kingdom generally contain nitrogen as well as carbon, hydrogen, and oxygen: urea and uric acid, for instance, are composed of these four elements; a few animal substances also contain sulphur and phosphorus.

Artificially prepared organic compounds may contain any element. Some—benzene, for example—are composed of carbon and hydrogen only, but the majority contain oxygen as well; nitrogen and the halogens are very often present in carbon compounds produced in the laboratory; so also are the metals calcium, sodium, silver, &c., which form salts with organic, just as they do with inorganic acids.

General Principles of Organic Analysis.—The qualitative analysis of organic compounds is carried out by methods quite different from those employed in the case of inorganic substances. Most organic compounds are insoluble in water and in acids, and could not be examined by the ordinary wet methods of analysis: even those which are soluble do not show, except in rare cases, a sufficiently characteristic behaviour to enable them to be identified by their reactions. There is, again, this wide difference between inorganic and organic analysis, that, whereas a mixture of inorganic compounds may be directly submitted first to qualitative and then to quantitative examination, in the case of a mixture of carbon compounds it is usually necessary to separate and purify each constituent before its composition can be determined.

* For these reasons organic analysis usually consists of several processes: Firstly, the substance is submitted to a preliminary qualitative examination, the object of which is to find out how many distinct compounds are present, and to separate and purify each of them. The nature of each constituent is then determined; this may sometimes be done by proving it to be identical with some known compound by methods to be described later. If this be impossible, a further qualitative examination is made to ascertain what elements the substance contains; the pure compound is then submitted to quantitative or elementary analysis, from the results of which its percentage composition is obtained.

Separation and Purification of Organic Compounds.—The separation of a pure organic compound from a mixture of any kind is often a matter of considerable difficulty, and it is usually necessary to employ different processes for different mixtures. Although, therefore, it is impossible to give a method which would be applicable in every case, the more important steps in the general examination and purification of organic substances may be briefly indicated.

In the case of any substance of unknown composition, a small portion is ignited on platinum foil, in order to ascertain

---

* Generally speaking, portions of the text which are printed in smaller type are intended only for those who have already acquired an elementary knowledge of organic chemistry.

whether it contains inorganic matter; if it leaves a non-combustible residue, it is probably a salt of some organic acid, or it contains inorganic compounds as impurity.

The separation of an organic from an inorganic substance can usually be accomplished by shaking or boiling the substance with some solvent, such as alcohol, ether, benzene, chloroform, petroleum, &c. Most organic compounds are soluble in one or other of these liquids, whereas the majority of inorganic compounds are insoluble, or nearly so. Water or dilute acids may often be employed for the same purpose, since many inorganic substances are soluble, many organic substances insoluble, in these liquids.

The separation of two or more organic substances may sometimes be effected in a similar manner. In the case of a mixture of cane-sugar, tartaric acid, and benzoic acid, for example, the last-named compound only can be dissolved out with ether, the tartaric acid being then separated from the sugar by treating with alcohol, in which it is much more readily soluble than sugar.

Solid or liquid organic substances in aqueous solution, or suspended in water in a fine state of division, may often be isolated by agitating the solution or mixture with some solvent, such as ether, benzene, chloroform, &c., which does not mix with water. For this purpose a **separating funnel** (fig. 1) is employed, and after being shaken vigorously, the mixture is allowed to stand until it forms two layers; the two solutions are now separated by turning the stopcock (*a*, *a′*) and running off that which is underneath, the extraction being repeated, if neces-

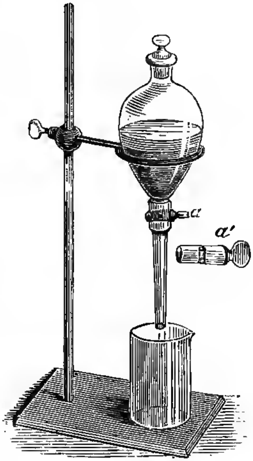


Fig. 1.

sary, with a fresh quantity of the organic solvent. The combined extracts are then dried (p. 17), and the solvent distilled or slowly evaporated.

The process of **crystallisation** is one of the simplest and best methods of separating and purifying organic substances, but before it can be successfully employed, a suitable solvent must be found. About a centigram of the substance is boiled for a short time in a test tube with 1–2 c.c. of some solvent (such as water, ether, alcohol, carbon bisulphide, benzene, light petroleum, &c.), and, if necessary, the hot liquid is filtered from any insoluble matter; if, on cooling, the substance be deposited in crystals, the rest of the material is treated in the same way, the insoluble portion, if any, being examined separately. Should no separation of crystals take place on cooling, the solution is concentrated by evaporation, and then allowed to cool; if, again, crystals be not deposited, some other solvent is tried. The crystals ultimately obtained are collected on a filter, washed with a small quantity of the solvent, and further purified by recrystallisation.

If only one constituent of a mixture be dissolved by the liquid employed, this particular substance is obtained in a state of purity without difficulty, because the others are easily got rid of by filtration; when, however, two or more of the constituents are soluble, their further separation can usually be effected by **fractional crystallisation.** In this process, advantage is taken of the difference in solubility of the substances. On slowly cooling the hot solution, the more sparingly soluble substance is first deposited, and can be separated by filtration from the more readily soluble compound, which does not crystallise until the solution is further cooled or concentrated; the two crops of crystals are then separately redissolved, and the process repeated until each substance is obtained in a pure state, as shown by a determination of its melting-point (p. 20).

Another method extensively used in the separation and purification of organic substances, both solid and liquid, is **distillation in a current of steam.** The substance and a little water are placed in a flask (A, fig. 2) which is connected with a condenser, and heated on a water- or sand-bath; a rapid current of steam, generated in a separate vessel (B), is then passed through the mixture. The distillate, which contains the volatile organic substance in solution, or in suspension, is afterwards extracted with ether, or filtered, or treated in some other way according to circumstances. In this simple manner it is often possible to isolate a compound when all other methods fail; it is, however, only applicable in the case of the comparatively few organic substances which are **volatile in steam.** Many compounds which cannot be distilled in the ordinary way because they undergo decomposition, are volatile in steam, and pass over unchanged, even when their boiling-points are much higher than that of water.

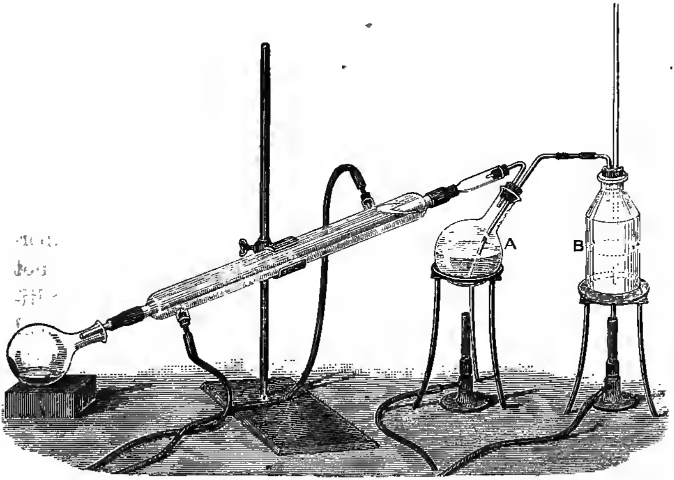


Fig. 2.

Organic substances which boil without decomposition can be purified by **distillation.** The substance is placed in a distilling flask (A, fig. 3), which is connected with a condenser, the neck of the flask being closed with a cork, through which a thermometer passes; the bulb of the thermometer is placed just below the opening of the side-tube (B), and a few scraps of unglazed porcelain or platinum are put in the distilling flask, to prevent 'bumping' or sudden ebullition. In the case of liquids which boil at temperatures above 130° or so, a long glass tube (C) without a water-jacket is used instead of a Liebig's condenser, which is apt to crack. If the compound to be purified contain only a small quantity of *non-volatile* impurities, the thermometer rises very rapidly as soon as the liquid begins to boil, but then remains practically stationary until almost the whole has distilled. Towards the end of the operation, however, it begins to rise again, and distillation is then stopped, the impurities remaining in the distilling flask. If the distillate be now transferred to a clean flask, and

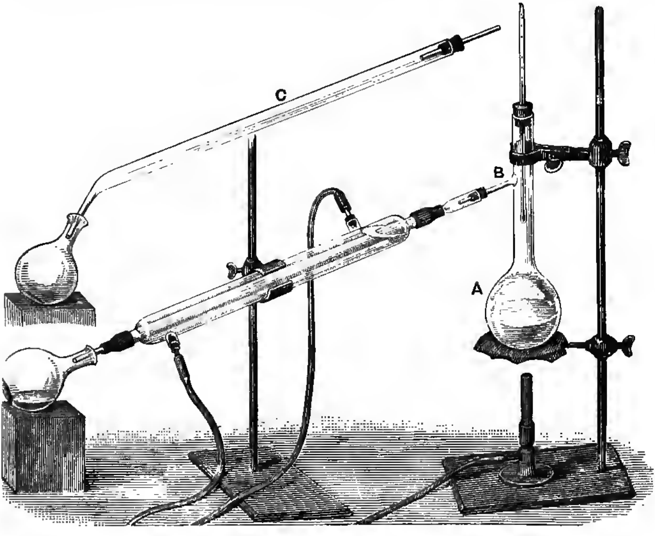


Fig. 3.

redistilled, it will boil at a constant temperature, which is the **boiling-point*** of the liquid.

All pure substances which boil without decomposition have a definite boiling-point (b.p.), which is dependent on the pressure. As the pressure diminishes, the boiling-point is lowered, so that, by carrying out the process under *reduced pressure*, it is often possible to distil a substance which would undergo decomposition under ordinary atmospheric pressure, because in the latter case it is heated more strongly.

The boiling-point is one of the most important physical constants of a substance, and affords a valuable means of identifying it. An observation of the boiling-point should always be made with an apparatus similar to that shown above, and a considerable quantity of the liquid should be distilled, in order to make sure that it has a constant boiling-point; if not, it is impure. Before distilling a substance, it should be carefully dried; in the case of liquids, this is done by shaking them with a few small pieces of fused calcium chloride, potassium carbonate, or other dehydrating agent, and then decanting or filtering.

When a mixture of two (or more) volatile substances is distilled in the manner described above, it begins to boil at some temperature lying between the boiling-points of the constituents. As distillation proceeds, the boiling-point rises, and towards the end of the operation, it usually becomes nearly the same as that of the liquid which boils at the higher temperature. In the case of a mixture of alcohol (b.p. 78·3°) and water (b.p. 100°), for example, the thermometer at first registers some temperature between 78·3 and 100° according to the proportion of the two substances, and the first portions of the distillate contain a larger proportion of alcohol than the original mixture. During distillation, the thermometer slowly and continuously rises, and at last registers 99–100°, the portions passing over at this temperature consisting of practically pure water. The change

---

* See foot-note, p. 21.

in boiling-point is due to a change in the composition of the mixture; the alcohol, being more volatile, passes off more quickly than the water. It is possible, therefore, to partially separate a mixture of liquids by collecting the distillate in portions or **fractions** at intervals of 5 or 10°, the operation being termed **fractional distillation.** By redistilling each fraction separately, a further separation is effected, and, after a sufficient number of operations, the constituents of the mixture are obtained in a practically pure condition, boiling at a constant temperature. Such a separation, however, can only be satisfactorily effected provided that there is a difference of at least 20–30° between the boiling-points of the liquids; in many cases, even when there is a greater difference than this, a complete separation cannot be accomplished.

As an illustration of the process of fractional distillation, the case of a mixture of 50 c.c. of benzene (b.p. 81°) and 50 c.c. of xylene (b.p. 140°) may be taken. The mixture begins to boil at about 87°, the thermometer rising gradually to 140°; if the receiver be changed every 10°, the following fractions are obtained:

87–100°	100–110°	110–120°	120–130°	130–140°
33 c.c.	16 c.c.	8·5 c.c.	8 c.c.	33 c.c.
(1)	(2)	(3)	(4)	(5)

The first and last are larger than the others, because the temperatures at which they are collected are approximately the boiling-points of the constituents. If, now, the fractions 1 and 5 be separately redistilled, they will yield a large fraction boiling at 81–85° and at 135–140° respectively, as well as small intermediate fractions, which are collected separately. By repeating these operations with the fractions 2, 3, and 4, a large proportion of the mixture is ultimately separated into two fractions, from which benzene and xylene respectively can be obtained in an almost pure condition by further fractional distillation.

The process of fractional distillation is greatly facilitated by employing a flask with a long neck, or by causing the mixed vapours to pass through a long vertical tube before they enter the condenser. By this means the vapour of the liquid of higher boiling-point is partially condensed, and runs back into the distilling flask instead of passing over with the more volatile liquid.

Fractional distillation is frequently carried out under reduced pressure for the reasons already stated in the case of ordinary distillation. A simple apparatus for this purpose is easily made by inserting the side-tube of one distilling flask (A, fig. 4) into the neck of a second flask (B), and connecting the side-tube (of B) with a water-pump. The liquid to be distilled is placed in A; the air is then exhausted, and the distillation carried out in the usual manner, the process being interrupted when the receiver is being changed.

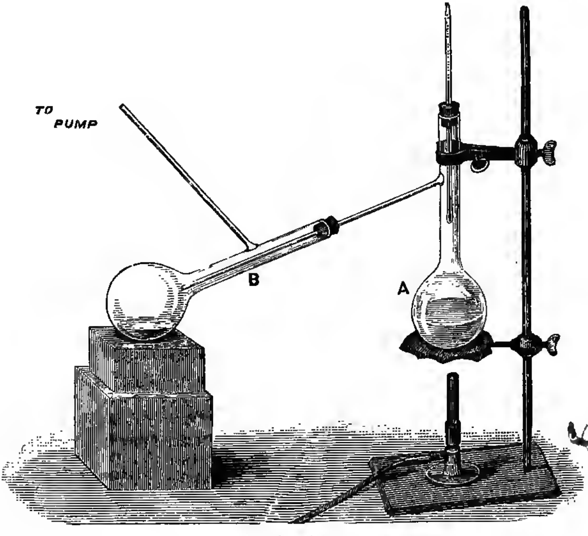


Fig. 4.

Tests of Purity.—Before attempting to determine the composition of an organic substance, its purity must be established. It would be useless to test for chlorine, for example, in an impure organic compound, since, even if a distinct indication were obtained, this element might be present (as a chloride) in the form of impurity. In the case of a compound, liquid or solid, which distils unchanged, its purity can generally be established by observing if its boiling-point is constant. A solid substance should be examined under the microscope in order to see whether it is homogeneous, and an observation of its melting-point should be made.

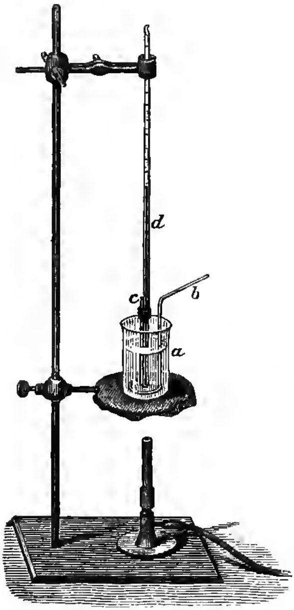


Fig. 5.

Pure substances which melt or liquefy without decomposition do so at a definite temperature, which is called the **melting-point** of the compound; when, however, the substance is impure, not only is the melting-point lowered, but it is also rendered indefinite, the mixture becoming soft and pasty at a certain temperature, and not melting completely until heated considerably above this point. The determination of the melting-point affords, therefore, a valuable test of purity, and also serves as a means of identifying a compound.

The apparatus generally employed for determining the melting-point consists of a small beaker (*a*, fig. 5) of about 50 c.c. capacity, containing concentrated sulphuric acid, and fitted with a glass stirrer (*b*). A minute quantity of the substance is placed in a capillary tube (*c*), closed below, which is attached to a thermometer (*d*) by means of a small india-rubber ring, or simply caused to adhere to it by capillary attraction. The acid is slowly heated, being constantly stirred, and the temperature at which the substance liquefies—that is to say, its melting-point (m.p.) *—is noted.

QUALITATIVE ELEMENTARY ANALYSIS.

A pure compound having been obtained, it is often possible, by noting its appearance, smell, crystalline form, solubility in various solvents, and by determining its melting- or boiling-point, to prove that it is identical with some substance the composition of which is known: when, however, this cannot be done, the next step is to ascertain of what *elements* the substance is composed.

In order, in the first place, to ascertain whether the substance contains **carbon**—that is to say, whether it really is an organic compound—a small quantity is heated on platinum foil. If it inflames and burns away, or swells up, giving a black mass, which on strongly heating entirely disappears, the substance is in all probability organic. The salts of organic acids usually char when treated in this way, and, on further heating, the carbonaceous matter burns away, leaving a residue which may be dissolved in water or acids and examined by the usual methods of inorganic analysis; sodium acetate, for example, yields sodium carbonate, silver acetate gives metallic silver, and copper acetate the oxide of the metal. If a halogen, or sulphur, be present in the acid, it is generally found in the residue in combination with the metal.

The behaviour of a substance when heated with concentrated sulphuric acid often affords an indication of the presence of carbon, as many organic substances blacken under these conditions owing to the separation of carbonaceous matter.

If neither of these tests give a decisive result, the compound is mixed with about ten times its weight of pure copper oxide, and the mixture heated to redness in a narrow tube of hard glass sealed at one end, the escaping gases being led into

---

* The *observed* melting- or boiling-point of a substance is usually rather lower than the true value, because, as a rule, the column of mercury is not wholly immersed in the heating liquid or vapour.

lime-water; under these conditions all organic substances* are decomposed, yielding carbon dioxide, the formation of which is proved by the lime-water becoming turbid.

The presence of **hydrogen** may sometimes be detected by heating the substance in a dry test tube and noticing whether any water is formed as the result of decomposition: as, however, many organic compounds do not yield water under these conditions, but simply distil unchanged, and as the detection of water itself in such small quantities is not a very simple matter, the only reliable test for hydrogen is to heat the substance with dry copper oxide in a stream of dry air or oxygen (see pp. 26–28); if hydrogen be present, it will be oxidised to water, the formation of which may be proved by passing the products of combustion through a weighed calcium chloride tube.

The presence of **chlorine, bromine**, or **iodine** in organic compounds cannot, as a rule, be detected by the methods employed in the examination of inorganic substances, as for example, by means of silver nitrate, or by heating with manganese dioxide and sulphuric acid; chloroform, for instance, contains a very large proportion of chlorine, but when pure it gives no precipitate with silver nitrate, and simply boils away when heated with manganese dioxide and sulphuric acid.

A simple but not quite conclusive test for the halogens is to take a piece of copper wire, and heat one end of it in the oxidising zone of the Bunsen flame until it is quite black and ceases to colour the flame green. A small quantity of the substance is then heated on the end of the wire in the flame, when, if a halogen be present, a green colouration is usually observed, due to the formation of a volatile halogen compound of copper. As, however, this test sometimes fails, and as, moreover, it does not give any information as to which of the halogens is present, one of the following methods is almost invariably adopted.

---

* Except the stable carbonates and cyanides of the alkalies and alkaline earths.

(*a*) A small quantity of the substance is placed in a narrow test tube, together with a bright piece of sodium (or potassium) about the size of a pea, and gently heated, care being taken, especially in the case of volatile compounds, that the metal is brought into contact with the substance and thoroughly chars it. The mixture is then heated more strongly, finally at a red heat, and after allowing to cool a little, the tube is broken by introducing the hot end into about 10 c.c. of water contained in an evaporating basin. The alkaline solution is filtered from carbonaceous matter, the filtrate acidified with pure nitric acid and a portion tested with silver nitrate; if a precipitate be formed, the presence of halogen in the original substance is proved, and its nature may be determined by submitting the rest of the solution, or the precipitate, to the usual examination. This test depends on the fact that when any organic substance containing chlorine, bromine, or iodine is heated with sodium, the halogen combines with the metal to form chloride, bromide, or iodide of sodium, which can then be tested for in the usual manner.

(*b*) A small quantity of the substance is heated with pure lime in a tube of hard glass, as described later (p. 35). The mixture is allowed to cool, carefully shaken into distilled water, the solution acidified with nitric acid, filtered from carbonaceous matter, and tested with silver nitrate. If the substance contained a halogen—chlorine, for instance—heating it with calcium oxide causes the formation of calcium chloride.

The presence of **nitrogen** in an organic substance is frequently indicated by the peculiar, unpleasant smell, like that of burning feathers, which is observed on heating the substance on platinum foil. A better test is to strongly heat a fairly large quantity of the substance with soda-lime * in a hard glass tube, when, if ammonia is evolved, the presence of

---

* Soda-lime is prepared by intimately mixing quicklime and caustic soda, and strongly heating the mixture until it is quite dry.

nitrogen is proved. As, however, certain organic compounds containing nitrogen do not yield ammonia when heated with soda-lime, the following test must be applied before the absence of nitrogen may be considered as satisfactorily proved. The substance is carefully heated with a bright piece of sodium or potassium exactly as described in testing for the halogens; the alkaline solution is filtered from carbonaceous matter, a few drops of ferrous sulphate added to the filtrate, the mixture warmed for a short time, acidified with pure hydrochloric acid, and tested with a drop of ferric chloride, when, if nitrogen were present in the original substance, a deep bluish-green coloration, or a precipitate of Prussian blue, is produced.

This test depends on the fact that the nitrogen and some of the carbon in the organic compound combine with the sodium to form sodium cyanide; when the alkaline solution of sodium cyanide is warmed with ferrous sulphate, ferrous hydrate is precipitated and sodium ferrocyanide is formed, $6NaCN + Fe(OH)_2 = Na_4Fe(CN)_6 + 2NaOH$, so that on afterwards adding a ferric salt* to the acidified solution, Prussian blue is produced.

Sulphur and **phosphorus** may be detected by gradually adding a small quantity of the substance to a fused mixture of potassium carbonate and nitre, heated on a piece of platinum foil; under these conditions the sulphur is oxidised to sulphuric acid, the phosphorus to phosphoric acid. The residue, which should be colourless, the carbon having been burned to carbon dioxide, is dissolved in water, and the solution of potassium salts tested for the above-mentioned acids in the usual way. Another method, similar in principle, consists in oxidising the substance with nitric acid in a sealed tube, as described later (pp. 33–35).

---

* During the operation some of the ferrous hydrate generally becomes oxidised to ferric hydrate, which, on acidifying with hydrochloric acid, is converted into ferric chloride; a precipitate of Prussian blue is thus at once produced.

Sulphur may also be detected by heating the substance with sodium or potassium in the manner described above, and bringing a portion of the alkaline solution into contact with a bright silver coin; if the original substance contained sulphur, an alkaline sulphide will have been produced, the presence of which will be at once recognised by the formation of a black stain on the silver coin.

QUANTITATIVE ELEMENTARY ANALYSIS.*

When the qualitative examination has been completed, the quantitative analysis may be proceeded with, but not before: the reason of this is, that the presence of certain elements necessitates a slight change in the methods to be employed, as will be shown below.

Estimation of Carbon and Hydrogen.—All organic compounds † are decomposed when brought into contact with red-hot copper oxide, or with any substance which readily gives up oxygen, the carbon being converted into *carbon dioxide*, the hydrogen into *water;* by employing a known weight of substance, and collecting and weighing these products of combustion, the percentage of carbon and hydrogen may be readily determined. The apparatus generally used for this purpose is shown in the accompanying figures.

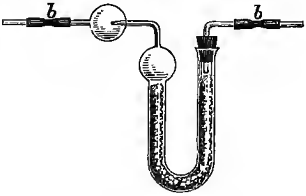


Fig. 6.

The **calcium chloride** or **drying tube** (fig. 6) is filled with granulated anhydrous calcium chloride, or with fragments of pumice moistened with concentrated sulphuric acid, and serves

---

[*] The following account of the methods most commonly adopted in the quantitative analysis of organic compounds is only intended to indicate the nature of the processes; the details of manipulation, upon which success depends, can only be learned by practice in the laboratory.

[†] With the exceptions already mentioned in the foot-note, p. 22.

to absorb the water; the **potash bulbs** (fig. 7) are partly filled, as shown, with strong potash (sp. gr. about 1·28), the small tube (*a*), which contains anhydrous calcium chloride, serving to retain the aqueous vapour which is taken up in the passage of the gases through the potash. The calcium chloride tube and the potash bulbs are carefully weighed before and after the combustion, the caps (*b*, *b*) with which they are closed being removed in both cases; the gain in weight of the former corresponds with the amount of water produced, that of the latter representing the amount of carbon dioxide absorbed.

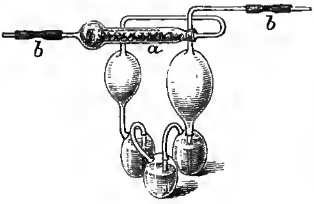


Fig. 7.

The combustion is carried out in a piece of hard glass combustion tube (*a*, *b*, fig. 8), which is usually about 90 cm. long, and open at both ends; part of the tube (*f* to *f*) is filled with a layer of granulated copper oxide kept in its place by loose asbestos plugs (*e*, *e*). Before commencing the analysis the tube is heated in a combustion furnace (*k*), at a dull red heat, a current of air, carefully freed from carbon dioxide and moisture—by passing first through potash contained in the wash bottle (*g*), and then through the two towers (*h*, *j*)* containing pumice moistened with concentrated sulphuric acid—being led through it in order that any moisture or traces of organic matter may be removed; the *empty* section of the tube (*a*, *f*) is then allowed to cool.

The drying tube (*l*) having been fitted into the end (*b*) through an india-rubber cork, and the potash bulbs (*m*) attached by means of a short piece of india-rubber tubing, 0·15 to 0·2 gram of the substance, accurately weighed out in a narrow porcelain or platinum *boat* (*d*), is introduced into the tube; a roll of platinum foil (*c*) is then placed behind

---

* In practice, two such sets of drying apparatus are usually employed, one for the air, the other for the oxygen.

the boat in order to prevent as far as possible any backward diffusion of the products of combustion. When a volatile liquid is to be analysed, the substance is weighed out in a thin glass bulb (shown on a larger scale at *n*), which is afterwards placed in the boat (at *d*).

A slow stream of air carefully freed from moisture and carbon dioxide, as before, is now passed through the tube, the combustion of the substance being started and regulated by turning on the gas taps (beginning at *c*). As soon as the whole of the tube has been gradually raised to a dull red heat, the current of air is turned off, and a stream of pure oxygen is passed, in order to burn any remaining organic matter, and to oxidise the copper which has been formed by the reduction of some of the copper oxide; finally, air is again passed until the oxygen is expelled from the apparatus. The whole operation occupies from $1\frac{1}{2}$ to 3 hours, according to the nature of the substance. The calcium chloride tube and the potash bulbs are then disconnected, their ends closed with the india-rubber caps, and allowed

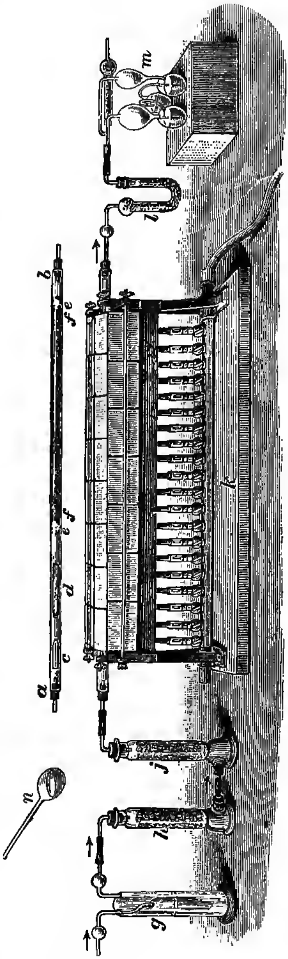


Fig. 8.

to stand for one or two hours, when they are again weighed.

Now, since the gain in weight of the potash bulbs is due to the absorption of carbon dioxide, which has been formed during the combustion, $\frac{12}{44}$ths or $\frac{3}{11}$ths (C/CO_2) of this gain in weight represents the quantity of carbon in the amount of substance taken; as also the gain in weight of the calcium chloride tube corresponds with the amount of water formed, $\frac{2}{18}$ths or $\frac{1}{9}$th (H_2/H_2O) of this increase represents the amount of hydrogen. The percentage of carbon and hydrogen may therefore be calculated.

Example.—0·1582 gram of substance gave on combustion 0·0614 gram of H_2O and 0·3620 gram of CO_2; therefore, 0·1582 gram of substance contains $0{\cdot}0614 \times \frac{1}{9} = 0{\cdot}0068$ gram of hydrogen, and $0{\cdot}3620 \times \frac{3}{11} = 0{\cdot}0987$ gram of carbon, so that 100 parts of the substance contain $\frac{0{\cdot}0068 \times 100}{0{\cdot}1582} =$ 4·31 parts of hydrogen, and $\frac{0{\cdot}0987 \times 100}{0{\cdot}1582} = 62{\cdot}40$ parts of carbon.

If the substance consist of carbon, hydrogen, and oxygen *only*, the difference between the sum of the above numbers and 100 must represent the quantity of oxygen; the percentage composition of the substance is therefore

C.........62·40 per cent.
H......... 4·31 "
O.........33·29 " (by difference).

The percentage of oxygen is always obtained by difference, there being no satisfactory method by which this element may be directly estimated.

The following points remain to be noticed in connection with the determination of carbon and hydrogen. If the substance contain *nitrogen*, it is necessary to insert a roll of bright copper gauze, about four inches long, into the front part (*b*) of the tube; this is kept red hot during the combustion, and serves to decompose any oxides of nitrogen* produced during the operation, which would otherwise be absorbed by the water in the calcium chloride tube and by the potash, and thus lead to erroneous results. When the substance contains a *halogen*, a roll of silver gauze must be used in order to prevent any halogen or halogen compound of copper from passing into the absorption apparatus; usually, in analysing a substance containing *halogens*, *sulphur*, or *phosphorus*, the space *f* to *f* (fig. 8) is filled with lumps of fused lead chromate instead of copper oxide. Lead chromate, like copper oxide, is a powerful oxidising agent at high temperatures, its action being probably represented by the equation

$$4PbCrO_4 = 4Pb + 2Cr_2O_3 + 10O.$$

Any sulphur dioxide, phosphorus pentoxide, or halogen produced during the combustion is completely retained by the lead chromate, as $PbSO_4$, $PbCl_2$, &c., and thus its passage into the absorption apparatus is prevented.

Quantitative Determination of Nitrogen.—Nitrogen may be estimated in two ways, either volumetrically by Dumas' method, or gravimetrically, as ammonia, by Will and Varrentrap's process.

1. **Volumetric Estimation by Dumas' Method.**—This process is based on the fact that when ignited with copper oxide, nitrogenous organic substances are entirely decomposed into carbon dioxide, water, and nitrogen. If the gaseous products of combustion be collected over potash, the carbon dioxide is absorbed, and the residual gas consists of practically pure nitrogen; by measuring the volume of the gas obtained

---

* $2NO_2 + 4Cu = N_2 + 4CuO$; $N_2O_3 + 3Cu = N_2 + 3CuO$. In order to render the roll of gauze as efficient as possible, it is heated in a blowpipe flame until thoroughly oxidised, and, while red hot, dropped into a little pure methyl alcohol contained in a test tube; the methyl alcohol reduces the copper oxide, giving a very bright surface of copper. The roll is then completely freed from methyl alcohol by heating at 160–180° for half an hour, just before commencing the combustion.

from a known weight of substance, the percentage of nitrogen can be readily ascertained.

The analysis is carried out in a combustion tube similar to that used in the determination of carbon and hydrogen (fig. 8), but containing in the front end (*b*) a roll of copper gauze, which serves to decompose any oxides of nitrogen formed during the combustion (see foot-note, p. 29). Instead, however, of placing the substance in a boat, the weighed quantity is intimately mixed with finely-powdered copper oxide, this mixture occupying the space *c* to *e*. Before commencing to heat the substance, a stream of carbon dioxide is passed through the tube until the air has been expelled, which is the case when the bubbles are almost entirely absorbed* in passing through the potash; at the same time the roll of copper gauze and the front part of the tube are raised to dull redness. The combustion is then started by gradually heating the mixture of substance and copper oxide, the escaping gases being either collected over mercury in a eudiometer containing potash, or more conveniently in the apparatus shown in fig. 9.

Fig. 9.

As soon as the whole of the tube has been raised to a dull or cherry-red heat, and gases cease to be evolved, a current

---

* The bubbles are never completely absorbed, as it is impossible to drive out the last traces of air.

of carbon dioxide is led through the combustion tube until the rest of the nitrogen has been expelled. The eudiometer is then closed with the thumb, inverted in a cylinder of water, and the thumb removed so that the mercury may fall out and the strong potash mix with the water. After about half an hour's time, the tube is held vertically in such a position that the level of the water inside and outside is the same, and the volume (v) of the nitrogen is observed, the temperature ($t°$) of the gas—that is, of the water surrounding the tube—and the height (P) of the barometer being also noted.

The apparatus (Schiff's nitrometer) shown in fig. 9, which is now very generally used in nitrogen determinations, consists of a graduated tube (*ac*), provided with a stopcock (*a*) and a reservoir (*d*), by means of which the tube may be filled with potash (sp. gr. 1·3), and which also serves for regulating the pressure in the apparatus; the lower part of the tube (*cb*) is filled with mercury, which forms a seal and prevents the passage of the potash into the combustion tube (*e*). After carbon dioxide has been passed through the combustion tube for a considerable time, the tube (*b*) is connected, and the reservoir (*d*) lowered. If the bubbles are almost completely absorbed as they ascend through the potash, the combustion is proceeded with, the nitrogen remaining in the tube at the end of the operation being swept into the apparatus by means of carbon dioxide, as described above. The apparatus is now placed aside for about an hour to cool; the reservoir (*d*) is then raised until the potash in it and in the tube (*ac*) is at the same level, and the volume of nitrogen (v) is read off, the temperature ($t°$) and the barometric pressure (P) being noted.

The weight of nitrogen in the quantity of substance taken is readily ascertained when its volume (in cubic centimetres) has been determined by either of the methods described. Since the volume v is measured at $t°$ under a pressure $P - w$, where w = the tension of aqueous vapour in mm. of mercury* at the temperature t°, the volume V at 0° and 760 mm. would be $v \times \frac{P - w}{760} \times \frac{273}{273 + t^\circ}$. As, now, 1 c.c. of nitrogen weighs 0·001256 gram at N.T.P.,† the weight of V c.c. will be V × 0·001256 gram.

Example.—0·2248 gram of substance gave 7·1 c.c. of nitrogen measured at 16°; P = 753·5 mm., w = 13·5 mm. The weight of the gas, therefore, is $7{\cdot}1 \times \frac{740}{760} \times \frac{273}{289} \times 0{\cdot}001256$ $= 0{\cdot}00805$ gram, and the percentage of nitrogen $\frac{0{\cdot}00805 \times 100}{0{\cdot}2248}$ $= 3{\cdot}58$.

2. **The Gravimetric Estimation of Nitrogen as Ammonia,** by Will and Varrentrap's method, depends on the fact already stated, that many nitrogenous organic substances, when heated with caustic alkalies, are decomposed in such a way that the whole of their nitrogen is converted into ammonia: by estimating the amount of ammonia produced by the decomposition of a known weight of the substance, the percentage of nitrogen can be determined.

The apparatus (fig. 10) employed for this purpose consists of a piece of hard glass tube (*ad*), about 35 cm. long, drawn out and sealed at one end (*a*); an asbestos wad is loosely fitted into the end (*a*), and the space *a* to *b* is filled with coarsely powdered soda-lime; the part *b* to *c* contains a mixture of the weighed substance and finely powdered soda-lime, the remainder of the tube (*c* to *d*) being filled with coarsely powdered soda-lime only, the whole being kept in position by an asbestos wad (at *d*).

---

* Some of the values of w which are most frequently required are the following:

t =	10°	12°	14°	16°	18°	20°
w =	9·14	10·43	11·88	13·51	15·33	17·36 mm.

When the apparatus shown in fig. 9 is employed, the vapour tension of the strong potash is much less than that of pure water; if the potash has a sp. gr. = 1·3 it is usual, in practice, to deduct from P half the tension of aqueous vapour at the temperature t.

† Normal temperature and pressure—that is, 0° and 760 mm.

The absorption apparatus (*e*) contains dilute hydrochloric acid, and serves to absorb the ammonia; it is fitted into the open end of the tube by means of an india-rubber cork. The tube is gradually heated in a combustion furnace, as in determining nitrogen volumetrically (commencing at *d*), and when the whole has been raised to a red heat, the ammonia remaining in the tube is drawn into the absorption bulb by breaking off the sealed end and aspirating air through the apparatus.

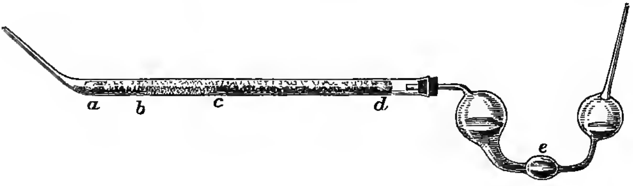


Fig. 10.

The amount of ammonia which has been produced may be determined gravimetrically by precipitation with platinic chloride, or, if a known volume of standard hydrochloric acid has been introduced into the bulbs, the quantity neutralised by the ammonia may be estimated volumetrically by titration with standard alkali.

The soda-lime method is not altogether satisfactory, because, owing to the decomposition of some of the ammonia formed during the operation, the results are usually too low. This decomposition may, to some extent, be prevented by adding a little sugar to the mixture of the substance and soda-lime. Furthermore, the method is not of universal application, as many nitrogenous organic substances, especially those belonging to the aromatic group, do not yield the whole of their nitrogen in the form of ammonia when heated with soda-lime.

Quantitative Determination of Chlorine, Bromine, and Iodine.—The halogens in an organic compound are very readily estimated by the method devised by Carius, which consists in oxidising the substance with nitric acid at a high temperature in presence of silver nitrate. Under these conditions the carbon is completely oxidised to carbon dioxide, and the hydrogen to water, the halogen combining with the silver; the chloride, bromide, or iodide of silver thus produced is collected and weighed in the ordinary way. The decomposition is carried out in a strong glass tube (*ab*, fig. 11), about 40 cm. long, sealed at one end (*a*); the substance is weighed out in a small glass receptacle, which is placed in the tube together with a few crystals of silver nitrate. Pure concentrated nitric acid having been added in quantity sufficient to fill $\frac{1}{6}$th to $\frac{1}{3}$d of the tube, the open end is drawn out and sealed, as shown at *b*. The tube is then placed in an iron case, and heated in a specially constructed apparatus (fig. 11) at a temperature necessary to ensure complete decomposition, usually at about 180°, for four hours; in the case of very stable substances, a much higher temperature and prolonged heating are required, and fuming nitric acid must be used. When *quite cold* the tube is opened,* the

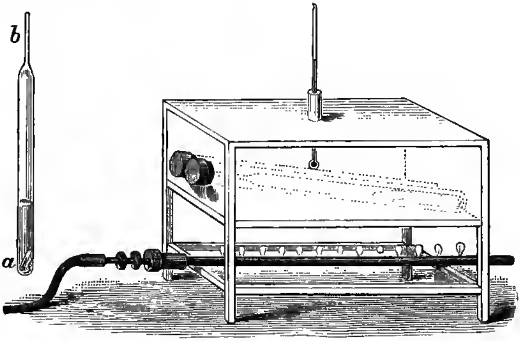


Fig. 11.

---

* Very great care must always be taken in working with sealed tubes, as they frequently explode, and serious accidents may occur. The tube is wrapped in a cloth as it is being removed from the iron case; after the pressure has been released by holding the capillary point in a flame, the tube is cut with a file in the usual way.

contents poured into distilled water, and the halogen silver salt treated in the usual way.

Another method of estimating the halogens, especially useful in the case of substances which are difficult to decompose, consists in heating the compound with pure, freshly ignited quicklime (prepared by calcining marble) in a narrow piece of combustion tube, about 50 cm. long, and closed at one end. In charging the tube a little lime is first introduced, and then the mixture of the substance with about ten times its weight of quicklime, the remainder of the tube being nearly filled with quicklime. After tapping gently to form a small channel for the passage of the gases, the tube is heated in a combustion furnace, the front part being raised to a bright red heat before the decomposition of the substance is proceeded with. When quite cold, the contents of the tube are cautiously shaken into excess of dilute nitric acid, the acid solution filtered from carbonaceous matter, and the halogen precipitated by the addition of silver nitrate.

Sulphur and **Phosphorus** may be estimated by heating the substance in a sealed tube with nitric acid, as described above, but without the addition of silver nitrate. The whole of the sulphur is oxidised to sulphuric acid, the phosphorus to phosphoric acid, which may then be estimated by the ordinary methods of analysis.

Another method for determining sulphur and phosphorus (applicable only in the case of organic acids and some non-volatile neutral compounds), consists in heating the substance with a mixture of potassium carbonate and nitre in a platinum crucible, until the product is colourless. Here, again, the substance is completely oxidised, and the sulphate or phosphate produced may be estimated in the solution of the residue.

CHAPTER II.

DEDUCTION OF A FORMULA FROM THE RESULTS OF ANALYSIS AND DETERMINATION OF MOLECULAR WEIGHT.

The quantitative analysis of an organic compound is usually made with one of two objects: either to prove that a particular compound is what it is supposed to be, or to ascertain the percentage composition of some pure substance, the nature of which is quite unknown.

In the first case, the results of the analysis are compared with the calculated percentage composition, and if the two series of values agree within the limits of experimental error, the fact is taken as evidence that the substance in question is what it was believed to be.

Example.—A substance obtained by oxidising a fat with nitric acid is suspected to be succinic acid, $C_4H_6O_4$, and, on analysis, it gives the following results: $C = 40{\cdot}56$, $H = 5{\cdot}12$, $O = 54{\cdot}32$ (by difference) per cent. Since the percentage composition of succinic acid, calculated from its formula, is $C = 40{\cdot}68$, $H = 5{\cdot}08$, $O = 54{\cdot}24$ per cent., the analysis affords strong confirmation of the conclusion previously arrived at.

In the second case, the nature of the substance being entirely unknown, it is necessary to deduce a formula from the analytical results—that is to say, to find the relative number of the atoms in the molecule of the compound.

Example.—The percentage composition of a substance is found to be $C = 84{\cdot}0$, $H = 16{\cdot}0$; deduce its formula. Since an atom of carbon weighs twelve times as much as an atom of hydrogen, the ratio between the number of *atoms* of carbon and the number of *atoms* of hydrogen is $\frac{84}{12} : \frac{16}{1}$ or 7 : 16; the formula C_7H_{16} may therefore be given to the substance, this formula having been obtained by dividing the percentage of each element by the atomic weight of that element.

Example.—The percentage composition of a substance is $C = 39{\cdot}95$, $H = 6{\cdot}69$, $O = 53{\cdot}36$; deduce its formula. Proceeding as before, the ratio between the number of atoms is found to be $3{\cdot}33 : 6{\cdot}69 : 3{\cdot}33$,

$$C = \frac{39{\cdot}95}{12} = 3{\cdot}33,\ H = \frac{6{\cdot}69}{1} = 6{\cdot}69,\ O = \frac{53{\cdot}36}{16} = 3{\cdot}33;$$

dividing now each term by 3·33 to simplify, and allowing for experimental errors, the ratio of the atoms $C : H : O = 1 : 2 : 1$; the formula obtained in this way is therefore CH_2O.

In order, then, to calculate a formula from the percentage composition, the quantity of each element is divided by the atomic weight of that element, and the ratio is then expressed in whole numbers by dividing each term by the smallest, or by some simple fraction of the smallest term.

Example.—The percentage composition of a substance is $C = 19{\cdot}88$, $H = 6{\cdot}88$, $N = 46{\cdot}86$, $O = 26{\cdot}38$; deduce its formula.

$$C = \frac{19{\cdot}88}{12} = 1{\cdot}657 \div 1{\cdot}649 = 1$$

$$H = \frac{6{\cdot}88}{1} = 6{\cdot}880 \div 1{\cdot}649 = 4$$

$$N = \frac{46{\cdot}86}{14} = 3{\cdot}347 \div 1{\cdot}649 = 2$$

$$O = \frac{26{\cdot}38}{16} = 1{\cdot}649 \div 1{\cdot}649 = 1$$

The formula, therefore, is CH_4N_2O; the ratio of the atoms determined experimentally is, of course, not exactly $1 : 4 : 2 : 1$, owing to unavoidable errors.

The formula calculated from the results of analysis is the *simplest* expression of the *ratio* of the atoms, and is termed an **empirical formula**; such a formula may, or may not, show how many atoms of each element the molecule of the substance contains, because substances such as formaldehyde, CH_2O, acetic acid, $C_2H_4O_2$, and lactic acid, $C_3H_6O_3$, have the same percentage composition, and would all be found, on analysis, to have the same empirical formula, CH_2O.

Determination of Molecular Weight.

Further investigation is necessary in order to deduce the **molecular formula** of a compound, by which is meant a formula expressing not only the ratio, but also the actual number of the atoms in the molecule; in other words, the **molecular weight** of the compound must be determined. If, for example, it can be proved that a compound of the empirical formula CH_2O has a molecular weight = 60, this fact shows that the molecular formula is $C_2H_4O_2$ ($C_2 = 24$, $H_4 = 4$, $O_2 = 32$; total 60), and not CH_2O or $C_3H_6O_3$; that is to say, the molecule consists of two atoms of carbon, four of hydrogen, and two of oxygen.

The determination of the molecular weight of a substance is therefore of great importance, and for this purpose certain physical methods, described later, are adopted whenever possible; no purely chemical methods are known by which the molecular weight can be established with certainty, although such methods often afford some indication of the probable molecular weight, as will be seen from the following examples.

Chemical Methods.—In the case of organic acids, the analysis of a salt of the acid is often of value; the silver salt is generally employed for this purpose, a weighed quantity being ignited in a porcelain crucible, when complete decomposition ensues, and a residue of pure silver is obtained.

Example.—The percentage composition of an organic acid is $C = 39{\cdot}95$, $H = 6{\cdot}69$, $O = 53{\cdot}36$; its empirical formula is therefore CH_2O. Its silver salt was prepared; 0·2960 gram of the pure salt gave on ignition 0·1620 gram of silver, so that the percentage of silver in the salt is $\dfrac{0{\cdot}1620 \times 100}{0{\cdot}2960} = 54{\cdot}73$.

Now, since 54·73 parts of silver are contained in 100 parts of the salt, 107·7 parts of silver will be contained in $\frac{100 \times 107 \cdot 7}{54 \cdot 73} = 196 \cdot 78$ parts of salt; but 107·7 is the atomic weight of silver, so that if the salt contain one atom of silver, its molecular weight must be 196·78, and, as the salt is formed from the acid by displacing 1 part of hydrogen by 107·7 parts of silver, the molecular weight of the acid must be $196 \cdot 78 - 107 \cdot 7 + 1 = 90 \cdot 08$. Since, however, the acid is composed of carbon, hydrogen, and oxygen, the atomic weights of which are all taken as whole numbers, the molecular weight of the acid must also be a whole number—that is to say, 90—the value found experimentally being not quite correct, owing to errors in the analysis. The molecular weight of the acid being 90, its *molecular formula* is not CH_2O (= 30) or $C_2H_4O_2$ (= 60), but $C_3H_6O_3$ (= 90), that of the silver salt being $C_3H_5O_3Ag$ (= 196·7).

This conclusion is based on the assumption that the silver salt contains only 1 atom of silver—that is to say, that the acid is monobasic; until this assumption is proved to be correct, the analysis of the silver salt does not establish the molecular formula of the acid. If the acid had the molecular formula $C_6H_{12}O_6$, and contained two atoms of displaceable hydrogen—that is to say, were dibasic—the silver salt $C_6H_{10}O_6Ag_2$ would contain, as before, 54·75 per cent. of silver, and the molecular weight, calculated as above, would again appear to be 90. But if the acid were dibasic, it would probably be possible to displace only one atom of hydrogen, and obtain an acid salt, $C_6H_{11}O_6Ag$, the analysis of which would point to the molecular formula $C_6H_{12}O_6$. If this were found impossible, the fact would be taken as evidence against this molecular formula, and the conclusion would be drawn that the probable molecular formula is $C_3H_6O_3$.

Most organic bases combine with hydrochloric acid to form salts which, like ammonium chloride, form double salts with platinic chloride and with auric chloride. These double salts usually have the composition B'_2,H_2PtCl_6, and $B',HAuCl_4$, where B′ represents one molecule of a monacid base, such as methylamine CH_5N, ethylamine C_2H_7N, &c. When these salts are ignited in a porcelain crucible, pure finely divided platinum, or gold, remains; so that the percentage of metal in the salt is very easily determined. Assuming that one molecule of the salt contains 1 atom of platinum or gold, and that the salt has the above composition, the molecular weight of the base can be calculated.

Example.—The platinum double salt (*platinochloride*) of an organic base gave on ignition 37·2 per cent. of platinum; what is its probable molecular weight? Since 37·2 parts of platinum are contained in 100 parts of the salt, 197 parts of the metal are contained in $\frac{100 \times 197}{37 \cdot 2} = 529 \cdot 4$ parts of salt, and, as 197 is the atomic weight of platinum, the molecular weight of the salt is 529·4. The molecular weight of the base (C_3H_9N) is therefore $\frac{B'_2,H_2PtCl_6 - H_2PtCl_6}{2}$ or

$$\frac{529{\cdot}4 - (2 + 197 + 212{\cdot}4)}{2} = \frac{529{\cdot}4 - 411{\cdot}4}{2} = 59.$$

As in the case of acids, so in that of bases, the molecular weight calculated from the analytical results may be incorrect, because it is not known whether the compound is a monacid base or not. Some bases are diacid, and form platinochlorides of the composition B'',H_2PtCl_6, so that a diacid base of the molecular weight 118 would yield a platinochloride containing the same percentage of platinum as the salt of a monacid base of the molecular weight 59.

It will be seen from the above examples, that, assuming that there is only one atom of any particular element in the molecule of the compound, the probable molecular weight may be calculated from the results of analysis.

This being the case, the probable molecular formula of a compound may often be determined by preparing and analysing some simple derivative.

Example.—A liquid hydrocarbon has the percentage composition C = 92·31, H = 7·69; its empirical formula is therefore CH. On treating this hydrocarbon with bromine, it yields hydrogen bromide and a bromo-derivative consisting of C = 45·86, H = 3·18, Br = 50·96 per cent. The empirical formula of this derivative is

$$\left.\begin{array}{l} \mathrm{C} = \dfrac{45{\cdot}86}{12} = 3{\cdot}82 \div 0{\cdot}637 = 6 \\ \mathrm{H} = \dfrac{3{\cdot}18}{1} = 3{\cdot}18 \div 0{\cdot}637 = 5 \\ \mathrm{Br} = \dfrac{50{\cdot}96}{80} = 0{\cdot}637 \div 0{\cdot}637 = 1 \end{array}\right\} = C_6H_5Br.$$

Now since, from experience, there are strong grounds for supposing that the number of atoms of carbon in the molecule is not changed on treating with bromine, the probable molecular formula of the hydrocarbon is C_6H_6; it cannot be less than this, but it may be greater. A hydrocarbon $C_{12}H_{12}$, for example, might give a bromo-derivative $C_{12}H_{10}Br_2$, and these compounds would have the same percentage composition as C_6H_6 and C_6H_5Br respectively.

The probable molecular weight may often be deduced with tolerable certainty by studying the methods of formation, and the chemical and physical properties of a substance. When, for example, acetone is distilled with concentrated sulphuric acid, it is converted into a hydrocarbon which, on analysis, is found to have the empirical formula C_3H_4. The fact that this hydrocarbon boils at 163° affords very strong evidence that the molecular formula is not C_3H_4, or C_6H_8, but probably C_9H_{12}, because other hydrocarbons which contain only 3 or 6 atoms of carbon boil at a temperature much below 163°, and an increase in molecular weight is generally accompanied by a rise in boiling-point.

Physical Methods.—One of the most important physical methods by which the molecular weight of a compound can be ascertained is by determining its vapour density. This method is based on the hypothesis that equal volumes of all gases measured under the same conditions of temperature and pressure, contain the same number of molecules (Avogadro's Law). If, therefore, the weights of equal volumes of various gases be determined under the same conditions, these weights must be in the same proportion as the weights of the molecules of the gases. In other words, the molecular weight of a substance can be determined by ascertaining the weight of a given volume of the vapour of the substance, compared with the weight of the same volume of hydrogen measured under the same conditions. The former divided by the latter is the *specific gravity* or *vapour density* (V.D.) of the gas compared with hydrogen as unity.

Now, since the vapour density is a number expressing how many times a given volume of the gas is heavier than the same volume of hydrogen, it also expresses how many times one molecule of the substance is heavier than one *molecule* of hydrogen (= 2), because equal volumes contain an equal number of molecules. The molecular weight, on the other hand, is a number expressing how many times one molecule of the substance is heavier than one *atom* of hydrogen (= 1); therefore the molecular weight is double the vapour density, because the standard with which it is compared is half as great: M.W. = V.D. × 2.

Sometimes air is taken as unit weight in stating the specific gravity or vapour density of a gas; since air is 14·43 times heavier than hydrogen, the sp. gr. compared with air is $\frac{1}{14{\cdot}43}$ of the value when compared with hydrogen; so that, in order to obtain the molecular weight, the sp. gr. is in such cases multiplied by $28{\cdot}86 = 2 \times 14{\cdot}43$.

Determination of Vapour Density.

The vapour density of a substance is ascertained experimentally, (*a*) by measuring the volume occupied by the vapour of a known weight of the substance at known temperature and pressure, or (*b*) by ascertaining the weight of a known volume of the vapour of the substance at known temperature and pressure. The observed volume of the vapour is then reduced to 0° and 760 mm., and the weight of a volume of hydrogen at 0° and 760 mm. equal to the corrected volume of the vapour is calculated; the weight of the vapour divided by that of the hydrogen is the vapour density.

Example.—An organic liquid has the empirical formula $C_4H_{10}O$; 0·062 gram of the liquid gave 23·2 c.c. of vapour at 50° and 720 mm., what is its molecular formula?

$$\text{The volume at } 0^\circ \text{ and } 760 = 23{\cdot}2 \times \frac{720}{760} \times \frac{273}{273+50} = 18{\cdot}57 \text{ c.c.}$$

and 1 c.c. of hydrogen at N.T.P. weighs 0·0000896 gram; therefore 18·57 c.c. weigh 0·00164 gram.

$$\frac{\text{The weight of the vapour}}{\text{The weight of the hydrogen}} = \frac{0{\cdot}062}{0{\cdot}00164} = 37{\cdot}7 = \text{V.D.}$$

$$\text{The molecular weight} = \text{V.D.} \times 2 \text{ or } 37{\cdot}7 \times 2 = 75{\cdot}4.$$

Since the molecular weight of a compound of the empirical formula $C_4H_{10}O$ is calculated to be 74, the determination of the vapour density proves that the molecular formula of the liquid is $C_4H_{10}O$, so that in this case the empirical is identical with the molecular formula. The molecular weight determined experimentally from the vapour density frequently differs from the theoretical value by several units, owing to experimental errors; this, however, is of little importance, since all that is required in most cases is to decide between multiples of the empirical formula, in the above example, between $C_4H_{10}O = 74$, $C_8H_{20}O_2 = 148$, &c.

The determination of the vapour density is only possible when a substance can be converted into vapour without decomposition under the conditions of the experiment. In many cases, however, a non-volatile compound, or a compound which cannot be vaporised without decomposition, can be converted into some simple derivative which is volatile, so that, by determining the vapour density of the latter, the molecular weight of the parent substance can be ascertained.

The following are some of the methods employed in determining vapour density:

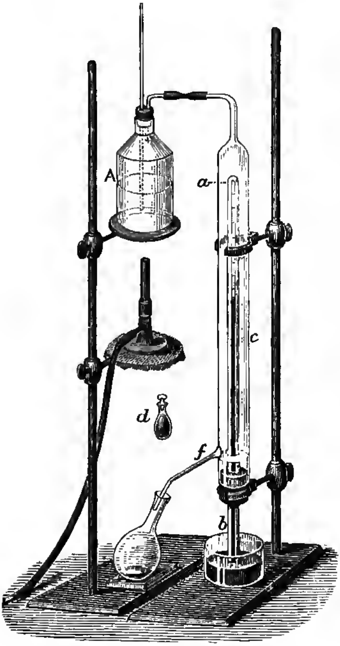


Fig. 12.

Gay-Lussac's or Hofmann's Method.—A graduated barometer tube (*ab*, fig. 12), about 85 cm. long, and 35 mm. wide, filled with and then inverted in mercury, is surrounded by a wider tube (*c*), through which the vapour of some liquid boiling at a known and constant temperature is passed. For this purpose the upper end of the outer tube (*c*) is connected with a vessel (A), usually made of copper, containing the heating liquid, which is kept in rapid ebullition. The liquids most commonly employed are water (b.p. 100°), xylene (b.p. 140°), aniline (b.p. 183°), and ethyl benzoate (b.p. 213°). The condensed liquid escapes through the side-tube (*f*), and is collected for subsequent use.

As soon as the barometer tube is at a constant temperature, a weighed quantity (about 0·05 gram) of the substance contained in a small stoppered vessel (*d*), which it fills completely, is introduced into the open end (*b*). The vessel immediately rises to the surface of the mercury in the tube, the substance vaporises into the Torricellian vacuum, and the mercury is forced downwards; as soon as the level remains stationary, the *volume* of the vapour is noted. The *temperature* of the vapour is the boiling-point of the liquid employed to heat the barometer tube. The *pressure* is determined by subtracting the height of the column of mercury in the inner tube (*ab*), above the level in the trough, from the height of the barometer, both readings having been first reduced to 0°.* The *weight* of the vapour is that of the substance taken.

The great advantage of this method lies in the fact that it affords a means of determining the vapour density of substances under greatly reduced pressures, and therefore at temperatures very much below their ordinary boiling-points, so that it can often be employed with success in the case of substances which are only volatile without decomposition under reduced pressure.

Dumas' Method.—A globe-shaped vessel of about 200 c.c. capacity (*a*, fig. 13), the neck of which is drawn out to a fine tube, is carefully weighed, the temperature ($t'°$) and pressure (P′) being noted. A fairly large quantity of the substance (about 8–10 grams) is now introduced by gently heating the globe and quickly dipping the tube into the liquid. The vessel is then immersed in an oil-bath (shown in section in fig. 13) containing a thermometer (*b*), and heated at a constant temperature, at least 20° above the boiling-point of the compound. The air in the apparatus is quickly expelled by the rapid vaporisation of the substance, and the vessel is filled with the vapour of the liquid. As soon as the whole of the liquid has been vaporised, which is known by the fact that gas ceases to issue from the fine tube, the point of the latter is sealed before the blowpipe, the *temperature* of the oil-bath ($t°$) and the *height of the barometer*

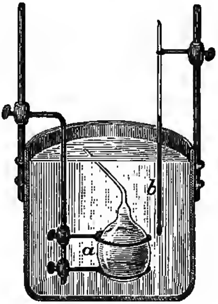


Fig. 13.

---

* By correcting for the expansion of the mercury.

(P) being noted. The globe is allowed to cool, and is then cleaned, dried, and weighed.

The point of the tube is now broken under water (or mercury), which rushes in and fills the globe completely, except for the minute quantity of liquid produced by the condensation of the vapour in the globe; the globe is again weighed, and its capacity or *volume* (v) calculated from the weight of the water contained in it, the weight in grams being equivalent to the volume in c.c. The volume may also be measured directly by transferring the liquid from the globe to a graduated vessel.

When the globe is weighed the first time it is full of air, but at the second weighing it is full of vapour; if, therefore, the first weight be subtracted from the second, the difference, W, is the weight of the volume, v, of vapour *less* the weight of the volume, v, of air.* The weight of the air is calculated by reducing the volume, v, at t'° and P′ to N.T.P., and multiplying by 0·001293, the weight of 1 c.c. of air at N.T.P.; this weight added to W gives the weight of the volume, v, of vapour at t° and P. The volume, v, of vapour at t° and P is then reduced to N.T.P., the weight of an equal volume of hydrogen at N.T.P. calculated, and divided into the weight of the vapour.

Victor Meyer's Method.—Owing to its simplicity, and the rapidity with which the determination may be made, this method is now used whenever possible; the apparatus is represented in fig. 14. The bulb tube (*ab*) is closed (at *a*) by means of an india-rubber stopper, and heated by the vapour of some constant boiling liquid† contained in the outer vessel (*c*); as the air expands it escapes through the narrow tube (*d*), which dips under the water in the vessel (*e*). As soon as the

---

* Changes in the temperature of the air, height of the barometer, and volume of the globe occurring during the experiment may be neglected.

† See page 44; in determining the vapour density of substances of high boiling-point, diphenylamine (b.p. 310°) or sulphur (b.p. 448°) may be used, or the bulb tube (*ab*) may be heated at a constant temperature in a metal bath.

temperature of the bulb tube (*ab*) becomes constant—that is to say, when bubbles of air cease to escape (from *d*)—the graduated tube (*g*) is filled with water and inverted over the end of *d*; the stopper (*a*) is now removed, and a small bottle or bulb (*d*, fig. 12) completely filled with a weighed quantity (about 0·1 gram) of the liquid dropped into the apparatus,* the stopper being replaced as quickly as possible. The substance immediately vaporises, and the vapour forces the air out of the apparatus into the graduated vessel (*g*). When air ceases to issue (from *d*), the stopper (*a*) is at once taken out to prevent the water (in *e*) from passing into the apparatus.

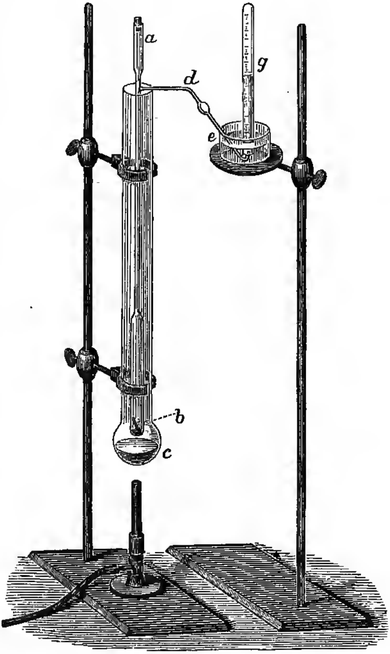


Fig. 14.

The *volume* of the vapour is ascertained by measuring the volume (*v*) of the air in the graduated tube, its *temperature* (t°) and the barometric *pressure* (P) being noted. The volume of the air (in *g*) is not the same as that actually occupied by the hot vapour (in *ab*), because the air displaced has been cooled, and is measured under a different pressure. Its volume now is equal to that which the given weight of vapour would

---

* In order to prevent fracture, a little mercury or sand is usually placed in *b*.

occupy under the same conditions of temperature and pressure.

The temperature of the volume, v, of air being t°, and the height of the barometer P, the volume at N.T.P. would be $v \times \frac{273}{273 + t} \times \frac{P - w}{760}$, w being the tension of aqueous vapour at t° (foot-note, p. 32). The weight of an equal volume of hydrogen at N.T.P. is then calculated and divided into the weight of the substance taken; the vapour density is thus obtained.

Determination of Molecular Weight from the depression of the freezing-point of a solvent.—When sugar is dissolved in water, the solution freezes at a lower temperature than pure water, and the extent to which the freezing-point is lowered or depressed is, within certain limits of concentration, directly proportional to the weight of sugar in solution; 1 part of sugar, for example, dissolved in 100 parts of water depresses the freezing-point about 0·058°—that is to say, the solution freezes at $-$ 0·058° instead of at 0°, the freezing-point of pure water; 2 parts of sugar dissolved in 100 parts of water lower the freezing-point 0·116°, 3 parts 0·174°, and so on.

Solutions of other organic compounds in other solvents, such as acetic acid, benzene, &c., behave in a similar manner, and, in sufficiently dilute solutions, the depression of the freezing-point is (approximately) proportional to the number of molecules of the dissolved substance in a given weight of the solvent, and independent of the nature of the substance. If, then, molecular proportions of various substances be separately dissolved in a given (and sufficiently large) quantity of the same solvent, the depression of the freezing-point is the same in all the solutions, but different with different solvents. In other words, if the molecular weight in grams of any substance be dissolved in 100 grams of a given solvent, the depression of the freezing-point is a constant quantity, K, which is termed the molecular depression of that solvent.

When, therefore, this constant has been determined for any solvent, the molecular weight, M, of a substance can be ascertained by observing the depression of the freezing-point of a sufficiently dilute solution, containing a known quantity of the substance. If 1 gram of the substance were dissolved in 100 grams of the solvent, the observed depression, D, would be $K \times \frac{1}{M}$, because K is the depression produced by the molecular weight in grams—that is to say, by M grams—and the depression varies directly with the weight of dissolved substance. If, again, P grams of the substance were dissolved in 100 grams of the solvent, the depression, $D = K \times \frac{P}{M}$; hence the molecular weight $M = \frac{K \times P}{D}$, so that K and P being known, if the depression be ascertained experimentally, the molecular weight, M, can be calculated.

This method of determining the molecular weight of organic compounds was first applied by Raoult, and is usually known as Raoult's or the *cryoscopic method.* The observation is usually made with the aid of the apparatus devised by Beckmann (fig. 15) in the following manner: A large tube (A), about one inch in diameter, and provided with a side-tube (B), is closed with a cork (C), through which pass a stirrer (*a*) and a thermometer (*b*) graduated to $\frac{1}{100}°$. A weighed quantity (about 25 grams) of the solvent is placed in the tube, which is then fitted into a wider tube (D), which serves as an air-jacket and prevents a too rapid change in temperature. The apparatus is now introduced through a hole in the metal plate (E) into a vessel which is partly filled with a liquid, the temperature of which is about 5° lower than the freezing-point of the solvent. The solvent (in A) is now constantly stirred, when the thermometer rapidly falls and sinks below the freezing-point of the solvent, until the latter begins to freeze; the thermometer now rises again, but soon becomes stationary at a temperature which is the *freezing-point of the solvent.* A weighed quantity of the substance is now introduced through the side-tube (B), and after first allowing the solvent to melt completely, the *freezing-point of the solution* is ascertained as before. The difference between the two freezing-points is the depression (D); the molecular weight of the substance is then calculated with the aid of the above formula.

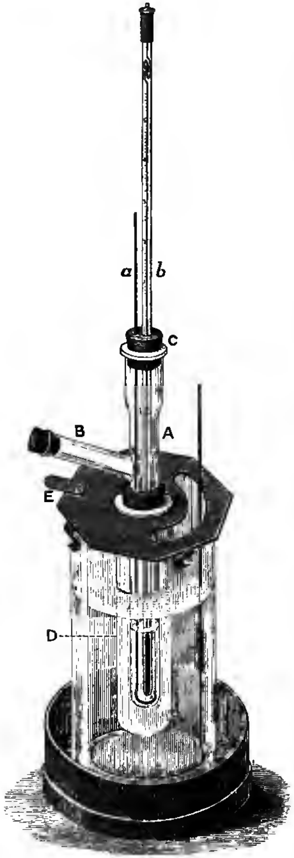


Fig. 15.

Example.—4·9818 grams of cane-sugar ($C_{12}H_{22}O_{11}$) dissolved in 96·94 grams of water caused a depression in the freezing-point of 0·295° (D). Since 96·94 grams of the solvent contain 4·9818 grams of substance P, the quantity in 100 grams = 5·139 grams. The constant, K, for water is 19; hence the molecular weight, M, of cane-sugar is found to be $\frac{19 \times 5{\cdot}139}{0{\cdot}295}$ = 331, the true value being 342.

As in the determination of molecular weight from the vapour density, the experimental and theoretical values frequently differ by several units, this is of little importance for the reasons already stated.

The constants, K, for the solvents most frequently used are: acetic acid, 39; benzene, 49; water, 19.

CHAPTER III.

CONSTITUTION OR STRUCTURE OF ORGANIC COMPOUNDS.

Even when the molecular formula of an organic compound has been established by the methods described in the foregoing pages, the most difficult and important steps in the investigation of the substance have still to be taken.

Many cases are known in which two or more compounds have the same molecular formula, and yet are different in chemical and physical properties; there are, for example, two compounds of the molecular formula $C_2H_4O_2$, three of the molecular formula C_5H_{12}, and so on. Now, if the properties of a compound depended simply on the nature and number of the atoms of which it is composed, there could not be two or more different substances having the same molecular formula.

The only possible conclusion to be drawn from the proved existence of such compounds is, therefore, that the difference between them is a difference in **constitution**; in other words, that the atoms of which their molecules are composed are differently arranged.

There is nothing at all improbable in this conclusion: in the case of simple inorganic compounds, the behaviour of any particular atom depends on the nature of the other atoms or groups of atoms with which it is united. The hydrogen atoms in ammonia, NH_3, for example, are not, but the hydrogen atoms in sulphuric acid, H_2SO_4, are displaceable by zinc, and the only difference between them is a difference in their state of combination. It is just the same in the case of organic compounds; the state of combination determines the behaviour of the atoms, and therefore the properties of the compound depend on the state of combination of all the atoms of which its molecule is composed.

Now, although the actual arrangement or structure of the molecule cannot be directly determined, it is possible to obtain some idea of the state of combination of the atoms by studying the chemical behaviour of the compound. Methyl alcohol, CH_4O, for example, is readily acted on by sodium, yielding a compound of the composition CH_3NaO, which is formed by the displacement of one hydrogen atom (*a*) by one atom of the metal; the other three hydrogen atoms in methyl alcohol cannot be displaced, no matter how large a quantity of sodium be employed. Again, when methyl alcohol is treated with hydrogen chloride under certain conditions, one atom of hydrogen and one atom of oxygen are displaced by one atom of chlorine, a compound of the composition CH_3Cl being formed,

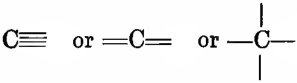
$$CH_4O + HCl = CH_3Cl + H_2O.$$

When this compound is heated with water, it is transformed into methyl alcohol, one atom of chlorine being displaced by one atom of oxygen and one atom of hydrogen; the change is, in fact, the reverse of that represented above.

From these and other experiments it is concluded that methyl alcohol contains one atom of hydrogen (*a*) combined differently from the other three; also that one atom of hydrogen is closely associated with the oxygen atom, because the two are constantly displaced and replaced together; as, further, the compound CH_3Cl does not contain a hydrogen atom which can be displaced by sodium, it is concluded that the particular hydrogen atom (*a*) in methyl alcohol which is displaceable by sodium is the same as that which is closely associated with the oxygen atom. These conclusions may be expressed by the formula $CH_3(OH)$.

Now any compound, such as ethyl alcohol, C_2H_6O, propyl alcohol, C_3H_8O, &c., which behaves like methyl alcohol under the same conditions, may be assumed to contain one atom of hydrogen and one atom of oxygen in the same state of combination as in methyl alcohol, and may be represented by formulæ such as $C_2H_5(OH)$, $C_3H_7(OH)$, &c.; in other words, the constitution of any compound may be ascertained by comparing its behaviour under various conditions with that of some compound of known constitution. Atoms or groups of atoms which are found to show the same behaviour are considered to be in a similar state of combination. In this way it is possible to determine the state of combination of many or of all the atoms of which the molecule is composed, and then, by using suitable formulæ, not only the state of combination or constitution, but also the chemical behaviour, of the substance may be expressed. Formulæ employed for this purpose are called **rational** or **constitutional** formulæ.

Another way of representing compounds is by means of **graphic formulæ,** the object of which is to express still more fully and clearly the constitution and chemical behaviour of the substance. Before giving examples of the use of graphic formulæ, it will be necessary to consider the molecular formulæ of some of the simpler organic compounds. For this purpose attention may be directed in the first place to compounds such as (*a*) CH_4 and $CHCl_3$; (*b*) CO_2 and COS; (*c*) $COCl_2$; and (*d*) HCN, which contain only one atom of carbon in the molecule. In all these compounds the atom of carbon is combined with (*a*) 4 monovalent or monad atoms, (*b*) 2 dyad atoms, (*c*) 1 dyad and 2 monad atoms, or (*d*) 1 triad and 1 monad atom—that is to say, with four monad atoms or their valency equivalent. With the doubtful exception of carbon monoxide, CO,* no compound containing only one carbon atom is known, in which the carbon atom is combined with *more* or *less* than four monad elements or their valency equivalent; carbon, therefore, is *tetravalent,* and this fact may be expressed by writing its symbol,



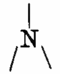
$$\mathrm{C}\text{≣} \quad \text{or} \quad =\mathrm{C}= \quad \text{or} \quad -\overset{|}{\underset{|}{\mathrm{C}}}-$$

or in any other way, four lines being drawn simply to express its tetravalent character.

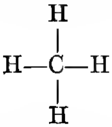
For similar reasons the monovalent hydrogen atom may be

---

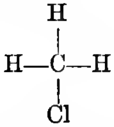
* Oxygen may be assumed to be a tetrad in CO.

represented by H—, divalent oxygen by O= or —O—, trivalent nitrogen by N≡ or  $\overset{|}{\mathrm{N}}\!\!\diagup\,\diagdown$, and so on, the number of lines serving to recall the valency of the atom.

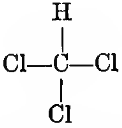
If, now, in the case of substances such as CH_4, CH_3Cl, $CHCl_3$, in which the carbon atom is united with four monad atoms, each of the latter be placed at the extremity of one of the four lines which represent the valency of carbon, the following formulæ are obtained:



$$\begin{array}{c}\mathrm{H}\\ |\\ \mathrm{H—C—H}\\ |\\ \mathrm{H}\end{array}$$



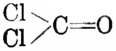
$$\begin{array}{c}\mathrm{H}\\ |\\ \mathrm{H—C—H}\\ |\\ \mathrm{Cl}\end{array}$$



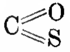
$$\begin{array}{c}\mathrm{H}\\ |\\ \mathrm{Cl—C—Cl}\\ |\\ \mathrm{Cl}\end{array}$$

If in the case of substances such as CO_2, $COCl_2$, COS, each of the dyad atoms be given two lines, the compounds will be represented by the formulæ

$O{=}C{=}O$

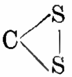


$$\begin{array}{l}\mathrm{Cl}\\ \mathrm{Cl}\end{array}\!>\!\mathrm{C{=}O}$$

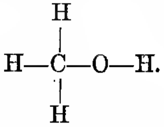


$$\mathrm{C}\!\begin{array}{l}\diagup\!\!\!\diagup \mathrm{O}\\ \diagdown\!\!\!\diagdown \mathrm{S}\end{array}$$

Similarly, HCN may be expressed by the formula $H{-}C{\equiv}N$.

Formulæ of this kind are termed *graphic formulæ.* They are intended to express in a purely diagrammatic manner the constitution of the several compounds—that is to say, the state of combination and the valency of each of the atoms in the molecule. In all such formulæ, therefore, the number of lines running to or from any given symbol must be the same as the number of monad atoms with which the element represented by that symbol is known to combine. The constitution of carbon bisulphide, for example, cannot be expressed by the formula , or that of carbon dioxide by a formula such as O—C—O, because the valency of the elements is not correctly indicated by the number of lines.

These lines are sometimes called **valencies,** more frequently **bonds** or **linkings**; in the graphic formula $H{-}C{\equiv}N$, the hydrogen atom is said to be combined with carbon by one bond or linking, the nitrogen atom by three. The hydrogen and nitrogen atoms are not directly combined, but are both united with carbon.

It must not be supposed, however, that these lines are intended to represent the actual force or attraction which causes the atoms to combine. They are simply expressions of valency or combining capacity, and may be shortened or lengthened at will without altering their significance: as a rule, they are shortened, as in the formulæ $H\cdot C\vdots N$ and $O:C:S$, or brackets are employed instead, as in $CH_3(OH)$, which signifies the same as $CH_3\cdot OH$ and  $H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-O-H$. All these, except the last, would be termed constitutional rather than graphic formulæ, but there is no sharp difference between them.

All such formulæ are based on considerations of valency and on a study of the chemical behaviour of the compounds which they represent; they express, in fact, in a concise and simple manner the most important chemical properties of the compound.

CHAPTER IV.

THE PARAFFINS, OR HYDROCARBONS OF THE METHANE SERIES.

It has already been noted that carbon differs from all other elements in forming an extraordinarily large number of compounds with hydrogen; these compounds, composed of hydrogen and carbon only, are called **hydrocarbons.**

Methane, or **Marsh-gas**, CH_4, is the simplest hydrocarbon. It is met with, as its name implies, in marshes and other places in which the decomposition or decay of vegetable matter is taking place under water. On stirring a marshy pond or swamp, bubbles consisting of marsh-gas, carbon dioxide, and other gases, frequently rise. It is one of the principal constituents of the gas which streams out of the earth in the petroleum districts of America and Russia; it also occurs in coal-mines, the gas (fire-damp) which issues from the fissures in the coal sometimes containing as much as 80–90 per cent. of methane, to the presence of which, mixed with air, explosions in coal-mines are due. Ordinary coal-gas usually contains about 40 per cent. of methane.

Methane is formed* when zinc methyl† (p. 216) is decomposed with water,

$$Zn(CH_3)_2 + 2H_2O = 2CH_4 + Zn(OH)_2.$$

It is also obtained when sulphuretted hydrogen or steam, together with the vapour of carbon bisulphide, is passed over heated copper,

$$CS_2 + 2H_2S + 8Cu = CH_4 + 4Cu_2S$$
$$CS_2 + 2H_2O + 6Cu = CH_4 + 2Cu_2S + 2CuO;$$

and by reducing carbon tetrachloride with sodium amalgam (p. 93),

$$CCl_4 + 4H_2 = CH_4 + 4HCl.$$

Since carbon bisulphide and hydrogen sulphide may be produced by the direct union of their constituent elements, and carbon tetrachloride is formed on treating carbon bisulphide with chlorine, these reactions are of considerable theoretical importance, as they afford a means of synthesising methane from its elements. They are often quoted as examples of the synthesis of an organic compound from inorganic materials, but such a view is rather misleading, because carbon and carbon bisulphide are just as truly 'organic' as methane.

---

* The words *formed*, *obtained*, and *produced* are used when the method is of theoretical importance, and not suitable for the actual *preparation* of the compound.

† Compounds, such as zinc methyl, are often unavoidably introduced long before their properties are described; in such cases references are given. The groups of atoms, CH_3-, C_2H_5-, C_3H_7-, and C_4H_9-, are termed *methyl*, *ethyl*, *propyl*, and *butyl* respectively.

Methane is prepared by heating one part of anhydrous sodium or potassium acetate with four parts of soda-lime in a hard glass tube or retort, and collecting the gas over water,

$$C_2H_3O_2Na + NaOH = CH_4 + Na_2CO_3.$$

The gas obtained in this way contains small quantities of hydrogen, ethylene (p. 72), and other impurities.

Pure methane is prepared by slowly running methyl iodide from a dropping funnel into a flask containing a zinc-copper couple* covered with dilute alcohol, to which a few drops of sulphuric acid have been added. The methyl iodide is reduced by the nascent hydrogen formed by the action of the dilute acid on the zinc-copper couple, and a constant stream of methane is obtained without application of heat,

$$CH_3I + 2H = CH_4 + HI.$$

In a similar manner, all halogen derivatives of marsh-gas (p. 171) are converted into marsh-gas on treatment with nascent hydrogen, generated from zinc and hydrochloric acid, from sodium amalgam and water, or in any other suitable manner (p. 93).

Methane is a colourless, tasteless gas; it condenses to a liquid at − 11° under a pressure of 180 atmospheres. It burns with a pale-blue, non-luminous flame, and forms a highly explosive mixture with certain proportions of air or oxygen,

$$\begin{array}{ccccccc} CH_4 & + & 2O_2 & = & CO_2 & + & 2H_2O \\ \text{2 vols.} & + & \text{4 vols.} & = & \text{2 vols.} & + & \text{4 vols.} \end{array}$$

It is almost insoluble in water, but rather more soluble in alcohol. It is very stable; when passed through bromine, potash, nitric acid, sulphuric acid, solution of potassium permanganate, and solution of chromic acid, it is not absorbed or changed in any way. When mixed with chlorine in the dark, no action takes place; but if a mixture of 1 vol. of

---

* Granulated zinc coated with a thin layer of copper by immersion in a dilute solution of copper sulphate and subsequent drying.

methane and 2 vols. of chlorine be exposed to direct sunlight, explosion ensues, and carbon is deposited,

$$CH_4 + 2Cl_2 = C + 4HCl.$$

In diffused sunlight there is no explosion, but after some time a mixture of hydrochloric acid and four other compounds is produced, the proportion of each depending on the quantity of chlorine present, and on the conditions of the experiment.

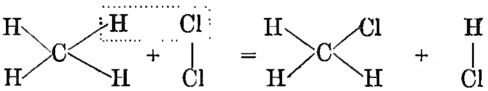
$CH_4 + Cl_2 = CH_3Cl + HCl.$
Methyl Chloride.

$CH_4 + 2Cl_2 = CH_2Cl_2 + 2HCl.$
Methylene Chloride.

$CH_4 + 3Cl_2 = CHCl_3 + 3HCl.$
Chloroform.

$CH_4 + 4Cl_2 = CCl_4 + 4HCl.$
Carbon Tetrachloride.

All these compounds are formed by the displacement of one or more hydrogen atoms by an equivalent quantity of chlorine. The carbon atom cannot combine with more than four monad atoms, so that hydrogen must be displaced if any action at all take place. Now it may be supposed that in the formation of methyl chloride, CH_3Cl, for example, one of the hydrogen atoms is drawn away from the carbon by the superior attraction of the chlorine, and that one atom of chlorine takes up the vacant place in the molecule without the other atoms being disturbed or their state of combination altered; this change may then be represented graphically thus:



In the formation of methylene chloride, CH_2Cl_2, it may be supposed that a repetition of this process occurs, and so also in the case of the other products; in other words, it may be assumed that in all the above examples the action of the chlorine is not such that the molecule of marsh-gas is completely broken up into atoms, which then, by combination with chlorine, form totally new molecules, but that certain atoms simply change places. To such changes as these, in which certain atoms are simply displaced by an equivalent quantity of other atoms, without the state of combination of the rest of the molecule being altered, the term **substitution** is applied, and the compounds formed as the result of the change are called **substitution products.**

The four compounds mentioned above are substitution products of methane and of one another: methyl chloride, CH_3Cl, is a mono-substitution product, methylene chloride, CH_2Cl_2, a di-substitution product of marsh-gas, and so on; chloroform, $CHCl_3$, is a tri-substitution product of methane, a di-substitution product of methyl chloride. If, by treatment with nascent hydrogen in the manner described above, any of these substitution products be reconverted into marsh-gas or into one another, the change would be termed **inverse substitution.**

The only way in which it is possible to produce a change in marsh-gas, or in any of its chloro-substitution products, is by a process of direct or inverse substitution. The atom of carbon already holds in combination the maximum number of atoms, and some of them must be displaced if any other atom enter the molecule. Compounds such as these, in which the maximum combining capacity of all the carbon atoms is exerted, and which can only yield derivatives by substitution, are termed **saturated.**

Ethane, ethyl hydride, or dimethyl, C_2H_6, like methane occurs in the gas which issues from the earth in the petroleum districts. It is formed when methyl chloride or methyl iodide, CH_3I, is treated with sodium,

$$2CH_3I + 2Na = C_2H_6 + 2NaI;$$

this reaction affords a means of preparing ethane from its elements, because methane can be formed from its elements, as already described, and then converted into methyl chloride by treatment with chlorine.

Ethane is also formed when zinc ethyl (p. 215) is decomposed with water,

$$Zn(C_2H_5)_2 + 2H_2O = 2C_2H_6 + Zn(OH)_2;$$

when ethylene (p. 72) is treated with nascent hydrogen,

$$C_2H_4 + 2H = C_2H_6;$$

and when methyl iodide is treated with zinc methyl,

$$2CH_3I + Zn(CH_3)_2 = 2C_2H_6 + ZnI_2.$$

Ethane is prepared by reducing ethyl iodide with the zinc-copper couple, exactly as described in the preparation of pure methane,

$$C_2H_5I + 2H = C_2H_6 + HI,$$

or by the electrolysis of dilute acetic acid, or of a concentrated aqueous solution of potassium acetate (Kolbe). When acetic acid is used, ethane and carbon dioxide are evolved at the positive, hydrogen at the negative pole,

$$\begin{array}{l} CH_3{\cdot}CO_2H \\ CH_3{\cdot}CO_2H \end{array} = \overbrace{C_2H_6 + 2CO_2} + H_2;$$

when potassium acetate is employed, the following decompositions occur:

$$\begin{array}{l} CH_3{\cdot}CO_2K \\ CH_3{\cdot}CO_2K \end{array} = \overbrace{C_2H_6 + 2CO_2} + 2K$$

and

$$2K + 2H_2O = 2KOH + H_2,$$

so that the same gases are evolved as before.

Ethane is a colourless, tasteless gas, which liquefies at 4° under a pressure of 46 atmospheres; it is practically insoluble in water, slightly soluble in alcohol. It is inflammable, burns with a feebly luminous flame, and can be exploded with air or oxygen.

$$\begin{array}{ccccccc} 2C_2H_6 & + & 7O_2 & = & 4CO_2 & + & 6H_2O \\ \text{4 vols.} & + & \text{14 vols.} & = & \text{8 vols.} & + & \text{12 vols.} \end{array}$$

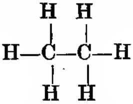
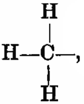
It is very stable, and is not acted on by alkalies, nitric acid, sulphuric acid, bromine, or oxidising agents at ordinary temperatures. When mixed with chlorine and exposed to diffused sunlight, it gives various substitution products, 1, 2, 3, 4, 5, or 6 atoms of hydrogen being displaced by an equivalent quantity of chlorine.

$C_2H_6 + Cl_2 = C_2H_5Cl + HCl$ Ethyl Chloride. $C_2H_6 + 2Cl_2 = C_2H_4Cl_2 + 2HCl$ Ethylene Chloride.

$$C_2H_6 + 6Cl_2 = C_2Cl_6 + 6HCl.$$

Perchlorethane.

Ethane, like methane, cannot combine directly with chlorine or with any element; it is a saturated compound.

The *constitution* of ethane may be deduced theoretically in the following manner: the two atoms of carbon must be directly united, because hydrogen, being monovalent, cannot link the two carbon atoms together; as, moreover, carbon is tetravalent, one of the six hydrogen atoms must be placed at the end of each of the remaining six lines; in this way the graphic formula  $\begin{array}{ccccc} & H & & H & \\ & | & & | & \\ H- & C & - & C & -H \\ & | & & | & \\ & H & & H & \end{array}$ is obtained. This view, based entirely on considerations of valency, is confirmed by a study of the methods of formation and properties of ethane. When methyl iodide is treated with sodium or with zinc methyl, the metal combines with the halogen, and a group of atoms, CH_3-, is left; as, however, carbon is tetravalent, this group  $\begin{array}{ccc} & H & \\ & | & \\ H- & C & - \\ & | & \\ & H & \end{array}$, like the atom of hydrogen H-, cannot exist alone, and immediately combines with a similar group forming ethane, CH_3-CH_3, or dimethyl, which is a saturated compound, because all the carbon atoms in the molecule are exerting their maximum valency or combining capacity.

Propane, propyl hydride, or methyl-ethyl, C_3H_8, occurs in petroleum, and can be obtained by reducing propyl iodide or isopropyl iodide (p. 178) with zinc and hydrochloric acid, or with the zinc-copper couple,

$$C_3H_7I + 2H = C_3H_8 + HI.$$

It is also obtained by treating a mixture of ethyl and methyl iodides with sodium,

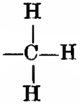
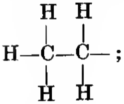
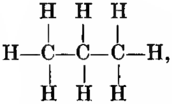
$$C_2H_5I + CH_3I + 2Na = C_3H_8 + 2NaI,$$

and by treating zinc ethyl with methyl iodide,

$$Zn(C_2H_5)_2 + 2CH_3I = 2C_3H_8 + ZnI_2.$$

Propane is a gas, and closely resembles methane and ethane in chemical properties. It condenses to a colourless liquid at temperatures below − 17° under ordinary atmospheric pressure. It burns with a more luminous flame than ethane. When treated with chlorine in diffused sunlight, it yields propyl chloride and other substitution products, one or more hydrogen atoms being displaced,

$$C_3H_8 + Cl_2 = C_3H_7Cl + HCl.$$

Constitution.—Since propane is produced by the action of sodium on a mixture of methyl and ethyl iodides, and also by the action of zinc ethyl on methyl iodide, it is concluded that propane is formed by the combination of  $-\overset{H}{\underset{H}{C}}-H$ and  $H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-$; its constitution is therefore represented by the formula  $H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$, or $CH_3\cdot CH_2\cdot CH_3$, and it may be regarded as derived from ethane, just as ethane may be considered as derived from methane, by substituting the monovalent group of atoms CH_3- for one atom of hydrogen.

Butanes, C_4H_{10}.—Two hydrocarbons of the molecular formula C_4H_{10} are known. One of them, **butane**, diethyl or methyl-propyl, occurs in petroleum, and can be obtained by treating ethyl iodide with sodium,

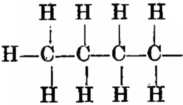
$$2C_2H_5I + 2Na = C_4H_{10} + 2NaI.$$

The other, **isobutane**, or trimethylmethane, is formed when tertiary butyl iodide (p. 178) is treated with nascent hydrogen,

$$C_4H_9I + 2H = C_4H_{10} + HI.$$

These two hydrocarbons have been proved to have the same molecular formula, but to be different in properties. Although they are both gases under ordinary conditions, butane liquefies at about 0°, isobutane not until about $-17°$ under atmospheric pressure, so that they are certainly distinct substances. In chemical properties they closely resemble propane and one another. They give substitution products with chlorine, but the compounds obtained from butane are not identical with those produced from isobutane, although they have the same molecular formula.

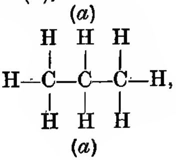
Constitution of the two Butanes.—The production of butane from ethyl iodide in the above-mentioned manner indicates that this hydrocarbon is di-ethyl. It is therefore represented by the formula



$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}H}$$, or $C_2H_5 - C_2H_5$, or $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_3$,

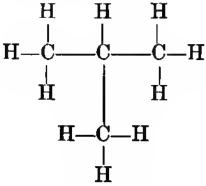
Butane.
(I.)

which not only brings to mind the method of formation of the hydrocarbon, but also indicates its relation to propane. Butane, in fact, may be regarded as propane in which one atom of hydrogen has been displaced by the monovalent CH_3- group. When, however, the graphic formula of propane is carefully considered, it will be seen that the eight atoms of hydrogen are not all in the same state of combination relatively to the rest of the molecule, but that two of them (*a*),

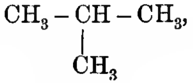


$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{\overset{(a)}{H}}{\underset{\underset{(a)}{H}}{C}}{-}\overset{H}{\underset{H}{C}}{-}H}$$, or $CH_3 - \underset{(a)}{CH_2} - CH_3$, or $\underset{(a)}{CH_2}(CH_3)_2$

are united with a carbon atom which is itself combined with two carbon atoms, whereas each of the other six atoms of hydrogen is combined with a carbon atom which is united with only one other. If, then, one of the (*a*) hydrogen atoms be displaced by a CH_3– group, the constitution of the product would be represented by the formula



or



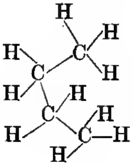
$$CH_3 - \underset{\underset{\displaystyle CH_3}{|}}{CH} - CH_3,$$

or $CH(CH_3)_3$

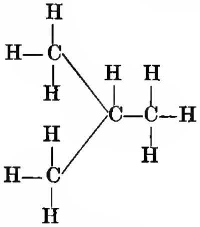
Isobutane.
(II.)

whereas, if one of the other hydrogen atoms were displaced, a hydrocarbon of the constitution represented by formula I. would be formed. As in these two cases the atoms would not all be in the same state of combination, the properties of the compounds represented by these formulæ would be different.

It is next important to note that the above two are the only formulæ which can be constructed with four atoms of carbon and ten atoms of hydrogen, if it be assumed that carbon is tetravalent and hydrogen monovalent. All formulæ such as



or

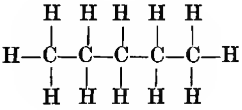


will, on examination, be found to be identical with I. or II., as they express the same state of combination. Since, then, formula I. represents the constitution of butane, that of isobutane or trimethylmethane is expressed by formula II. This conclusion is confirmed by a study of the methods of formation and chemical behaviour of isobutane.

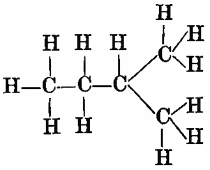
Pentanes.—Three hydrocarbons of the molecular formula C_5H_{12} are known; two of them—namely **pentane** (b.p. 37°), and **isopentane** (b.p. 30°)—occur in petroleum, and are colourless mobile liquids. The third, **tetramethylmethane** (b.p. 9·5°), can be obtained by treating tertiary butyl iodide with zinc methyl,

$$2(CH_3)_3CI + Zn(CH_3)_2 = 2(CH_3)_3C \cdot CH_3 + ZnI_2.$$

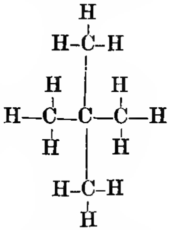
For reasons similar to those stated in the case of the simpler hydrocarbons, the constitutions of the three pentanes are represented by the formulæ



Pentane.



Isopentane.



Tetramethylmethane.

They may all be regarded as derived from the butanes (pentane and isopentane from normal butane, tetramethylmethane from isobutane) by the substitution of a CH_3– group for one atom of hydrogen.

Isomerism.—Compounds, such as the two hydrocarbons C_4H_{10}, and the three hydrocarbons C_5H_{12}, which have respectively the same molecular formula, but different properties, are said to be **isomeric.** The phenomenon is spoken of as **isomerism,** and the compounds themselves are called **isomers** or **isomerides.** Isomerism is due to a difference in constitution or arrangement of the atoms.

When graphic formulæ are employed to represent the constitutions of the hydrocarbons, it will be found possible to construct as many different formulæ as there are isomerides. It is possible, for example, to construct three different graphic formulæ for a substance of the molecular formula C_5H_{12}, and three isomerides only are known; more could not be represented by graphic formulæ, assuming always that carbon is tetravalent. This agreement between theoretical conclusions and observed facts is strong evidence of the tetravalent character of carbon.

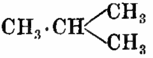
Ethane may be regarded as derived from methane, propane from ethane, and the butanes from the propanes by substituting the monovalent group of atoms CH_3– for one atom of hydrogen, and, theoretically, this process can be continued without limit. If one hydrogen atom in each of the three pentanes be displaced by a CH_3– group, a number of isomeric hydrocarbons, C_6H_{14}, would be obtained, from each of which, by a repetition of the same process, at least one hydrocarbon, C_7H_{16}, might be formed, and so on. It is evident then, that, theoretically, a great number of hydrocarbons may exist, and, as a matter of fact, very many have actually been isolated from petroleum (p. 70). As the number of carbon atoms in the molecule increases, the number of possible isomerides rapidly becomes larger; 7 isomerides of the molecular formula C_7H_{16}, 18 of the formula C_8H_{18}, and no less than 802 of the formula $C_{13}H_{28}$ could, theoretically, be formed. In many cases, all the possible isomerides have not been prepared, but there can be little doubt that they could be obtained by suitable reactions.

The several isomerides are usually distinguished by the terms *normal* or *primary*, *iso-* or *secondary*, and *tertiary*. A normal or primary hydrocarbon is one in which no carbon atom is directly combined with more than two others, as, for example,

$CH_3\cdot CH_2\cdot CH_2\cdot CH_3$ Normal Butane.

$CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_3$. Normal Hexane.

A secondary or iso-hydrocarbon contains at least one carbon atom directly united with three others,



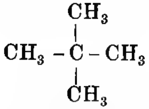
$CH_3\cdot CH<\begin{matrix}CH_3\\CH_3\end{matrix}$

Isobutane or Trimethylmethane.

$\begin{matrix}CH_3\\CH_3\end{matrix}>CH\cdot CH<\begin{matrix}CH_3\\CH_3\end{matrix}$

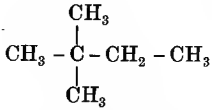
Di-isopropyl.

A tertiary hydrocarbon contains at least one carbon atom directly combined with four others,



$$\begin{array}{ccccc} & & CH_3 & & \\ & & | & & \\ CH_3 & - & C & - & CH_3 \\ & & | & & \\ & & CH_3 & & \end{array}$$

Tertiary Pentane
(or Tetramethylmethane).



$$\begin{array}{ccccccc} & & CH_3 & & & & \\ & & | & & & & \\ CH_3 & - & C & - & CH_2 & - & CH_3 \\ & & | & & & & \\ & & CH_3 & & & & \end{array}$$

Tertiary Hexane
(or Trimethylethylmethane).

In the case of iso- and tertiary hydrocarbons, it is convenient to use a name which readily expresses the constitution of the compound; examples of such names are given above in brackets.

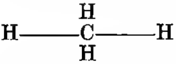
The hydrocarbons methane, ethane, propane, &c., are not only all produced by similar reactions, but they also show very great similarity in chemical properties; for these reasons they are classed together as the **paraffins**, or hydrocarbons of the methane series. The class, or generic name 'paraffin,' was assigned to this group because paraffin-wax consists principally of the higher members of the methane series. Paraffin-wax is a remarkably inert and stable substance, and is not acted on by strong acids or alkalies; the name paraffin, from the Latin *parum affinis* (small or slight affinity), was given to it for this reason.

Homologous Series.—When the paraffins are arranged in order of molecular weight, they form a series, each member of which contains one atom of carbon and two atoms of hydrogen more than the preceding member.

Methane,	CH_4	difference CH_2
Ethane,	C_2H_6	" CH_2
Propane,	C_3H_8	" CH_2
Butane,	C_4H_{10}	" CH_2.
Pentane,	C_5H_{12}	

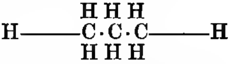
The members of this series are similar in constitution and in chemical properties; but, as the molecular weight increases, the physical properties undergo a gradual and regular variation. Such a series is termed **homologous**, and the several members are spoken of as **homologues** of one another; there are many homologous series of organic compounds.

General Formulæ.—The molecular composition of all the members of a homologous series can be expressed by a **general formula.** In the case of the paraffin series the general formula is C_nH_{2n+2}, which means, that in any member containing n atoms of carbon in the molecule, there are $2n + 2$ atoms of hydrogen; in propane, C_3H_8, for example, $n = 3$; $2n + 2 = 8$. That this is so can be readily seen by writing the graphic formulæ of some of the paraffins in the following manner:



$\mathrm{H}\text{———}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\text{———}\mathrm{H}$

$\mathrm{H}\text{———}\overset{\mathrm{H\,H}}{\underset{\mathrm{H\,H}}{\mathrm{C\cdot C}}}\text{———}\mathrm{H}$



$\mathrm{H}\text{———}\overset{\mathrm{H\,H\,H}}{\underset{\mathrm{H\,H\,H}}{\mathrm{C\cdot C\cdot C}}}\text{———}\mathrm{H}$

when it is at once obvious that for every atom of carbon there are two atoms of hydrogen, the molecule containing, in addition, two extra hydrogen atoms.

Since the members of a homologous series can, as a rule, be obtained by similar or *general methods*, if these be given it is usually unnecessary to describe the preparation of each member separately. In view, also, of the great similarity in chemical properties, a detailed account of each compound may be omitted if the *general properties* of the members of the series be described; the physical properties may also be treated in a general manner, since they undergo a regular and gradual variation as the molecular weight increases.

The following is a summary of the principal facts relating to the paraffins treated in this way; it will be found advantageous to omit this and other summaries until some knowledge of other series has been acquired.

SUMMARY AND EXTENSION.

The Paraffin or Methane Series.—Saturated hydrocarbons of the general formula C_nH_{2n+2}. The more important members of the series are the following, the number of possible isomers being indicated by the figures in brackets:

Methane (1),	CH_4	Hexane (5),	C_6H_{14}
Ethane (1),	C_2H_6	Heptane (9),	C_7H_{16}
Propane (1),	C_3H_8	Octane (18),	C_8H_{18}
Butane (2),	C_4H_{10}	Nonane (35),	C_9H_{20}
Pentane (3),	C_5H_{12}	Decane (75),	$C_{10}H_{22}$

Nomenclature.—The names of all the hydrocarbons of this series have the distinctive termination **ane**, those of the higher members having prefixes which denote the number of carbon atoms in the molecule.

Occurrence.—The paraffins are found in nature in enormous quantities as petroleum or mineral naphtha, in smaller quantities as natural gas, and as earth-wax, or ozokerite.

Methods of Preparation.—(1) By the dry distillation of an alkali salt of a fatty acid (p. 142) with potash, soda, or soda-lime,

$$CH_3\cdot COONa + NaOH = CH_4 + Na_2CO_3$$
$$C_3H_7\cdot COOK + KOH = C_3H_8 + K_2CO_3.$$

(2) By the action of nascent hydrogen on the alkyl* halogen compounds,

$$CH_3Cl + 2H = CH_4 + HCl$$
$$C_2H_5I + 2H = C_2H_6 + HI.$$

(3) By the action of sodium or zinc on the alkyl halogen compounds (Frankland),

$$2C_2H_5I + 2Na = C_2H_5\cdot C_2H_5 + 2NaI$$
$$2CH_3I + 2Na = CH_3\cdot CH_3 + 2NaI.$$

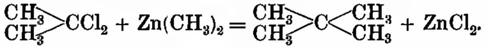
(4) By decomposing the zinc alkyl compounds (p. 215) with water,

$$Zn(CH_3)_2 + 2H_2O = 2CH_4 + Zn(OH)_2$$
$$Zn(C_3H_7)_2 + 2H_2O = 2C_3H_8 + Zn(OH)_2.$$

(5) By the action of the alkyl halogen compounds on the zinc alkyl derivatives,

$$2CH_3I + Zn(CH_3)_2 = 2CH_3\cdot CH_3 + ZnI_2$$
$$2CH_3I + Zn(C_2H_5)_2 = 2CH_3\cdot C_2H_5 + ZnI_2.$$

Tertiary hydrocarbons, such as tetramethylmethane, may be similarly prepared by acting with the zinc alkyl compounds on certain dihalogen derivatives of the paraffins (p. 139),



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CCl_2 + Zn(CH_3)_2 = \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C<\!\!\begin{matrix}CH_3\\CH_3\end{matrix} + ZnCl_2.$$

(6) By the electrolysis of aqueous solutions of the sodium or potassium salts of the fatty acids,

$$2CH_3\cdot COOK + 2H_2O = CH_3\cdot CH_3 + 2KHCO_3 + H_2.$$

(7) By the destructive distillation of coal, cannel, turf, shale, and other products of vegetable origin.

Physical Properties.—The first four members of the series are colourless gases under ordinary conditions, but on the application of pressure at a low temperature they condense to liquids, and the

---

* The meaning of the word *alkyl* is given on p. 115.

more readily the greater the number of carbon atoms in the molecule. Methane liquefies at – 11° under a pressure of 180 atmospheres, ethane at 4° under 46 atmospheres, butane at 0° under ordinary atmospheric pressure. The hydrocarbons containing from 4 to about 16 atoms of carbon are colourless liquids under ordinary conditions, the boiling-point rising as the series is ascended. Normal pentane boils at 37°, normal hexane at 69°, and normal heptane at 98°, the difference between the boiling-points of consecutive normal hydrocarbons being about 30°. The higher members of the series, from about $C_{16}H_{34}$ (m.p. 18°), are colourless solids, the melting-point rising with increasing molecular weight.

The specific gravity of the hydrocarbons from butane, C_4H_{10}, to octane, C_8H_{18}, varies from 0·600 to about 0·718; from octane upwards the sp. gr. increases until the solid hydrocarbons are reached, when it becomes almost constant at 0·775 – 0·780, this value being determined at the melting-point.

The paraffins are insoluble, or nearly so, in water, but soluble in alcohol, ether, and other organic liquids.

Chemical Properties.—The paraffins are all characterised by great stability. At ordinary temperatures they are not acted on by nitric acid, fuming sulphuric acid, alkalies, or such powerful oxidising agents as chromic acid and potassium permanganate, and even at higher temperatures only a very slow action occurs. They are, however, attacked by chlorine and, less readily, by bromine in sunlight with formation of substitution products. Iodine has no action on the paraffins.

The paraffins are saturated compounds, and cannot combine directly with any element.

Paraffins of Commercial Importance.—In Pennsylvania, North America, in Baku, South-east Russia, and in other parts of the world, a gas escapes from the earth under considerable pressure. This *natural gas* is variable in composition, but usually contains a large proportion of methane and hydrogen, small quantities of other gaseous paraffins, and other hydrocarbons. It is employed as a fuel at Pittsburgh in Pennsylvania for a variety of industrial purposes.

In the localities already mentioned, enormous quantities of *petroleum* or *mineral naphtha* are also obtained, either from natural springs or from artificial borings. The origin of natural gas and petroleum is unknown, but it is supposed that they are produced by the destructive distillation in the lower layers of the earth's crust of the fatty remains of (sea) animals.

Crude petroleum is specifically lighter than water, and varies greatly in consistency and colour, being generally a thick yellow or brown liquid with a greenish colour when viewed by reflected light. It consists almost entirely of a mixture of hydrocarbons, that obtained from Pennsylvania being composed chiefly of paraffins, that from Baku of hydrocarbons belonging to a different (naphthene) series.

Petroleum is not only, next to coal-gas, one of the most important illuminating agents of the present day, but is also the source of a number of substances of considerable commercial value. The crude oil is not directly employed for illuminating purposes, owing partly to the fact that it contains very volatile hydrocarbons which render it too inflammable. In order to obtain the various substances in a condition suitable to the purposes for which they are required, the crude oil is distilled from large iron vessels and the distillate collected in fractions. American petroleum, treated in this way, yields: *Petroleum ether* (b.p. 40–70°), *gasoline* (b.p. 70–90°), and *ligroin* or *light petroleum* (b.p. 80–120°), colourless mobile liquids used as solvents for resins, oils, caoutchouc, &c.; *cleaning oil* (b.p. 120–170°), employed for cleaning purposes, and as a substitute for oil of turpentine in the preparation of varnishes; *refined petroleum, kerosene*, or burning oil (b.p. 150–300°), used for illuminating purposes; the portions collected above 300° are employed as lubricating oils. The residue consists of heavy lubricating oils, *vaseline*, and tarry matter. Russian petroleum also yields a variety of products, such as *benzine*, *kerosene*, *Vulcan oil*, *vaseline*, and tarry matter, which, though slightly different in composition, are similar in properties and uses to those obtained from American oil.

Ordinary paraffin-wax is obtained from the tar which is produced by the destructive distillation of cannel-coal or shale. When this tar is fractionally distilled, it yields several liquid products similar to those obtained from petroleum—such as *photogene* and *solar oil*, which are used as solvents and for illuminating purposes—and solid paraffins, or paraffin-wax, which is purified by treatment with concentrated sulphuric acid and redistillation. Paraffin-wax is a colourless, semi-crystalline, waxy substance, soluble in ether, &c., but insoluble in water; its melting-point ranges from about 45–65°, according to its composition; its principal use is for the preparation of candles (p. 170).

Ozokerite is a naturally occurring solid paraffin or *earth-wax* which is found in Galicia and Roumania; it is purified by treatment with concentrated sulphuric acid and distillation.

CHAPTER V.

UNSATURATED HYDROCARBONS—
THE OLEFINES, OR HYDROCARBONS OF THE ETHYLENE SERIES.

When the halogen mono-substitution products of the paraffins, such as ethyl bromide (p. 176), propyl chloride, &c., are heated with an alcoholic solution of potash, they are converted into hydrocarbons,

$$C_2H_5Br + KOH = C_2H_4 + KBr + H_2O$$
$$C_3H_7Cl + KOH = C_3H_6 + KCl + H_2O.$$

The compounds obtained in this way, and by other methods to be described later, contain two atoms of hydrogen less than the corresponding paraffins, and form a homologous series of the general formula C_nH_{2n}; their names are derived from those of the corresponding paraffins by changing the termination *ane* into *ylene*,

Methane, CH_4; Ethane, C_2H_6; Propane, C_3H_8; Butane, C_4H_{10}.
—— Ethylene, C_2H_4; Propylene, C_3H_6; Butylene, C_4H_8.

The simplest member of the series is *ethylene;* the hydrocarbon CH_2 (methylene), which would correspond with methane, is unknown, and all attempts to prepare it have been unsuccessful.

The word 'olefine' is derived from 'olefiant' or 'oil-making' gas, a name originally given to ethylene on account of its property of forming an oily liquid (ethylene dichloride or Dutch liquid) with chlorine; the generic or class name 'olefine' is now applied to all the hydrocarbons of the series.

Ethylene, ethene, or olefiant gas, C_2H_4, is formed during the destructive distillation of many organic substances, and occurs in coal-gas, of which it forms about 6 per cent. by volume; the luminosity of the burning gas is to a great extent due to ethylene.

It is formed when acetylene (p. 81) is reduced with zinc dust and ammonia,

$$C_2H_2 + 2H = C_2H_4,$$

and when methylene iodide is heated with copper,

$$2CH_2I_2 + 4Cu = C_2H_4 + 2Cu_2I_2,$$

a reaction which is very similar to the formation of ethane by the action of sodium on methyl iodide (p. 59); also when ethyl bromide is heated with alcoholic potash,

$$C_2H_5Br + KOH = C_2H_4 + KBr + H_2O,$$

and when a solution of potassium succinate (p. 235) is submitted to electrolysis,

$$C_2H_4(COOK)_2 = C_2H_4 + 2CO_2 + 2K.$$

In the latter case, a mixture of ethylene and carbon dioxide is obtained at the positive pole, the alkali metal which separates at the negative pole acting on the water with liberation of hydrogen. This interesting method of formation of ethylene is similar to the production of ethane by the electrolysis of potassium acetate (p. 60).

Ethylene is prepared by heating a mixture of 1 vol. of ethyl alcohol and 6 vols. of concentrated sulphuric acid in a capacious flask (fig. 16), the gas thus produced being passed through wash-bottles containing potash, to free it from sulphur dioxide and carbon dioxide, and then collected over water; when the evolution of gas slackens, a further supply may be obtained by dropping a mixture of 1 vol. of alcohol and 2 vols. of sulphuric acid through the funnel. The reaction may be expressed by the equation

$$C_2H_5{\cdot}OH = C_2H_4 + H_2O,$$

but in reality it is not quite so simple (p. 183).

Ethylene is a colourless gas, has a peculiar sweet but not unpleasant smell, and liquefies at 10° under a pressure of 60 atmospheres; it is only sparingly soluble in water, more readily in alcohol and ether. It burns with a luminous flame, and forms a highly explosive mixture with air or oxygen,

$$\begin{array}{ccccccc} C_2H_4 & + & 3O_2 & = & 2CO_2 & + & 2H_2O \\ 2 \text{ vols.} & + & 6 \text{ vols.} & = & 4 \text{ vols.} & + & 4 \text{ vols.} \end{array}$$

Its chemical behaviour is totally different from that of the paraffins. It combines directly with hydrogen at high temperatures (in presence of spongy platinum at ordinary temperatures) forming ethane,

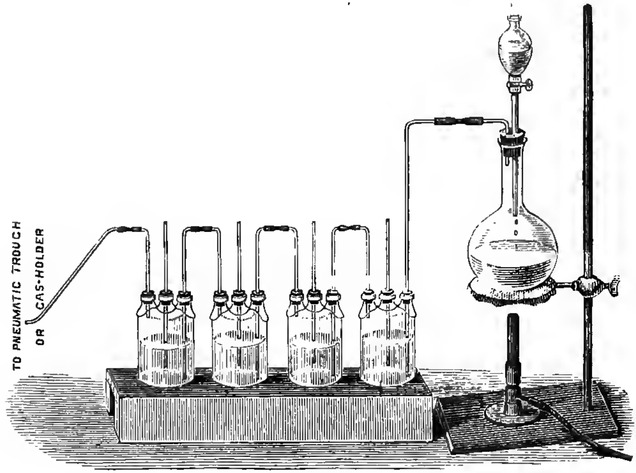


Fig. 16.

$$C_2H_4 + H_2 = C_2H_6.$$

Although it is not acted on by hydrochloric acid, it combines directly with concentrated hydrobromic and hydriodic acids at 100°, forming ethyl bromide and ethyl iodide respectively,

$$C_2H_4 + HBr = C_2H_5Br \qquad C_2H_4 + HI = C_2H_5I.$$

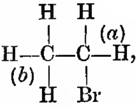
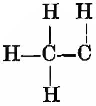
It is absorbed by, and combines with, fuming sulphuric acid, and, more slowly, with ordinary sulphuric acid, yielding ethyl hydrogen sulphate (p. 182), from which ethyl alcohol is produced on boiling with water,

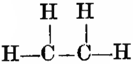
$$C_2H_4 + H_2SO_4 = C_2H_5{\cdot}HSO_4$$
$$C_2H_5{\cdot}HSO_4 + H_2O = C_2H_5{\cdot}OH + H_2SO_4.$$

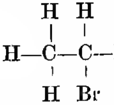
It combines directly with chlorine and bromine, and also with iodine in alcoholic solution,

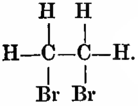
$$C_2H_4 + X_2 = C_2H_4X_2 \qquad (X = Cl, Br, I).$$

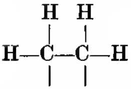
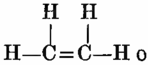
Constitution of Ethylene.—Ethylene is formed when ethyl bromide, a mono-substitution product of ethane, is heated with alcoholic potash, which simply takes away one atom of hydrogen and one atom of bromine ($C_2H_5Br = C_2H_4 + HBr$); since, therefore, the constitution of ethyl bromide is represented by the formula

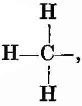
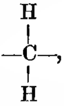
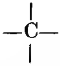

$\begin{array}{ccccc} & H & & H & \\ & | & & |^{(a)} & \\ H- & C & - & C & -H, \\ {}^{(b)} & | & & | & \\ & H & & Br & \end{array}$ that of ethylene would be 
$\begin{array}{cccc} & H & & H \\ & | & & | \\ H- & C & - & C \\ & | & & \\ & H & & \end{array}$ (I.), assuming that one of the (*a*) hydrogen atoms were taken away,


$\begin{array}{ccccc} & H & & H & \\ & | & & | & \\ H- & C & - & C & -H \end{array}$ (II.) if one of the (*b*) hydrogen atoms were removed.

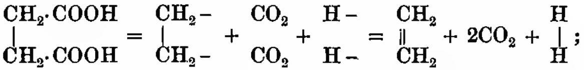
But if ethylene have the constitution (I.), ethylene dibromide $C_2H_4Br_2$ (p. 78), the compound formed by the *direct combination* of ethylene with bromine, must be represented by the formula (III.), 
$\begin{array}{ccccc} & H & & H & \\ & | & & | & \\ H- & C & - & C & -Br, \\ & | & & | & \\ & H & & Br & \end{array}$ because, from the behaviour of the paraffins, it is known that the carbon atom in the CH_3- group cannot combine with bromine except by substitution. As, however, a substance $C_2H_4Br_2$ (ethylidene dibromide, p. 78), whose constitution must be represented by the formula (III.), is known, and is not identical with ethylene dibromide,

the latter cannot have the same constitution, but must be represented by the only alternative formula  $\mathrm{H{-}\underset{\underset{Br}{|}}{\overset{\overset{H}{|}}{C}}{-}\underset{\underset{Br}{|}}{\overset{\overset{H}{|}}{C}}{-}H}$.

This being the case, the constitution of ethylene might be expressed by formula (II.). But such a formula does not indicate that carbon is tetravalent, nor does it recall the fact that ethylene combines directly with Cl_2, Br_2, HBr, &c. These deficiencies might be remedied by writing ethylene  $\mathrm{H{-}\underset{|}{\overset{\overset{H}{|}}{C}}{-}\underset{|}{\overset{\overset{H}{|}}{C}}{-}H}$ to show that the carbon atoms are tetravalent, but that their combining capacity is not fully exercised; this formula would express the fact that each of the carbon atoms has still the power of combining with one monad atom or group. It is usual, however, to represent the constitution of ethylene by the formula  $\mathrm{H{-}\overset{\overset{H}{|}}{C}{=}\overset{\overset{H}{|}}{C}{-}H}$ or $CH_2 = CH_2$ or $CH_2{:}CH_2$, the two carbon atoms being joined by two lines, **bonds**, or **linkings**; this formula is not quite the same as that just given, because it indicates that the particular portion of the combining power of each of the carbon atoms, which before was represented as doing nothing, or free, is in some way exerted in 'satisfying,' or combining with, the other carbon atom.

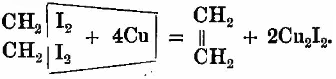
There are at least two very good reasons for writing the formula in this way and not with unoccupied lines, or **free bonds**; firstly, because it has been found impossible to prepare hydrocarbons such as  $\mathrm{H{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}}$,  $\mathrm{{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}}$, or  $\mathrm{{-}\underset{|}{\overset{|}{C}}{-}H}$, a fact which indicates that no carbon compound, in which the maximum combining capacity of the carbon atom or atoms is not exerted in some way, can exist; secondly, because whenever a compound contains one carbon atom which is not combined with the maximum quantity of four monad atoms or their valency equivalent, the carbon atom directly united with it is in the same 'unsatisfied' condition. One has never been found to exist without the other, and so it is assumed that they have some action on one another.

The above view of the constitution of ethylene receives support from the formation of the gas by the electrolysis of succinic acid, as is clearly seen if the decomposition be represented thus:



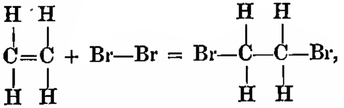
$$\begin{array}{l}CH_2\cdot COOH\\ |\\ CH_2\cdot COOH\end{array} = \begin{array}{l}CH_2-\\ |\\ CH_2-\end{array} + \begin{array}{c}CO_2\\ \\ CO_2\end{array} + \begin{array}{c}H-\\ \\ H-\end{array} = \begin{array}{c}CH_2\\ \|\\ CH_2\end{array} + 2CO_2 + \begin{array}{c}H\\ |\\ H\end{array};$$

again, the formation of ethylene by the action of copper on methylene iodide can only be explained on the assumption that ethylene has this constitution,



$$\begin{array}{l}CH_2\\ CH_2\end{array}\left|\begin{array}{l}I_2\\ I_2\end{array} + 4Cu\right| = \begin{array}{c}CH_2\\ \|\\ CH_2\end{array} + 2Cu_2I_2.$$

All organic compounds, which, like ethylene, contain carbon atoms having the power of combining directly with other atoms or groups, are said to be **unsaturated.** In the graphic formulæ of all such substances, these particular carbon atoms are represented as joined by a **double bond** or **double linking.** When an unsaturated compound enters into direct combination, the double bond is said to be broken, and the two carbon atoms, which before were written with two lines between them, are now joined by only one; the combination of ethylene with bromine, for example, is expressed graphically,



$$\begin{array}{c}H\quad H\\ |\quad\ |\\ C{=}C\\ |\quad\ |\\ H\quad H\end{array} + Br{-}Br = Br{-}\begin{array}{c}H\quad H\\ |\quad\ |\\ C{-}C\\ |\quad\ |\\ H\quad H\end{array}{-}Br,$$

to show that ethylene dibromide, like the paraffins, is a saturated substance, and cannot combine except by substitution.

The substances formed by the direct union of unsaturated compounds with atoms or groups of atoms are called **additive products,** in contradistinction to substitution products. Unsaturated compounds always combine with 2, 4, 6, &c. monovalent atoms or groups, because they always contain an even number of unsaturated carbon atoms.

Derivatives of Ethylene.—*Ethylene dichloride*, $C_2H_4Cl_2$, or $CH_2Cl{\cdot}CH_2Cl$, was originally called Dutch liquid, or oil of Dutch chemists, by whom it was discovered. It is obtained by the direct combination of ethylene and chlorine, and is a colourless liquid of sp. gr. 1·28 at 0°, boiling at 85°. It is isomeric with ethylidene chloride, $CH_3{\cdot}CHCl_2$ (p. 139). *Ethylene dibromide*, $C_2H_4Br_2$, or $CH_2Br{\cdot}CH_2Br$, is prepared by passing ethylene into bromine until the colour of the latter disappears; the product is purified by fractional distillation. It is a colourless crystalline substance, melts at 9·5°, and boils at 131°; its sp. gr. is 2·21 at 0°. It is isomeric with ethylidene bromide, $CH_3{\cdot}CHBr_2$.

Substitution products of ethylene, such as *chlorethylene* or *vinyl chloride*, $CH_2{:}CHCl$, *bromethylene* or *vinyl bromide*, $CH_2{:}CHBr$, cannot be obtained by treating ethylene with a halogen, because additive products are produced in this way. They are prepared by heating the halogen additive products of ethylene with alcoholic potash,

$$CH_2Br{\cdot}CH_2Br + KOH = CH_2{:}CHBr + KBr + H_2O.$$

Vinyl chloride is a gas, vinyl bromide a colourless liquid, boiling at 16°; they are unsaturated compounds, and combine directly with Br_2, HBr, &c.

Propylene or methyl-ethylene, C_3H_6, or $CH_3{\cdot}CH{:}CH_2$, is formed by the dehydrating action of phosphorus pentoxide on propyl alcohol (p. 104),

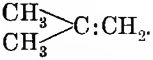
$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}OH = CH_3{\cdot}CH{:}CH_2 + H_2O.$$

It is prepared by boiling either propyl or isopropyl bromide with alcoholic potash,

$$\left.\begin{array}{ll}\text{Propyl bromide,} & CH_3{\cdot}CH_2{\cdot}CH_2Br\\ \text{Isopropyl bromide,} & CH_3{\cdot}CHBr{\cdot}CH_3\end{array}\right\} = CH_3{\cdot}CH{:}CH_2 + HBr.$$

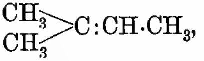
It is a gas very similar to ethylene in properties; it liquefies at ordinary temperatures under a pressure of 7–8 atmospheres, and being an unsaturated compound, combines readily with bromine, forming *propylene dibromide*, $CH_3{\cdot}CHBr{\cdot}CH_2Br$, an oily liquid boiling at 141°.

The higher members of the olefine series are obtained by methods similar to those employed in the case of propylene. Three isomeric **butylenes** of the molecular formula C_4H_8 are known, namely,

$CH_3{\cdot}CH_2{\cdot}CH{:}CH_2$	$CH_3{\cdot}CH{:}CH{\cdot}CH_3$	 $\begin{matrix}CH_3\\CH_3\end{matrix}\!>C{:}CH_2.$
Normal or α-butylene.	β-Butylene.	Iso- or γ-butylene.

They are all colourless gases, and combine directly with chlorine, bromine, hydrobromic acid, &c.

Five isomeric **amylenes** or **pentylenes**, C_5H_{10}, are known, the most important being *trimethylethylene* or *β- iso-amylene*,

 $\begin{matrix}CH_3\\CH_3\end{matrix}\!>C{:}CH{\cdot}CH_3$, which is obtained by treating fusel oil (pp. 99, 104–5) with zinc chloride; it is a colourless liquid, and boils at 32°.

SUMMARY AND EXTENSION.

The Olefine or **Ethylene Series.**—Unsaturated hydrocarbons of the general formula C_nH_{2n}. The following are the more important members of this series, the number of possible isomerides being given in brackets:

Ethylene (1),	C_2H_4	Amylene (5),	C_5H_{10}
Propylene (1),	C_3H_6	Hexylene (13),	C_6H_{12}.
Butylene (3),	C_4H_8		

Methods of Preparation.—By the action of dehydrating agents, such as H_2SO_4, $ZnCl_2$, P_2O_5, &c., on the alcohols (p. 88),

$$CH_3{\cdot}CH_2{\cdot}OH = CH_2{:}CH_2 + H_2O.$$

By the action of alcoholic potash on the alkyl halogen compounds (p. 171),

$$CH_3{\cdot}CH_2Br + KOH = CH_2{:}CH_2 + KBr + H_2O$$
$$CH_3{\cdot}CHBr{\cdot}CH_3 + KOH = CH_3{\cdot}CH{:}CH_2 + KBr + H_2O.$$

By the electrolysis of certain dibasic acids (p. 229), or, better, of their potassium salts,

$$\begin{array}{l} \mathrm{CH_2{\cdot}COOH} \\ | \\ \mathrm{CH_2{\cdot}COOH} \end{array} = \begin{array}{l} \mathrm{CH_2} \\ \| \\ \mathrm{CH_2} \end{array} + \mathrm{2CO_2 + H_2}.$$

Physical Properties.—The first four members of the series are gases; the following fourteen or so, liquids; the higher members, solids at ordinary temperatures: the boiling-point and the melting-point rise on passing up the series, as in the case of the paraffins. They are insoluble, or nearly so, in water, but more readily soluble in alcohol.

Chemical Properties.—The olefines burn with a luminous smoky flame, and can be exploded with oxygen or air. They are unsaturated hydrocarbons, and differ very considerably in chemical properties from the saturated hydrocarbons of the paraffin series; whereas the latter are either not acted on, or form substitution products when treated with Cl_2, Br_2, HCl, HBr, HClO, H_2SO_4, &c., the olefines, as a rule, readily enter into direct combination with all these substances, forming saturated additive products.

The olefines are converted into paraffins on treatment with nascent hydrogen,

$$C_nH_{2n} + 2H = C_nH_{2n+2}.$$

They combine with chlorine and bromine, sometimes with iodine, forming saturated compounds which may be regarded as di-substitution products of the paraffins,

$$\mathrm{CH_3{\cdot}CH{:}CH_2 + Cl_2 = CH_3{\cdot}CHCl{\cdot}CH_2Cl.}$$

They combine with hydrobromic and hydriodic acids, but not, as a rule, with hydrochloric acid, yielding alkyl halogen compounds,

$$\mathrm{CH_2{:}CH_2 + HBr = C_2H_5Br} \qquad \mathrm{CH_3{\cdot}CH{:}CH_2 + HI = CH_3{\cdot}CHI{\cdot}CH_3},$$

combination generally taking place in such a manner that the halogen atom unites with that carbon atom which is combined with the smallest number of hydrogen atoms; propylene, for example, yields with hydrobromic acid isopropyl bromide, $CH_3{\cdot}CHBr{\cdot}CH_3$, and not propyl bromide, $CH_3{\cdot}CH_2{\cdot}CH_2Br$; normal butylene, $CH_3{\cdot}CH_2{\cdot}CH{:}CH_2$, with hydriodic acid, gives secondary butyl iodide, $CH_3{\cdot}CH_2{\cdot}CHI{\cdot}CH_3$, and so on.

Fuming sulphuric acid, in some cases ordinary sulphuric acid, readily absorbs the olefines, forming alkyl hydrogen sulphates,

$$\mathrm{CH_2{:}CH_2 + H_2SO_4 = C_2H_5{\cdot}HSO_4.}$$

Hypochlorous acid, in aqueous solution, converts the olefines into chlorohydrins (p. 222),

$$\mathrm{CH_2{:}CH_2 + HOCl = CH_2Cl{\cdot}CH_2{\cdot}OH.}$$

Unlike the paraffins, the olefines are readily oxidised by chromic acid and potassium permanganate. When oxidation is carried out carefully under suitable conditions, products containing the same number of carbon atoms as the original olefine are obtained; ethylene, for example, giving ethylene glycol (p. 219); butylene, the corresponding butylene glycol,

$$CH_2{:}CH_2 + O + H_2O = CH_2(OH){\cdot}CH_2{\cdot}OH$$

$$CH_3{\cdot}CH_2{\cdot}CH{:}CH_2 + O + H_2O = CH_3{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH.$$

Generally speaking, when a substance contains the group $—CH = CH—$, this group, on oxidation, is in the first place converted into the group $—CH(OH){\cdot}CH(OH)—$. The compounds thus formed readily undergo further oxidation in such a way that the originally unsaturated carbon atoms are forced asunder. Propylene, on vigorous oxidation, yields acetic and formic acids; α-butylene gives propionic and formic acids,

$$CH_3{\cdot}CH{:}CH_2 + 4O = CH_3{\cdot}COOH + H{\cdot}COOH$$

$$CH_3{\cdot}CH_2{\cdot}CH{:}CH_2 + 2O_2 = CH_3{\cdot}CH_2{\cdot}COOH + H{\cdot}COOH.$$

HYDROCARBONS OF THE ACETYLENE SERIES.

The relation between the hydrocarbons of the acetylene series and those of the olefine series is the same as that between the olefines and the paraffins; in other words, the members of the acetylene series contain two atoms of hydrogen less than the corresponding olefines, and the general formula of the series is C_nH_{2n-2}.

Paraffins, C_nH_{2n+2}	*Olefines*, C_nH_{2n}	*Acetylenes*, C_nH_{2n-2}
Methane, CH_4	——	——
Ethane, C_2H_6	Ethylene, C_2H_4	Acetylene, C_2H_2
Propane, C_3H_8	Propylene, C_3H_6	Allylene, C_3H_4

Acetylene, C_2H_2, the simplest member of the series, occurs in small quantities (about 0·06 per cent. by vol.) in coal-gas. It is produced during the incomplete combustion of methane, ethyl alcohol, coal-gas, and other substances; also when the vapour of such substances is passed through a red-hot tube. It is formed when hydrogen is led through a globe in which the electric arc is passing between carbon poles,

$$C_2 + H_2 = C_2H_2.$$

This synthesis of acetylene from its elements is of great interest, because ethylene can be produced from acetylene by the action of nascent hydrogen, and ethylene is readily converted into ethyl alcohol by treating with sulphuric acid and water consecutively (p. 75). As, moreover, a large number of organic substances can be produced from ethyl alcohol, it is possible to prepare all these compounds, starting with carbon and hydrogen.

Acetylene is also produced by the electrolysis of a solution of the potassium salt of fumaric or maleïc acid (p. 241), hydrogen being evolved at the negative pole (as the result of the action of the liberated potassium on the water) a mixture of acetylene and carbon dioxide at the positive pole,

$$C_2H_2(COOK)_2 = C_2H_2 + 2CO_2 + 2K.$$

Acetylene is prepared by heating ethylene dibromide with excess of alcoholic potash,

$$C_2H_4Br_2 + 2KOH = C_2H_2 + 2KBr + 2H_2O.$$

In the first place, the potash takes away one molecule of hydrogen bromide ($C_2H_4Br_2 + KOH = C_2H_3Br + KBr + H_2O$), and the vinyl bromide thus produced is then further acted on ($C_2H_3Br + KOH = C_2H_2 + KBr + H_2O$). A more convenient method of preparation is to burn coal-gas with a supply of oxygen insufficient for complete combustion, the products being aspirated through an ammoniacal solution of cuprous chloride, when the red copper derivative of acetylene is precipitated. When this compound is decomposed with hydrochloric acid, acetylene is evolved.

Acetylene is a colourless gas, which liquefies at 1° under a pressure of 48 atmospheres. It has a characteristic smell, resembling that of garlic, and quite different from that which is noticed when a Bunsen is burning below, although the latter is often erroneously ascribed to the presence of acetylene. It is slightly soluble in water, much more readily in alcohol. It burns with a luminous, very smoky flame, this behaviour being shown by all hydrocarbons which contain a very large percentage of carbon.

Copper acetylene, the brownish-red amorphous compound which is precipitated when acetylene is passed into a solution of cuprous chloride in ammonia, has probably the composition $C_2H_2Cu_2O$, and its formation serves as a delicate test for acetylene. The dry substance explodes when struck on an anvil or when heated at about 120°. It is decomposed by hydrochloric acid with formation of acetylene and traces of vinyl chloride, but when warmed with a solution of potassium cyanide, it yields pure acetylene. Silver acetylene, $C_2H_2Ag_2O$, is a colourless amorphous compound obtained on passing acetylene into an ammoniacal solution of silver nitrate. It is more explosive than the copper compound.

When acetylene is passed over heated sodium or potassium, hydrogen is evolved, and a metallic substitution product formed,

$$2C_2H_2 + 2Na = 2C_2HNa + H_2.$$

Acetylene combines directly with nascent hydrogen, being converted first into ethylene, then into ethane,

$$C_2H_2 + 2H = C_2H_4 \qquad C_2H_2 + 4H = C_2H_6.$$

It combines directly with chlorine, forming dichlorethylene and tetrachlorethane,

$$C_2H_2 + Cl_2 = C_2H_2Cl_2 \qquad C_2H_2 + 2Cl_2 = C_2H_2Cl_4,$$

with bromine, forming dibromethylene and tetrabromethane, and with halogen acids under certain conditions, giving in the first place substitution products of ethylene. Thus, when the copper compound of acetylene is decomposed with hydrochloric acid, small quantities of vinyl chloride or chlorethylene are produced.

Sulphuric acid absorbs acetylene. When the solution is diluted with H_2O, and then distilled, acetaldehyde (p. 120) passes over,

$$C_2H_2 + H_2O = C_2H_4O.$$

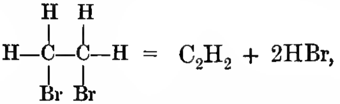
Acetaldehyde is also formed when acetylene is passed through an aqueous solution of mercuric bromide.

This remarkable reaction—that is, the addition of the elements of water to the group $HC\equiv CH$, by treatment with sulphuric acid or with halogen mercuric salts—appears to be a general one, and is frequently employed as a method of synthesis in organic investigations.

When acetylene is heated at a dull red heat, it is converted into benzene (part ii.),

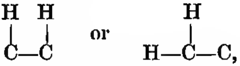
$$3C_2H_2 = C_6H_6.$$

Constitution of Acetylene.—The formation of acetylene from ethylene dibromide may be expressed by the equation



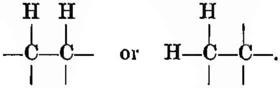
$$H-\underset{\underset{Br}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{Br}{|}}{\overset{\overset{H}{|}}{C}}-H = C_2H_2 + 2HBr,$$

so that the constitution of the hydrocarbon might be represented by one of the formulæ



$$\overset{\overset{H}{|}}{C}-\overset{\overset{H}{|}}{C} \quad \text{or} \quad H-\overset{\overset{H}{|}}{C}-C,$$

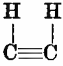
which, in order to recall the fact that carbon is tetravalent, and that acetylene combines directly with four monad atoms, must then be written



$$-\underset{|}{\overset{\overset{H}{|}}{C}}-\underset{|}{\overset{\overset{H}{|}}{C}}- \quad \text{or} \quad H-\underset{|}{\overset{\overset{H}{|}}{C}}-\underset{|}{\overset{|}{C}}-.$$

I. II.

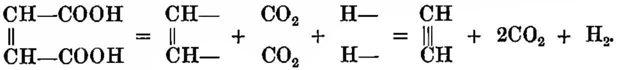
Since, however, as stated in discussing the constitution of ethylene, one unsaturated carbon atom is never found to exist alone, but requires the presence of another, it must be assumed that the particular portion of the combining capacity of each of the carbon atoms which is not exerted in uniting with hydrogen, is in some way exerted in combining with or satisfying the other carbon atom. For these reasons, formula I. is written



$$\overset{\overset{H}{|}}{C}\equiv\overset{\overset{H}{|}}{C} \quad \text{or} \quad CH : CH.$$

But it is impossible to write formula II. in any such manner, and at the same time to represent both carbon atoms as actively tetravalent. For these and other reasons the constitution of acetylene is expressed by the formula $CH:CH$, which recalls the fact that it contains *doubly unsaturated* carbon atoms, and is capable of combining directly with two pairs of monad groups or atoms to form additive compounds. This view of the constitution of acetylene accords well with its whole chemical behaviour.

The formation of acetylene by the electrolysis of fumaric acid affords support to this view, as will be readily understood if the decomposition be represented thus :



$$\begin{matrix}\mathrm{CH{-}COOH}\\ \| \\ \mathrm{CH{-}COOH}\end{matrix} = \begin{matrix}\mathrm{CH{-}}\\ \| \\ \mathrm{CH{-}}\end{matrix} + \begin{matrix}\mathrm{CO_2}\\ \\ \mathrm{CO_2}\end{matrix} + \begin{matrix}\mathrm{H{-}}\\ \\ \mathrm{H{-}}\end{matrix} = \begin{matrix}\mathrm{CH}\\ ||| \\ \mathrm{CH}\end{matrix} + 2CO_2 + H_2.$$

Fumaric Acid.

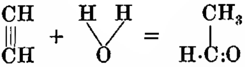
When the hydrocarbon combines with two monovalent atoms, such as 2H, Cl_2, Br_2, HBr, &c., it loses part of its unsaturated character, and the two carbon atoms, which before were represented as joined by three lines, or by a **treble binding** or **treble linking,** are now represented as joined by two only, as in the olefines,

$$CH:CH + 2H = CH_2:CH_2 \qquad CH:CH + Br_2 = CHBr:CHBr.$$

If, now, these compounds, which are still unsaturated, again combine with $2H, Br_2$, &c., they are converted into saturated compounds,

$$CH_2:CH_2 + 2H = CH_3 \cdot CH_3$$
$$CHBr:CHBr + Br_2 = CHBr_2 \cdot CHBr_2.$$

Acetylene can also combine with the valency equivalent of four monad atoms, with one atom of oxygen and two atoms of hydrogen, for example,



$$\begin{matrix}\mathrm{CH}\\ ||| \\ \mathrm{CH}\end{matrix} + \begin{matrix}\mathrm{H}\quad\mathrm{H}\\ \diagdown\diagup \\ \mathrm{O}\end{matrix} = \begin{matrix}\mathrm{CH_3}\\ | \\ \mathrm{H{\cdot}C{:}O}\end{matrix}$$

Homologues of Acetylene.—Two hydrocarbons of the molecular formula C_3H_4 are known; they may be represented by the formulæ

$$\underset{\text{Allylene or Methylacetylene.}}{CH_3{\cdot}C{:}CH} \quad \text{and} \quad \underset{\text{Allene.}}{CH_2{:}C{:}CH_2.}$$

Allylene, like acetylene, contains two doubly unsaturated carbon atoms, whereas allene resembles rather ethylene in constitution, and may be considered as containing two pairs of (singly) unsaturated carbon atoms, $\overbrace{CH_2{:}C}\underbrace{{:}CH_2}.$ This example shows that isomerism in the acetylene series may be due to a difference in the *position* of the unsaturated carbon atoms in the molecule, as well as to a difference in the *extent* of unsaturation, and consequently the number of isomerides in any given case is, theoretically, even greater than in the olefine series.

Allylene is prepared by heating propylene dibromide (dibromopropane) with alcoholic potash,

$$CH_3{\cdot}CHBr{\cdot}CH_2Br + 2KOH = CH_3{\cdot}C{:}CH + 2KBr + 2H_2O.$$

It is a gas, very similar to acetylene in properties, and gives characteristic copper and silver compounds.

Allene is said to be produced in small quantities by heating allyl bromide (p. 255) with alcoholic potash,

$$CH_2{:}CH{\cdot}CH_2Br + KOH = CH_2{:}C{:}CH_2 + KBr + H_2O.$$

It is also a gas, but it differs from allylene in not forming metallic derivatives. Only those hydrocarbons which contain the group $-C{:}CH$ yield metallic compounds with ammoniacal solutions of cuprous chloride and silver nitrate.

The higher homologues of acetylene have been comparatively little investigated.

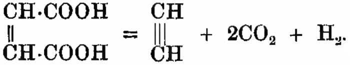
SUMMARY AND EXTENSION.

The Acetylene Series: Unsaturated hydrocarbons of the general formula C_nH_{2n-2}. The most important members of this series are *acetylene*, $CH{:}CH$, *allylene*, $CH_3{\cdot}C{:}CH$, and its isomeride allene, $CH_2{:}C{:}CH_2$, and *crotonylene*, $CH_3{\cdot}C{:}C{\cdot}CH_3$.

Methods of Preparation.—By treating the monohalogen substitution products of the olefines, or the dihalogen substitution products of the paraffins, with alcoholic potash,

$$CH_2{:}CHBr + KOH = CH\vdots CH + KBr + H_2O$$
$$CH_3{\cdot}CHBr{\cdot}CH_2Br + 2KOH = CH_3{\cdot}C\vdots CH + 2KBr + 2H_2O.$$

By the electrolysis of the alkali salts of unsaturated dibasic acids,



$$\begin{array}{l} CH{\cdot}COOH \\ \| \\ CH{\cdot}COOH \end{array} = \begin{array}{l} CH \\ ||| \\ CH \end{array} + 2CO_2 + H_2.$$

Physical and Chemical Properties.—The members of the acetylene series up to $C_{12}H_{22}$ are gases or volatile liquids having a peculiar odour. They are sparingly soluble in water, more readily in alcohol, and burn with a luminous, very smoky flame. The hydrocarbons, C_nH_{2n-2} may be classed in two groups: (1) The true acetylene series, consisting of those compounds which, like *acetylene*, contain the group $—C\vdots C—$; and (2) the *di-olefines*, or hydrocarbons, such as *allene*, $CH_2{:}C{:}CH_2$, and *diallyl*, $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2$, which resemble the olefines in constitution. The former behave on the whole like acetylene, whereas the latter are similar to the olefines.

Those hydrocarbons of the true acetylene series which contain the group $-C\vdots CH$ form metallic compounds such as copper acetylene, $C_2H_2Cu_2O$, and silver acetylene, $C_2H_2Ag_2O$, when treated with ammoniacal solutions of cuprous chloride and silver nitrate. The copper compounds are red, the silver compounds white, and both classes are explosive, the latter more so than the former. These compounds are decomposed by hydrochloric acid, and by warm potassium cyanide solution, the acetylenes being regenerated. The di-olefines, and those members of the true acetylene series, such as $CH_3{\cdot}C\vdots C{\cdot}CH_3$, which do not contain the group $—C\vdots CH$, do not form these metallic derivatives.

The hydrocarbons of the true acetylene series may be caused to combine with the elements of water either by dissolving them in strong sulphuric acid, and then adding water and warming; or by shaking them with a concentrated aqueous solution of mercuric chloride or bromide, and then decomposing the precipitate which is formed with a dilute mineral acid,

$$CH\vdots CH + H_2O = CH_3{\cdot}CHO \quad CH_3{\cdot}C\vdots CH + H_2O = CH_3{\cdot}CO{\cdot}CH_3.$$

In the case of all the higher members, combination takes place in such a way that the oxygen atom becomes united with the carbon atom which is not combined with hydrogen; allylene, for example, yields acetone, as shown above, and not propaldehyde, $CH_3{\cdot}CH_2{\cdot}CHO$.

All the hydrocarbons of the C_nH_{2n-2} series combine directly with two molecules of chlorine, bromine, halogen acids, and with nascent hydrogen, &c., the action taking place in two stages,

$$C_2H_2 + 2H = C_2H_4 \qquad C_2H_2 + 4H = C_2H_6$$
$$CH_3{\cdot}C{:}CH + Br_2 = CH_3{\cdot}CBr{:}CHBr$$
$$CH_3{\cdot}CBr{:}CHBr + Br_2 = CH_3{\cdot}CBr_2{\cdot}CHBr_2.$$

Like the olefines, they are readily oxidised and converted into compounds containing a smaller number of carbon atoms in the molecule.

CHAPTER VI.

THE MONOHYDRIC ALCOHOLS.

The monohydric alcohols form a homologous series of the general formula $C_nH_{2n+1}{\cdot}OH$, or $C_nH_{2n+2}O$. They may be regarded as derived from the paraffins by the substitution of the monovalent hydroxyl-group HO– for one atom of hydrogen.

Methyl alcohol,	$CH_3{\cdot}OH$,	derived from	methane,	$CH_3{\cdot}H$
Ethyl "	$C_2H_5{\cdot}OH$,	"	ethane,	$C_2H_5{\cdot}H$
Propyl "	$C_3H_7{\cdot}OH$,	"	propane,	$C_3H_7{\cdot}H$, &c.

Methyl alcohol, *wood spirit*, or carbinol, $CH_3{\cdot}OH$, occurs in nature in several substances, amongst others in combination with salicylic acid, as methyl salicylate, in oil of wintergreen (*Gaultheria procumbens*). When this oil is distilled with dilute potash, an aqueous solution of pure methyl alcohol collects in the receiver. Methyl alcohol may be obtained from methane, by first converting the hydrocarbon into methyl chloride, and then heating the latter with dilute aqueous potash in closed vessels,

$$CH_3Cl + KOH = CH_3{\cdot}OH + KCl.$$

Methyl alcohol is prepared from the products of the destructive distillation of wood. When wood is heated in iron retorts out of contact with air, gases are evolved, water, tar, and other products collect in the receiver, and wood-coke or charcoal remains. After allowing the distillate to settle, the brown aqueous layer, which contains methyl alcohol, acetic acid, acetone, and other substances, is drawn off from the wood-tar and distilled from a copper vessel, the vapours being passed through hot milk of lime, to free them from acetic acid, and then collected in a receiver; this distillate is diluted with water to precipitate oily impurities, and then submitted to careful fractional distillation over quicklime. The liquid obtained in this way contains 98–99 per cent. of methyl alcohol. In order to free it from acetone and other impurities, it is mixed with powdered calcium chloride, with which the methyl alcohol combines, forming a crystalline compound of the composition $CaCl_2 + 4CH_4O$. This substance is freed from acetone by pressure between cloths, and then decomposed by distilling with water; the aqueous methyl alcohol is finally dehydrated by repeated distillation with quicklime, but it still contains traces of acetone and other impurities.

Pure methyl alcohol can be prepared by warming the impure product with oxalic acid, when methyl oxalate is produced (p. 233),

$$2CH_3{\cdot}OH + C_2O_4H_2 = C_2O_4(CH_3)_2 + 2H_2O\,;$$

this crystalline substance is decomposed by distilling with potash, and the aqueous solution of pure methyl alcohol dehydrated with caustic lime as before.

Methyl alcohol is a colourless, mobile liquid of sp. gr. 0·796 at 20°; it boils at 66°, has an agreeable vinous or wine-like odour, and a burning taste. It mixes with water in all proportions, a slight contraction in volume taking place, and heat being developed; it burns with a pale, non-luminous flame, and its vapour forms an explosive mixture with air or oxygen,

$$2CH_3{\cdot}OH + 3O_2 = 2CO_2 + 4H_2O.$$

It is largely used in the manufacture of organic dyes and varnishes, and for the preparation of methylated spirit (p. 100).

Sodium and potassium dissolve readily in methyl alcohol with evolution of hydrogen and formation of metallic compounds called *methylates* or *methoxides*,

$$2CH_3{\cdot}OH + 2Na = 2CH_3{\cdot}ONa + H_2,$$

a reaction which is similar to the decomposition of water by sodium. Sodium methoxide is readily soluble in methyl alcohol, but can be obtained in a solid condition by evaporating the solution in a stream of hydrogen; it is a colourless, crystalline, very deliquescent compound, which rapidly absorbs carbon dioxide from the air, and is immediately decomposed by water with regeneration of methyl alcohol,

$$CH_3{\cdot}ONa + H_2O = CH_3{\cdot}OH + NaOH.$$

Potassium methoxide has similar properties.

Although neutral to test-paper, methyl alcohol acts like a weak base, and combines with acids to form salts; when saturated with hydrogen chloride, it yields methyl chloride, corresponding with potassium chloride,

$$\begin{gathered} CH_3{\cdot}OH + HCl = CH_3Cl + H_2O \\ KOH + HCl = KCl + H_2O, \end{gathered}$$

and when warmed with sulphuric acid, it gives methyl hydrogen sulphate, corresponding with potassium hydrogen sulphate, and methyl sulphate, corresponding with potassium sulphate,

$$\begin{gathered} CH_3{\cdot}OH + H_2SO_4 = CH_3{\cdot}HSO_4 + H_2O \\ 2CH_3{\cdot}OH + H_2SO_4 = (CH_3)_2SO_4 + 2H_2O. \end{gathered}$$

When phosphorus pentachloride, trichloride, or oxychloride is added to methyl alcohol, a considerable development of heat occurs, and methyl chloride is formed,

$$\begin{gathered} CH_3{\cdot}OH + PCl_5 = CH_3Cl + HCl + POCl_3 \\ 3CH_3{\cdot}OH + PCl_3 = 3CH_3Cl + H_3PO_3 \\ 3CH_3{\cdot}OH + POCl_3 = 3CH_3Cl + H_3PO_4. \end{gathered}$$

The corresponding bromides of phosphorus act in a similar manner.

Methyl alcohol is readily oxidised,* being first converted into formaldehyde and then into formic acid,

$$\underset{}{CH_3{\cdot}OH + O = \underset{\text{Formaldehyde.}}{CH_2O} + H_2O} \qquad CH_2O + O = \underset{\text{Formic Acid.}}{CH_2O_2}.$$

Constitution of Methyl Alcohol.—Since only one of the four hydrogen atoms in methyl alcohol, CH_4O, is displaceable by potassium or sodium, it must be concluded that this particular hydrogen atom is in a different state of combination from the other three; but methyl alcohol is formed by the action of dilute alkalies on methyl chloride,

$$CH_3Cl + KOH = CH_3{\cdot}OH + KCl,$$

---

* The substances most frequently used in oxidising organic compounds are: *Chlorine water*, *bromine water*, *nitric acid*, *chromic acid*, *manganese dioxide and sulphuric acid*, and *potassium permanganate*. Chlorine and bromine, in presence of water, act as oxidising agents by liberating oxygen,

$$Cl_2 + H_2O = 2HCl + O.$$

Nitric acid gives up some of its oxygen and is reduced to an oxide of nitrogen, the nature of which depends on that of the substance undergoing oxidation, and on the conditions of the experiment,

$$2HNO_3 = H_2O + N_2O_3 + 2O \qquad 2HNO_3 = H_2O + 2NO_2 + O, \text{ \&c.}$$

Chromic acid in the presence of sulphuric or acetic acid gives oxygen and a chromic salt,

$$2CrO_3 = Cr_2O_3 + 3O, \text{ or } 2CrO_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + 3H_2O + 3O.$$

A mixture of potassium dichromate and sulphuric acid, which is very often used instead of chromic acid, yields oxygen and a mixture of chromic sulphate and potassium sulphate, which frequently crystallises out in dark purple octahedra of chrome-alum, $K_2SO_4, Cr_2(SO_4)_3 + 24H_2O$,

$$K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O.$$

Potassium permanganate, in *alkaline* solution, is decomposed, yielding a precipitate of hydrated manganese dioxide,

$$2KMnO_4 + H_2O = 2MnO_2 + 2KOH + 3O;$$

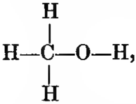
but in *acid* solution the same quantity of permanganate gives five instead of three atoms of oxygen,

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O,$$

because manganese dioxide and sulphuric acid yield oxygen,

$$2MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O.$$

and the three hydrogen atoms in methyl chloride, which are known to be combined with carbon, are not displaceable by metals. It is evident, therefore, that the displaceable hydrogen atom in methyl alcohol is not combined with carbon; the only other possibility is that it is combined with oxygen, and that methyl alcohol has the constitution



$H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-O-H$, which is usually written $CH_3{\cdot}OH$. When represented in this way, the whole chemical behaviour of methyl alcohol is summarised in its graphic formula; the fact that the oxygen atom cannot be taken away without one of the hydrogen atoms accompanying it—as, for example, when the alcohol is treated with HCl, PCl_5, PBr_5, &c.—is recalled by the two atoms being represented as directly united. The similarity between methyl alcohol and the metallic hydroxides is also accounted for; the alcohol may be regarded as derived from water, H–O–H, by substituting the monovalent CH_3–group for one atom of hydrogen, just as sodium hydroxide, Na–OH, is obtained by the substitution of one atom of sodium. Methyl alcohol, in fact, is *methyl hydroxide*, and, like other hydroxides, it forms salts and water when treated with acids,

$$CH_3{\cdot}OH + HCl = CH_3Cl + H_2O$$
$$Na{\cdot}OH + HCl = NaCl + H_2O.$$

Like water and certain metallic hydroxides, it contains displaceable hydrogen,

$$2CH_3{\cdot}OH + 2Na = 2CH_3{\cdot}ONa + H_2$$
$$Zn(OH)_2 + 2KOH = Zn(OK)_2 + 2H_2O.$$

It may also be considered as a hydroxy-substitution product of the paraffin, methane; it is termed a monohydric alcohol because it contains one hydroxyl-group.

Ethyl alcohol, *spirits of wine*, alcohol, or methyl carbinol, $C_2H_5{\cdot}OH$, has been known from the earliest times, as it is contained in all wines prepared by the fermentation (p. 97) of grape juice.

It may be obtained from ethane by converting the hydrocarbon into ethyl chloride and heating the latter with dilute alkalies under pressure,

$$C_2H_5Cl + KOH = C_2H_5{\cdot}OH + KCl,$$

and by passing ethylene into fuming sulphuric acid, and then boiling the solution with water, a reaction of considerable theoretical importance,

$$C_2H_4 + H_2SO_4 = C_2H_5{\cdot}HSO_4$$
$$C_2H_5{\cdot}HSO_4 + H_2O = C_2H_5{\cdot}OH + H_2SO_4\,;$$

also by reducing* acetaldehyde in aqueous solution with sodium amalgam,

$$C_2H_4O + 2H = C_2H_6O.$$

Alcohol may be prepared by placing a weak aqueous

---

* The substances most frequently used in reducing organic compounds are, *sodium, zinc, tin, iron, sodium amalgam, hydrogen iodide, sulphuretted hydrogen*, and *sulphur dioxide* in aqueous, acid, alkaline or alcoholic solution.

Sodium, acting on the alcoholic or moist ethereal solution of the substance, is one of the most powerful reducing agents known,

$$2Na + 2C_2H_5{\cdot}OH = 2C_2H_5{\cdot}ONa + 2H$$
$$2Na + 2H_2O = 2NaOH + 2H.$$

Sodium Amalgam, an alloy of sodium and mercury, acts on aqueous or dilute alcoholic solutions in the same way as metallic sodium, the action being, however, greatly moderated by the presence of the mercury.

Zinc and hydrochloric or sulphuric acid, or zinc dust and acetic acid, are perhaps the most commonly employed reducing agents; in some cases the action is much accelerated by coating the zinc with copper in the form of the zinc-copper couple (p. 57). Zinc dust is sometimes employed in alkaline solution, as, for instance, in the presence of potash, soda, or ammonia,

$$Zn + 2KOH = Zn(OK)_2 + 2H.$$

Substances which are reduced only with great difficulty are frequently mixed with zinc dust and heated at a high temperature.

Tin and hydrochloric acid act as reducing agents, stannous chloride being first produced,

$$Sn + 2HCl = SnCl_2 + 2H.$$

Stannous chloride is not acted on by hydrochloric acid alone, but, in solution of cane- or grape-sugar in a capacious flask, adding a small quantity of brewer's yeast, and keeping the mixture in a warm place (at about 20°). After some time it begins to froth and ferment (p. 97), and, if the flask be fitted with a cork and delivery tube, it can be proved that carbon dioxide is being evolved by passing the gas into lime-water. After about 24 hours' time the yeast is filtered off, and the solution distilled from a flask or retort connected with a condenser, the process being stopped when about one-third has passed over. In this way the more volatile alcohol is partially separated from the water (fractional distillation). The distillate has an unpleasant vinous smell, and consists of an aqueous solution of slightly impure alcohol. It is poured into a retort or flask connected with a condenser, and a considerable quantity of freshly-burnt lime in the form of small lumps is then slowly added; after some hours, the alcohol is distilled by heating on a water-bath. By repeating this process several times, employing fresh caustic lime in sufficient quantity, alcohol containing only about 0·2 per cent. of water is obtained, but it is impossible to free it completely from water by distillation over lime. When the alcohol contains less than about 0·5 per cent. of water, it is known commercially as *absolute* alcohol.

Wines, beers, and spirits contain alcohol, and its preparation from these liquids is very simple. The liquid is distilled, and the alcohol, thus freed from colouring matter and other

presence of reducible substances, it is a very powerful reducing agent, being converted into stannic chloride,

$$SnCl_2 + 2HCl = SnCl_4 + 2H.$$

Hydriodic Acid, in concentrated aqueous solution, is a very powerful reducing agent at high temperatures, the hydrogen iodide being decomposed into hydrogen and iodine.

Sulphuretted Hydrogen, being readily decomposed into sulphur and hydrogen, is frequently used as a mild reducing agent, generally in the form of ammonium sulphide.

Sulphur Dioxide has only a limited use; in presence of water and reducible substances, it is converted into sulphuric acid,

$$SO_2 + 2H_2O = H_2SO_4 + 2H.$$

solid substances, is then dehydrated by distillation with caustic lime.

Alcohol is a colourless, mobile liquid of sp. gr. 0·8062 at 0°; it has a pleasant vinous odour and a burning taste; it boils at 78°, but does not solidify until about – 130° (hence its use in alcohol thermometers). It burns with a pale, non-luminous flame, and its vapour forms an explosive mixture with air or oxygen,

$$C_2H_5{\cdot}OH + 3O_2 = 2CO_2 + 3H_2O.$$

It mixes with water in all proportions with development of heat and diminution of volume; 52 vols. of alcohol and 48 vols. of water give a mixture occupying only 96·3 vols.

Ethyl alcohol closely resembles methyl alcohol in chemical properties. It quickly dissolves sodium and potassium with evolution of hydrogen and formation of *ethylates* or *ethoxides*,

$$2C_2H_5{\cdot}OH + 2Na = 2C_2H_5{\cdot}ONa + H_2.$$

These compounds are readily soluble in alcohol, but may be obtained in a solid condition by evaporating the solution in a stream of hydrogen. They are colourless, hygroscopic substances, rapidly absorb carbon dioxide from the air, and are immediately decomposed by water with regeneration of alcohol,

$$C_2H_5{\cdot}OK + H_2O = C_2H_5{\cdot}OH + KOH.$$

Although it has a neutral reaction, alcohol acts like a weak base, and when treated with acids, is converted into salts with formation of water,

$$C_2H_5{\cdot}OH + HI = C_2H_5I + H_2O.$$

When treated with the chlorides or bromides of phosphorus, it is converted into ethyl chloride or ethyl bromide, an energetic action taking place,

$$C_2H_5{\cdot}OH + PBr_5 = C_2H_5Br + HBr + POBr_3.$$

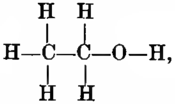
Alcohol is readily oxidised by chromic acid, yielding acetaldehyde, which on further oxidation is converted into acetic acid,

$$C_2H_5{\cdot}OH + O = \underset{\text{Acetaldehyde.}}{C_2H_4O} + H_2O \qquad C_2H_4O + O = \underset{\text{Acetic Acid.}}{C_2H_4O_2}.$$

By the action of the ferment, *mycoderma aceti*, it is, under certain conditions (p. 148), oxidised to acetic acid at ordinary temperatures by the oxygen of the air.

The presence of alcohol in aqueous solution may be detected by Lieben's *iodoform reaction* (p. 175). A small quantity of iodine is placed in the solution, and then caustic potash is added drop by drop until the colour of the iodine disappears. If alcohol be present in considerable quantity, a yellow precipitate of iodoform is produced almost immediately. In very dilute solutions of alcohol only a very slight precipitate is formed even after some time, but it may be recognised as iodoform by its odour, and by the characteristic appearance of its six-sided crystals when viewed under the microscope. By means of this reaction it is possible to detect 1 part of alcohol in 2000 parts of water. It is especially valuable as affording a means of distinguishing between ethyl and methyl alcohols, as the latter does not give the iodoform reaction, although many other substances, such as acetone, aldehyde, &c., do so.

The presence of water in alcohol can be detected by adding a little anhydrous copper sulphate. If water be present, the colourless powder turns blue, owing to the formation of the hydrated salt, but this test is not very delicate.

Constitution.—The formation of alcohol from ethyl chloride, the fact that only one of its six atoms of hydrogen is displaceable by metals, and its close resemblance to methyl alcohol in chemical properties, lead to the conclusion that it is a *hydroxide* of the constitution  $H{-}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}{-}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}{-}O{-}H$, or $C_2H_5{\cdot}OH$. It may be regarded as a mono-hydroxy-substitution product of ethane.

Production of Wines and Beers; Alcoholic Fermentation.

When the juice of grapes is kept for a few days at ordinary temperatures, it changes into wine; the sugars, dextrose and levulose (p. 262), present in the juice being decomposed into alcohol and carbon dioxide. This change is brought about by a small vegetable organism; the process is called *fermentation*, and the active agent which causes the change is termed a *ferment*. All wines, beers, and spirits, and the whole of the alcohol of commerce are prepared by the process of fermentation.

The ferment which brings about the conversion of grape-juice into wine is present on the grapes and stalks and in the air; it is a living organism, and during fermentation it rapidly grows and multiplies, feeding on the sugar, mineral salts, and nitrogenous substances contained in the juice. In order that fermentation may take place, the conditions must be favourable to the life and growth of the living ferment; sufficient food of a suitable kind must be at hand, and the temperature must be kept within certain limits.

Beer is prepared from malt and hops. Malt is the grain of barley which has been caused to sprout or germinate by first soaking it in water and then keeping it in a moist atmosphere at a suitable temperature. During the process of germination a ferment, *diastase*, is formed in the grain. The malt is now heated at 50–100° in order to stop germination and to cause the production of various substances which impart to it both colour and flavour, the character of the beer depending largely on the temperature and the duration of heating. It is then stirred up with water and kept at 60–65°, when fermentation sets in, the diastase converting the starch in the malt into *dextrin* and a sugar, *maltose*. This solution is now boiled in order to stop the *diastatic fermentation*, and then hops, the flower of the hop-plant, are added in order to impart a slight bitter taste, and also on account of the preservative properties of the hops. After cooling to from 5° to 20°, *yeast* is added, when *alcoholic fermentation* sets in, the sugar maltose being gradually converted into alcohol and carbon dioxide. The beer is then run off and kept until ready for consumption.

Beer usually contains 3–6 per cent. of alcohol, small quantities of dextrin, sugars, and colouring matters, and traces of succinic acid, glycerol, and other substances. It contains, moreover, carbon dioxide, to which it owes its refreshing taste, and small quantities of *fusel oil*, which help to give it a flavour.

The production of beer involves two distinct fermentations. In the first place, the starch in the malt is converted into maltose and dextrin by the diastase,

$$\underset{\text{Starch.}}{3(C_6H_{10}O_5)} + H_2O = \underset{\text{Maltose.}}{C_{12}H_{22}O_{11}} + \underset{\text{Dextrin.}}{C_6H_{10}O_5};$$

in the second place, the maltose is transformed into alcohol by the yeast,

$$C_{12}H_{22}O_{11} + H_2O = 4C_2H_6O + 4CO_2.$$

One of the ferments cannot do the work of the other; yeast cannot convert starch into maltose, nor can diastase set up the alcoholic fermentation of sugar. Diastase is an amorphous substance, without definite form or structure, and apparently lifeless. Such ferments are termed *enzymes*, in contradistinction to living *organised* ferments of definite structure, of which yeast is an example.

Yeast (*saccharomyces*) consists of rounded, almost transparent living cells, which are usually grouped together in chain-like clusters. When placed in solutions of certain sugars containing small quantities of mineral substances, &c., which the organism requires for food, the cells soon begin to bud and multiply, provided also that the temperature is kept between about 5° and 30°; if it exceeds these limits, the plant stops growing, and fermentation ceases.

There are several sugars which can be fermented with yeast, the most important being dextrose or grape-sugar, $C_6H_{12}O_6$, levulose or fruit-sugar, $C_6H_{12}O_6$, and maltose, $C_{12}H_{22}O_{11}$. Cane-sugar, $C_{12}H_{22}O_{11}$, does not ferment with pure yeast, but does so with ordinary yeast, because the latter contains other ferments which rapidly convert the cane-sugar into equal molecules of dextrose and levulose:

$$C_{12}H_{22}O_{11} + H_2O = \underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Levulose.}}{C_6H_{12}O_6}.$$

The alcoholic fermentation of these sugars is expressed approximately by the equation,

$$C_6H_{12}O_6 = 2C_2H_6O + 2CO_2;$$

but small quantities of succinic, acetic, lactic, and butyric acids, glycerol, fusel oil, and other substances are also formed. *Fusel oil* is a mixture of the higher homologues of ethyl alcohol; it is usually present in small quantities in beers and spirits.

Manufacture of Alcohol and Spirits.—Alcohol is prepared on the large scale from potatoes, grain, rice, and other substances rich in starch. The raw material is reduced to a pulp or paste with water, mixed with a little malt, and the mixture kept at about 60° for 30–60 minutes, when diastatic fermentation takes place, and the starch is converted into dextrin and maltose. After cooling to about 15°, yeast is added, and the mixture kept until alcoholic fermentation is at an end. It is possible to obtain alcohol from starch without the use of malt, since starch is converted into dextrose when heated with dilute sulphuric acid, and, after neutralising with lime, the solution can be fermented with yeast. Alcohol is also prepared from beet-root, molasses (treacle), and other substances rich in sugar, by direct fermentation with yeast.

The weak solution of alcohol obtained by any of these methods is submitted to fractional distillation in specially constructed apparatus. The distillate is known as 'raw spirit,' and contains from 80–95 per cent. of alcohol and a small quantity of fusel oil, which passes over in spite of the fact that its constituents boil at a higher temperature than alcohol or water.

For the preparation of spirits, liqueurs, and other articles of consumption, the raw spirit must be freed as much as possible from fusel oil, which is very injurious to health. For this purpose it is diluted with water and filtered through charcoal, which absorbs some of the fusel oil. Finally, the spirit is again fractionally distilled, the portions which pass over first ('first runnings') and last ('last runnings') being collected separately; the intermediate portions consist of 'refined' or 'rectified spirit,' most of the fusel oil, which has not been removed, being present in the last runnings.

For most other purposes the separation of the fusel oil is unnecessary, and if a stronger alcohol be required, the raw spirit is again fractionated, or distilled over lime.

Alcohol is used in large quantities for the manufacture of ether, chloroform, &c., and in the purification of the alkaloids. It is employed as a solvent for gums, resins, and other substances, in the preparation of tinctures, varnishes, perfumes, &c., and is also used in spirit-lamps. In this country a heavy excise duty has long been levied on spirits of wine, a fact which acted as a serious impediment to its extended use; but since 1856 the Government has permitted the manufacture and sale of methylated spirit free of duty.

Methylated spirit contains about 90 per cent. of raw spirit (ethyl alcohol), about 10 per cent. of partially purified wood-spirit or methyl alcohol, and a small quantity of paraffin-oil, the addition of which renders the alcohol unfit for drinking purposes, without affecting its value as a solvent; methylated spirit is therefore used instead of alcohol whenever possible, as it is so much cheaper. Methylated spirit cannot be separated into its constituents by any commercial process, but the water and tarry and oily impurities can be got rid of almost completely by distilling with a little potash, and then dehydrating over lime; the purified spirit may be employed in most chemical experiments in the place of pure ethyl alcohol.

Alcoholometry.—In order to ascertain the strength of a sample of alcohol—that is, the percentage of alcohol in pure aqueous spirit, it is only necessary to determine its specific gravity at some particular temperature, and then to refer to published tables, in which the sp. gr. of all mixtures of alcohol and water is given. If, for example, the sp. gr. is found to be 0·8605 at 15·5°, reference to the tables would show that the sample contained 75 per cent. of alcohol by weight.

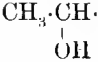
For excise and general purposes the sp. gr. is determined with the aid of hydrometers graduated in such a manner that the percentage of alcohol can be read off directly on the scale. The standard referred to in this country is *proof-spirit*, which contains 49·3 per cent. by weight, or 57·1 per cent. by volume of alcohol: it is defined by act of parliament as being 'such a spirit as shall at a temperature of 51° F. weigh exactly $\frac{12}{13}$ths of an equal measure of distilled water.' Spirits are termed *under* or *over* proof according as they are weaker or stronger than proof-spirit: thus 20° over proof means that 100 vols. of this spirit diluted with water would yield 120 vols. of proof-spirit, whilst 20° under proof means that 100 vols. of the sample contain as much alcohol as 80 vols. of proof-spirit. The name *proof-spirit* owes its origin to the practice in vogue during the last century, of testing the strength of samples of alcohol by pouring them on to gunpowder and applying a light. If the sample contained much water, the alcohol burned away, and the water made the powder so damp that it did not ignite; but if the spirit were strong enough, the gunpowder took fire. A sample which just succeeded in igniting the powder was called proof-spirit.

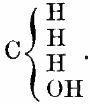
For the *determination of alcohol* in beers, wines, and spirits, a measured quantity of the sample is distilled from a flask connected with a condenser until about $\frac{1}{3}$d has passed over. The distillate, which contains the whole of the alcohol, is then diluted with water to the volume of the sample taken, and its sp. gr. determined with a hydrometer; the percentage of alcohol is found by referring to the tables already mentioned.

Distillation is necessary because the sugary and other extractive matters contained in the sample influence the sp. gr. to such an extent that a direct observation would be of no value.

The percentage of alcohol by weight in some of the best-known fermented liquors may be roughly taken as being as follows :

Brandy	50 %	Port	20 %	Hock	8 %
Whisky	50 %	Sherry	16 %	Burton Ale	5·5 %
Gin	40 %	Claret	7 %	Lager-bier	3 %

Homologues of Ethyl Alcohol.—The members of the series of monohydric alcohols may all be considered as derived from the paraffins by the substitution of the monovalent HO– group for one atom of hydrogen. Like the paraffins, they exist in isomeric forms, but, as two or more isomeric alcohols may be derived from one hydrocarbon, the number of isomerides is greater in the alcohol than in the paraffin series. Propane, $CH_3\cdot CH_2\cdot CH_3$, for example, exists in only one form, but two isomeric alcohols may be derived from it —namely, propyl alcohol, $CH_3\cdot CH_2\cdot CH_2\cdot OH$, and isopropyl alcohol,  $CH_3\cdot\underset{OH}{\underset{|}{CH}}\cdot CH_3$, or $CH_3\cdot CH(OH)\cdot CH_3$.

In order to distinguish between the various isomerides, the alcohols may be considered as derivatives of methyl alcohol or *carbinol*, $CH_3\cdot OH$, or  $C\left\{\begin{matrix}H\\H\\H\\OH\end{matrix}\right.$. Thus, propyl alcohol, $CH_3\cdot CH_2\cdot CH_2\cdot OH$, may be termed ethyl-carbinol, because it may be considered as derived from carbinol by displacing one atom of hydrogen by the ethyl group C_2H_5–. Isopropyl alcohol, $(CH_3)_2CH\cdot OH$, may be called dimethyl-carbinol, and regarded as derived from carbinol, by substituting two methyl or CH_3– groups for two atoms of hydrogen. Such names as these serve to express the constitution of the substance, as will be seen by considering the case of the four isomeric butyl alcohols, $C_4H_9\cdot OH$,

$CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH,$	or $C\left\{\begin{array}{l}CH_2\cdot CH_2\cdot CH_3\\H\\H\\OH\end{array}\right.$	Normal butyl alcohol, or propyl carbinol (primary).
$\begin{array}{l}CH_3\\CH_3\end{array}\!\!>CH\cdot CH_2\cdot OH,$	or $C\left\{\begin{array}{l}CH{<}\begin{array}{l}CH_3\\CH_3\end{array}\\H\\H\\OH\end{array}\right.$	Isobutyl alcohol, or isopropyl carbinol (primary).
$\begin{array}{l}CH_3\\C_2H_5\end{array}\!\!>CH\cdot OH,$	or $C\left\{\begin{array}{l}CH_3\\C_2H_5\\H\\OH\end{array}\right.$	Methylethyl carbinol (secondary).
$\begin{array}{l}CH_3\diagdown\\CH_3-\\CH_3\diagup\end{array}\!\!C\cdot OH,$	or $C\left\{\begin{array}{l}CH_3\\CH_3\\CH_3\\OH\end{array}\right.$	Trimethyl carbinol (tertiary).

The alcohols are divided into three classes, namely, normal or primary, iso- or secondary, and tertiary alcohols.

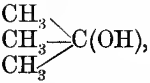
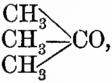
Primary or *normal alcohols* (such as normal propyl alcohol, $CH_3\cdot CH_2\cdot CH_2\cdot OH$), contain the group $-CH_2\cdot OH$, and may be considered as mono-substitution products of carbinol. On oxidation with chromic acid, &c., they are converted first into aldehydes (p. 116) and then into fatty acids, (p. 142), the group $-CH_2\cdot OH$ being transformed first into $-C\begin{array}{l}\diagup H\\ \diagdown\!\!\diagdown O\end{array}$, and then into $-C\begin{array}{l}\diagup O-H\\ \diagdown\!\!\diagdown O\end{array}$

$$CH_3\cdot CH_2\cdot OH + O = CH_3\cdot CHO + H_2O$$
$$CH_3\cdot CHO + O = CH_3\cdot COOH.$$

These oxidation products contain the *same* number of carbon atoms in the molecule as the alcohols from which they are obtained.

Secondary or *iso-alcohols,* such as isopropyl alcohol, $CH_3\cdot CH(OH)\cdot CH_3$, contain the group $>CH\cdot OH$, and may be regarded as di-substitution products of carbinol. On oxidation they are converted into ketones (p. 127) containing the *same* number of carbon atoms, the group $>CH\cdot OH$ becoming $>CO$,

$$CH_3\cdot CH(OH)\cdot CH_3 + O = CH_3\cdot CO\cdot CH_3 + H_2O.$$

Tertiary alcohols, such as tertiary butyl alcohol,  $\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\!\!>C(OH)$, contain the group —C·OH, and may be regarded as tri-substitution products of carbinol. On oxidation they yield both ketones and fatty acids, which contain a *smaller* number of carbon atoms than the alcohol from which they are derived, the molecule of the latter being broken up. Tertiary butyl alcohol, or trimethyl carbinol, $(CH_3)_3C{\cdot}OH$, for example, yields acetone, $CH_3{\cdot}CO{\cdot}CH_3$, acetic acid, $CH_3{\cdot}CO{\cdot}OH$, carbon dioxide, and other products. It could not be converted by simple loss of hydrogen into a compound,  $\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\!\!>CO$, containing the same number of carbon atoms—a change which would be analogous to that undergone by primary and secondary alcohols—because carbon is tetravalent and not pentavalent, as represented in this formula.

Propyl alcohol (normal ethyl carbinol), $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, is one of the principal constituents of fusel oil, from which it is prepared by fractional distillation. It is formed when propyl iodide is heated with freshly precipitated silver hydroxide,

$$C_3H_7I + Ag{\cdot}OH = C_3H_7{\cdot}OH + AgI.$$

It is a colourless liquid of sp. gr. 0·817 at 0°, boils at 97°, and is miscible with water in all proportions. On oxidation with chromic acid, it is converted first into propaldehyde and then into propionic acid,

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}OH + O = \underset{\text{Propaldehyde.}}{CH_3{\cdot}CH_2{\cdot}CHO} + H_2O$$

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}OH + 2O = \underset{\text{Propionic Acid.}}{CH_3{\cdot}CH_2{\cdot}CO{\cdot}OH} + H_2O.$$

Isopropyl alcohol, or dimethyl carbinol, $(CH_3)_2CH{\cdot}OH$, is best prepared by the reduction of acetone in aqueous solution with sodium amalgam,

$$CH_3{\cdot}CO{\cdot}CH_3 + 2H = CH_3{\cdot}CH(OH){\cdot}CH_3.$$

It is a colourless liquid of sp. gr. 0·789 at 0°, and boils at 81°, or about 16° lower than normal propyl alcohol. On oxidation it yields acetone,

$$CH_3\cdot CH(OH)\cdot CH_3 + O = CH_3\cdot CO\cdot CH_3 + H_2O.$$

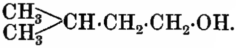
There are four isomeric **butyl alcohols,** $C_4H_9\cdot OH$. *Normal butyl alcohol,* or propyl carbinol, $CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$, may be prepared by the reduction of butaldehyde, $CH_3\cdot CH_2\cdot CH_2\cdot CHO$, and is produced during the fermentation of glycerol by certain bacteria. It boils at 117°.

Isobutyl alcohol, or isopropyl carbinol, $(CH_3)_2\cdot CH\cdot CH\cdot_2OH$, is contained in large quantities in fusel oil. It boils at 107°.

Methylethyl carbinol, $(CH_3)\cdot CH(OH)\cdot C_2H_5$, is obtained by the reduction of methyl ethyl ketone, $CH_3\cdot CO\cdot C_2H_5$ (p. 136), by means of sodium amalgam. It boils at 100°.

Trimethyl carbinol, $(CH_3)_3C\cdot OH$, may be prepared by the action of zinc methyl, $Zn(CH_3)_2$, on acetyl chloride, $CH_3\cdot COCl$, a reaction which is described below (p. 107). It may also be obtained from isobutyl alcohol, as explained later (p. 108). Trimethyl carbinol is one of the few alcohols which are solid at ordinary temperatures. It melts at 28°, and boils at 83–84°.

Amyl alcohols, $C_5H_{11}\cdot OH$.—Of the eight isomerides theoretically capable of existing, the following two occur in fusel oil:

Isobutyl carbinol, (Isoamyl alcohol.)	 $\begin{matrix}CH_3\\CH_3\end{matrix}>CH\cdot CH_2\cdot CH_2\cdot OH.$	B.p. 131°.
Secondary butyl carbinol, (Active amyl alcohol.)	 $\begin{matrix}CH_3\\CH_3\cdot CH_2\end{matrix}>CH\cdot CH_2\cdot OH.$	B.p. 127°.

These alcohols always occur in commercial amyl alcohol, and their boiling-points lie so close together that they cannot be separated by fractional distillation. A separation may, however, be accomplished by treating the mixture with sulphuric acid, and thus converting both alcohols into the alkyl hydrogen sulphates,

$$C_5H_{11}\cdot OH + H_2SO_4 = C_5H_{11}\cdot HSO_4 + H_2O.$$

By neutralising these acid salts with barium hydrate, the barium salts, $(C_5H_{11}\cdot SO_4)_2Ba$, are obtained; and, as the barium salt of isobutyl carbinol is more sparingly soluble than that of active amyl alcohol, the two may be separated by fractional crystallisation.

From the pure salts the respective alcohols are then obtained in a pure condition by distillation with dilute mineral acids,

$$C_5H_{11}\cdot HSO_4 + H_2O = C_5H_{11}\cdot OH + H_2SO_4.$$

Commercial amyl alcohol is prepared from fusel oil by fractionation, and is a mixture of about 87 per cent. of isobutyl carbinol and about 13 per cent. of active amyl alcohol. It has a pungent, unpleasant smell, boils at about 131°, and is used as a solvent, and in the preparation of essences and perfumes (p. 189).

SUMMARY AND EXTENSION.

The Monohydric Alcohols.—Hydroxy-derivatives of the paraffins of the general formula $C_nH_{2n+1}\cdot OH$.

The more important members of the series are the following. The letters p., s., t., in brackets, denote primary, secondary, and tertiary.

Name and composition.		B.p.	Sp. gr.
Methyl alcohol (p.)...........	$CH_3\cdot OH$,	66°	0·812 at 0°
Ethyl alcohol (p.).............	$C_2H_5\cdot OH$,	78°	0·806 „
Propyl alcohol (p.)..........	$C_3H_7\cdot OH$,	97°	0·817 „
Isopropyl alcohol (s.).......		83°	0·816 „
Butyl alcohol, (p.)	$C_4H_9\cdot OH$,	117°	0·823 „
Isobutyl alcohol (p.)		108°	0·816 „
Tertiary butyl alcohol (t.)		83°	0·786 at 20°
Methylethyl carbinol (s.)		99°	0·827 „
Active amyl alcohol (p.)..	$C_5H_{11}\cdot OH$,	128°	— „
Isoamyl alcohol (p.)		132°	0·825 „
Six other isomerides of little importance..........			

Methods of Preparation.—Methyl alcohol is prepared from the products of the dry distillation of wood. Ethyl alcohol is obtained by the alcoholic fermentation of sugar by means of yeast; the fusel oil produced at the same time contains propyl, isobutyl, active amyl, and isoamyl alcohols.

The alcohols are formed when the halogen substitution products of the paraffins are heated with water, dilute aqueous alkalies, or freshly precipitated silver hydroxide,

$$CH_3Br + KOH = CH_3\cdot OH + KBr \quad C_3H_7I + Ag\cdot OH = C_3H_7\cdot OH + AgI;$$

more readily by heating these halogen derivatives with silver or potassium acetate, and decomposing the products with potash,

$$C_2H_5I + \underset{\text{Silver Acetate.}}{C_2H_3O_2Ag} = \underset{\text{Ethyl Acetate.}}{C_2H_5\cdot C_2H_3O_2} + AgI$$

$$C_2H_5\cdot C_2H_3O_2 + KOH = C_2H_5\cdot OH + C_2H_3O_2K.$$

This method gives very good results, and is much used in the preparation of the higher alcohols, because the halogen derivatives of the higher paraffins (such as hexyl chloride, $C_6H_{13}Cl$), when treated directly with alkalies, are mainly converted into olefines,

$$CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2Cl + KOH$$
$$= CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH{:}CH_2 + KCl + H_2O,$$

so that the yield of alcohol is small.

Alcohols are also formed when the hydrocarbons of the olefine series are dissolved in sulphuric acid, and the solutions boiled with water,

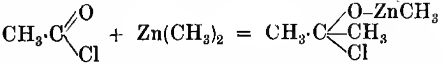
$$C_3H_6 + H_2SO_4 = C_3H_7\cdot HSO_4$$
$$C_3H_7\cdot HSO_4 + H_2O = C_3H_7\cdot OH + H_2SO_4,$$

and when aldehydes and ketones are reduced with nascent hydrogen, aldehydes giving primary, ketones secondary alcohols,

$$CH_3\cdot CH_2\cdot CHO + 2H = CH_3\cdot CH_2\cdot CH_2\cdot OH$$
$$CH_3\cdot CO\cdot CH_3 + 2H = CH_3\cdot CH(OH)\cdot CH_3.$$

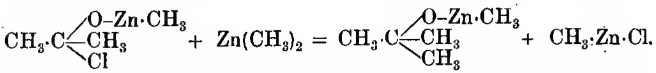
Tertiary alcohols are, as a rule, more difficult to obtain than the primary or secondary compounds; they are usually prepared by gradually adding the chloride of a fatty acid to excess of a zinc alkyl derivative. Thus acetyl chloride, $CH_3\cdot COCl$, acts on zinc methyl, $Zn(CH_3)_2$, forming a compound which, when treated with water, yields trimethyl carbinol, $(CH_3)_3C\cdot OH$.

In this reaction the zinc methyl and acetyl chloride form a crystalline compound



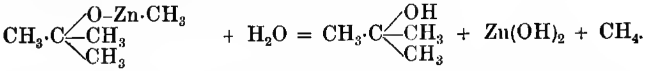
$$CH_3\cdot C\begin{array}{l}\diagup\!\!\!\diagup O\\ \diagdown Cl\end{array} + Zn(CH_3)_2 = CH_3\cdot C\begin{array}{l}\diagup O\text{–}ZnCH_3\\ \text{—}CH_3\\ \diagdown Cl\end{array}$$

which is then very slowly acted on by a further quantity of zinc methyl,



$$CH_3\cdot C\begin{array}{l}\diagup O\text{–}Zn\cdot CH_3\\ \text{—}CH_3\\ \diagdown Cl\end{array} + Zn(CH_3)_2 = CH_3\cdot C\begin{array}{l}\diagup O\text{–}Zn\cdot CH_3\\ \text{—}CH_3\\ \diagdown CH_3\end{array} + CH_3\cdot Zn\cdot Cl.$$

This product is decomposed by water, when trimethyl carbinol, methane, and zinc hydroxide are obtained,



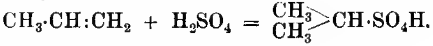
$$CH_3\cdot C\begin{array}{l}\diagup O\text{–}Zn\cdot CH_3\\ \text{—}CH_3\\ \diagdown CH_3\end{array} + H_2O = CH_3\cdot C\begin{array}{l}\diagup OH\\ \text{—}CH_3\\ \diagdown CH_3\end{array} + Zn(OH)_2 + CH_4.$$

Other tertiary alcohols may be prepared by employing other zinc alkyl compounds and other acid chlorides.

Conversion of Primary into Secondary and Tertiary Alcohols.—A secondary alcohol may be prepared from the corresponding primary compound by first converting the latter into an olefine by treating with dehydrating agents such as H_2SO_4, $ZnCl_2$, and P_2O_5,

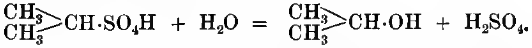
$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}OH = CH_3{\cdot}CH{:}CH_2 + H_2O.$$

The olefine is then dissolved in fuming sulphuric acid, when an alkyl hydrogen sulphate is formed, the SO_4H- group uniting with that carbon atom which is combined with the least number of hydrogen atoms,



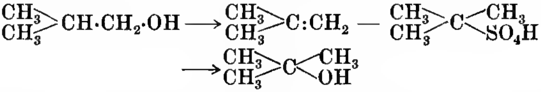
$$CH_3{\cdot}CH{:}CH_2 + H_2SO_4 = \left.\begin{matrix}CH_3\\CH_3\end{matrix}\right>CH{\cdot}SO_4H.$$

The alkyl hydrogen sulphate is finally converted into a secondary alcohol by boiling with water,



$$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right>CH{\cdot}SO_4H + H_2O = \left.\begin{matrix}CH_3\\CH_3\end{matrix}\right>CH{\cdot}OH + H_2SO_4.$$

In a similar manner, a primary alcohol, such as isobutyl alcohol, may be converted into the tertiary alcohol, trimethyl carbinol,



$$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right>CH{\cdot}CH_2{\cdot}OH \longrightarrow \left.\begin{matrix}CH_3\\CH_3\end{matrix}\right>C{:}CH_2 - \left.\begin{matrix}CH_3\\CH_3\end{matrix}\right>C\left<\begin{matrix}CH_3\\SO_4H\end{matrix}\right.$$
$$\longrightarrow \left.\begin{matrix}CH_3\\CH_3\end{matrix}\right>C\left<\begin{matrix}CH_3\\OH\end{matrix}\right.$$

Physical Properties.—No gaseous alcohols are known. The members up to $C_{12}H_{26}O$ are, with few exceptions, neutral, colourless liquids, possessing a characteristic odour and a burning taste. Trimethyl carbinol and all the higher alcohols, such as cetyl alcohol, $C_{16}H_{33}{\cdot}OH$, which occurs in spermaceti in combination with palmitic acid, and melissyl alcohol, $C_{30}H_{61}{\cdot}OH$, which is found in beeswax, also in combination with palmitic acid, are solids. Methyl, ethyl, and the propyl alcohols are miscible with water, but as the series is ascended, the solubility in water rapidly decreases, the amyl alcohols, for example, being only sparingly soluble. The alcohols are miscible in all proportions with most organic liquids.

The sp. gr. gradually increases, and the boiling-point rises on passing up the series; moreover, the primary alcohols boil at a higher temperature than the secondary, and the latter at a higher temperature than the tertiary isomerides, as shown in the table (p. 106).

Chemical Properties.—The fact that the alcohols interact with other compounds so much more readily than the paraffins is due to the presence of the hydroxyl group, the rest of the molecule remaining unchanged, except under exceptional circumstances. In many reactions the alcohols behave as alkyl substitution products of water; in others, their similarity to metallic hydroxides is more marked.

They dissolve sodium and potassium with evolution of hydrogen,

$$2C_3H_7{\cdot}OH + 2Na = 2C_3H_7{\cdot}ONa + H_2.$$

They interact with acids, forming neutral or acid ethereal salts, such as CH_3Cl, C_2H_5Br, $(C_2H_5)_2SO_4$, $C_3H_7{\cdot}HSO_4$.

They are converted into halogen derivatives of the paraffins, when treated with PCl_5, PCl_3, $POCl_3$, or with the corresponding bromo-derivatives,

$$PCl_5 + C_3H_7{\cdot}OH = C_3H_7Cl + POCl_3 + HCl.$$

They are converted into olefines by dehydrating agents, such as H_2SO_4, and $ZnCl_2$,

$$CH_3{\cdot}CH_2{\cdot}OH = CH_2{:}CH_2 + H_2O.$$

The action of oxidising agents varies with the nature of the alcohol. Primary alcohols are converted into aldehydes, and then into fatty acids, secondary alcohols into ketones, and in both cases the oxidation products contain the same number of carbon atoms in the molecule as the alcohol from which they are formed,

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}OH + O = CH_3{\cdot}CH_2{\cdot}CHO + H_2O$$
$$CH_3{\cdot}CH(OH){\cdot}CH_3 + O = CH_3{\cdot}CO{\cdot}CH_3 + H_2O.$$

Tertiary alcohols do not yield oxidation products containing the same number of carbon atoms as the alcohol, but are decomposed, giving simpler acids or ketones.

CHAPTER VII.

THE ETHERS.

The ethers, such as methyl ether, $CH_3{\cdot}O{\cdot}CH_3$, methyl ethyl ether, $CH_3{\cdot}O{\cdot}C_2H_5$, &c., are substances which contain an oxygen atom united to two hydrocarbon groups, such as CH_3-, C_2H_5-, and C_3H_7-. They are related to the metallic oxides in the same way as the alcohols to the metallic hydroxides.

$CH_3{\cdot}OH$ corresponds to $K{\cdot}OH$
$CH_3{\cdot}O{\cdot}CH_3$ " " $K{\cdot}O{\cdot}K$.

Methyl ether, $CH_3{\cdot}O{\cdot}CH_3$, may be prepared by the action of sulphuric acid or other suitable dehydrating agent on methyl alcohol,

$$2CH_3{\cdot}OH = CH_3{\cdot}O{\cdot}CH_3 + H_2O.$$

It is a gas which liquefies at −23°, and dissolves readily in water (1 vol. of water dissolves 37 vols. of methyl ether).

Ethyl ether, ether, or sulphuric ether,

$$C_4H_{10}O \text{ or } C_2H_5{\cdot}O{\cdot}C_2H_5,$$

is formed, together with sodium iodide, when sodium ethoxide is warmed with ethyl iodide,

$$C_2H_5{\cdot}ONa + C_2H_5I = C_2H_5{\cdot}O{\cdot}C_2H_5 + NaI.$$

It is also produced when ethyl alcohol is heated with sulphuric acid, zinc chloride, or other dehydrating agent,

$$2C_2H_5{\cdot}OH = C_2H_5{\cdot}O{\cdot}C_2H_5 + H_2O.$$

Ethyl ether is prepared by the following method:

A mixture of five parts of 90 per cent. alcohol and nine parts of concentrated sulphuric acid is heated in a flask fitted with a tap funnel and thermometer, and connected with a condenser (fig. 17). As soon as the temperature rises to 140°

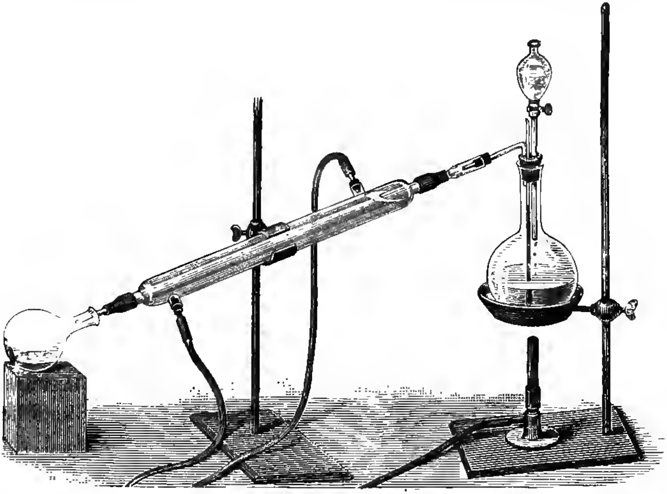


Fig. 17.

the mixture begins to boil, and ether distils over. Alcohol is now slowly run in from the tap funnel, the temperature being kept at 140–145°, and the process continued until a considerable quantity of ether has collected. The crude product in the receiver is a mixture of ether, alcohol, and water, and contains sulphur dioxide. It is shaken with dilute soda in a separating funnel; the layer of ether which collects on the surface is then separated, dried over calcium chloride or quicklime, and purified by redistillation from a water-bath. The ether still contains traces of water and alcohol, which may be got rid of by adding pieces of bright sodium, allowing to stand for some time, and again distilling. Sodium ethoxide and sodium hydroxide remain, and pure ether passes over.

The formation of ether from alcohol takes place in two stages. When alcohol is heated with sulphuric acid, it is converted into ethyl hydrogen sulphate (p. 182),

$$C_2H_5{\cdot}OH + H_2SO_4 = C_2H_5{\cdot}HSO_4 + H_2O\,;$$

this compound then interacts with alcohol, yielding ether and sulphuric acid,

$$C_2H_5{\cdot}HSO_4 + C_2H_5{\cdot}OH = C_2H_5{\cdot}O{\cdot}C_2H_5 + H_2SO_4.$$

That this is the true explanation of the formation of ether, is shown by the fact that ether is formed when pure ethyl hydrogen sulphate is heated with alcohol.

Now, since the sulphuric acid necessary for the conversion of the alcohol into ethyl hydrogen sulphate is regenerated when the latter is heated with alcohol, a given quantity of the acid might, theoretically, convert an unlimited quantity of alcohol into ether. As a matter of fact, a small quantity of sulphuric acid can transform a very large quantity of alcohol into ether, but the process has a limit, because the acid becomes diluted by the water formed in the first stage of the reaction, and part of it is reduced by the alcohol with formation of sulphur dioxide. This method of preparing ether, by the *continuous* addition of alcohol to a solution of alcohol in sulphuric acid, is termed the *continuous process.*

Ether is a colourless, mobile, neutral, pleasant-smelling liquid of sp. gr. 0·736 at 0°. It boils at 35°, and does not solidify at $-80°$. It is very volatile, and highly inflammable, its vapour forming an explosive mixture with air or oxygen,

$$C_4H_{10}O + 6O_2 = 4CO_2 + 5H_2O,$$

so that all experiments in which ether is used should be conducted at a considerable distance from all flames or hot objects. Ether is soluble in about ten times its own volume of water, and is miscible with alcohol and other organic liquids in all proportions.

Compared with alcohol, ether is a very indifferent substance. It is not acted on by sodium or potassium, by alkalies or weak acids, or by phosphorus pentachloride in the cold. Concentrated acids, however, decompose ether, with formation of ethereal salts (p. 171),

$$(C_2H_5)_2O + 2H_2SO_4 = 2C_2H_5{\cdot}HSO_4 + H_2O$$
$$(C_2H_5)_2O + 2HI = 2C_2H_5I + H_2O.$$

Ether is used in considerable quantities in surgery as an anæsthetic, since, like chloroform, it causes insensibility when inhaled; it is also very largely employed as a solvent for resins, fats, oils, alkaloids, &c.

Constitution of Ether.—Since ether is produced by the action of ethyl iodide, C_2H_5I, on sodium ethoxide, $C_2H_5{\cdot}ONa$, it may be concluded that it is formed by the substitution of the monovalent C_2H_5- group for the sodium atom, and its constitution may be expressed by the formula $C_2H_5{\cdot}O{\cdot}C_2H_5$. The same conclusion is arrived at from the fact that ether is formed when 1 mol. of H_2O is taken away from 2 mols. of alcohol by the action of dehydrating agents,

$$C_2H_5\boxed{OH \quad H}OC_2H_5 = C_2H_5{\cdot}O{\cdot}C_2H_5 + H_2O.$$

When represented by this formula, several facts concerning the behaviour of ether are brought to mind. Ether, unlike alcohol, contains no HO– group, and therefore it is not acted on by sodium or potassium, or by phosphorus pentachloride; and, not being a hydroxide, it does not interact with acids to form an ethereal salt and water. Ether may be regarded as the *anhydride* of alcohol, as it is formed from alcohol (2 mols.) by the removal of the elements of water, just in the same way as nitric anhydride is formed from nitric acid,

$$2C_2H_5{\cdot}OH = (C_2H_5)_2O + H_2O \qquad 2NO_2{\cdot}OH = (NO_2)_2O + H_2O.$$

Ether may also be compared with the metallic oxides and regarded as *ethyl oxide,* since it is related to alcohol or ethyl hydroxide in the same way as the metallic oxides to the metallic hydroxides,

$$\begin{array}{llll} C_2H_5{\cdot}OH & C_2H_5{\cdot}O{\cdot}C_2H_5 & \text{or} & (C_2H_5)_2O \\ K{\cdot}OH & K{\cdot}O{\cdot}K & \text{or} & K_2O. \end{array}$$

Finally, it may be regarded as a di-substitution product of water, the mono-substitution product being the corresponding alcohol,

$$H{\cdot}O{\cdot}H \qquad C_2H_5{\cdot}O{\cdot}H \qquad C_2H_5{\cdot}O{\cdot}C_2H_5.$$

The *homologues* of ether are very similar to ethyl ether in properties.

SUMMARY AND EXTENSION.

Some of the more important higher ethers are the following:

Dipropyl ether $(CH_3{\cdot}CH_2{\cdot}CH_2)_2O$	B.p.	90·7°
Di-isopropyl ether $\left(\begin{matrix}CH_3\\CH_3\end{matrix}{>}CH\right)_2O$	"	69°
Di-isobutyl ether $\left(\begin{matrix}CH_3\\CH_3\end{matrix}{>}CH{\cdot}CH_2\right)_2O$	"	122°
Di-isoamyl ether $(C_5H_{11})_2O$	"	170–175°

General Methods of Formation.—The ethers may be obtained by treating the sodium compounds of the alcohols with the alkyl halogen compounds,

$$CH_3{\cdot}ONa + CH_3I = CH_3{\cdot}O{\cdot}CH_3 + NaI;$$

but they are usually prepared by heating the alcohols with sulphuric acid. If a mixture of two alcohols be treated with sulphuric acid, *three* ethers are formed. A mixture of methyl and ethyl alcohols, for example, yields *methyl ether*, *ethyl ether*, and *methyl ethyl ether*, $CH_3{\cdot}O{\cdot}C_2H_5$. The formation of the two first-named compounds will be understood from the equations given above in the case of ethyl ether. Methyl ethyl ether is produced by the interaction (*a*) of methyl hydrogen sulphate, and ethyl alcohol, (*b*) of ethyl hydrogen sulphate and methyl alcohol,

$$CH_3{\cdot}HSO_4 + C_2H_5{\cdot}OH = CH_3{\cdot}O{\cdot}C_2H_5 + H_2SO_4$$
$$C_2H_5{\cdot}HSO_4 + CH_3{\cdot}OH = C_2H_5{\cdot}O{\cdot}CH_3 + H_2SO_4.$$

All ethers, such as methyl ethyl ether, $CH_3{\cdot}O{\cdot}C_2H_5$, which contain two different hydrocarbon groups, are termed *mixed ethers*, to distinguish them from *simple ethers*, such as ethyl ether, $C_2H_5{\cdot}O{\cdot}C_2H_5$, and those given in the above table, which contain two identical groups. Mixed ethers can also be obtained by treating the sodium compounds of the alcohols with alkyl halogen compounds,

$$CH_3{\cdot}ONa + C_3H_7I = CH_3{\cdot}O{\cdot}C_3H_7 + NaI.$$

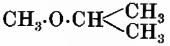
General Properties.—With the exception of methyl ether, which is a gas, the ethers are mobile, volatile, inflammable liquids, specifically lighter than water; they all boil at a much lower temperature than the corresponding alcohols. In chemical properties they closely resemble ethyl ether. They are not acted on by alkalies or alkali metals, and do not combine with dilute acids; but they are decomposed when heated with strong acids, yielding ethereal salts,

$$(C_2H_5)_2O + 2H_2SO_4 = 2C_2H_5{\cdot}HSO_4 + H_2O$$
$$CH_3{\cdot}O{\cdot}C_2H_5 + 2HBr = CH_3Br + C_2H_5Br + H_2O.$$

Chlorine and bromine act on ethers, forming substitution products such as

$$CH_2Cl{\cdot}O{\cdot}CH_3,\ CH_2Br{\cdot}O{\cdot}CH_2Br,\ C_2H_5{\cdot}O{\cdot}C_2H_4Cl,\ \&c.$$

Metamerism.—The ethers exist in isomeric forms. There are, for example, three compounds of the formula $C_4H_{10}O$,

$CH_3{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$	 $CH_3{\cdot}O{\cdot}CH{<}^{CH_3}_{CH_3}$	$CH_3{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_3.$
Methyl Propyl Ether.	Methyl Isopropyl Ether.	Ethyl Ether.

Substances such as these, which have the same molecular formula, but in which *all* the carbon atoms in the molecule are not directly united, are called *metameric;* the phenomenon is called *metamerism*, and the several compounds, *metamers.* Metamerism is simply a particular form of isomerism, and there is no real distinction between the two, the different terms being used purely for the sake of convenience.

RADICLES.

On studying the equations which represent the interactions of alcohols, ethers, &c., it is evident that certain groups of atoms often remain unchanged during a whole series of double decompositions. Ethyl chloride, for example, may be converted into ethyl alcohol, the latter may be transformed into ethyl iodide, and this again may be converted into butane, but during all these interactions the group C_2H_5- remains unchanged, and behaves, in fact, as if it were a single atom,

$$C_2H_5{\cdot}Cl + H{\cdot}OH = C_2H_5{\cdot}OH + HCl$$
$$C_2H_5{\cdot}OH + HI = C_2H_5{\cdot}I + H_2O$$
$$2C_2H_5{\cdot}I + 2Na = C_2H_5{\cdot}C_2H_5 + 2NaI.$$

Numerous examples of a similar kind might be quoted; amongst others, the changes by which the five compounds, $CH_3{\cdot}Cl$, $CH_3{\cdot}OH$ $CH_3{\cdot}O{\cdot}CH_3$, $CH_3{\cdot}I$, and $CH_3{\cdot}CH_3$, may be successively transformed one into the other.

Groups of atoms, such as C_2H_5- and CH_3-, which act like *single atoms*, and which *enter unchanged* into a number of compounds, are termed **radicles**, or sometimes compound radicles.

Radicles may be monovalent, divalent, &c., according as they act like monad, dyad, &c., atoms; the radicles C_2H_5- and CH_3-, for example, are monad radicles, because they combine with one atom of hydrogen or its valency equivalent, as shown in the above equations.

The name **alkyl** or alcohol radicle is given to all the *monovalent* groups of atoms which are, theoretically, obtained on taking away one atom of hydrogen from the paraffins, methane, ethane, propane, butane, &c.; the distinctive names of these radicles are derived from those of the hydrocarbons by changing *ane* into *yl*, thus: *methyl*, CH_3-; *ethyl*, C_2H_5- or $CH_3{\cdot}CH_2-$; *propyl*, C_3H_7- or $CH_3{\cdot}CH_2{\cdot}CH_2-$; *isopropyl*, C_3H_7- or $(CH_3)_2CH-$; *butyl*, C_4H_9- or $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2-$; *isobutyl*, C_4H_9- or $(CH_3)_2CH{\cdot}CH_2-$, &c.

The compounds formed by the combination of these hypothetical alkyl radicles with hydrogen, as, for example, $CH_3{\cdot}H$, $C_2H_5{\cdot}H$, $C_3H_7{\cdot}H$, are named collectively the *alkyl hydrides*, and are identical with the paraffins; the corresponding chlorine compounds, such as $CH_3{\cdot}Cl$, $C_2H_5{\cdot}Cl$, $C_3H_7{\cdot}Cl$, are termed the *alkyl chlorides*, and so on. The letter R is frequently employed to represent an alkyl radicle, as, for example, in the formulæ $R{\cdot}OH$ (alcohols) and $R{\cdot}O{\cdot}R$ (simple ethers).

The name **alkylene** is given to the *divalent* radicles, which (except methylene) may be actually obtained by taking away two atoms of hydrogen from the paraffins. The alkylenes are *methylene*, $CH_2=$; *ethylene*, $C_2H_4=$; *propylene*, $C_3H_6=$; *butylene*, $C_4H_8=$, &c. ; and the compounds which they form, with chlorine, for example, such as $CH_2{:}Cl_2$, $C_2H_4{:}Cl_2$, are termed collectively the *alkylene chlorides*, &c.

Trivalent hydrocarbon radicles, such as *glyceryl*, $C_3H_5\equiv$, are seldom met with, and will be mentioned later.

Other radicles frequently met with are: hydroxyl, $-OH$; carbonyl, $=CO$; carboxyl, $-CO{\cdot}OH$; cyanogen, $-CN$; acetyl, $-CO{\cdot}CH_3$, &c. The true significance of the term radicle will be more easily understood when a greater number of organic compounds has been considered.

CHAPTER VIII.

ALDEHYDES AND KETONES.

The aldehydes form a homologous series of the general formula $C_nH_{2n}O$, or $C_nH_{2n+1}{\cdot}CHO$; they are derived from the primary alcohols $C_nH_{2n+1}{\cdot}CH_2{\cdot}OH$ by the removal of two atoms of hydrogen from the $-CH_2{\cdot}OH$ group,

Paraffins.	Alcohols.	Aldehydes.
$H{\cdot}CH_3$	$H{\cdot}CH_2{\cdot}OH$	$H{\cdot}CHO$
$CH_3{\cdot}CH_3$	$CH_3{\cdot}CH_2{\cdot}OH$	$CH_3{\cdot}CHO$
$C_2H_5{\cdot}CH_3$	$C_2H_5{\cdot}CH_2{\cdot}OH$	$C_2H_5{\cdot}CHO.$

The word aldehyde is a contraction of *al*cohol *dehyd*rogenatum, this name having been originally given to acetaldehyde, because it is formed when hydrogen is taken from alcohol by a process of oxidation.

Formaldehyde, or methaldehyde, $H{\cdot}CHO$, is said to occur in those plant cells which contain the green colouring matter, chlorophyll, and is possibly an intermediate product in that wonderful process—the formation of starch and sugars from the carbon dioxide which the plant absorbs from the air.

Formaldehyde is produced when calcium formate is subjected to dry distillation,

$$(H{\cdot}COO)_2Ca = H{\cdot}CHO + CaCO_3,$$

and is prepared by passing a stream of air, saturated with the vapour of methyl alcohol, through a tube containing a copper spiral, or platinised asbestos, heated to dull redness;* the change is a process of oxidation,

$$CH_3{\cdot}OH + O = H{\cdot}CHO + H_2O.$$

The pungent-smelling liquid which collects in the receiver may contain, under favourable conditions, as much as 30–40 per cent. of formaldehyde, together with methyl alcohol and water. On evaporating the solution on a water-bath or even at ordinary temperatures, the formaldehyde gradually undergoes change (polymerisation), and is converted into paraformaldehyde, which remains as a white solid.

The formation of formaldehyde may be readily demonstrated by heating a spiral of platinum wire to dull redness and quickly suspending it over methyl alcohol contained in a beaker; the spiral begins to glow, and irritating vapours are rapidly evolved, a slight but harmless explosion usually taking place.

Formaldehyde is only known in dilute solution and in the state of a gas at high temperatures (see below). That it would probably be a gas at ordinary temperatures may be inferred by considering the boiling-points of the next higher members of the series. Since the difference between the boiling-points of two consecutive aldehydes such as

---

* Unless special precautions be taken, explosions frequently occur.

propaldehyde, $C_2H_5{\cdot}CHO$ (49°), and acetaldehyde, $CH_3{\cdot}CHO$ (20°·8), is about 28°, formaldehyde would probably boil at about $-7°$, or 28° lower than acetaldehyde.* Aqueous solutions of formaldehyde have a very penetrating, suffocating odour and a neutral reaction; they have also a powerful reducing action, since formaldehyde readily undergoes oxidation, yielding formic acid,

$$H{\cdot}CHO + O = H{\cdot}COOH.$$

When its aqueous solution is mixed with an ammoniacal solution of silver oxide, the latter is reduced, a silver mirror being obtained,

$$H{\cdot}CHO + Ag_2O = H{\cdot}COOH + 2Ag;$$

mercuric chloride is also reduced, first to mercurous chloride, then to mercury.

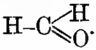
When formaldehyde is treated with reducing agents, it is converted into methyl alcohol,

$$H{\cdot}CHO + 2H = H{\cdot}CH_2{\cdot}OH.$$

When a concentrated aqueous solution of formaldehyde is mixed with a saturated solution of sodium hydrogen sulphite, direct combination takes place, a compound of the constitution $OH{\cdot}CH_2{\cdot}SO_3Na$ being formed. Formaldehyde interacts with hydroxylamine in aqueous solution, yielding *formaldoxime*,

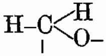
$$H{\cdot}CHO + NH_2{\cdot}OH = H{\cdot}CH:NOH + H_2O,$$

a substance which is only known in solution since it very readily undergoes polymerisation.

Constitution.—Since carbon is tetravalent, there is only one way of expressing graphically the constitution of formaldehyde, CH_2O, namely, by the formula  $H{-}C\begin{smallmatrix}\diagup H\\ \diagdown O\end{smallmatrix}$. In the formation of formaldehyde by the oxidation of methyl alcohol, $CH_3{-}O{-}H$, the hydrogen atom of the $HO{-}$ group and one of the atoms combined directly with carbon are

---

* As a rule, the lowest member of a homologous series shows a somewhat abnormal behaviour, and its properties cannot be foretold with as much certainty as in the case of the higher members.

taken away. The carbon and oxygen atoms in formaldehyde are therefore represented in a state of combination different from that existing in methyl alcohol—namely, as joined by two lines instead of one. Formaldehyde behaves in some ways like an unsaturated compound, capable of forming additive products, because, under certain conditions, it may act as if it had the constitution  $H-\underset{|}{C}\genfrac{}{}{0pt}{}{\diagup H}{\diagdown O-}$ In aqueous solution it probably exists to some extent as the hydrate $CH_2(OH)_2$.

Paraformaldehyde, $(CH_2O)_n$, is formed, as stated above, when an aqueous solution of formaldehyde is evaporated; it is a colourless, amorphous substance, sublimes readily, and melts at 171°. When strongly heated, it is completely decomposed into pure, *gaseous formaldehyde*, CH_2O, as is proved by vapour density determinations; but as the gas cools, paraformaldehyde is again produced. When paraformaldehyde is heated with a large quantity of water, it is reconverted into formaldehyde.

The relation between formaldehyde and paraformaldehyde is similar to that between yellow and red phosphorus, or between the allotropic modifications of elements in general. Just as yellow is converted into red phosphorus on heating, so formaldehyde is converted into paraformaldehyde; and just as red is changed into yellow phosphorus on heating more strongly, so paraformaldehyde is changed into formaldehyde. Here, however, the similarity in behaviour ends, since the gaseous formaldehyde changes into paraformaldehyde on cooling.

The different forms in which a definite compound may exist are termed **polymeric** forms or modifications, such forms being in many respects similar to the allotropic forms of the elements—that is to say, a polymeric form is simply an aggregate of the molecules of the original substance, and the change of the simple into a complex form is spoken of as **polymerisation**. Paraformaldehyde is a polymeric form or a **polymeride** or **polymer** of formaldehyde, and its molecule consists of two or more (n) molecules of formaldehyde united to form a complex molecule $(CH_2O)_n$.

Formaldehyde forms several polymeric modifications, and the readiness with which it undergoes polymerisation is one of its most characteristic properties. When its aqueous solution is treated with lime-water or other weak alkali, formaldehyde undergoes polymerisation into *formose*, a mixture of substances, some of which have the composition $(CH_2O)_6$ or $C_6H_{12}O_6$, and belong to the sugar group. This reaction is of great interest, since it shows that complex vegetable substances such as the sugars may be formed by very simple means.

Methylal, $CH_2(OCH_3)_2$, is an important derivative of formaldehyde. It may be obtained by boiling aqueous formaldehyde with methyl alcohol and a small quantity of sulphuric acid, but is usually prepared by oxidising methyl alcohol with manganese dioxide and sulphuric acid, the formaldehyde first produced combining with the unchanged methyl alcohol,

$$H{\cdot}CHO + 2CH_3{\cdot}OH = H{\cdot}CH(OCH_3)_2 + H_2O.$$

Methylal, a pleasant-smelling liquid, which boils at 42° and is readily soluble in water, is used in medicine as a soporific. When distilled with dilute sulphuric acid, it is resolved into methyl alcohol and formaldehyde, a reaction which may be conveniently employed for preparing the latter.

Acetaldehyde, or ethaldehyde, $CH_3{\cdot}CHO$, is contained in the 'first runnings' obtained in the rectification of refined spirit (p. 100), having been formed by the oxidation of the alcohol during the process of filtration through charcoal; it is formed when a mixture of calcium acetate and calcium formate is submitted to dry distillation,

$$(CH_3{\cdot}COO)_2Ca + (H{\cdot}COO)_2Ca = 2CH_3{\cdot}CHO + 2CaCO_3,$$

and is prepared by oxidising alcohol with potassium bichromate and sulphuric acid,

$$CH_3{\cdot}CH_2{\cdot}OH + O = CH_3{\cdot}CHO + H_2O.$$

Coarsely powdered potassium bichromate (3 parts) and water (12 parts) are placed in a capacious flask fitted with a tap-funnel and attached to a condenser, and a mixture of alcohol (3 parts) and concentrated sulphuric acid (4 parts) is then run in moderately rapidly, the flask being gently heated on a water-bath during the operation. A vigorous action sets in, and a liquid, which consists of aldehyde, alcohol, water, and small quantities of acetal (see below), collects in the receiver. This liquid is now distilled from a water-bath, the temperature of which is not allowed to rise above 50°, when the aldehyde, being very volatile, passes over, most of the impurities remaining in the flask; the distillate is then mixed with ether, and the mixture saturated with dry ammonia, when a crystalline precipitate of *aldehyde ammonia* (see below) is obtained. This substance is transferred to a filter, washed with ether, and then decomposed by distillation with dilute sulphuric acid at as low a temperature as possible; the aldehyde is finally dehydrated by distillation with coarsely powdered anhydrous calcium chloride, the receiver being well cooled with ice in this and in the previous operations.

Acetaldehyde, or aldehyde, as it is usually called, is a colourless, mobile, very volatile liquid of sp. gr. 0·801 at 0°; it boils at 20·8°. It has a peculiar penetrating and suffocating odour, somewhat like that of sulphur dioxide, and when inhaled it produces cramp in the throat, and for some seconds takes away the power of respiration; it is very inflammable, and mixes with water, alcohol, and ether in all proportions. Aldehyde is slowly oxidised to acetic acid on exposure to the air, and, like formaldehyde, it has powerful reducing properties; it precipitates silver, in the form of a mirror, from ammoniacal solutions of silver oxide, being itself oxidised to acetic acid,

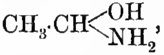
$$CH_3{\cdot}CHO + Ag_2O = CH_3{\cdot}COOH + 2Ag.$$

On treatment with reducing agents, it is converted into alcohol, just as formaldehyde is reduced to methyl alcohol,

$$CH_3{\cdot}CHO + 2H = CH_3{\cdot}CH_2{\cdot}OH$$
$$H{\cdot}CHO + 2H = H{\cdot}CH_2{\cdot}OH.$$

Aldehyde interacts readily with hydroxylamine in aqueous solution, yielding a crystalline compound, *acetaldoxime*,

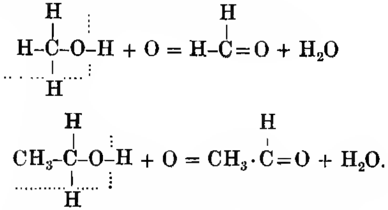
$$CH_3{\cdot}CHO + NH_2{\cdot}OH = CH_3{\cdot}CH{:}NOH + H_2O.$$

When aldehyde is shaken with a concentrated solution of sodium hydrogen sulphite (sodium bisulphite), direct combination occurs, and a colourless substance of the composition $CH_3{\cdot}CHO,NaHSO_3$ separates in crystals. This compound is readily decomposed by acids, alkalies, and alkali carbonates, aldehyde being liberated. Aldehyde also combines directly with dry ammonia, yielding a colourless, crystalline substance, *aldehyde ammonia*, $CH_3{\cdot}CHO,NH_3$, or  $CH_3{\cdot}CH{<}^{OH}_{NH_2}$, which is decomposed by acids, aldehyde being regenerated.

Aldehyde very readily undergoes polymerisation on treatment with acids, dehydrating agents, and other substances (see below). Its behaviour with alkalies is very characteristic; when it is warmed with potash or soda, a violent action sets in, and the aldehyde is converted into a brown substance called *aldehyde resin*.

Aldehyde may be detected by its smell, by its reducing action on silver oxide, and by the 'magenta' or 'rosaniline test' (Schiff's reaction), which is carried out as follows: Sulphurous acid is added to a dilute solution of rosaniline hydrochloride until the pink colour is just discharged; the solution to be tested is now added, when, if it contain a trace of aldehyde, a violet or pink colour immediately appears. This behaviour is not characteristic of acetaldehyde, as, with very few exceptions, all aldehydes give this reaction.

Constitution.—Aldehyde is formed by the oxidation of ethyl alcohol, just as formaldehyde is produced by the oxidation of methyl alcohol, two atoms of hydrogen being removed in both cases. Now, as regards formaldehyde, it must be assumed that the hydrogen atom of the HO– group takes part in the change; probably, therefore, this is also true in the case of acetaldehyde, because the two substances are so very similar in chemical properties that they must be similar in constitution. The two reactions may therefore be expressed in a similar manner,



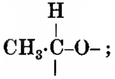
$$H\!-\!\overset{H}{\underset{H}{C}}\!-\!O\!-\!H + O = H\!-\!\overset{H}{C}\!=\!O + H_2O$$

$$CH_3\!-\!\overset{H}{\underset{H}{C}}\!-\!O\!-\!H + O = CH_3\cdot\overset{H}{C}\!=\!O + H_2O.$$

Judging from analogy, then, the constitution of aldehyde is expressed by the formula $CH_3\cdot C\genfrac{}{}{0pt}{}{\diagup H}{\diagdown O}$; this view accords very well with the whole chemical behaviour of the compound. Aldehyde, unlike alcohol, does not contain a hydrogen atom displaceable by sodium or potassium, and does not form salts with acids; these facts are expressed by the above formula, which shows that aldehyde does not contain an HO– group. When aldehyde is treated with phosphorus pentachloride, one atom of oxygen is displaced by *two* atoms of chlorine, a change which is very different from that which occurs when alcohol is acted on, and which affords further evidence that aldehyde is not a hydroxy-compound. This point is rendered very clear if the behaviour of aldehyde and alcohol respectively with phosphorus pentachloride be represented side by side,

$$CH_3\cdot CH\mathbf{O} + PCl_5 = CH_3\cdot CHCl_2 + POCl_3$$
$$CH_3\cdot CH_2\cdot\mathbf{OH} + PCl_5 = CH_3\cdot CH_2Cl + POCl_3 + HCl.$$

The fact that aldehyde has the power of combining directly with ammonia, sodium hydrogen sulphite, alcohol (see below), &c., is also indicated by the above constitutional formula. Under certain conditions the nature of the union between the carbon and oxygen atoms may undergo change, and the aldehyde may then act as if it had the constitution



$$\mathrm{CH_3\cdot\overset{H}{\underset{|}{\overset{|}{C}}}{-}O{-}}\ ;$$

in other words, it may behave like an unsaturated compound and combine directly with two monad atoms or groups, as in its reduction to ethyl alcohol, in its conversion into aldehyde ammonia, &c.

It will be seen that both formaldehyde and acetaldehyde contain the monovalent group $-\mathrm{C}{<}^{\mathrm{H}}_{\mathrm{O}}$, which is usually written $-\mathrm{CHO}$ (not COH); it is the presence of this *aldehyde group* which determines their characteristic properties, and all aldehydes are assumed to contain a group of this kind.

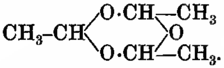
Polymerisation of Acetaldehyde.—Three well-defined polymerides of aldehyde are known—namely, aldol, paraldehyde, and metaldehyde.

Aldol, $(C_2H_4O)_2$, or $CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CHO$, is produced by the action of dilute hydrochloric acid, or of zinc chloride, on aldehyde at ordinary temperatures. It is a colourless, inodorous liquid, miscible with water, and shows all the ordinary properties of an aldehyde. It can be distilled under reduced pressure without decomposition, but when distilled under ordinary pressure, or when treated with dehydrating agents, it is converted into *crotonaldehyde* (p. 256) and water,

$$CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CHO = CH_3{\cdot}CH{:}CH{\cdot}CHO + H_2O.$$

Paraldehyde, $(C_2H_4O)_3$, is readily produced by adding a drop of concentrated sulphuric acid to aldehyde, an almost explosive action taking place. It is a colourless, pleasant-smelling liquid, boils at 124°, and solidifies in the cold. It is soluble in water, its cold saturated solution becoming turbid on warming, as it is less soluble in hot than in cold water; when distilled with dilute sulphuric acid, it is converted into aldehyde. Paraldehyde is used in medicine as a soporific.

Paraldehyde shows none of the ordinary properties of an aldehyde, and probably, therefore, does not contain the aldehyde or -CHO group; in other words, it is not a true aldehyde, and its constitution is usually represented by the formula



Metaldehyde, $(C_2H_4O)_n$, is produced by the action of acids on aldehyde at low temperatures. It crystallises in colourless needles, and is insoluble in water; it can be sublimed without decomposition, but on prolonged heating, it is converted into aldehyde, a change which is also readily brought about by distilling it with dilute sulphuric acid. Metaldehyde is probably isomeric with paraldehyde.

Derivatives of Aldehyde.—**Acetal,** $CH_3{\cdot}CH(OC_2H_5)_2$, is produced when a mixture of aldehyde and alcohol is heated at 100°, or when alcohol is oxidised with manganese dioxide and sulphuric acid (compare methylal, p. 120),

$$CH_3{\cdot}CHO + 2C_2H_5{\cdot}OH = CH_3{\cdot}CH(OC_2H_5)_2 + H_2O.$$

It is a colourless liquid, possessing an agreeable smell, and boiling at 104°; when distilled with dilute acids, it is decomposed into alcohol and aldehyde,

$$CH_3{\cdot}CH(OC_2H_5)_2 + H_2O = CH_3{\cdot}CHO + 2C_2H_5{\cdot}OH.$$

Chloral, or trichloraldehyde, $CCl_3{\cdot}CHO$, cannot be prepared by the direct action of chlorine on aldehyde; it is manufactured on a large scale by saturating alcohol with chlorine, first at ordinary temperatures, and then at the boiling-point, the operation taking some days. The crystalline product, which consists for the greater part of *chloral alcoholate,* $CCl_3{\cdot}CH\Big\langle\begin{matrix}OC_2H_5\\OH\end{matrix}$, is distilled with concentrated sulphuric acid, and the oily distillate of crude chloral converted into chloral hydrate (see below). After purifying the hydrate by recrystallisation from water, it is distilled with sulphuric acid, when pure chloral passes over.

The formation of chloral alcoholate may be represented by the equations

$$CH_3{\cdot}CH_2{\cdot}OH + O = CH_3{\cdot}CHO + H_2O$$
$$CH_3{\cdot}CHO + C_2H_5{\cdot}OH = CH_3{\cdot}CH(OH){\cdot}OC_2H_5$$
$$CH_3{\cdot}CH(OH){\cdot}OC_2H_5 + 3Cl_2 = CCl_3{\cdot}CH(OH){\cdot}OC_2H_5 + 3HCl,$$

the aldehyde first produced by the oxidising action of the chlorine (p. 91), combining with alcohol, and being finally converted into chloral alcoholate by substitution.

It is, however, very doubtful whether the action is quite so simple. A more probable explanation is that acetal is first produced by the combination of the aldehyde with the unchanged alcohol, and then converted into trichloracetal, $CCl_3{\cdot}CH(OC_2H_5)_2$, by the further action of chlorine; this substance is finally decomposed by the hydrogen chloride produced during the reaction, giving chloral alcoholate and ethyl chloride,

$$CCl_3{\cdot}CH(OC_2H_5)_2 + HCl = CCl_3{\cdot}CH{<}{\begin{matrix}OC_2H_5\\OH\end{matrix}} + C_2H_5Cl.$$

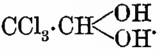
Chloral is an oily liquid of sp. gr. 1·512 at 20°, and boils at 97°. It has a penetrating and irritating smell, and in chemical properties closely resembles aldehyde, a fact which was only to be expected, since it is a simple substitution product of aldehyde, and contains the characteristic aldehyde group. It has reducing properties, combines directly with ammonia, sodium hydrogen sulphite, &c., and on oxidation it is converted into trichloracetic acid (p. 163), just as aldehyde is converted into acetic acid,

$$CCl_3{\cdot}CHO + O = CCl_3{\cdot}COOH.$$

On the addition of small quantities of acids, it readily undergoes polymerisation, being transformed into a white amorphous modification called *metachloral;* the same change takes place when chloral is kept for a considerable time. One of the most interesting reactions of chloral is its behaviour with boiling potash, by which it is quickly decomposed, giving chloroform (p. 172) and potassium formate,

$$CCl_3{\cdot}CHO + KOH = CHCl_3 + H{\cdot}COOK.$$

Pure chloroform is often prepared in this way.

Chloral Hydrate, $CCl_3{\cdot}CH(OH)_2$.—When chloral is poured into water, it sinks as an oil at first, but in a few seconds the oil changes to a mass of colourless crystals of chloral hydrate, a considerable rise in temperature taking place. Chloral hydrate melts at 57°, is readily soluble in water, and is decomposed on distillation with sulphuric acid, chloral passing over. In some respects it is a very stable substance; it does not polymerise, and does not give the rosaniline reaction of aldehydes. These facts point to the conclusion that chloral hydrate does not contain the aldehyde group, but that by combination with water the chloral has been converted into a substance of the constitution  $CCl_3{\cdot}CH\begin{smallmatrix}\diagup OH\\ \diagdown OH\end{smallmatrix}$.

Chloral hydrate is extensively used in medicine as a soporific.

Homologues of Acetaldehyde.—The higher members of the homologous series of aldehydes, such as *propaldehyde*, $C_2H_5{\cdot}CHO$, *butaldehyde*, $C_3H_7{\cdot}CHO$, may be produced by the oxidation of the corresponding primary alcohols, or by the dry distillation of the calcium salts of the corresponding fatty acids with calcium formate; they resemble acetaldehyde in chemical properties.

Heptaldehyde, or **Œnanthol**, $C_6H_{13}{\cdot}CHO$, is of considerable interest because it is one of the products of the dry distillation of castor-oil. It is a colourless oil, boils at 154°, and has a penetrating, disagreeable odour; on oxidation it yields normal heptylic acid, $C_6H_{13}{\cdot}COOH$ (p. 158), and on reduction, normal heptyl alcohol, $C_6H_{13}{\cdot}CH_2{\cdot}OH$.

KETONES.

The ketones, of which the simplest, acetone, $CH_3{\cdot}CO{\cdot}CH_3$, may be taken as an example, are derived from the secondary alcohols, such as isopropyl alcohol, $CH_3{\cdot}CH(OH){\cdot}CH_3$, by the removal of two atoms of hydrogen from the $-CH(OH)$

group, the process being, in fact, strictly analogous to the formation of aldehydes from the primary alcohols. Ketones are characterised by containing the divalent group $>C=O$ united with two alkyl radicles, as in $CH_3{\cdot}CO{\cdot}C_2H_5$, $C_2H_5{\cdot}CO{\cdot}C_2H_5$, and their composition may be expressed by the general formula $C_nH_{2n}O$; they are isomeric with the aldehydes:

$$\left.\begin{array}{ll}\text{Propaldehyde,} & CH_3{\cdot}CH_2{\cdot}CHO \\ \text{Dimethyl ketone,} & CH_3{\cdot}CO{\cdot}CH_3\end{array}\right\} C_3H_6O$$

$$\left.\begin{array}{ll}\text{Butaldehyde,} & CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CHO \\ \text{Ethylmethyl ketone,} & CH_3{\cdot}CH_2{\cdot}CO{\cdot}CH_3\end{array}\right\} C_4H_8O.$$

Acetone, or dimethyl ketone, $CH_3{\cdot}CO{\cdot}CH_3$, occurs in small quantities in normal urine, and in cases of *diabetes mellitus* and *acetonuria* the quantity increases considerably. It also occurs in small quantities in the blood.

Acetone is formed when isopropyl alcohol is oxidised with potassium bichromate and sulphuric acid,

$$CH_3{\cdot}CH(OH){\cdot}CH_3 + O = CH_3{\cdot}CO{\cdot}CH_3 + H_2O,$$

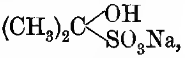
and is produced in considerable quantities during the dry distillation of wood and many other organic compounds, such as sugar, gum, &c. Crude wood-spirit, which has been freed from acetic acid (p. 89), consists in the main of a mixture of acetone and methyl alcohol. These two substances may be roughly separated by the addition of calcium chloride, which combines with the methyl alcohol; on subsequent distillation, crude acetone passes over, and may be purified by conversion into the bisulphite compound (see below).

Acetone is usually prepared by the dry distillation of crude calcium or barium acetate,

$$(CH_3{\cdot}COO)_2Ca = CH_3{\cdot}CO{\cdot}CH_3 + CaCO_3.$$

The distillate is fractionated, and the portion boiling between 50 and 60° mixed with a strong solution of sodium bisulphite. The crystalline cake of 'acetone sodium bisulphite,' which separates on standing, is well pressed, to free it from impurities, decomposed by distillation with dilute sodium carbonate, and the aqueous distillate of pure acetone dehydrated over calcium chloride.

Acetone is a colourless, mobile liquid of sp. gr. 0·792 at 20°; it boils at 56·5°, has a peculiar, pleasant, ethereal odour, and is miscible with water, alcohol, and ether in all proportions.

In chemical properties acetone resembles aldehyde in several important particulars. When shaken with a concentrated aqueous solution of sodium bisulphite, direct combination takes place with considerable development of heat, and a colourless, crystalline substance, *acetone sodium bisulphite*, $CH_3{\cdot}CO{\cdot}CH_3{,}NaHSO_3$, or  $(CH_3)_2C\begin{smallmatrix}\diagup OH\\ \diagdown SO_3Na\end{smallmatrix}$, separates. This compound is readily soluble in water, and is quickly decomposed by dilute acids and alkalies, acetone being regenerated. Acetone, like aldehyde, interacts with hydroxylamine in aqueous solution, forming acetoxime,

$$(CH_3)_2CO + NH_2{\cdot}OH = (CH_3)_2C{:}NOH + H_2O,$$

a crystalline substance, melting at 59°. When treated with phosphorus pentachloride, the oxygen atom in acetone is displaced by two atoms of chlorine, and β-dichloropropane is formed,

$$(CH_3)_2CO + PCl_5 = (CH_3)_2CCl_2 + POCl_3;$$

on reduction, acetone is converted into secondary propyl alcohol,

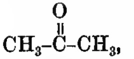
$$(CH_3)_2CO + 2H = (CH_3)_2CH{\cdot}OH.$$

At the same time acetone differs from aldehyde very widely in one or two important respects. It does not undergo polymerisation, and does not reduce ammoniacal solutions of silver oxide; it is oxidised only by moderately powerful agents, by which its molecule is broken up into acetic acid and carbon dioxide,

$$CH_3{\cdot}CO{\cdot}CH_3 + 4O = CH_3{\cdot}COOH + CO_2 + H_2O.$$

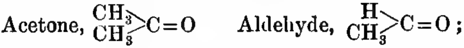
Acetone gives the iodoform reaction (p. 96), and is employed for the preparation of iodoform, chloroform, &c.; it is also used as a solvent.

Constitution.—Acetone is formed when isopropyl alcohol, $\genfrac{}{}{0pt}{}{CH_3}{CH_3}\!>\!CH{-}OH$ (p. 104), loses two atoms of hydrogen by oxidation. It does not contain a hydroxyl-group, because, unlike the alcohols, it does not form salts with acids. That the oxygen atom is combined with carbon only—that is, that acetone contains a $-CO-$ group, is shown by the behaviour of acetone with phosphorus pentachloride, which is similar to that of aldehyde. Furthermore, the $-CO-$ group must be united with two methyl groups, as in the formula $CH_3{\cdot}CO{\cdot}CH_3$, because if it were not, acetone would be identical with propaldehyde, $CH_3{\cdot}CH_2{\cdot}C\genfrac{}{}{0pt}{}{{\diagup\!\!\diagup}O}{\diagdown H}$. These facts, and many others which might be mentioned, show that acetone has the constitution



$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3$, or $(CH_3)_2CO$; its characteristic properties are determined by the presence of the divalent **carbonyl** or **ketonic** group $>\!C=O$, which is assumed to be contained in all ketones.

The similarity in chemical behaviour between acetone and aldehyde is at once brought to mind on considering their graphic formulæ; they both contain the carbonyl group,



$$\text{Acetone, } \genfrac{}{}{0pt}{}{CH_3}{CH_3}\!>\!C=O \qquad \text{Aldehyde, } \genfrac{}{}{0pt}{}{H}{CH_3}\!>\!C=O\,;$$

and therefore those changes, in which only this group takes part, are common to both substances. Such changes are, for example, interaction with hydroxylamine, behaviour with phosphorus pentachloride, and direct combination with sodium bisulphite, hydrogen, &c.; in the last two reactions, acetone acts as if it had the constitution $(CH_3)_2C\genfrac{}{}{0pt}{}{\diagup O-}{\diagdown}$. As regards oxidation, the difference between the two compounds is also readily understood; acetone does not contain the readily oxidisable hydrogen atom of the aldehyde group, and does not combine with oxygen without the molecule being broken up; it is therefore less readily acted on than aldehyde, and does not reduce silver oxide or give the rosaniline test, since both these reactions are the result of oxidation.

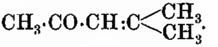
Condensation of Acetone.—When acetone is treated with certain dehydrating agents, it undergoes a peculiar change, two or more molecules combining together with elimination of one or more molecules of water,

$$2(CH_3)_2CO = \underset{\text{Mesityl Oxide.}}{C_6H_{10}O} + H_2O \quad 3(CH_3)_2CO = \underset{\text{Phorone.}}{C_9H_{14}O} + 2H_2O.$$

This, and similar changes, in which two or more molecules of the same or of different substances combine, with separation of water, are termed **condensations**, and the substances formed, **condensation products**; the process differs from polymerisation in this, that water is eliminated. Acetone yields three interesting condensation products. When it is saturated with dry hydrogen chloride, and the solution kept for some time, a mixture of *mesityl oxide* and *phorone* is formed, in accordance with the above equations; but when distilled with concentrated sulphuric acid, acetone yields a hydrocarbon, *mesitylene*, (part ii.), a derivative of benzene,

$$3(CH_3)_2CO = C_9H_{12} + 3H_2O.$$

Mesityl Oxide, $C_6H_{10}O$, is a colourless oil, boiling at 130°, and having a strong peppermint-like smell: when boiled with dilute sulphuric acid, it is decomposed with regeneration of acetone. Its constitution may be represented by the formula $CH_3{\cdot}CO{\cdot}CH{:}C{<}^{CH_3}_{CH_3}$.



$$CH_3{\cdot}CO{\cdot}CH{:}C\begin{matrix}\diagup CH_3\\ \diagdown CH_3\end{matrix}$$

Phorone, $C_9H_{14}O$, crystallises in almost colourless prisms, melting at 28°; it boils at 196°, has a pleasant aromatic odour, and is decomposed by boiling dilute sulphuric acid with formation of acetone.

Substitution Products of Acetone.—Acetone is readily attacked by chlorine with formation of *monochloracetone*, $CH_3{\cdot}CO{\cdot}CH_2Cl$ (b.p. 119), and *asymmetrical dichloracetone*, $CH_3{\cdot}CO{\cdot}CHCl_2$ (b.p. 120°). *Symmetrical dichloracetone*, $CH_2Cl{\cdot}CO{\cdot}CH_2Cl$, is produced by the oxidation of dichlorisopropyl alcohol, or dichlorohydrin (p. 252), $CH_2Cl{\cdot}CH(OH){\cdot}CH_2Cl$; it is a colourless, crystalline solid (m.p. 45°; b.p. 172·5°). Higher substitution products of acetone have been obtained by indirect methods. The final product, *hexachloracetone*, or *perchloracetone*, $CCl_3{\cdot}CO{\cdot}CCl_3$, is a colourless liquid, boiling at 204°. Corresponding bromo-substitution products of acetone have also been prepared.

These halogen substitution products are characterised by their exceedingly irritating action on the eyes, the presence of a mere trace of these substances in the air being sufficient to cause a copious flow of tears; when dropped on the skin, they produce very painful blisters.

Homologues of Acetone may be obtained by the oxidation of the corresponding secondary alcohols and by the dry distillation of the calcium salts of the higher fatty acids; they resemble acetone in chemical properties.

Methylnonyl Ketone, $CH_3\cdot CO\cdot C_9H_{19}$, is the chief constituent of oil of rue, the essential oil obtained by distilling rue (*Ruta graveolens*) with steam. It is a colourless, crystalline substance, melts at 15°, boils at 224°, and possesses an odour resembling that of oranges.

Hydroximes and Hydrazones.—Aldehydes and ketones interact readily with hydroxylamine, $NH_2\cdot OH$, and with phenylhydrazine, $C_6H_5\cdot NH\cdot NH_2$ (part ii.), forming condensation products. This property is not only highly characteristic of all aldehydes and ketones, with one or two exceptions, but is also of the greatest value in the isolation and identification of the compounds in question.

The substances formed by the action of hydroxylamine on aldehydes are called *aldoximes*, those obtained from ketones, *ketoximes*, the term *oxime* or *hydroxime* being applied to both. Acetaldehyde, for example, yields acetaldoxime,

$$CH_3\cdot CHO + NH_2\cdot OH = CH_3\cdot CH{:}N\cdot OH + H_2O,$$

acetone giving acetoxime or dimethyl ketoxime,

$$(CH_3)_2CO + NH_2\cdot OH = (CH_3)_2C{:}N\cdot OH + H_2O,$$

the interactions being expressed by the general equation

$$>C\boxed{O + H_2}N\cdot OH = >C{:}N\cdot OH + H_2O.$$

The oximes are usually prepared by mixing an aqueous or alcoholic solution of the aldehyde or ketone (2 mols.) with an aqueous solution of hydroxylamine hydrochloride,

$NH_2 \cdot OH,HCl$ (2 mols.), and then adding sodium carbonate (1 mol.) in order to decompose the hydrochloride and set the base free,

$$2NH_2 \cdot OH,HCl + Na_2CO_3 = 2NH_2 \cdot OH + 2NaCl + CO_2 + H_2O.$$

The mixture is now heated gently, or kept at the ordinary temperature for some hours, and the oxime then extracted from the acidified solution by shaking with ether, or in some other suitable manner.

The lower aldoximes are mostly colourless, volatile, solid compounds, which distil without decomposition under reduced pressure, and mix with water in all proportions; the higher members are only sparingly soluble in water. The ketoximes have similar properties. Most oximes are decomposed, on treatment with boiling moderately strong hydrochloric acid, with formation of hydroxylamine hydrochloride, and regeneration of the aldehyde or ketone,

$$CH_3 \cdot CH:N \cdot OH + HCl + H_2O = CH_3 \cdot CHO + NH_2 \cdot OH,HCl.$$

They are usually readily soluble in caustic alkalies, with which they form compounds, such as

$$CH_3 \cdot CH:N \cdot ONa \text{ and } (CH_3)_2C:N \cdot OK;$$

but they are not decomposed by alkalies, even on boiling. One important difference between aldoximes and ketoximes is, that the former are decomposed by acetyl chloride, yielding cyanides or nitriles (p. 284),

$$CH_3 \cdot CH:N \cdot OH = CH_3 \cdot CN + H_2O,$$

whereas the latter are converted into acetyl derivatives,

$$(CH_3)_2C:N \cdot OH + CH_3 \cdot COCl = (CH_3)_2C:N \cdot O \cdot CO \cdot CH_3 + HCl.$$

The condensation products of aldehydes and ketones with phenylhydrazine are called *phenylhydrazones*, or simply *hydrazones.* They are formed according to the general equation,

$$>C\boxed{O + H_2}N \cdot NH \cdot C_6H_5 = >C:N \cdot NH \cdot C_6H_5,$$

as, for example, *acetaldehyde hydrazone*, $CH_3 \cdot CH:N \cdot NH \cdot C_6H_5$, and *acetone hydrazone*, $(CH_3)_2C{:}N{\cdot}NH{\cdot}C_6H_5$. The hydrazones are referred to later (part ii.), but it may be mentioned here that, like the hydroximes, they are usually decomposed by hot concentrated hydrochloric acid, with regeneration of the aldehyde or ketone.

SUMMARY AND EXTENSION.

The **Aldehydes** form a homologous series of the general formula $C_nH_{2n+1}{\cdot}CHO$, or $R{\cdot}CHO$, and are derived from the primary alcohols by the removal of two atoms of hydrogen from the $-CH_2{\cdot}OH$ group. The more important members of the series are—

			B.p.
Formaldehyde,	CH_2O	$H{\cdot}CHO$	—
Acetaldehyde,	C_2H_4O	$CH_3{\cdot}CHO$	20·8°
Propaldehyde,	C_3H_6O	$CH_3{\cdot}CH_2{\cdot}CHO$	49°
Butaldehyde,	C_4H_8O	$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CHO$	74°
Isobutaldehyde,		$(CH_3)_2CH{\cdot}CHO$	63°
Valeraldehyde,	$C_5H_{10}O$	$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHO$	102°
Isovaleraldehyde,		$(CH_3)_2CH{\cdot}CH_2{\cdot}CHO$	92°
Capraldehyde,	$C_6H_{12}O$	$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHO$	128°
Heptaldehyde, or Œnanthol,	$C_7H_{14}O$	$CH_3{\cdot}[CH_2]_5{\cdot}CHO$*	155°

The **Ketones** are derived from the secondary alcohols by the removal of two atoms of hydrogen from the $>CH{\cdot}OH$ group, and have the general formula $R{\cdot}CO{\cdot}R'$, where R and R′ may be the same or different radicles; in the former case the substance is a *simple ketone*, but when R and R′ are different, it is a *mixed ketone* (compare ethers, p. 114). The more important ketones are—

Acetone, or dimethyl ketone	$(CH_3)_2CO$	B.p.	56·5°
Propione, or diethyl ketone	$(C_2H_5)_2CO$	"	103°
Butyrone, or dipropyl ketone	$(C_3H_7)_2CO$	"	144°
Isobutyrone, or di-isopropyl ketone		"	125°
Œnanthone, or dihexyl ketone	$(C_6H_{13})_2CO$	M.p.	30·5°
Laurone	$(C_{11}H_{23})_2CO$	"	69°
Palmitone	$(C_{15}H_{31})_2CO$	"	83°
Stearone	$(C_{17}H_{35})_2CO$	"	88°

When the less important mixed ketones are also considered, the ketones form a homologous series,

$$C_3H_6O,\ C_4H_8O,\ C_5H_{10}O,\ C_6H_{12}O,\ \&c.,$$

---

* $[CH_2]_5$ is a convenient way of writing $-CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2-$.

in which numerous cases of isomerism occur. The first two members, acetone, $CH_3{\cdot}CO{\cdot}CH_3$, and methylethyl ketone, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_3$, exist in only one form, but there are three ketones of the composition $C_5H_{10}O$, namely,

Diethyl Ketone, or Propione.	Methylpropyl Ketone.	Methylisopropyl Ketone.
$CH_3{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CH_3$	$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$	 $CH_3{\cdot}CO{\cdot}CH{<}\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$,

and the number of possible isomerides rapidly increases on passing up the series.

Both aldehydes and ketones may be regarded as derived from the paraffins, by substituting one atom of oxygen for two atoms of hydrogen; they are, therefore, isomeric. In the case of aldehydes, two atoms of hydrogen of one of the CH_3– groups in the paraffin are displaced,

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3, \text{ giving } CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CHO;$$

but in the case of ketones, the oxygen atom is substituted for two hydrogen atoms of a $–CH_2–$ group,

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3, \text{ giving } CH_3{\cdot}CH_2{\cdot}CO{\cdot}CH_3.$$

Nomenclature.—The aldehydes (from *alcohol dehydrogenatum*) are conveniently named after the fatty acids which they yield on oxidation;

Formaldehyde,	$H{\cdot}CHO$,	giving	formic acid, $H{\cdot}COOH$.
Acetaldehyde,	$CH_3{\cdot}CHO$,	"	acetic acid, $CH_3{\cdot}COOH$.
Propaldehyde,	$C_2H_5{\cdot}CHO$,	"	propionic acid, $C_2H_5{\cdot}COOH$.

Simple ketones, having been first obtained by the dry distillation of a salt of a fatty acid, are usually named after that acid from which they are in this way obtained; acetone, for example, from acetic acid, propione from propionic acid. Mixed ketones are named according to the alkyl groups which they contain, as exemplified above in the case of the isomerides of the composition $C_5H_{10}O$. Ketones in general may also be named after the hydrocarbons from which they are theoretically derived, employing the prefix 'keto' and a numeral, as, for example, 2-ketopropane, $\overset{1}{C}H_3{\cdot}\overset{2}{C}O{\cdot}\overset{3}{C}H_3$, and 3-ketohexane, $\overset{1}{C}H_3{\cdot}\overset{2}{C}H_2{\cdot}\overset{3}{C}O{\cdot}\overset{4}{C}H_2{\cdot}\overset{5}{C}H_2{\cdot}\overset{6}{C}H_3$.

Methods of Preparation.—*Aldehydes* are formed by the oxidation of primary alcohols,

$$CH_3{\cdot}CH_2{\cdot}OH + O = CH_3{\cdot}CHO + H_2O;$$

whereas *ketones* are produced from secondary alcohols by similar treatment,

$$CH_3{\cdot}CH(OH){\cdot}CH_3 + O = CH_3{\cdot}CO{\cdot}CH_3 + H_2O.$$

Aldehydes may be prepared from the fatty acids by the dry distillation of their calcium salts with calcium formate :

$$(CH_3{\cdot}COO)_2Ca + (H{\cdot}COO)_2Ca = 2CH_3{\cdot}CHO + 2CaCO_3,$$
$$(CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}COO)_2Ca + (H{\cdot}COO)_2Ca$$
$$= 2CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CHO + 2CaCO_3.$$

In its simplest form this reaction may be considered as being due to the removal of water and carbon dioxide from one molecule of the fatty acid and one molecule of formic acid ; thus,

$$\begin{array}{r}R{\cdot}CO\vdots\text{-}O\ \vdots\text{-}H\\ H\vdots CO\vdots\text{-}OH\end{array} = R{\cdot}CHO + CO_2 + H_2O.$$

Ketones may be prepared by the distillation of the calcium salts of the fatty acids alone,

$$(CH_3{\cdot}COO)_2Ca = 2CH_3{\cdot}CO{\cdot}CH_3 + CaCO_3.$$

If a mixture of the calcium salts of two fatty acids (other than formic acid) be employed, a mixed ketone is formed,

$$\underset{\text{Calcium Acetate.}}{(CH_3{\cdot}COO)_2Ca} + \underset{\text{Calcium Propionate.}}{(C_2H_5{\cdot}COO)_2Ca} = \underset{\text{Methylethyl Ketone.}}{2CH_3{\cdot}CO{\cdot}C_2H_5} + 2CaCO_3\,;$$

at the same time two simple ketones (acetone and propione) are produced by the independent decomposition of the two salts.

This method of formation is readily understood if, for the sake of simplicity, the free acids instead of their calcium salts be considered,

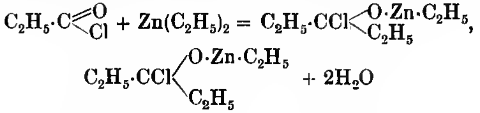
$$\begin{array}{r}RCO\vdots\ \text{-}O\text{-}\ \vdots H\\ R'\vdots\text{-}CO\text{-}\vdots OH\end{array} = R{\cdot}CO{\cdot}R' + CO_2 + H_2O.$$

Ketones may, in fact, be prepared by heating the higher fatty acids with phosphoric anhydride at about 200°,

$$\underset{\text{Stearic Acid.}}{2C_{17}H_{33}{\cdot}COOH} = \underset{\text{Stearone.}}{C_{17}H_{33}{\cdot}CO{\cdot}C_{17}H_{33}} + CO_2 + H_2O,$$

a method especially useful in the preparation of the higher ketones, such as laurone, palmitone, &c., which are obtained only with difficulty by any other method.

A very important synthetical method for the preparation of ketones consists in treating the acid chlorides (1 mol.) with the zinc alkyl compounds (1 mol.); in the first place, an additive product is formed, and this, on decomposition with water, yields the ketone,



$$C_2H_5{\cdot}C\Big<\begin{matrix}O\\Cl\end{matrix} + Zn(C_2H_5)_2 = C_2H_5{\cdot}CCl\Big<\begin{matrix}O{\cdot}Zn{\cdot}C_2H_5\\C_2H_5\end{matrix},$$

$$C_2H_5{\cdot}CCl\Big<\begin{matrix}O{\cdot}Zn{\cdot}C_2H_5\\C_2H_5\end{matrix} + 2H_2O$$

$$= C_2H_5{\cdot}CO{\cdot}C_2H_5 + C_2H_6 + Zn(OH)_2 + HCl$$

(Compare formation of tertiary alcohols by the action of *excess* of the zinc alkyl compound, p. 107).

Ketones may also be prepared by the hydrolysis of ethyl acetoacetate and its derivatives, a synthetical method of great practical importance (p. 193).

When hydrocarbons of the acetylene series are treated with 80 per cent. sulphuric acid (or with a solution of mercuric chloride or bromide), they combine directly with the elements of water, an aldehyde or a ketone being formed according to the constitution of the hydrocarbon (p. 87).

Physical Properties.—Excluding formaldehyde, the physical properties of which are unknown, the aldehydes and ketones up to about $C_{11}H_{22}O$ are colourless, mobile, neutral, volatile liquids. Aldehydes have usually a disagreeable, irritating smell, and their sp. gr. (at 20°) varies from about 0·780 in the case of acetaldehyde, to 0·834 in the case of caprylic aldehyde, $C_7H_{15}\cdot CHO$. Ketones have generally a not unpleasant odour, and their sp. gr. (at 20°) varies from 0·792 in the case of acetone, to 0·830 in the case of caprone, $(C_5H_{11})_2CO$. The boiling-point rises fairly regularly on passing up both series. The lowest members of both classes of compounds are readily soluble in water, but the solubility rapidly decreases as the number of carbon atoms in the molecule increases.

The higher aldehydes and ketones are usually colourless, waxy solids, insoluble or nearly so in water, but readily soluble in alcohol and ether.

Chemical Properties.—Aldehydes and ketones have many chemical properties in common, because they are similar in constitution, both classes of substances containing the carbonyl group $>CO$. Owing to the presence of this group, they have the power of combining directly under certain conditions with two monad atoms or their valency equivalent

All the lower aldehydes and many* of the lower ketones form crystalline additive compounds when shaken with a concentrated aqueous solution of sodium bisulphite. This property is of great value in purifying aldehydes and ketones, and especially in separating them from substances which do not form 'bisulphite compounds,' as illustrated in the preparation of acetone from crude wood-spirit (p. 128). These 'bisulphite compounds' are soluble in water, but usually insoluble or nearly so in alcohol and ether. They may be regarded as salts of *hydroxy-sulphonic*

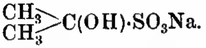
---

* With few exceptions, only those ketones containing the group $CH_3\cdot CO$— combine readily with $NaHSO_3$.

acids,* the compounds formed by aldehyde and acetone respectively being

$CH_3\cdot CH(OH)\cdot SO_3Na$

Sodium Hydroxyethylsulphonate.



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C(OH)\cdot SO_3Na.$$

Sodium Hydroxyisopropylsulphonate.

All these compounds are readily decomposed on warming with dilute alkalies or acids, the aldehydes or ketones being regenerated,

$$CH_3\cdot CH_2\cdot CH(OH)\cdot SO_3Na + HCl = CH_3\cdot CH_2\cdot CHO + NaCl + H_2O + SO_2.$$

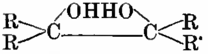
The characteristic behaviour of aldehydes and ketones with hydroxylamine and with phenylhydrazine has been described above.

Aldehydes and ketones are readily acted on by reducing agents, such as sodium amalgam and water, zinc and hydrochloric acid, with formation of primary and secondary alcohols respectively,

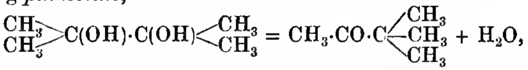
$$CH_3\cdot CH_2\cdot CH_2\cdot CHO + 2H = CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$$
$$CH_3\cdot CO\cdot CH_2\cdot CH_3 + 2H = CH_3\cdot CH(OH)\cdot CH_2\cdot CH_3.$$

A secondary alcohol is not the sole product of the reduction of ketones, but is usually accompanied by varying quantities of interesting substances belonging to the class of *pinacones*. Acetone, for example, yields not only isopropyl alcohol, $CH_3\cdot CH(OH)\cdot CH_3$, but also *acetone pinacone*,

$$2(CH_3)_2CO + 2H = (CH_3)_2C(OH)\cdot C(OH)(CH_3)_2.$$

The formation of a pinacone may be accounted for by assuming that the first product of reduction of a ketone is a substance, $\begin{matrix}R\\R\end{matrix}\!\!>C\!<\!\begin{matrix}OH\\ \ \end{matrix}$, produced by combination with one atom of hydrogen. This intermediate product may then combine with another atom of hydrogen to form a secondary alcohol, $\begin{matrix}R\\R\end{matrix}\!\!>C\!<\!\begin{matrix}OH\\H\end{matrix}$, or two molecules may unite to form a pinacone,  $\begin{matrix}R\\R\end{matrix}\!\!>\overset{/OH}{C}\text{———}\overset{HO\backslash}{C}\!<\!\begin{matrix}R\\R\end{matrix}$. Similar products are formed in the reduction of aldehydes, but in smaller quantities.

Pinacone is decomposed on distillation with dilute sulphuric acid, yielding *pinacoline*,



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C(OH)\cdot C(OH)\!<\!\begin{matrix}CH_3\\CH_3\end{matrix} = CH_3\cdot CO\cdot C\!\!\begin{matrix}/CH_3\\-CH_3\\ \backslash CH_3\end{matrix} + H_2O,$$

a very remarkable change, and one which has not been satisfactorily accounted for. Pinacoline is a colourless liquid, boils at 106°,

---

* A sulphonic acid is an organic acid containing the group $—SO_2\cdot OH$.

and has a very strong odour of peppermint. That it has the constitution given above, is shown by the facts that on oxidation with chromic acid, it yields trimethylacetic acid and carbon dioxide,

$$(CH_3)_3C{\cdot}CO{\cdot}CH_3 + 4O = (CH_3)_3C{\cdot}COOH + CO_2 + H_2O,$$

and that it is formed by the action of zinc methyl on trimethylacetyl chloride, $(CH_3)_3{\cdot}COCl$. (Compare preparation of ketones, p. 136).

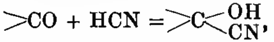
Aldehydes and ketones are readily acted on by phosphorus pentachloride with formation of dihalogen derivatives of the paraffins, the oxygen atom of the $>CO$ group being displaced by two atoms of chlorine. Aldehyde, for example, gives a *dichlorethane*, called *ethylidene chloride* (because it contains the ethylidene group $CH_3{\cdot}CH=$),

$$CH_3{\cdot}CHO + PCl_5 = CH_3{\cdot}CHCl_2 + POCl_3,$$

and acetone gives *β-dichloropropane* or *acetone dichloride*,

$$(CH_3)_2CO + PCl_5 = (CH_3)_2CCl_2 + POCl_3.$$

Aldehydes and ketones combine directly with hydrocyanic acid, forming additive products, termed *hydroxycyanides*. This reaction may be expressed by the general equation



$$>CO + HCN = >C<\begin{matrix}OH\\CN\end{matrix},$$

aldehyde, for example, giving *hydroxyethyl cyanide*,

$$CH_3{\cdot}CH(OH){\cdot}CN,$$

and acetone, *hydroxyisopropyl cyanide*, $(CH_3)_2C(OH){\cdot}CN$. These compounds are decomposed by hot concentrated alkalies and mineral acids, yielding *hydroxycarboxylic acids*, the $-CN$ group being transformed into $-COOH$ (compare p. 285),

$$CH_3{\cdot}CH(OH){\cdot}CN + 2H_2O = CH_3{\cdot}CH(OH){\cdot}COOH + NH_3.$$

Aldehydes *differ* from ketones in the following important respects: They usually undergo oxidation to a fatty acid on exposure to the air, and are readily oxidised by an ammoniacal solution of silver oxide, especially in presence of a little potash or soda, a silver mirror being formed. They also reduce alkaline solutions of copper (Fehling's solution, p. 263). Ketones, on the other hand, are only attacked by powerful oxidising agents, and the difference between their behaviour on oxidation and that of aldehydes is so characteristic that it may be made use of for determining whether a substance of doubtful constitution be an aldehyde or a ketone.

Aldehydes, on oxidation, are converted into fatty acids containing *the same number* of carbon atoms:

$$\underset{\text{Propaldehyde.}}{CH_3{\cdot}CH_2{\cdot}CHO} + O = \underset{\text{Propionic Acid.}}{CH_3{\cdot}CH_2{\cdot}COOH},$$

$$\underset{\text{Heptaldehyde.}}{CH_3{\cdot}[CH_2]_5{\cdot}CHO} + O = \underset{\text{Heptylic Acid.}}{CH_3{\cdot}[CH_2]_5{\cdot}COOH}.$$

Ketones, on oxidation, are decomposed with formation, usually, of a mixture of acids, each of which contains *a smaller number* of carbon atoms than the original ketone,

$$CH_3{\cdot}CO{\cdot}CH_3 + 4O = CH_3{\cdot}COOH + CO_2 + H_2O.$$

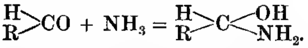
$$CH_3{\cdot}CO{\cdot}\vdots\,[CH_2]_4{\cdot}CH_3 + 3O = CH_3{\cdot}COOH + CH_3{\cdot}[CH_2]_3{\cdot}COOH.$$

In the case of mixed ketones, several acids may be formed. Methylamyl ketone, for example, might yield acetic acid, and valeric acid on oxidation, in which case the molecule would be decomposed as indicated by the dotted line in the above equation, or it might give carbon dioxide and caproic acid, the molecule being attacked in a different manner,

$$CH_3\,\vdots\,CO{\cdot}[CH_2]_4{\cdot}CH_3 + 4O = CH_3{\cdot}[CH_2]_4{\cdot}COOH + H_2O + CO_2.$$

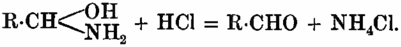
It frequently happens, therefore, that, in oxidising mixed ketones, several products are formed, the nature of which may afford important evidence as to the constitution of the ketone. Generally speaking, the oxidation of a mixed ketone follows the rule (Popoff's law) that the ketonic group –CO– remains united with the smaller alkyl group, in which case the decomposition represented in the above example by the first equation would take place almost entirely. Later experiments have shown, however, that Popoff's rule does not hold good in all cases, and must be considered as only approximately correct.

Aldehydes differ from ketones in combining readily with ammonia, forming additive products,



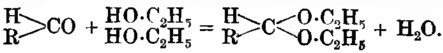
$$\begin{matrix}H\\R\end{matrix}\!\!>CO + NH_3 = \begin{matrix}H\\R\end{matrix}\!\!>C<\!\!\begin{matrix}OH\\NH_2\end{matrix}.$$

These compounds, of which aldehyde ammonia is an example, are usually crystalline, and very readily soluble in water. They are decomposed on distillation with dilute acids, with regeneration of the aldehyde,



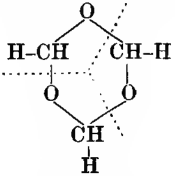
$$R{\cdot}CH<\!\!\begin{matrix}OH\\NH_2\end{matrix} + HCl = R{\cdot}CHO + NH_4Cl.$$

Aldehydes differ again from ketones in combining with alcohols with elimination of water, to form substances called *acetals*,

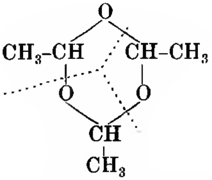


$$\begin{matrix}H\\R\end{matrix}\!\!>CO + \begin{matrix}HO{\cdot}C_2H_5\\HO{\cdot}C_2H_5\end{matrix} = \begin{matrix}H\\R\end{matrix}\!\!>C<\!\!\begin{matrix}O{\cdot}C_2H_5\\O{\cdot}C_2H_5\end{matrix} + H_2O.$$

Aldehydes, especially the lower members of the series, very readily undergo polymerisation, a property which distinguishes them from ketones in a very striking manner. Polymerisation may take place spontaneously, as in the case of formaldehyde, but usually only on addition of a small quantity of some mineral acid or of some substance, such as $ZnCl_2$, SO_2, &c., which acts in a manner as yet unexplained. The most common form of polymerisation is the combination of three molecules of the aldehyde to form substances called *paraldehydes*, such as paraformaldehyde, $(CH_2O)_3$, and paracetaldehyde $(C_2H_4O)_3$, the constitutions of which are usually represented by the formulæ



Paraformaldehyde.



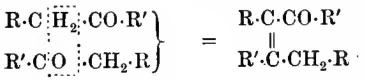
Paracetaldehyde, or Paraldehyde.

The method of combination of the three molecules to form a paraldehyde will be readily understood with the aid of the dotted lines. The paraldehydes are decomposed into the original aldehydes on distillation with dilute mineral acids. They do not show the characteristic reactions of aldehydes, consequently they are not true aldehydes, and do not contain the aldehyde group.

Aldehydes are generally very unstable in presence of alkalies, by which they are converted into brown resins of unknown nature.

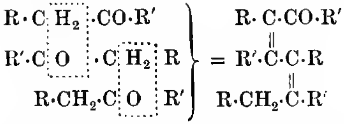
Ketones, as mentioned above, are much more stable than aldehydes; they do not reduce alkaline solutions of silver, copper, &c., or combine directly with ammonia or with alcohols, and they do not polymerise like the aldehydes.

When treated with dehydrating agents, both aldehydes and ketones readily undergo condensation, two or more molecules combining with loss of water, as illustrated in the case of aldehyde (p. 124) and acetone (p. 131). When condensations of this nature take place, the hydrogen atoms of one of the $-CH_2-$ or CH_3- groups, which is in direct combination with the $>CO$ group, are invariably eliminated, as shown in the following schemes, in which R, R′ may be either hydrogen atoms or similar or different alkyl groups :



$$\left.\begin{array}{l} R{\cdot}CH_2{\cdot}CO{\cdot}R' \\ R'{\cdot}CO{\cdot}CH_2{\cdot}R \end{array}\right\} = \begin{array}{l} R{\cdot}C{\cdot}CO{\cdot}R' \\ \quad\| \\ R'{\cdot}C{\cdot}CH_2{\cdot}R \end{array}$$

(Type of Mesityl Oxide).



$$\left.\begin{array}{l} R{\cdot}CH_2{\cdot}CO{\cdot}R' \\ R'{\cdot}CO{\cdot}CH_2{\cdot}R \\ R{\cdot}CH_2{\cdot}CO\,R' \end{array}\right\} = \begin{array}{l} R{\cdot}C{\cdot}CO{\cdot}R' \\ \quad\| \\ R'{\cdot}C{\cdot}C{\cdot}R \\ \qquad\| \\ R{\cdot}CH_2{\cdot}C{\cdot}R' \end{array}$$

(Type of Phorone).

It is not necessary that the molecules undergoing condensation be identical; two different ketones, two different aldehydes, or an aldehyde and a ketone may condense together, always provided that the group $-CH_2-CO-$ be present in the molecule of one at least of the substances.

CHAPTER IX.

THE FATTY ACIDS.

The fatty acids form a homologous series of the general formula $C_nH_{2n+1}{\cdot}COOH$, or $C_nH_{2n}O_2$; they may be regarded as derivatives of the paraffins, the alcohols, or the aldehydes.

Paraffins.	Alcohols.	Aldehydes.	Fatty Acids.
$H{\cdot}CH_3$	$H{\cdot}CH_2{\cdot}OH$	$H{\cdot}CHO$	$H{\cdot}COOH$
$CH_3{\cdot}CH_3$	$CH_3{\cdot}CH_2{\cdot}OH$	$CH_3{\cdot}CHO$	$CH_3{\cdot}COOH$
$C_2H_5{\cdot}CH_3$	$C_2H_5{\cdot}CH_2{\cdot}OH$	$C_2H_5{\cdot}CHO$	$C_2H_5{\cdot}COOH$.

The term '*fatty*' was given to the acids of this series because many of the higher members occur in natural fats, and resemble fats in physical properties.

Formic Acid, CH_2O_2, or $H{\cdot}COOH$, occurs in nature in nettles, ants (*formicæ*), and other living organisms; the sting of ants and nettles owes part, at least, of its irritating effect to the presence of formic acid. When nettles or ants are macerated with water and the mixture distilled, weak aqueous formic acid collects in the receiver.

Formic acid can be obtained from its elements by simple methods. When carbon monoxide is passed over moistened potassium hydroxide heated at 100°, it is slowly absorbed, and potassium formate is produced,

$$CO + KOH = H{\cdot}COOK.$$

When moist carbon dioxide is passed over potassium, formate and carbonate of potassium are formed, the carbon dioxide being reduced by the nascent hydrogen evolved during the interaction of the potassium and water,

$$2H_2O + 2K = 2KOH + 2H, \text{ and } CO_2 + 2H + KOH = H{\cdot}COOK + H_2O,$$

$$\text{or } 3CO_2 + 4K + H_2O = 2H{\cdot}COOK + K_2CO_3.$$

The acid may be obtained from the potassium salt by distilling with dilute sulphuric acid.

Formic acid can also be obtained by oxidising methyl alcohol or formaldehyde with platinum black (precipitated platinum),

$$CH_3{\cdot}OH + 2O = H{\cdot}COOH + H_2O \qquad H{\cdot}CHO + O = H{\cdot}COOH,$$

and by heating hydrocyanic acid with alkalies or mineral acids,

$$HCN + 2H_2O = H{\cdot}COOH + NH_3.^*$$

Formic acid is prepared by heating oxalic acid with glycerol (glycerin); it can be obtained by heating oxalic acid alone,

$$C_2O_4H_2 = H{\cdot}COOH + CO_2,$$

but a large proportion of the acid sublimes without decomposition. Glycerol (about 50 c.c.) is placed in a retort connected with a condenser, crystallised oxalic acid (about 30 grams) added, and the mixture heated to about 100–110°; rather below this temperature, evolution of carbon dioxide commences, and dilute formic acid distils, but after keeping for some time at 100–110°, action ceases. A further quantity of oxalic acid is then added, and the heating continued, when carbon dioxide is again evolved, and a more concentrated solution of formic acid collects in the receiver. By adding

---

* If an alkali be used, ammonia is liberated, and a salt of formic acid obtained; whereas when a mineral acid is employed, free formic acid and an ammonium salt are produced.

more oxalic acid from time to time, a large quantity of formic acid can be obtained, the glycerol, like the sulphuric acid in the manufacture of ether, being able, theoretically, to convert an unlimited quantity of oxalic into formic acid.

When crystallised oxalic acid, $C_2O_4H_2 + 2H_2O$, is heated with glycerol, it loses its water of crystallisation; the anhydrous acid is then decomposed into carbon dioxide and formic acid; part of the latter distils with the water, part combining with the hydroxide, glycerol, to form the salt, glycerol formate, or monoformin,

$$C_2O_4H_2,2H_2O = H{\cdot}COOH + CO_2 + 2H_2O$$
$$C_3H_5(OH)_3 + H{\cdot}COOH = C_3H_5(OH)_2{\cdot}O{\cdot}CHO + H_2O.$$

On adding more crystallised oxalic acid, the monoformin is decomposed by part of the water expelled from the oxalic acid crystals, yielding glycerol and formic acid,

$$C_3H_5(OH)_2{\cdot}O{\cdot}CHO + H_2O = C_3H_5(OH)_3 + H{\cdot}COOH.$$

The regenerated glycerol and the anhydrous oxalic acid then interact as before, yielding monoformin, carbon dioxide, and water.

In order to prepare anhydrous formic acid, the aqueous distillate is gently warmed and excess of litharge added in small quantities at a time, the solution being gradually heated to boiling; as soon as the litharge ceases to be dissolved, the solution is filtered hot, and the filtrate evaporated to a small bulk, when colourless crystals of lead formate are obtained,

$$2H{\cdot}COOH + PbO = (H{\cdot}COO)_2Pb + H_2O.$$

This salt is carefully dried, and about $\frac{19}{20}$ths of it introduced in the form of coarse powder, between plugs of cotton wool, into the inner tube of an upright Liebig's condenser, which is connected above with an apparatus for generating hydrogen sulphide, and below with a suitable receiver closed with a calcium chloride drying tube; the lead formate is heated by passing steam through the outer tube of the condenser, and carefully dried hydrogen sulphide is led over it, when anhydrous formic acid collects in the receiver,

$$(H{\cdot}COO)_2Pb + SH_2 = 2H{\cdot}COOH + PbS.$$

The acid is now placed in a retort connected with a condenser, the remainder of the dried lead salt added, and, after warming gently for a short time, the acid is distilled, care being taken to prevent absorption of moisture; this rectification or distillation over lead formate is necessary in order to free the acid from hydrogen sulphide.

Formic acid is a colourless, mobile, hygroscopic liquid of sp. gr. 1·241 at 0°; it solidifies at low temperatures, melting again at 8°, and boiling at 101°. It has a pungent, irritating odour, recalling that of sulphur dioxide, and it blisters the skin like a nettle sting does; it is miscible with water and alcohol in all proportions. The anhydrous substance and its aqueous solution have an acid reaction, decompose carbonates, and dissolve certain metallic oxides; formic acid, in fact, behaves like a weak mineral acid. Like the aldehydes, it has reducing properties, and precipitates silver from warm solutions of ammoniacal silver nitrate, being itself oxidised to carbon dioxide,

$$H{\cdot}COOH + Ag_2O = 2Ag + CO_2 + H_2O.$$

When mixed with concentrated sulphuric acid, it is rapidly decomposed into carbon monoxide and water,

$$H{\cdot}COOH = CO + H_2O,$$

and when heated alone at 160° in closed vessels, it yields carbon dioxide and hydrogen,

$$H{\cdot}COOH = CO_2 + H_2.$$

The **Formates**, or salts of formic acid, are prepared by neutralising the acid with alkalies, hydroxides, &c., or by double decomposition; they are all soluble in water, but some, such as the lead and silver salts, only moderately easily; they are all decomposed by warm concentrated sulphuric acid, with evolution of carbon monoxide, and by dilute mineral acids, yielding formic acid. The *sodium* salt, $H{\cdot}COONa$, and the *potassium* salt, $H{\cdot}COOK$, are deliquescent; when heated at about 250°, they are converted into oxalates with evolution of hydrogen, a reaction which may be made use of for the preparation of pure hydrogen,

$$2H{\cdot}COONa = C_2O_4Na_2 + H_2.$$

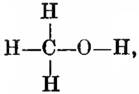
When *ammonium formate* is strongly heated, it is first converted into formamide (p. 162), then into hydrogen cyanide, water being eliminated in both stages,

$$H{\cdot}COONH_4 = H{\cdot}CO{\cdot}NH_2 + H_2O$$
$$H{\cdot}CO{\cdot}NH_2 = HCN + H_2O.$$

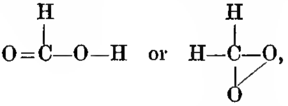
Silver formate, $H{\cdot}COOAg$, is precipitated in colourless crystals on adding silver nitrate to a concentrated solution of an alkali formate, but it is unstable, and quickly darkens on exposure to light, very rapidly on boiling.

In order to test for formic acid or a formate, the solution, if acid, is neutralised with soda, and a portion warmed with an ammoniacal solution of silver nitrate; if a black precipitate of silver be produced, the presence of formic acid is confirmed by evaporating the rest of the neutral solution to dryness, and then warming the residue *very gently* with concentrated sulphuric acid, when carbon monoxide is evolved, and may be ignited at the mouth of the test tube.

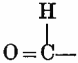
Constitution.—Formic acid is produced from methyl alcohol,



$H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}O{-}H$, by the substitution of one atom of oxygen for two atoms of hydrogen, and must, therefore, have the constitution



$O{=}\overset{\displaystyle H}{C}{-}O{-}H$ or

because these are the only formulæ which can be constructed, assuming, as usual, that the atoms have the indicated valencies. But the second formula does not correctly indicate the behaviour of formic acid; it represents the two hydrogen atoms as being in the same state of combination, which is very improbable, since one of them is, the other is not, readily displaced by metals; it does not recall the fact that formic acid behaves in some respects like an aldehyde, which is indicated in the first formula by the presence of the aldehyde group  $\overset{\displaystyle\overset{H}{|}}{O{=}C{-}}$ For these and other reasons, which will be seen more clearly after considering the case of acetic acid (p. 152), the constitution of formic acid is represented by the first formula, which is usually written H·CO·OH, or simply H·COOH. From analogy with methyl alcohol and other compounds, it may be assumed that it is the hydrogen atom of the HO– group, and not that directly combined with carbon, which is displaced when the acid forms salts.

Acetic Acid, $C_2H_4O_2$, or $CH_3{\cdot}COOH$, occurs in nature in combination with alcohols in the essences or odoriferous oils of many plants, and is formed during the decay of many organic substances. It can be produced by gently heating sodium methoxide in a stream of carbon monoxide, just as formic acid may be obtained from sodium or potassium hydroxide under the same conditions,

$$CH_3{\cdot}ONa + CO = CH_3{\cdot}COONa;$$

also by boiling methyl cyanide (p. 285) with alkalies or mineral acids,

$$CH_3{\cdot}CN + 2H_2O = CH_3{\cdot}COOH + NH_3;$$

and by exposing alcohol or aldehyde in contact with platinum black to the oxidising action of the air,

$$C_2H_6O + 2O = C_2H_4O_2 + H_2O \qquad 2C_2H_4O + 2O = 2C_2H_4O_2.$$

Acetic acid is manufactured on the large scale from the products of the dry distillation of wood. The brown aqueous portion of the distillate, obtained on heating wood in iron retorts (p. 89), contains a large quantity of acetic acid, and is called *pyroligneous acid;* it is first distilled with lime, as already described, to separate the methyl alcohol, acetone, and other volatile neutral substances, and the solution of calcium acetate is then evaporated in iron pans, when tarry or 'empyreumatic' matter rises as a scum and is skimmed off. The solution is finally evaporated to dryness, and the calcium salt distilled with concentrated hydrochloric acid from copper vessels, care being taken not to employ excess of acid,

$$(C_2H_3O_2)_2Ca + 2HCl = 2C_2H_4O_2 + CaCl_2.$$

The concentrated aqueous acetic acid which collects in the receiver is now mixed with a little potassium permanganate or bichromate, and again distilled, by which means most of the impurities are oxidised, and commercial acetic acid is obtained.

Vinegar.—When beer, or a weak wine such as claret, is left exposed to the air, it soon becomes sour, the alcohol which it contains being converted into acetic acid,

$$C_2H_6O + O_2 = C_2H_4O_2 + H_2O.$$

This change is not a simple oxidation, as represented by the equation, but a process of fermentation brought about by a living ferment, *mycoderma aceti.* This ferment, being in the atmosphere, soon finds its way into the solution, where it grows and multiplies and in some way causes the alcohol to combine with the oxygen of the air to form acetic acid. Strong wines, such as port and sherry, do not turn sour on exposure to the air, nor does an aqueous solution of pure alcohol, no matter how dilute, because the ferment is killed by strong alcohol, and cannot live in pure aqueous alcohol, since the latter does not contain nitrogenous substances, mineral salts, &c., which the ferment requires for food, and which are present in beers and wines.

Vinegar is simply a dilute solution of acetic acid, containing colouring matter and other substances, obtained by the acetous fermentation of poor wine or wine residues, of beer which has turned sour, and of other dilute alcoholic liquids; it is manufactured by one of the two following processes.

In the old *French* or *Orléans* process, a small quantity of wine is placed in large vats covered with perforated lids, the vats having been previously soaked inside with hot vinegar; the ferment soon gets into the wine, and vinegar is produced, the solution gradually becoming coated with a slimy film, known as 'mother-of-vinegar,' which is simply a mass of the living ferment. After some time more wine is added, the process being repeated at intervals until the vat is about half full; most of the vinegar is then drawn off, and the operations repeated with fresh quantities of wine.

In the modern *German* or '*quick vinegar process,*' large vats, provided with perforated sides, and fitted near the top and bottom with perforated discs, are employed, the space between the discs being filled with beech-wood shavings, which are first moistened with vinegar in order that they may become coated with a growth of the ferment; diluted 'raw-spirit,' containing 6–10 per cent. of alcohol, mixed with about 20 per cent. of vinegar, or with beer, or malt extract, to provide food for the ferment, is then poured in at the top, when it slowly trickles through the shavings in contact with the ferment, and provided with a free supply of air. The liquid which collects at the bottom is again poured over the shavings, the operations being continued until it is converted into vinegar—that is to say, until almost the whole of the alcohol has been oxidised to acetic acid. This process is much more rapid than the French method, since oxidation is hastened by the exposure of a large surface of the liquid; in both processes the fermenting liquid must be kept at a temperature of 25–40°.

Vinegar produced by the French process contains 6–10 per cent. of acetic acid; whereas that produced by the German process from diluted raw-spirit contains only 4–6 per cent. of acetic acid. Vinegar is used for table purposes and in the manufacture of white-lead and verdigris (see below); it is too dilute to be economically employed for the preparation of commercial acetic acid.

Pure acetic acid is prepared by distilling anhydrous sodium acetate with concentrated sulphuric acid; this salt is obtained by neutralising the impure commercial acid with sodium carbonate, recrystallising, and then fusing to expel the water of crystallisation. The distillate from this process contains only a small quantity of water, and solidifies, when cooled, to a mass of colourless crystals; it is then termed *glacial acetic acid* in contradistinction to the weaker acid, which does not crystallise so readily. The small quantity of water in glacial acetic acid can be got rid of by separating the crystals from the more dilute mother-liquors by pressure, melting them, and then cooling again, repeating the processes if necessary.

Anhydrous acetic acid is a colourless, crystalline, hygroscopic solid, melts at 16·5°, boils at 118°, and has the sp. gr. 1·080 at 0°; it has a pungent, penetrating smell, a burning action on the skin, and a sharp sour taste; it is inflammable when near its boiling-point, burning with a feebly luminous flame. It is miscible with water, alcohol, and ether in all proportions, and is an excellent solvent for most organic compounds, and for many inorganic substances, such as sulphur, iodine, &c., which are insoluble in water. It is a fairly strong acid, dissolves certain metals, and acts readily on metallic hydroxides; unlike formic acid, it has not reducing properties. The pure acid does not decolourise potassium permanganate; if impure, it will probably do so.

Acetic acid is largely used in medicine, in chemical laboratories, and in the manufacture of organic dyes, as well as for the preparation of many acetates of considerable commercial importance; the uses of vinegar have been mentioned.

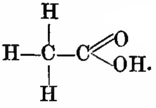
The **Acetates**, or salts of acetic acid, are prepared by neutralising the acid with carbonates, hydroxides, &c., or by double decomposition; they are crystalline compounds, soluble in water, and decomposed by mineral acids with liberation of acetic acid. *Sodium acetate*, $C_2H_3O_2Na + 3H_2O$, is extensively used in the laboratory; it melts in its water of crystallisation when heated, but as the water is expelled, it solidifies again. The anhydrous salt is hygroscopic, and is used as a dehydrating agent. *Potassium acetate*, $C_2H_3O_2K$, is deliquescent. *Ammonium acetate* is gradually decomposed into acetamide (p. 162) and water on dry distillation, $C_2H_3O_2 \cdot NH_4 = CH_3 \cdot CO \cdot NH_2 + H_2O$. *Silver acetate* is precipitated in colourless crystals on adding silver nitrate to a concentrated neutral solution of an acetate; it is moderately soluble in cold water, and does not darken on exposure to light. *Copper acetate*, $(C_2H_3O_2)_2Cu + H_2O$, is obtained by dissolving cupric oxide in acetic acid; it is a dark, greenish-blue substance. *Verdigris* is a blue, basic copper acetate, $(C_2H_3O_2)_2Cu + Cu(OH)_2$, containing water of crystallisation, and is manufactured by leaving sheet-copper in contact with vinegar, or with grape-skins, the sugars in which have undergone fermentation first into alcohol, then into acetic acid. When washed with water, part of the salt dissolves and green verdigris is obtained; both these basic acetates are used as pigments. Copper acetate and copper arsenite unite to form a beautiful emerald green, insoluble double salt, $(C_2H_3O_2)_2Cu + (AsO_3)_2Cu_3$, known as *Schweinfurth's green.* This substance was formerly employed in large quantities in colouring wall-papers, carpets, blinds, &c.; but as its dust is poisonous, and as it is liable to decompose in presence of decaying starch or other organic matter, with evolution of hydrogen arsenide, its use is now almost abandoned. *Lead acetate*, or 'sugar of lead,' $(C_2H_3O_2)_2Pb + 3H_2O$, prepared by dissolving litharge in commercial acetic acid, has a sweet (sugary) astringent taste, and is very poisonous; when its solution is boiled with litharge, a soluble basic lead acetate is formed. *Ferric acetate* is prepared on the large scale by dissolving scrap iron in pyroligneous acid, the greenish ferrous salt first produced being rapidly oxidised in contact with the air and excess of acetic acid to the deep reddish-brown ferric salt; the solution is known in commerce as 'iron liquor,' or 'black liquor.' When a solution of ferric acetate containing traces of other salts is heated, an insoluble basic iron salt is precipitated, the solution becoming clear; this property is made use of in separating the metals of the iron group, also in dyeing and 'printing' cotton, for which purpose 'iron liquor' is used as a mordant. *Aluminium acetate* is prepared by precipitating a solution of aluminium sulphate with sugar of lead, or by dissolving precipitated aluminium hydroxide in acetic acid; its solution is known as 'red liquor,' and is used as a mordant, as, when heated, it loses acetic acid, an insoluble basic salt being formed. *Chromic acetate* is prepared by similar methods, and is also used as a mordant.

If a solution is to be tested for acetic acid or an acetate, it is boiled with a few drops of strong sulphuric acid, when the characteristic smell of acetic acid is observed. A fresh portion of the solution is then neutralised with soda, if necessary, evaporated to dryness, and the residue warmed with a few drops of alcohol and a little strong sulphuric acid, when ethyl acetate (p. 185) is formed; this substance is recognised by its pleasant fruity odour (which should be compared with that of alcohol and of ether).

Constitution.—The formation of acetic acid by the oxidation of ethyl alcohol is clearly a process similar to that by which formic acid is produced from methyl alcohol; if, therefore, the two changes be represented in a similar manner,

$$\begin{aligned} H{\cdot}CH_2{\cdot}OH + 2O &= H{\cdot}CO{\cdot}OH + H_2O \\ CH_3{\cdot}CH_2{\cdot}OH + 2O &= CH_3{\cdot}CO{\cdot}OH + H_2O, \end{aligned}$$

the constitution of acetic acid will be expressed by the formula $CH_3{\cdot}CO{\cdot}OH$, or



$$H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}{-}C\begin{matrix}{\diagup\!\!\diagup O}\\{\diagdown OH.}\end{matrix}$$

Again, formic acid is produced when hydrogen cyanide is boiled with mineral acids (p. 143), whilst acetic acid is formed from methyl cyanide under the same conditions. Expressing these two changes in a similar manner,

$$\begin{aligned} H\cdot CN + 2H_2O &= \quad H\cdot CO\cdot OH + NH_3 \\ CH_3\cdot CN + 2H_2O &= CH_3\cdot CO\cdot OH + NH_3, \end{aligned}$$

the constitution of acetic acid will be represented by the same formula as before.

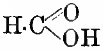
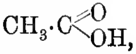
If now the properties of acetic acid be considered, it will be evident that the constitutional formula arrived at in this manner indicates the chemical behaviour of the acid, and accounts for its methods of formation, decompositions, and relations to other compounds better than any other formula.

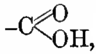
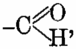
From the numerous arguments which might be advanced in support of this statement, the following only will be quoted: (1) Acetic acid contains an HO– group, because its behaviour with phosphorus pentachloride is similar to that of alcohols (p. 95). (2) It contains a methyl or CH_3– group—that is to say, three of the four atoms of hydrogen in acetic acid are *directly* combined with carbon. This is shown by the fact that three of the four hydrogen atoms behave like those in CH_4, C_2H_6, &c., and are displaceable by free chlorine (p. 162); also by the production of ethane by the electrolysis of potassium acetate, a change which can be formulated in a simple manner, only by assuming the presence of a CH_3– group,

$$\begin{matrix} CH_3\cdot COOK \\ CH_3\cdot COOK \end{matrix} = \begin{matrix} CH_3 \\ | \\ CH_3 \end{matrix} + \begin{matrix} CO_2 \\ CO_2 \end{matrix} + 2K.$$

Since, then, judging by its chemical behaviour, acetic acid contains a CH_3– and an HO– group, it must have the constitution $CH_3\cdot C\Big\langle\begin{matrix} O \\ OH \end{matrix}$, which confirms the conclusion previously arrived at.

The relation between formic and acetic acids, and their similarity in certain chemical properties, are satisfactorily accounted for by the constitutional formulæ

 and 

which thus confirm one another. The acids are both represented as containing the monovalent group of atoms  which has not been met with in any of the *neutral* compounds yet considered; it may be concluded, therefore, that their characteristic *acid* properties are due to the presence of this group. As, moreover, aldehydes contain the group  but do not contain hydrogen displaceable by metals, it must be the hydrogen atom of the HO– group which is displaced when the acids form salts. The particular monovalent group of atoms common to formic and acetic acids is named the *carboxyl*-group, and is usually written –CO·OH, or simply, for convenience, –COOH.

Homologues of Acetic Acid.—As all the higher members of the series of fatty acids resemble formic and acetic acids in chemical properties, may be produced by similar methods, and undergo similar changes, it is assumed that they all contain a carboxyl-group. With the exception of formic acid, they may, in fact, be regarded as derived from the paraffins, by the substitution of the monovalent carboxyl-group for one atom of hydrogen; acetic acid, $CH_3{\cdot}COOH$, from methane, CH_4; propionic acid, $C_2H_5{\cdot}COOH$, from ethane; and so on. They form, therefore, a homologous series of the general formula $C_nH_{2n+1}{\cdot}COOH$, or $C_nH_{2n}O_2$, and are all monobasic or *monocarboxylic* acids.

As in other homologous series, the higher members exist in isomeric forms, the number of isomerides theoretically possible in any given case being the same as that of the corresponding primary alcohols. The two isomeric acids, butyric acid,

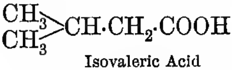
$CH_3\cdot CH_2\cdot CH_2\cdot COOH$, and isobutyric acid, $\begin{matrix}CH_3\\CH_3\end{matrix}\!>CH\cdot COOH$, for example, correspond with the two primary alcohols, $CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$, and $\begin{matrix}CH_3\\CH_3\end{matrix}\!>CH\cdot CH_2\cdot OH$, respectively.

Those isomerides which are derived from the normal paraffins, by substituting $-COOH$ for one atom of hydrogen in the CH_3- group, are termed *normal* or primary acids, as normal butyric acid, $CH_3\cdot CH_2\cdot CH_2\cdot COOH$, normal heptylic acid, $CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot COOH$; those which contain the group $\begin{matrix}CH_3\\CH_3\end{matrix}\!>CH-$ are usually termed *iso*-acids, as, for example, isobutyric acid, $\begin{matrix}CH_3\\CH_3\end{matrix}\!>CH\cdot COOH$, isovaleric acid, $\begin{matrix}CH_3\\CH_3\end{matrix}\!>CH\cdot CH_2\cdot COOH$, but the term is not used very systematically.

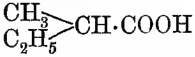
With the exception of the normal acids and one or two well-known iso-acids, such as those just quoted, it is usual, to avoid confusion, to name the fatty acids as if they were derived from acetic acid, just as the alcohols are regarded as derivatives of carbinol; the four isomerides of the molecular formula $C_5H_{10}O_2$, for example, are named as follows:

$CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot COOH$

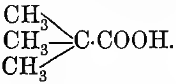
Normal Valeric Acid
(Propylacetic Acid).


$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>CH\cdot CH_2\cdot COOH$$

Isovaleric Acid
(Isopropylacetio Acid).


$$\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>CH\cdot COOH$$

Methylethylacetic Acid.


$$\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\!>C\cdot COOH.$$

Trimethylacetic Acid.

Propionic acid, $C_3H_6O_2$, or $CH_3\cdot CH_2\cdot COOH$, exists in only one form, and occurs in crude pyroligneous acid; it is formed when acrylic acid (p. 257) is reduced with sodium amalgam,

$$C_3H_4O_2 + 2H = C_3H_6O_2,$$

and when lactic acid (p. 225) is heated with concentrated hydriodic acid, which, at a high temperature, is a powerful reducing agent,*

$$CH_3{\cdot}CH(OH){\cdot}COOH + 2HI = CH_3{\cdot}CH_2{\cdot}COOH + H_2O + I_2.$$

It is prepared by oxidising propyl alcohol with chromic acid,

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}OH + 2O = CH_3{\cdot}CH_2{\cdot}COOH + H_2O.$$

Propionic acid is a colourless liquid, boils at 141°, and has a pungent sour smell; it is miscible with water in all proportions, but on adding a little calcium chloride to the solution, part of the acid separates at the surface, forming an oily layer. This property is characteristic of all fatty acids, which are readily soluble in water, except formic and acetic acids. Propionic acid is a mono-carboxylic acid, and closely resembles acetic acid in chemical properties; its salts, the **propionates**, are soluble in water, and of little importance.

There are two acids of the molecular formula $C_4H_8O_2$. **Normal butyric acid**, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, occurs in the vegetable and animal kingdoms, both in the free state and in combination with glycerol; it is an important constituent of butter. It is formed during the decay of nitrogenous animal matter, and during the butyric fermentation of lactic acid. When milk is left exposed to the air, it turns sour, the milk sugar which it contains being converted into lactic acid by a minute organism, the *lactic ferment*, which is present in the air, and finds its way into the milk,

$$\underset{\text{Milk Sugar.}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Lactic Acid.}}{4C_3H_6O_3}.$$

The lactic ferment has the power of converting other sugars besides milk sugar (or lactose) into lactic acid. If now a little decaying cheese be added to the sour milk, and the solu-

---

* In the reduction of lactic acid the following changes occur:

$$CH_3{\cdot}CH(OH){\cdot}COOH + HI = CH_3{\cdot}CHI{\cdot}COOH + H_2O$$

$$CH_3{\cdot}CHI{\cdot}COOH + H\vdots I = CH_3{\cdot}CH_2{\cdot}COOH + I_2.$$

In such reductions it is usual to add a pinch of amorphous phosphorus to the mixture, in order that the iodine may be reconverted into hydriodic acid ($3I + P + 3H_2O = H_3PO_3 + 3HI$).

tion be kept neutral by adding some chalk,* *butyric fermentation* sets in, the lactic acid being converted into butyric acid by the action of another organism, the *butyric ferment*, which is present in the decomposing cheese,

$$2C_3H_6O_3 = C_4H_8O_2 + 2CO_2 + 2H_2.$$

Butyric acid is usually prepared by a combination of these two processes of fermentation.

Butyric acid is a thick sour liquid, boiling at 163°. It has a very disagreeable odour, like that of rancid butter and stale perspiration, in which it occurs; it is miscible with water in all proportions, but separates on adding calcium chloride.

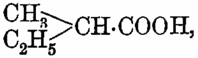
The **butyrates**, or salts of butyric acid, are soluble in water; the *calcium salt* $(C_4H_7O_2)_2Ca + H_2O$ is more soluble in cold than in hot water, so that when a cold saturated solution is heated, part of the salt separates in crystals, and the solution becomes turbid.

Isobutyric acid, or dimethylacetic acid, $(CH_3)_2CH\cdot COOH$, may be prepared by the oxidation of isobutyl alcohol,

$$(CH_3)_2CH\cdot CH_2\cdot OH + 2O = (CH_3)_2CH\cdot COOH + H_2O.$$

It boils at 155°, and resembles the normal acid very closely, but is not miscible with water in all proportions, one part of the acid requiring about five parts of water for solution. The *calcium salt* $(C_4H_7O_2)_2Ca + 5H_2O$, unlike that of butyric acid, is more soluble in hot than in cold water.

Of the four isomerides of the molecular formula $C_5H_{10}O_2$, **isovaleric acid**, or isopropylacetic acid, $(CH_3)_2CH\cdot CH_2\cdot COOH$, and **active valeric acid**, or methylethylacetic acid,



$$\begin{matrix}CH_3\\C_2H_5\end{matrix}\!\!>CH\cdot COOH,$$

are the most important. These acids occur together in the plant all-heal, or valerian, and in angelica root; the mixture of acids obtained by distilling the macerated plants with water is known as valeric or valerianic acid, and is an oily liquid, boiling at about 174°. A mixture of these two acids may

---

* The ferment ceases to act if the solution become too strongly acid.

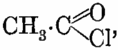
be prepared by oxidising commercial amyl alcohol (p. 105) with chromic acid.

The **hexylic acids**, $C_6H_{12}O_2$, are of little importance; seven of the eight isomerides theoretically possible are known, including normal hexylic acid (caproic acid).

Normal heptylic acid, $C_7H_{14}O_2$, or $C_6H_{13}{\cdot}COOH$, one of the seventeen theoretically possible isomerides, of which only nine are known, is prepared by oxidising castor-oil or œnanthaldehyde (p. 127) with nitric acid; it is an oily, rather unpleasant smelling liquid, sparingly soluble in water; it boils at 223°, and, like all the lower members of the series, is readily volatile in steam.

Palmitic acid, $C_{16}H_{32}O_2$, or $C_{15}H_{31}{\cdot}COOH$, and **stearic acid**, $C_{18}H_{36}O_2$, or $C_{17}H_{35}{\cdot}COOH$, occur in large quantities in animal and vegetable fats and oils (p. 166), from which they are prepared on the large scale principally for the manufacture of stearin candles; they are colourless, waxy substances, melting at 62° and 69° respectively, and insoluble in water, but soluble in alcohol, ether, &c. Their sodium and potassium salts are soluble in pure water, and are the principal constituents of soaps (p. 168), but their calcium, magnesium, and other salts are insoluble. A mixture of these two acids was at one time thought to be a definite compound, and named *margaric acid;* this name is now given to an artificially prepared acid, $C_{17}H_{34}O_2$, or $C_{16}H_{33}{\cdot}COOH$, which stands between palmitic and stearic acids in the series, and which seems not to occur in nature.

Derivatives of the Fatty Acids.

Acid Chlorides.—When phosphorus pentachloride is added to anhydrous acetic acid, an energetic action takes place, and **acetyl chloride**,  $CH_3{\cdot}C\begin{smallmatrix}\nearrow\!\!\!\nearrow O\\ \searrow Cl\end{smallmatrix}$, is formed, with evolution of hydrogen chloride; this change is analogous to that which occurs when an alcohol is treated with phosphorus pentachloride,

$$CH_3{\cdot}CO{\cdot}OH + PCl_5 = CH_3{\cdot}COCl + POCl_3 + HCl$$
$$CH_3{\cdot}CH_2{\cdot}OH + PCl_5 = CH_3{\cdot}CH_2Cl + POCl_3 + HCl.$$

Phosphorus trichloride and oxychloride also convert acetic acid into acetyl chloride.

Acetyl chloride is best prepared by adding phosphorus trichloride, or oxychloride, from a tap funnel to anhydrous sodium or potassium acetate contained in a retort connected with a condenser, and then distilling from a water-bath; a phosphite, or a mixture of metaphosphate and chloride, is left in the retort,

$$3CH_3{\cdot}COONa + PCl_3 = 3CH_3{\cdot}COCl + Na_3PO_3$$
$$2CH_3{\cdot}COOK + POCl_3 = 2CH_3{\cdot}COCl + KPO_3 + KCl.$$

It is a colourless, pungent-smelling liquid, boils at 55°, and fumes in moist air; when poured into water, it is rapidly decomposed, with formation of acetic acid,

$$CH_3{\cdot}COCl + H_2O = CH_3{\cdot}COOH + HCl.$$

Acetyl chloride bears the same relation to acetic acid as ethyl chloride to alcohol; it may, in fact, be produced by passing hydrogen chloride into anhydrous acetic acid containing phosphorus pentoxide, which combines with the water formed, and thus prevents the reverse change (compare ethereal salts, p. 187),

$$CH_3{\cdot}COOH + HCl = CH_3{\cdot}COCl + H_2O.$$

Acetyl chloride is not only quickly decomposed by alkalies and by water, but also, more or less rapidly, by all compounds containing one or more hydroxyl-groups; the interaction always takes place in such a way that hydrogen chloride is produced, the monovalent *acetyl*-group $CH_3{\cdot}C{<}^{O}$ displacing the hydrogen of the hydroxyl-group,

$$C_2H_5{\cdot}OH + CH_3{\cdot}COCl = C_2H_5{\cdot}O{\cdot}CO{\cdot}CH_3 + HCl$$
$$C_3H_7{\cdot}OH + CH_3{\cdot}COCl = C_3H_7{\cdot}O{\cdot}CO{\cdot}CH_3 + HCl.$$

Acetyl chloride may therefore be employed as a reagent for determining the presence of a hydroxyl-group. All that is necessary is to add the dry substance, in the state of a fine powder, if a solid, to excess of acetyl chloride, and then heat the mixture or solution for some time. The substance may be recovered unchanged, indicating that it is not a hydroxy-compound, or it may be converted into a new substance, an *acetyl* derivative, by the substitution of the acetyl-group for hydrogen; in the latter case, a combustion of the substance is usually made, in order to ascertain its composition, from which the number of times the acetyl-group has displaced hydrogen is determined;* or, since acetyl derivatives are decomposed by boiling acids and alkalies, the percentage of acetic acid obtained from the substance may be directly estimated,

$$C_2H_5 \cdot O \cdot CO \cdot CH_3 + KOH = C_2H_5 \cdot OH + CH_3 \cdot COOK.$$

All the fatty acids except formic acid may be converted into *acid chlorides*, such as *propionyl chloride*, $CH_3 \cdot CH_2 \cdot COCl$, by the methods described above; the products resemble acetyl chloride in chemical properties, and may be employed for the detection of hydroxyl-groups. *Acid bromides*, such as $CH_3 \cdot COBr$, can be obtained in a similar manner.

Anhydrides.—The hydrogen atom in a carboxyl-group $-COOH$ is not, as a rule, displaced by the acetyl-group on treatment with acetyl chloride, but, when an alkali salt of a fatty acid is heated with acetyl chloride, an acetyl derivative of the acid is formed,

$$CH_3 \cdot COOK + CH_3 \cdot COCl = CH_3 \cdot CO \cdot O \cdot CO \cdot CH_3 + KCl.$$

The compound obtained from an acetate in this way may be regarded as acetyl oxide, $(CH_3 \cdot CO)_2O$, or as an **anhydride** of acetic acid, derived from 2 mols. of the acid by loss of 1 mol. of water, just as ethers are derived from alcohols, and inorganic anhydrides from the corresponding acids,

---

* Except when the acetyl derivative has the same, or nearly the same percentage composition as the original substance, in which case the number of acetyl groups in the molecule is determined by boiling with standard alkali or acid, and then estimating by titration the amount of acetic acid which has been formed.

$$\begin{array}{l} CH_3\cdot CO\,\vdots\,OH \\ CH_3\cdot COO\,\vdots\,H \end{array} = \left.\begin{array}{l} CH_3\cdot CO \\ CH_3\cdot CO \end{array}\right> O + H_2O$$

$$\begin{array}{l} C_2H_5\cdot OH \\ C_2H_5\cdot OH \end{array} = \left.\begin{array}{l} C_2H_5 \\ C_2H_5 \end{array}\right> O + H_2O \qquad \begin{array}{l} NO_2\cdot OH \\ NO_2\cdot OH \end{array} = \left.\begin{array}{l} NO_2 \\ NO_2 \end{array}\right> O + H_2O.$$

Acetic anhydride, $(CH_3\cdot CO)_2O$, may be prepared by heating the anhydrous alkali acetates (4 mols.) with phosphorus oxychloride (1 mol.); the salt is first acted on by the oxychloride yielding acetyl chloride (see above), which interacts with more salt, forming acetic anhydride, or, expressed in one equation,

$$4CH_3\cdot COONa + POCl_3 = 2(CH_3\cdot CO)_2O + NaPO_3 + 3NaCl.$$

Acetic anhydride is a mobile liquid, boils at 137°, and has an unpleasant, irritating odour; it is decomposed by alkalies, by water, and by nearly all substances (except acids) which contain the hydroxyl-group, acetyl derivatives being formed,

$$(CH_3\cdot CO)_2O + H_2O = 2CH_3\cdot COOH$$

$$(CH_3\cdot CO)_2O + C_2H_5\cdot OH = CH_3\cdot CO\cdot O\cdot C_2H_5 + CH_3\cdot COOH.$$

Acetic anhydride may therefore be employed in ascertaining whether a substance contains a hydroxyl-group just as well as acetyl chloride, the operations being carried out as already described.

All the fatty acids, except formic acid, may be converted into anhydrides by treating the acid chloride with an alkali salt, or by heating excess of an alkali salt with phosphorus oxychloride. If an acid chloride be treated with a salt of a different acid, *mixed anhydrides*, corresponding with the mixed ethers, are obtained. All these anhydrides resemble acetic anhydride in chemical properties.

Amides.—Acetyl chloride and acetic anhydride interact not only with compounds containing a hydroxyl-group, but also with anhydrous ammonia; the compound obtained in this way may be regarded as derived from ammonia by the substitution of the acetyl-group for one atom of hydrogen, and is named acetamide.

$$CH_3{\cdot}COCl + 2NH_3 = CH_3{\cdot}CO{\cdot}NH_2 + NH_4Cl$$
$$(CH_3{\cdot}CO)_2O + 2NH_3 = CH_3{\cdot}CO{\cdot}NH_2 + CH_3{\cdot}CO{\cdot}ONH_4.$$

Acetamide, $CH_3{\cdot}CO{\cdot}NH_2$, may also be produced by heating ethyl acetate (p. 185) with concentrated ammonia under pressure,

$$CH_3{\cdot}CO{\cdot}OC_2H_5 + NH_3 = CH_3{\cdot}CO{\cdot}NH_2 + C_2H_5{\cdot}OH,$$

but it is best prepared by slowly distilling ammonium acetate in a stream of dry ammonia,

$$CH_3{\cdot}CO{\cdot}ONH_4 = CH_3{\cdot}CO{\cdot}NH_2 + H_2O.$$

As one distillation is not sufficient to insure complete decomposition, that portion of the distillate boiling above 140° is collected separately and redistilled, these operations being repeated three or four times.

Acetamide crystallises in colourless needles, melts at 80–82°, and boils at 222°. When pure, it has only a faint odour, but as usually prepared, it has a strong smell of mice, owing to the presence of traces of impurity; it is readily soluble in water and alcohol. When heated with mineral acids or alkalies, it is decomposed into acetic acid and ammonia, or their salts (compare foot-note, p. 143),

$$CH_3{\cdot}CO{\cdot}NH_2 + H_2O = CH_3{\cdot}COOH + NH_3;$$

on distillation with phosphoric anhydride, it loses 1 mol. of water, and is converted into methyl cyanide or acetonitrile,

$$CH_3{\cdot}CO{\cdot}NH_2 = CH_3{\cdot}CN + H_2O.$$

Formic acid and all the higher fatty acids may be converted into amides by methods similar to those given above; *formamide*, $H{\cdot}CO{\cdot}NH_2$, for example, may be prepared by distilling ammonium formate. These amides closely resemble acetamide in chemical and physical properties, but their solubility in water rapidly diminishes on passing up the series. It is a remarkable fact that the melting-points of the amides of the fatty acids lie very close together, most of them melting between 95° and 110°, and all within the limits of 79° and 129°.

Substitution Products of Acetic Acid.—Since acetic acid, like methyl chloride, is a mono-substitution product of marsh-gas, and contains three atoms of hydrogen combined with carbon, it might be expected to give halogen substitution products, just as does methyl chloride. As a matter of fact, acetic acid yields three substitution products on treatment with chlorine in sunlight,

$$\begin{aligned} CH_3{\cdot}COOH + Cl_2 &= CH_2Cl{\cdot}COOH + HCl \\ CH_3{\cdot}COOH + 2Cl_2 &= CHCl_2{\cdot}COOH + 2HCl \\ CH_3{\cdot}COOH + 3Cl_2 &= CCl_3{\cdot}COOH + 3HCl. \end{aligned}$$

If the constitutions of acetic acid and of these three compounds be correctly represented by these formulæ, it would be expected that, as the chloro-substitution products still contain the carboxyl-group, they would behave like monocarboxylic acids, and, like acetic acid, form salts, acid chlorides, anhydrides, &c. This again is the fact; the three substitution products are monobasic acids, similar to acetic acid and to one another in chemical properties.

The three chloracetic acids may be prepared by passing chlorine into boiling acetic acid, to which a little iodine has been added. When iodine is present, the process can be carried out in absence of sunlight, because the iodine is converted into iodine trichloride, which acts on the acetic acid even in the dark,

$$CH_3{\cdot}COOH + ICl_3 = CH_2Cl{\cdot}COOH + HCl + ICl.$$

The iodine chloride is again converted into trichloride by direct combination with chlorine, and so the process continues, a very small quantity of iodine being sufficient to insure chlorination. The iodine, or rather the iodine chloride, is spoken of as a chlorine *carrier*.

Chloracetic acid, $CH_2Cl{\cdot}COOH$, is a crystalline substance; it melts at 62°, and boils at 185–187°.

Dichloracetic acid, $CHCl_2{\cdot}COOH$, is a liquid, and boils at 190–191°; it is best prepared by treating chloral hydrate with potassium cyanide in aqueous solution,

$$KCN + CCl_3{\cdot}CH(OH)_2 = CHCl_2{\cdot}COOH + HCN + KCl.$$

Trichloracetic acid, $CCl_3{\cdot}COOH$, is best prepared by oxidising the corresponding aldehyde, chloral, with concentrated nitric acid,

$$CCl_3\cdot CHO + O = CCl_3\cdot COOH.$$

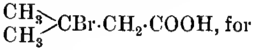
It melts at 52°, boils at 195°, and is decomposed by hot alkalies into chloroform and a carbonate,

$$CCl_3\cdot COOH + KOH = CHCl_3 + KHCO_3.$$

The three bromacetic and iodacetic acids are similar in properties. On treating any of these halogen substitution products with nascent hydrogen, they are reconverted into acetic acid by inverse substitution. The higher fatty acids may be converted into halogen substitution products, which, however, unlike those of acetic acid, exist in isomeric forms. Propionic acid, for example, gives two monochloro-propionic acids—namely, α-chloro-propionic acid, $CH_3\cdot CHCl\cdot COOH$, and β-chloro-propionic acid, $CH_2Cl\cdot CH_2\cdot COOH$. For the purpose of distinguishing between these substitution products, the carbon atoms are lettered α, β, γ, δ, &c., commencing always with that which is combined with the carboxyl-group

$$\underset{\delta}{CH_3}\cdot\underset{\gamma}{CH_2}\cdot\underset{\beta}{CH_2}\cdot\underset{\alpha}{CH_2}\cdot COOH\,;$$

the acid of the constitution $\genfrac{}{}{0pt}{}{CH_3}{CH_3}\!>\!CBr\cdot CH_2\cdot COOH$, for example, is named β-bromisopropylacetic acid.



$$\genfrac{}{}{0pt}{}{CH_3}{CH_3}\!>\!CBr\cdot CH_2\cdot COOH$$

SUMMARY AND EXTENSION.

The Fatty Acids.—Carboxy-derivatives of the paraffins of the general formula $C_nH_{2n+1}\cdot COOH$, or $C_nH_{2n}O_2$. The more important members of this homologous series are the following, the number of *known* isomerides being given by the figures in brackets:

		M.p.	B.p.	Sp. gr.	
Formic acid, $H\cdot COOH$ (1)		8·3°	101°	1·241	at 0°
Acetic acid, $CH_3\cdot COOH$ (1)		16·5°	118°	1·080	"
Propionic acid, $C_2H_5\cdot COOH$ (1)		-24°	141°	1·013	"
Butyric acid, $C_3H_7\cdot COOH$ (2)	Normal	-4°	163°	0·978	"
	Iso-	—	155°	0·965	"
Valeric acid, $C_4H_9\cdot COOH$ (4)	Normal	—	186°	0·957	"
	Iso-	—	174°	0·947	"
Heptylic acid, $C_6H_{13}\cdot COOH$ (8)		—	223°	0·945	"
Lauric acid, $C_{11}H_{23}\cdot COOH$ (3)		43·6°	—	0·875	At the melting-point.
Myristic acid, $C_{13}H_{27}\cdot COOH$ (2)		54°	—	0·862	
Palmitic acid, $C_{15}H_{31}\cdot COOH$ (2)		62°	—	0·853	
Stearic acid, $C_{17}H_{35}\cdot COOH$ (3)		69°	—	0·845	

Heptylic acid and all the higher members named in this table are normal acids; they occur in nature in fats and oils, and contain an even number of carbon atoms. The higher normal acids containing an odd number of carbon atoms, $C_8H_{17}\cdot COOH$, $C_{10}H_{21}\cdot COOH$, &c., are known, but they do not occur in nature.

Formic acid is prepared by heating oxalic acid with glycerol, acetic acid from pyroligneous acid, and by the acetous fermentation of alcohol, butyric acid by the butyric fermentation of lactic acid, and palmitic and stearic acids by the hydrolysis of glycerides occurring in fats and oils.

Methods of Preparation.—By the oxidation of primary alcohols and of aldehydes,

$$C_2H_5\cdot CH_2\cdot OH + 2O = C_2H_5\cdot COOH + H_2O$$
$$C_6H_{13}\cdot CHO + O = C_6H_{13}\cdot COOH.$$

By boiling alkyl cyanides with alkalies or mineral acids,

$$C_2H_5\cdot CN + 2H_2O = C_2H_6\cdot COOH + NH_3.$$

By heating those dicarboxylic acids in which the two carboxyl-groups are combined with one and the same carbon atom (p. 234),

$$CH_2(COOH)_2 = CH_3\cdot COOH + CO_2.$$

By the hydrolysis of derivatives of ethyl acetoacetate (p. 189),

$$CH_3\cdot CO\cdot CH(C_3H_7)\cdot COOC_2H_5 + 2KOH = C_3H_7\cdot CH_2\cdot COOK$$
$$+ CH_3\cdot COOK + C_2H_5\cdot OH.$$

Physical Properties.—At ordinary temperatures, the lower members are colourless liquids (except acetic acid), miscible with water, alcohol, and ether in all proportions. On passing up the series, they become more oily in character, gradually lose their pungent smell, and become less readily soluble in water. The higher members, from $C_{10}H_{20}O_2$, are solid, waxy, or fatty substances, have only a faint smell, and are insoluble in water, but soluble in alcohol and ether. They are all volatile in steam except the highest members, which, however, may be distilled in super-heated steam. The first three members are specifically heavier than water, but the sp. gr. decreases as the series is ascended (see table). With the exception of the highest members, they boil without decomposition under ordinary atmospheric pressure, the boiling-point rising about 19° for every addition of $-CH_2-$ to the molecule; the melting-point also rises, but not continuously, acids containing an odd number of carbon atoms melting at a lower temperature than the preceding members containing an even number of carbon atoms,

$C_{12}H_{24}O_2$	$C_{13}H_{26}O_2$	$C_{14}H_{28}O_2$	$C_{15}H_{30}O_2$	$C_{16}H_{32}O_2$	$C_{17}H_{34}O_2$.
43·6°	40·5°	54°	51°	62°	60°

Chemical Properties.—The fatty acids are very stable, and are only with difficulty oxidised and broken up; nevertheless, owing to the presence of the carboxyl-group, they readily undergo a variety of double decompositions. They are all monobasic acids, but the acid character becomes less and less pronounced on passing up the series; whereas formic and acetic acids readily decompose carbonates, and dissolve metals and metallic hydroxides, the higher members, such as palmitic and stearic acids, are with difficulty recognised as acids by ordinary tests. The metallic salts of the lower members are soluble in water; but on passing up the series, the solubility decreases, until, in the case of the higher acids, only the alkali salts (soaps) are soluble.

Fatty acids interact with alcohols, especially in presence of dehydrating agents, forming ethereal salts and water,

$$CH_3{\cdot}COOH + C_2H_5{\cdot}OH = CH_3{\cdot}COOC_2H_5 + H_2O.$$

When treated with phosphorus pentachloride, &c., they are converted into acid chlorides,

$$C_2H_5{\cdot}COOH + PCl_5 = C_2H_5{\cdot}COCl + POCl_3 + HCl.$$

These acid chlorides interact readily with hydroxy-compounds, giving ethereal salts,

$$C_2H_5{\cdot}COCl + CH_3{\cdot}OH = C_2H_5{\cdot}CO{\cdot}OCH_3 + HCl;$$

on distillation with an alkali salt of a fatty acid, they yield anhydrides of the acids,

$$C_2H_5{\cdot}COCl + C_2H_5{\cdot}COOK = (C_2H_5{\cdot}CO)_2O + KCl;$$

and when treated with ammonia, they give amides,

$$CH_3{\cdot}COCl + NH_3 = CH_3{\cdot}CO{\cdot}NH_2 + HCl.$$

The fatty acids yield halogen substitution products under suitable conditions. From the alkali salts of the fatty acids, ketones, aldehydes, and paraffins can be prepared without difficulty, and, as the aldehydes and ketones are easily reduced to alcohols, which again are readily converted into ethers and olefines, all these compounds may be obtained from the fatty acids.

Fats, Oils, Soaps, Stearin, and Butter.

Composition of Fats and Oils.—When beef or mutton suet is kneaded in a muslin bag in a basin of hot water, the fat melts and passes out, leaving the membrane or tissue in the bag; the melted fat solidifies on cooling, and is known as *tallow.* The fat obtained from pigs, in a similar manner, is much softer, and is called *lard*

When tallow is heated with water in closed vessels at about 200°, or treated with superheated steam (steam which has been passed through tubes heated at about 200°), it is decomposed into glycerol (p. 248) and fatty acids; if the mixture be now distilled in superheated steam, these products pass over, the distillate being an aqueous solution of glycerol, at the surface of which floats the mixture of fatty acids. A similar decomposition takes place when tallow is heated with dilute sulphuric acid, but in this case it is not necessary to heat so strongly.

All animal fats, such as lard, goose-fat, bone-fat, butter, &c., and the fatty oils, such as olive-, linseed-, rape-, palm-, and cotton-seed oils, which are obtained by pressing the seeds or fruit of certain plants, behave in a similar manner, and when heated with dilute sulphuric acid, or with water under pressure, are decomposed into glycerol and a mixture of fatty acids. The occurrence of these acids in natural fats and oils, and the fact that the higher members of the series resemble fats in physical properties, led to the use of the term 'fatty acid,' which is now applied to all the members of the series.

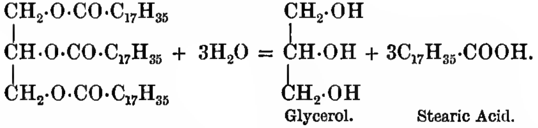
The chemical compounds of which these fats are composed are called *glycerides;* they are ethereal salts (p. 171), formed, together with water, by the combination of the fatty acids with the alcohol, glycerol, which acts as a hydroxide or weak base. Glycerol is a *tri-acid* base, and can combine with and neutralise three molecules of a monobasic or monocarboxylic acid, forming neutral salts, just as can the tri-acid bismuth hydroxide,

$$C_3H_5(OH)_3 + 3CH_3{\cdot}COOH = C_3H_5(O{\cdot}CO{\cdot}CH_3)_3 + 3H_2O$$
$$Bi(OH)_3 + 3HCl = BiCl_3 + 3H_2O.$$

These glycerides or salts are named after the acids from which they are formed. The salt formed from acetic acid is called *triacetin;* that from palmitic acid, *tripalmitin;* and that from stearic acid, *tristearin,* and so on.

Now the chief constituents of fats and oils are tristearin and tripalmitin, which are solid at ordinary temperatures, and a liquid glyceride, *trioleïn*, which is formed by the combination of glycerol with *oleïc acid.*[*] When a fat contains a relatively large proportion of tristearin and tripalmitin, it is solid and comparatively hard (tallow) at ordinary temperatures; when, however, it contains a relatively large proportion of trioleïn, it is soft and pasty (lard), or liquid (olive-oil).

These glycerides, like other salts formed from weak acids and weak bases, are not very stable, and at moderately high temperatures they are decomposed by water and by dilute mineral acids, being converted into glycerol and an acid; in the case of tristearin, for example,



$$\begin{array}{l} CH_2{\cdot}O{\cdot}CO{\cdot}C_{17}H_{35} \\ | \\ CH{\cdot}O{\cdot}CO{\cdot}C_{17}H_{35} \\ | \\ CH_2{\cdot}O{\cdot}CO{\cdot}C_{17}H_{35} \end{array} + 3H_2O = \underset{\text{Glycerol.}}{\begin{array}{l} CH_2{\cdot}OH \\ | \\ CH{\cdot}OH \\ | \\ CH_2{\cdot}OH \end{array}} + \underset{\text{Stearic Acid.}}{3C_{17}H_{35}{\cdot}COOH.}$$

Since fats and oils are mixtures of glycerides, they yield mixtures of fatty acids.

Soaps.—On treatment with alkalies the glycerides are decomposed much more readily than by water, yielding alkali salts, the weak base, glycerol, being liberated, just as ammonia or methyl alcohol is liberated from its salts on adding a stronger base. In manufacturing soaps, a fat or oil, such as tallow or cotton-seed oil, is heated in an iron pan with a small but sufficient quantity of caustic soda, when it is converted after some time into a thick, homogeneous, frothy solution, which contains glycerol and the sodium salts of the various acids which were present in the glycerides—that is to say, the sodium salts of stearic, palmitic, and oleïc acids. Some common salt is now added, whereupon the sodium

---

[*] *Oleïc acid*, $C_{17}H_{33}{\cdot}COOH$ (p. 258), is a liquid at ordinary temperatures. It contains two atoms of hydrogen less than stearic acid, $C_{17}H_{35}{\cdot}COOH$, and is, therefore, an *unsaturated* acid, belonging to a different series; its lead salt is soluble in ether, a property very rarely met with in other lead salts.

salts separate from the solution of glycerol and salt as a curd, because they are insoluble in salt water. The curd, after having been drained off, and allowed to cool, slowly solidifies, and is then known as *hard soap*, which is simply a mixture of the sodium salts of palmitic, stearic, and oleïc acids with water and alkali. When fats or oils are boiled with potash, instead of with soda, similar chemical changes take place, and the potassium salts of the acids are formed; if common salt be now added to the solution, the potassium are partially converted into sodium salts, and a hard soap is finally obtained; if, however, without adding salt, the homogeneous solution be allowed to cool, it sets to a jelly-like mass of *soft soap*, which is a mixture of the potassium salts of the above-named acids, containing glycerol and a large percentage of water.

The decomposition of fats and oils in this way in the process of soap-making originally received the name *saponification*, and the fats and oils were said to be *saponified*. The term saponification was then applied generally to the analogous decomposition of other ethereal salts by alkalies, in spite of the fact that the products were not soaps, but the word *hydrolysis* has now to a great extent taken its place. Hydrolysis may be roughly defined as the decomposition of one compound into two or more, with fixation of the elements of water or of some hydroxide. The decomposition of glycerides by water, acids, and alkalies, and the changes expressed by the following equations, are examples of hydrolysis,

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6$$
$$C_2H_3O_2{\cdot}C_2H_5 + H_2O = C_2H_4O_2 + C_2H_5{\cdot}OH$$
$$C_2H_5Cl + KOH = C_2H_5{\cdot}OH + KCl.$$

Stearin and Glycerol.—Stearin consists principally of a mixture of stearic and palmitic acids, and is manufactured by decomposing tallow with water, superheated steam, dilute sulphuric acid, or milk of lime under pressure (see above). After distilling the products in a current of superheated steam — first acidifying with sulphuric acid, if lime has been used—the pasty mixture of fatty acids is separated from the aqueous solution of glycerol, and pressed, in order to squeeze out as much of the liquid oleïc acid as possible. The pressed mass is then gently warmed, and pressed again between warm plates, when a further quantity of oleïc acid is squeezed out, together with some palmitic and stearic acids. The hard mass that remains is called *stearin;* it is mixed with a little paraffin to make it less brittle, and employed in large quantities in the manufacture of stearin candles. The pasty mass of oleïc, palmitic, and stearic acids, separated from the stearin, is known as *oleomargarine* (from oleïc and 'margaric' acids), and is employed for the preparation of artificial butter. Glycerol (p. 248) is obtained from the aqueous distillate, after separating the fatty acids; the solution is decolourised by filtration through charcoal, and evaporated to a syrup.

Butter and Margarine.—Butter, prepared from cream, is a mixture of fat (about 87 per cent.), water (about 12 per cent.), and small quantities of caseïn, milk-sugar, and salts. Pure butter-fat contains about 92 per cent. of a mixture of tristearin, tripalmitin, and trioleïn, about 7·7 per cent. of tributyrin, and traces of other glycerides, and substances which impart flavour; it differs from all other fats and oils, in containing a large proportion of *tributyrin,* the glyceride of butyric acid.

Artificial butter, or *margarine,* is prepared from oleomargarine (see above), which has been carefully manufactured from the best ox-suet; the oleomargarine is flavoured and coloured by churning it with milk, sometimes also by the addition of artificial colouring and flavouring substances. When carefully prepared, it is a wholesome substitute for butter, and probably just as nutritious, although perhaps not quite so easily digested.

CHAPTER X.

ETHEREAL SALTS.

It has been pointed out that the alcohols behave in some respects like metallic hydroxides, and combine with acids, forming salts and water,

$$C_2H_5{\cdot}OH + HCl = C_2H_5Cl + H_2O$$
$$C_2H_5{\cdot}OH + H_2SO_4 = C_2H_5{\cdot}HSO_4 + H_2O$$
$$CH_3{\cdot}OH + CH_3{\cdot}COOH = CH_3{\cdot}COOCH_3 + H_2O.$$

These compounds are called **ethereal salts** or **esters**, in contradistinction to the metallic salts.

Halogen Ethereal Salts and Halogen Derivatives of the Paraffins.

The ethereal salts of the halogen acids are identical with the *halogen mono-substitution products of the paraffins*, and may be obtained either from the alcohols or from the paraffins; they form homologous series of the general formula $C_nH_{2n+1}{\cdot}X$ where X = Cl, Br, or I.

Methyl chloride,	CH_3Cl	Methyl bromide,	CH_3Br	Methyl iodide,	CH_3I
Ethyl ″	C_2H_5Cl	Ethyl ″	C_2H_5Br	Ethyl ″	C_2H_5I
Propyl ″	C_3H_7Cl	Propyl ″	C_3H_7Br	Propyl ″	C_3H_7I

The di-, tri-, &c. halogen substitution products of the paraffins, such as methylene dichloride, CH_2Cl_2, chloroform, $CHCl_3$, iodoform, CHI_3, and carbon tetrachloride, CCl_4, cannot be regarded as ethereal salts, but, being closely related to the halogen ethereal salts, are conveniently considered in this chapter.

Methyl chloride, or chloromethane, CH_3Cl, is one of the four substitution products obtained on treating methane with chlorine in sunlight, and is formed in small quantities when methyl alcohol is heated with *concentrated* hydrochloric acid,

$$CH_3{\cdot}OH + HCl = CH_3Cl + H_2O.$$

It is prepared by passing hydrogen chloride into methyl alcohol containing anhydrous zinc chloride (Groves' process), as described in the case of ethyl chloride (p. 175); also by heating methyl alcohol with sodium chloride and concentrated sulphuric acid.

It is a colourless gas, and liquefies at very low temperatures, boiling at –24°; it burns with a green-edged flame, is moderately easily soluble in water, and when heated with water or dilute potash under pressure, it is converted into methyl alcohol,

$$CH_3Cl + H_2O = CH_3{\cdot}OH + HCl.$$

Methyl chloride is employed on the large scale in the preparation of organic dyes, the compressed gas being also used for the artificial production of a low temperature; for these purposes it is manufactured by heating trimethylamine hydrochloride (p. 207) with hydrochloric acid,

$$N(CH_3)_3,HCl + 3HCl = 3CH_3Cl + NH_4Cl.$$

Methylene (or methene) **dichloride**, CH_2Cl_2, is prepared by reducing chloroform with zinc and hydrochloric acid in alcoholic solution,

$$CHCl_3 + 2H = CH_2Cl_2 + HCl;$$

it is a colourless, heavy liquid, boiling at 41°.

Chloroform, or trichloromethane, $CHCl_3$, is formed when methane, methyl chloride, or methylene dichloride, is treated with chlorine in sunlight, and when many simple organic substances containing oxygen, such as ethyl alcohol, acetone, &c., are heated with bleaching powder, which acts as an oxidising as well as a chlorinating agent (see below).

Chloroform may be prepared by distilling alcohol or acetone with bleaching powder: Some strong bleaching powder (about 450 grams) is made into a cream with about 1½ litres of water contained in a large flask, and alcohol, methylated spirit, or acetone (about 100 c.c.) is gradually added; the flask is then connected with a condenser, and slowly heated on a water-bath, when a mixture of chloroform, water, and alcohol or acetone distils. If the operation has been successful, the chloroform collects as a heavy oil at the bottom of the receiver; but if too much alcohol or acetone be present, the chloroform must be precipitated by adding water. It is then separated with the aid of a funnel, washed with water, shaken once or twice with a little concentrated sulphuric acid, which frees it from water, alcohol, &c., and redistilled from a water-bath.

The chloroform prepared in this way is not quite pure; the pure substance is best prepared by distilling chloral or chloral hydrate (p. 125) with caustic soda, the product being separated in the manner just described,

$$CCl_3{\cdot}CHO + NaOH = CHCl_3 + H{\cdot}COONa.$$

The changes which occur in the preparation of chloroform from alcohol are complex; it is probable that aldehyde is first formed by oxidation, and then converted into chloral, which is decomposed by the calcium hydroxide which is always produced during the reaction, yielding chloroform and calcium formate. When acetone is employed, trichloracetone is probably formed in the first place; this compound is then decomposed by the calcium hydroxide, giving chloroform and calcium acetate,

$$2CH_3{\cdot}CO{\cdot}CCl_3 + Ca(OH)_2 = 2CHCl_3 + (CH_3{\cdot}COO)_2Ca.$$

Chloroform is a heavy, pleasant-smelling liquid of sp. gr. 1·498 at 15°, and boils at 61°; when strongly heated, it burns with a green-edged flame, but it is not inflammable at ordinary temperatures. It is readily decomposed by warm alcoholic potash, yielding potassium formate and chloride,

$$CHCl_3 + 4KOH = H{\cdot}COOK + 3KCl + 2H_2O.$$

If a drop of chloroform be added to a mixture of aniline (part ii.) and alcoholic potash, an intensely nauseous smell is observed on warming gently, owing to the formation of *phenylcarbylamine* or *phenylisocyanide*,[*]

$$CHCl_3 + 3KOH + C_6H_5{\cdot}NH_2 = C_6H_5{\cdot}NC + 3KCl + 3H_2O, \text{ or}$$
$$C_6H_5{\cdot}NH_2 + H{\cdot}COOH = C_6H_5{\cdot}NC + 2H_2O.$$

---

[*] The experiment should be performed in a test tube, only one drop of aniline being employed, and the contents of the test tube should afterwards be carefully poured into the sink-pipe, in a draught closet if possible.

This reaction affords a very delicate test for chloroform and for aniline, and is spoken of as the **carbylamine reaction** (p. 202).

Chloroform is extensively employed in surgery as an anæsthetic, its vapour when inhaled causing unconsciousness. For this purpose pure chloroform must be employed, as the impure substance is dangerous, and produces bad after-effects.* Pure chloroform gives no precipitate with silver nitrate, and does not darken when shaken with concentrated sulphuric acid or with strong potash.

Carbon tetrachloride, or tetrachloromethane, CCl_4, the final product of the action of chlorine on CH_4, CH_3Cl, CH_2Cl_2, and $CHCl_3$, is prepared by passing chlorine into boiling chloroform in sunlight, or by passing chlorine into carbon bisulphide in presence of antimony pentachloride, which acts as a chlorine carrier (p. 163),

$$CS_2 + 3SbCl_5 = CCl_4 + S_2Cl_2 + 3SbCl_3,$$
$$SbCl_3 + Cl_2 = SbCl_5;$$

in the latter case the sulphur dichloride is got rid of, after a preliminary distillation, by shaking the product with potash, the carbon tetrachloride being purified by redistillation. Carbon tetrachloride is a very heavy, pleasant-smelling liquid, boiling at 76–77°; on treatment with nascent hydrogen, it is converted into $CHCl_3$, CH_2Cl_2, CH_3Cl, and CH_4 successively, by inverse substitution. It is decomposed by hot alcoholic potash,

$$CCl_4 + 4KOH = 4KCl + CO_2 + 2H_2O.$$

The halogen ethereal salts, *methyl bromide*, CH_3Br (b.p. 4·5°), and *methyl iodide*, CH_3I (b.p. 44°), are prepared by methods similar to those employed in the case of the corresponding

---

* In the presence of air, chloroform gradually undergoes decomposition, especially under the influence of light, carbonyl chloride (phosgene gas, $COCl_2$) and hydrochloric acid being produced, $CHCl_3 + O = COCl_2 + HCl$. As carbonyl chloride is very poisonous, it is necessary to keep all chloroform required for anæsthetic purposes in the dark, the bottle being kept as full as possible, so as to exclude air.

ethyl salts (see below), which they closely resemble in chemical properties.

Iodoform, or triiodomethane, CHI_3, a halogen tri-substitution product of methane, is closely related to chloroform, and may be considered here. It is formed when ethyl alcohol (but *not* methyl alcohol), acetone, aldehyde, and other simple organic substances containing oxygen united with a $CH_3{\cdot}C\equiv$ group are warmed with iodine and an alkali or alkali carbonate; the changes which occur are doubtless similar to those which take place in the preparation of chloroform.

Iodoform is prepared by gradually adding iodine to an aqueous solution of sodium carbonate containing a little alcohol and heated at 60–80°; the precipitated iodoform is separated by filtration, and purified by recrystallisation from dilute alcohol. It crystallises in lustrous, yellow, six-sided plates, melts at 119°, and has a peculiar, very characteristic odour; it sublimes readily, and is volatile in steam. It is used in medicine and surgery as an antiseptic.

Ethyl chloride, or chlorethane, C_2H_5Cl, is formed when ethane is treated with chlorine in sunlight, and when alcohol is heated with concentrated hydrochloric acid, or treated with phosphorus pentachloride, or trichloride, at ordinary temperatures,

$$C_2H_5{\cdot}OH + PCl_5 = C_2H_5Cl + POCl_3 + HCl.$$

Ethyl chloride is prepared by Groves' process: Hydrogen chloride, carefully dried with concentrated sulphuric acid, is passed into a flask containing absolute alcohol, to which about half its weight of coarsely powdered anhydrous zinc chloride has been added; the flask is connected with a reflux condenser (p. 186), and is provided with a safety tube. As soon as the solution is saturated with hydrogen chloride, it is gently warmed on the water-bath, when ethyl chloride and alcohol pass off; the alcohol vapour is cooled in passing through the condenser, the liquid running back into the flask. The gaseous ethyl chloride now passes through three wash-bottles containing water, dilute potash, and concentrated sulphuric acid respectively, by which means it is freed from hydrogen chloride, alcohol, and moisture; the pure ethyl chloride is then collected in a U-tube immersed in a freezing mixture.

Zinc chloride is a powerful dehydrating agent, and combines with the water produced during the interaction,

$$C_2H_5{\cdot}OH + HCl = C_2H_5Cl + H_2O.$$

Unless some dehydrating agent be present, very little ethyl chloride is formed, because it is decomposed by water, or rather its formation cannot take place in presence of much water.

Ethyl chloride may also be prepared by warming a mixture of absolute alcohol, concentrated sulphuric acid, and sodium chloride, the gas being purified and condensed in the same way as before; the sulphuric acid not only interacts with the salt, forming hydrogen chloride, but also acts as a dehydrating agent.

Ethyl chloride is a colourless, very volatile liquid, boiling at 12·5°; it burns with a greenish, smoky flame, and is only sparingly soluble in water, but miscible with alcohol, ether, &c. When heated with water or potash under pressure, it yields ethyl alcohol,

$$C_2H_5Cl + H_2O = C_2H_5{\cdot}OH + HCl;$$

on treatment with chlorine in sunlight, it gives di-, tri-, &c. substitution products of ethane. It gives no immediate precipitate with aqueous silver nitrate, but when warmed with an *alcoholic* solution of silver nitrate, silver chloride is quickly precipitated, ethyl nitrate remaining in solution,

$$C_2H_5Cl + AgNO_3 = C_2H_5{\cdot}NO_3 + AgCl.$$

Ethyl bromide, or bromethane, C_2H_5Br, is formed when alcohol is heated with concentrated hydrobromic acid, or treated with phosphorus tribromide or pentabromide, at ordinary temperatures,

$$C_2H_5{\cdot}OH + PBr_5 = C_2H_5Br + POBr_3 + HBr.$$

It is prepared by dropping bromine from a stoppered funnel into a mixture of alcohol (60 grams) and amorphous phosphorus (10 grams) contained in a distilling-flask, connected with a condenser and immersed in cold water; after adding the whole of the bromine, the mixture is distilled. The distillate is shaken with dilute potash to free it from bromine, hydrobromic acid, and alcohol, and then washed by shaking with water; after drying with calcium chloride, the ethyl bromide is purified by fractional distillation,

$$3C_2H_5{\cdot}OH + P + 3Br = 3C_2H_5Br + H_3PO_3.$$

It may also be prepared by distilling a mixture of alcohol, concentrated sulphuric acid, and potassium bromide.

Ethyl bromide is a colourless, pleasant-smelling, heavy liquid, and boils at 39°; it resembles ethyl chloride in its behaviour with water, potash, and silver nitrate.

Ethyl iodide, or iodethane, C_2H_5I, is formed when alcohol is heated with concentrated hydriodic acid; it is prepared by gradually adding iodine (100 grams), in small quantities at a time, to a mixture of alcohol (50 grams) and amorphous phosphorus (10 grams), and then distilling from a water-bath, the product being purified exactly as described in the case of ethyl bromide,

$$3C_2H_5{\cdot}OH + P + 3I = 3C_2H_5I + H_3PO_3.$$

Ethyl iodide is a colourless, pleasant-smelling, highly refractive, very heavy liquid, boiling at 72°; on exposure to light, it turns yellowish-brown, owing to the separation of traces of iodine, this phenomenon being observed in the case of nearly all organic compounds containing iodine. In chemical properties it closely resembles ethyl chloride and ethyl bromide.

Other halogen ethereal salts or halogen mono-substitution products of the paraffins, such as **propyl bromide**, C_3H_7Br, **butyl iodide**, C_4H_9I, &c., may be prepared by methods similar to those given above; they are all colourless, neutral, pleasant-smelling liquids, as a rule specifically heavier than water, in which they are insoluble, or nearly so. They are slowly decomposed, or hydrolysed (p. 188), by boiling water and by aqueous alkalies, yielding the alcohols,

$$C_3H_7Br + KOH = C_3H_7{\cdot}OH + KBr;$$

when boiled with *alcoholic* potash, they are converted into olefines,

$$C_3H_7I + KOH = C_3H_6 + KI + H_2O.$$

They do not give an immediate precipitate with silver nitrate in aqueous solution; but in alcoholic solution, especially on warming, a halogen silver salt is quickly precipitated, and an organic *nitrate* remains in solution,

$$C_2H_5I + AgNO_3 = C_2H_5{\cdot}NO_3 + AgI.$$

Although these compounds closely resemble one another in chemical properties, their physical properties depend to a considerable extent on the halogen which they contain, the sp. gr. and boiling-point rising on displacing chlorine by bromine, or bromine by iodine:

		Sp. gr. at 0°	B.p.			Sp. gr. at 0°	B.p.
Methyl chloride,	CH_3Cl	—	−22°	Ethyl chloride,	C_2H_5Cl	0·921	12·5°
Methyl bromide,	CH_3Br	1·73	+4·5°	Ethyl bromide,	C_2H_5Br	1·47	39°
Methyl iodide,	CH_3I	2·33	45°	Ethyl iodide,	C_2H_5I	1·975	72°

Although the monohalogen derivatives of methane and ethane exist in only one form, those of propane and the higher paraffins show isomerism. There are, for example, two compounds of the molecular formula, C_3H_7I, corresponding with the two alcohols, $C_3H_7{\cdot}OH$, namely, *normal propyl iodide*, $CH_3{\cdot}CH_2{\cdot}CH_2I$ (b.p. 102°), and *isopropyl iodide*, $CH_3{\cdot}CHI{\cdot}CH_3$ (b.p. 89·9°). The monohalogen derivatives of butane exist theoretically in four isomeric forms, two of which, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2X$, and $CH_3{\cdot}CH_2{\cdot}CHX{\cdot}CH_3$, are derived from normal butane; the other two, $\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}CH{\cdot}CH_2X$, and $\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}CX{\cdot}CH_3$, from isobutane.

Tertiary butyl iodide, $(CH_3)_3CI$, has been previously mentioned. It may be obtained by treating isobutyl alcohol with zinc chloride or sulphuric acid, and then dissolving the isobutylene formed in this way in concentrated hydriodic acid,

$$(CH_3)_2CH{\cdot}CH_2{\cdot}OH = (CH_3)_2C:CH_2 + H_2O$$
$$(CH_3)_2C:CH_2 + HI = (CH_3)_2CI{\cdot}CH_3;$$

also by heating trimethylcarbinol with hydriodic acid,

$$(CH_3)_3C{\cdot}OH + HI = (CH_3)_3I + H_2O.$$

It is a colourless oil, boils at 100° with slight decomposition, and is readily acted on by alkalies, being converted into isobutylene.

Ethereal Salts of Nitric Acid.

The ethereal salts of nitric acid are formed when the halogen ethereal salts are warmed with silver nitrate in alcoholic solution,

$$CH_3I + AgNO_3 = CH_3 \cdot NO_3 + AgI;$$

they are also produced, together with nitrites (see below), when the alcohols are treated with concentrated nitric acid,

$$C_3H_7 \cdot OH + HNO_3 = C_3H_7 \cdot NO_3 + H_2O.$$

Ethyl nitrate, $C_2H_5 \cdot NO_3$, is formed when alcohol is treated with ordinary concentrated nitric acid,

$$C_2H_5 \cdot OH + HNO_3 = C_2H_5 \cdot NO_3 + H_2O,$$

but so much heat is developed that, unless care be taken, the reaction becomes almost explosive in violence; even when the mixture is cooled, only a comparatively small quantity of ethyl nitrate is produced, owing to the acid oxidising some of the alcohol, and being itself reduced to nitrous acid, which then interacts with the alcohol, forming ethyl nitrite. If, however, the nitric acid be mixed with a little urea (p. 289), a substance which decomposes nitrous acid,

$$CO(NH_2)_2 + 2NO \cdot OH = CO_2 + 3H_2O + 2N_2,$$

the reaction takes place with much less violence, and ethyl nitrate is the sole product.

For these reasons ethyl nitrate is prepared by gradually adding alcohol (not more than 30 grams) to half its volume of nitric acid (sp. gr. 1·4), to which about 5 grams of urea have been added; the mixture is then *very slowly* heated on a water-bath in a large retort provided with a condenser. The mixture of ethyl nitrate, alcohol, and acid which collects in the receiver is shaken with water in a separating funnel, the heavy oil dried with calcium chloride, and distilled from a water-bath.

Ethyl nitrate is a colourless liquid of sp. gr. 1·11 at 20°, and boils at 87°; it has a pleasant fruity odour, and is almost insoluble in water, but readily soluble in alcohol, &c. It burns with a luminous flame, and when dropped on to a hot surface it sometimes explodes. It is slowly decomposed by boiling water, quickly by hot alkalies, yielding alcohol and nitric acid or a nitrate,

$$C_2H_5{\cdot}NO_3 + H_2O = C_2H_5{\cdot}OH + HNO_3.$$

On reduction with tin and hydrochloric acid it yields *hydroxylamine*,

$$C_2H_5{\cdot}NO_3 + 6H = C_2H_5{\cdot}OH + NH_2{\cdot}OH + H_2O.$$

Methyl nitrate, $CH_3{\cdot}NO_3$ (b.p. 66°), and the higher homologues closely resemble ethyl nitrate in properties.

Ethereal Salts of Nitrous Acid.

The ethereal salts of nitrous acid are produced by the action of nitrous acid on the alcohols,

$$C_2H_5{\cdot}OH + HNO_2 = C_2H_5{\cdot}NO_2 + H_2O.$$

They may be prepared by saturating the alcohols with the fumes evolved by the interaction of arsenic trioxide and nitric acid,* or by distilling alcohol with sodium nitrite and sulphuric acid, or with copper and nitric acid.†

Ethyl nitrite, $C_2H_5{\cdot}NO_2$, is usually prepared by slowly dropping concentrated nitric acid (3 c.c.) into a cold mixture of alcohol (20 c.c.) and concentrated sulphuric acid (2 c.c.), then adding copper turnings (about 4 grams), and distilling carefully from a water-bath.

The distillate consists of a mixture of ethyl nitrite, alcohol, and its oxidation products; when mixed with alcohol, it is employed in medicine as 'sweet spirits of nitre.' In order to prepare pure ethyl nitrite, the distillate is shaken with water, the oil dried over calcium chloride, and redistilled.

Ethyl nitrite is a colourless liquid of sp. gr. 0·900 at 15·5°; it boils at 17°, and has a pleasant fruity odour like that of apples; it is insoluble in water, and is readily hydrolysed by boiling water or dilute alkalies,

$$C_2H_5{\cdot}NO_2 + KOH = C_2H_5{\cdot}OH + KNO_2.$$

---

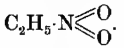
* $As_2O_3 + 2HNO_3 + 2H_2O = 2H_3AsO_4 + N_2O_3$.

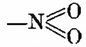
† $2Cu + 6HNO_3 = 2Cu(NO_3)_2 + 2H_2O + 2HNO_2$.

Methyl nitrite, $CH_3{\cdot}NO_2$, is a gas; the higher homologues resemble ethyl nitrite.

Nitro-paraffins.—When ethyl iodide is heated with silver nitrite, very interesting changes occur: part of the ethyl iodide interacts with the silver nitrite, yielding *ethyl nitrite*, the rest being converted into *nitro-ethane*, both changes being expressed by the equation

$$C_2H_5I + AgNO_2 = C_2H_5{\cdot}NO_2 + AgI.$$

Ethyl nitrite and nitro-ethane are isomeric; the former is simply a salt of nitrous acid, $HO{\cdot}N{:}O$, and has the constitution $C_2H_5{\cdot}O{\cdot}N{:}O$, whereas the latter contains pentavalent nitrogen, and has the constitution  $C_2H_5{\cdot}N{\lessgtr}\begin{matrix}O\\O\end{matrix}$.

Compounds, similar to nitro-ethane in constitution and isomeric with the corresponding nitrites, may be obtained from other halogen ethereal salts in the above manner; they are termed *nitro-paraffins*, because they are derived from the paraffins by the substitution of the nitro group  $—N{\lessgtr}\begin{matrix}O\\O\end{matrix}$ for one atom of hydrogen.

The nitro-paraffins are colourless, pleasant-smelling liquids, and distil without decomposition, but their boiling-points are much higher than those of the corresponding nitrites; nitro-ethane, for example, boils at 114°, ethyl nitrite at 17°. They differ from the nitrites in certain important particulars: the nitro-paraffins are soluble in, but are not decomposed by caustic alkalies, whereas the nitrites, like all other ethereal salts, undergo hydrolysis, yielding an alcohol and a nitrite. The nitro-paraffins are converted into amines on reduction,

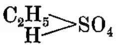
$$C_2H_5{\cdot}NO_2 + 6H = C_2H_5{\cdot}NH_2 + 2H_2O,$$

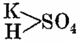
whilst the nitrites yield hydroxylamine, or ammonia, and an alcohol,

$$C_5H_{11}{\cdot}O{\cdot}N{:}O + 6H = C_5H_{11}{\cdot}OH + NH_3 + H_2O.$$

Ethereal Salts of Sulphuric Acid.

Dibasic acids, such as sulphuric acid, form two classes of salts with alcohols—namely, acid salts, corresponding with the acid sulphates, and normal or neutral salts, corresponding with the neutral sulphates,

Ethyl hydrogen sulphate,  $\begin{matrix}C_2H_5\\H\end{matrix}{>}SO_4$ Ethyl sulphate, $(C_2H_5)_2SO_4$.

Potassium hydrogen sulphate,  $\begin{matrix}K\\H\end{matrix}{>}SO_4$ Potassium sulphate, K_2SO_4.

Ethyl hydrogen sulphate, ethylsulphuric acid, or *sulphovinic acid* (from sulphuric acid and spirits of wine), $C_2H_5{\cdot}HSO_4$, is formed when ethylene is passed into fuming sulphuric acid, or heated with ordinary sulphuric acid,

$$C_2H_4 + H_2SO_4 = C_2H_5{\cdot}HSO_4.$$

It is prepared in the following manner: A mixture of equal volumes of alcohol and concentrated sulphuric acid is heated at 100° for about an hour, when part of the alcohol is converted into ethyl hydrogen sulphate,

$$C_2H_5{\cdot}OH + H_2SO_4 = C_2H_5{\cdot}HSO_4 + H_2O.$$

The solution is cooled, diluted with water, and treated with a slight excess of barium carbonate, when barium sulphate and barium ethylsulphate are formed,

$$2C_2H_5{\cdot}HSO_4 + BaCO_3 = (C_2H_5{\cdot}SO_4)_2Ba + CO_2 + H_2O.$$

After filtering from the barium sulphate and excess of barium carbonate, the cold solution of barium ethylsulphate is treated with dilute sulphuric acid as long as a precipitate is produced, and filtered again to separate the barium sulphate,

$$(C_2H_5{\cdot}SO_4)_2Ba + H_2SO_4 = 2C_2H_5{\cdot}HSO_4 + BaSO_4.$$

The filtrate is now free from sulphuric acid; it is evaporated at ordinary temperature under reduced pressure over sulphuric acid, when alcohol and water pass off and are absorbed by the sulphuric acid, and ethyl hydrogen sulphate remains as a thick sour liquid.

Ethyl hydrogen sulphate has an acid reaction, decomposes carbonates, and is, in fact, like potassium hydrogen sulphate, a monobasic acid, since it contains one atom of hydrogen displaceable by metals. The *potassium* salt, $C_2H_5{\cdot}KSO_4$, may be prepared by neutralising the acid with potassium carbonate, or by treating a solution of the barium salt with potassium carbonate, and, after filtering, evaporating to dryness; it is a colourless, crystalline, neutral compound, readily soluble in water. The *barium* salt, $(C_2H_5{\cdot}SO_4)_2Ba$, is also readily soluble in water, so that ethylsulphuric acid does not give a precipitate with barium chloride.

Ethyl hydrogen sulphate is a very interesting substance, as it is an intermediate product in the conversion of alcohol into ethylene and ether, and of ethylene into alcohol. When boiled with water it yields alcohol, so that it cannot be obtained from its aqueous solution by evaporating at 100°,

$$C_2H_5{\cdot}HSO_4 + H_2O = C_2H_5{\cdot}OH + H_2SO_4;$$

when heated with alcohol it gives ether,

$$C_2H_5{\cdot}HSO_4 + C_2H_5{\cdot}OH = (C_2H_5)_2O + H_2SO_4;$$

and when heated alone, or with concentrated sulphuric acid, it yields ethylene,

$$C_2H_5{\cdot}HSO_4 = C_2H_4 + H_2SO_4.$$

Other alcohols combine with sulphuric acid, yielding acid salts corresponding with ethyl hydrogen sulphate; these compounds, the *alkyl hydrogen sulphates*, closely resemble ethyl hydrogen sulphate in properties, and undergo similar decompositions.

Ethyl sulphate, $(C_2H_5)_2SO_4$, the normal or neutral salt, is of comparatively little importance; it may be prepared by warming silver sulphate with ethyl iodide, when double decomposition takes place, just as when silver sulphate is treated with potassium iodide,

$$Ag_2SO_4 + 2C_2H_5I = (C_2H_5)_2SO_4 + 2AgI.$$

It is a colourless liquid, boiling at 208°, with decomposition.

MERCAPTANS AND SULPHIDES.

Alcohols form two classes of compounds with hydrogen sulphide—namely, the hydrosulphides and the sulphides; the former bear the same relation to the metallic hydrosulphides as the alcohols to the metallic hydroxides, whereas the sulphides are related to the metallic sulphides just as the ethers to the metallic oxides,

Ethyl hydrosulphide,	$C_2H_5{\cdot}SH$	Ethyl sulphide,	$(C_2H_5)_2S$
Potassium hydrosulphide,	$K{\cdot}SH$	Potassium sulphide,	K_2S
Ethyl hydroxide,	$C_2H_5{\cdot}OH$	Ethyl oxide,	$(C_2H_5)_2O$
Potassium hydroxide,	$K{\cdot}OH$	Potassium oxide,	K_2O

The organic hydrosulphides or sulphhydrates are usually called **mercaptans** (*mercurium captans*) on account of their property of combining readily with mercuric oxide, forming crystalline compounds; they may be regarded as *sulphur-* or *thio-alcohols*, and the organic sulphides, as *thio-ethers*.

Ethyl mercaptan, $C_2H_5{\cdot}SH$, may be obtained by treating alcohol with phosphorus pentasulphide,

$$5C_2H_5{\cdot}OH + P_2S_5 = 5C_2H_5{\cdot}SH + P_2O_5;$$

it is prepared by distilling a concentrated solution of ethyl potassium sulphate with potassium hydrosulphide,

$$C_2H_5{\cdot}KSO_4 + KSH = C_2H_5{\cdot}SH + K_2SO_4.$$

It is a colourless, very unpleasant-smelling liquid, boiling at 36°. The hydrogen atom in the HS– group is displaceable by metals more readily than that in the HO– group of the alcohols; when ethyl mercaptan is treated with sodium or potassium, it yields *sodium* or *potassium mercaptide*, $C_2H_5{\cdot}SNa$, or $C_2H_5{\cdot}SK$, with evolution of hydrogen; when shaken with mercuric oxide, it yields *mercuric mercaptide*,

$$2C_2H_5{\cdot}SH + HgO = (C_2H_5{\cdot}S)_2Hg + H_2O,$$

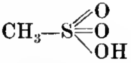
a crystalline compound, which is decomposed by hydrogen sulphide, giving ethyl mercaptan,

$$(C_2H_5{\cdot}S)_2Hg + SH_2 = 2C_2H_5{\cdot}SH + HgS.$$

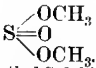
Other mercaptans can be obtained by similar reactions; they are characterised by having a highly unpleasant, garlic-like smell, and in chemical properties they resemble ethyl mercaptan; on oxidation with nitric acid they are converted into *sulphonic acids,*

$$\underset{\text{Ethylsulphonic Acid.}}{C_2H_5{\cdot}SH + 3O = C_2H_5{\cdot}SO_2{\cdot}OH.}$$

Sulphonic acids contain the group $—SO_2{\cdot}OH$, the alkyl group being attached to the sulphur atom, and not to oxygen, as in the alkyl sulphites,



Methylsulphonic Acid.



Methyl Sulphite.

They are powerful acids, forming salts, such as potassium ethylsulphonate, $C_2H_5{\cdot}SO_2{\cdot}OK$; and they differ from the sulphites in not being hydrolysed when boiled with dilute aqueous potash. They stand, therefore, in much the same relationship to the sulphites as the nitro-paraffins to the nitrites (p. 181).

Ethyl sulphide, $(C_2H_5)_2S$, may be obtained by treating ether with phosphorus pentasulphide,

$$5(C_2H_5)_2O + P_2S_5 = 5(C_2H_5)_2S + P_2O_5,$$

and by distilling a concentrated aqueous solution of ethyl potassium sulphate with potassium sulphide,

$$2C_2H_5{\cdot}KSO_4 + K_2S = (C_2H_5)_2S + 2K_2SO_4.$$

It is a colourless, neutral, unpleasant-smelling liquid, and boils at 91°; like the ethers, it does not contain hydrogen displaceable by metals, and is a comparatively inert substance.

Other sulphides can be obtained by similar methods, and have similar properties.

Ethereal Salts of Organic Acids.

Ethyl acetate, acetic ether,

$$C_2H_3O_2{\cdot}C_2H_5, \text{ or } CH_3{\cdot}CO{\cdot}OC_2H_5,$$

is formed when acetyl chloride or acetic anhydride is treated with alcohol,

$$CH_3{\cdot}COCl + C_2H_5{\cdot}OH = CH_3{\cdot}COOC_2H_5 + HCl$$
$$(CH_3{\cdot}CO)_2O + C_2H_5{\cdot}OH = CH_3{\cdot}COOC_2H_5 + CH_3{\cdot}COOH;$$

also when a metallic salt of acetic acid is heated with a halogen salt of ethyl alcohol,

$$CH_3{\cdot}COOK + C_2H_5Br = CH_3{\cdot}COOC_2H_5 + KBr,$$

and when alcohol is heated with glacial acetic acid,

$$CH_3{\cdot}COOH + C_2H_5{\cdot}OH = CH_3{\cdot}COOC_2H_5 + H_2O.$$

It is prepared by gradually adding a mixture of equal volumes of alcohol and acetic acid to a mixture of equal volumes of alcohol and concentrated sulphuric acid, heated at about 140° in a retort connected with a condenser; this process, like that by which ether is prepared, is theoretically continuous, the alcohol and sulphuric acid combining to form ethyl hydrogen sulphate, which then interacts with acetic acid, forming ethyl acetate and sulphuric acid,

$$C_2H_5{\cdot}OH + H_2SO_4 = C_2H_5{\cdot}HSO_4 + H_2O$$
$$C_2H_5{\cdot}HSO_4 + C_2H_4O_2 = C_2H_3O_2{\cdot}C_2H_5 + H_2SO_4.$$

The distillate is shaken with a concentrated solution of sodium chloride, when the alcohol dissolves, the ethyl acetate separating as an oil; it is dried with calcium chloride, and purified by fractional distillation.

Ethyl acetate is a colourless, mobile liquid, having a pleasant fruity odour, and boiling at 77°; it is specifically lighter than water, in which it is moderately easily soluble. It is readily hydrolysed (see below) by hot alkalies, more slowly by hot mineral acids, and by water,

$$CH_3{\cdot}COOC_2H_5 + H_2O = CH_3{\cdot}COOH + C_2H_5{\cdot}OH.$$

When treated with concentrated ammonia it yields acetamide and alcohol,

$$CH_3{\cdot}COOC_2H_5 + NH_3 = CH_3{\cdot}CO{\cdot}NH_2 + C_2H_5{\cdot}OH.$$

Sodium acts readily on ethyl acetate, with formation of ethyl acetoacetate (p. 189).

Since ethyl acetate has a rather characteristic smell, and is formed when acetic acid or any of its salts is warmed with alcohol and concentrated sulphuric acid, the presence of acetic acid or an acetate may be readily detected by this reaction, the so-called 'acetic-ether' test.

In hydrolysing ethereal salts, and in many other operations, as, for example, in the preparation of ethylene from ethyl bromide, it is often necessary to boil the aqueous, alcoholic, ethereal, or other solution for a long time; in order, therefore, to avoid loss of solvent, or of the substances present in solution, the flask or other vessel is connected with a *reflux* condenser (*b*, fig. 18), so that the vapours, which would otherwise pass away, are condensed, the liquid running back into the flask. The latter may be heated over a piece of wire-gauze or on a sand-bath, but when alcohol, ether, or other substances of low-boiling point are being used, a water-bath is usually employed. A very convenient form of water-bath (*c*) is that shown in the figure. During use, water slowly but continuously runs from the tube (*d*), which is connected with the water-supply; the water in the bath

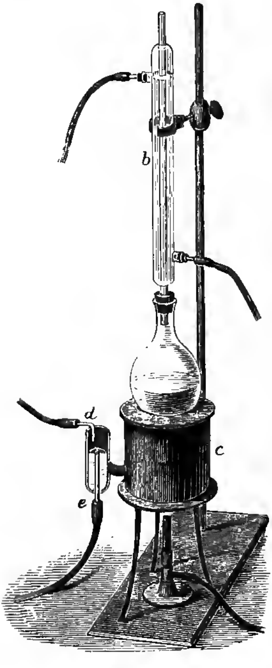


Fig. 18.

is thus kept at a constant level, the surplus running away through (*e*). With apparatus similar to that shown, a liquid may be kept constantly boiling for days without requiring any attention.

SUMMARY AND EXTENSION.

Although the ethereal salts of mineral acids are, on the whole, very similar in chemical properties, they are derived from acids of such diverse characters that slight differences in behaviour is only to be expected. The ethereal salts of organic acids, on the other hand, being derived from acids of similar nature, resemble one another in chemical properties so very closely that they may be described in a general manner.

The ethereal salts of organic acids may all be produced by treating an alcohol with the chloride or anhydride of the acid,

$$C_3H_7{\cdot}COCl + CH_3{\cdot}OH = C_3H_7{\cdot}COOCH_3 + HCl,$$

and by heating a metallic salt of the acid with a halogen salt of an alcohol,

$$C_2H_5{\cdot}COOAg + CH_3I = C_2H_5{\cdot}COOCH_3 + AgI.$$

They are all formed when an alcohol is treated with an acid, but the change is never complete, because, after the interaction has proceeded for some time, the quantity of ethereal salt decomposed by the water produced is the same as that formed by the combination of the acid with the alcohol; in other words, a condition of equilibrium is established when the two changes represented by the equations

$$CH_3{\cdot}OH + C_2H_4O_2 = C_2H_3O_2{\cdot}CH_3 + H_2O$$
$$C_2H_3O_2{\cdot}CH_3 + H_2O = CH_3{\cdot}OH + C_2H_4O_2$$

balance one another; this is usually expressed by writing the equations thus,

$$CH_3{\cdot}OH + C_2H_4O_2 \rightleftarrows C_2H_3O_2{\cdot}CH_3 + H_2O,$$

which indicates that the change takes place in either direction.

The proportion of ethereal salt produced depends on the nature of the alcohol and acid, and on their relative quantities; it is independent of the temperature, but the higher the temperature the sooner the condition of equilibrium is established. If the water produced during the interaction be prevented in some way from decomposing the ethereal salt, the desired change is far more complete; when, for example, methyl alcohol is heated with excess of anhydrous oxalic acid, it is almost completely converted into methyl oxalate, because the anhydrous oxalic acid combines with the water as fast as it is formed, and thus the inverse change is prevented,

$$C_2O_4H_2 + 2CH_3{\cdot}OH = C_2O_4(CH_3)_2 + 2H_2O.$$

In order, then, to prepare an ethereal salt from an acid and an alcohol, some dehydrating agent, such as hydrogen chloride, sulphuric acid, zinc chloride, &c., should be present. Based on these considerations, the two methods usually employed in preparing ethereal salts of organic acids are (*a*) by passing hydrogen chloride into a mixture of the acid and alcohol, and then warming the saturated solution; (*b*) by warming a mixture of the acid and alcohol with concentrated sulphuric acid. In both cases the mineral acids act as dehydrating agents. If the ethereal salt be readily volatile (ethyl acetate), the mixture is now distilled; if not, it is poured into water and the ethereal salt isolated by filtration, if a solid, by extraction with ether, if a liquid, or if it be soluble in water.

When only a small quantity of acid is at disposal, and it is desired to prepare one of its ethereal salts, it is converted into the silver salt, and the latter is warmed with a halogen ethereal salt (see above).

Normal ethereal salts are usually colourless, neutral, pleasant-smelling liquids, which distil unchanged under atmospheric pressure, and are volatile in steam; a few, such as *cetyl palmitate*, $C_{16}H_{31}O_2 \cdot C_{16}H_{33}$, which occurs in spermaceti, are solid at ordinary temperatures, and distil with decomposition. They are all comparatively inert substances, and resemble the ethers perhaps more closely than any other class of compounds, although, at the same time, they differ from them in several important respects. The acid ethereal salts are usually non-volatile, and act like feeble acids.

All ethereal salts are decomposed by water, mineral acids, and alkalies, the change which they undergo being spoken of as hydrolysis (or saponification, p. 169),

$$CH_3 \cdot COOC_3H_7 + KOH = CH_3 \cdot COOK + C_3H_7 \cdot OH$$
$$2H \cdot COOCH_3 + Ba(OH)_2 = (H \cdot COO)_2Ba + 2CH_3 \cdot OH.$$

The rapidity with which hydrolysis takes place depends on the temperature and concentration of the solution, as well as on the nature of the ethereal salt and of the hydrolysing agent; as a rule, potash, soda, and barium hydroxide are the most powerful hydrolysing agents. Since ethereal salts are generally insoluble in water, if they be boiled with aqueous alkalies or mineral acids they are not attacked very quickly; it is usual, therefore, to employ *alcoholic* potash, &c., in which the ethereal salts are soluble.

All ethereal salts of organic acids yield amides on treatment with concentrated aqueous or alcoholic ammonia,

$$C_3H_7 \cdot COOCH_3 + NH_3 = C_3H_7 \cdot CO \cdot NH_2 + CH_3 \cdot OH,$$

whereas the halogen ethereal salts give amines with alcoholic ammonia (p. 200),

$$C_2H_5I + NH_3 = C_2H_5 \cdot NH_2,\ HI.$$

The ethereal salts of organic acids afford an excellent example of the special form of isomerism known as metamerism; ethyl formate, $H{\cdot}CO{\cdot}O{\cdot}CH_2{\cdot}CH_3$, for example, is metameric with methyl acetate, $CH_3{\cdot}CO{\cdot}O{\cdot}CH_3$; propyl formate, $H{\cdot}COOC_3H_7$, is metameric with ethyl acetate, $CH_3{\cdot}COOC_2H_5$, and with methyl propionate, $C_2H_5{\cdot}COOCH_3$.

Many ethereal salts occur in the fruit, flower, and other parts of plants, and it is to their presence in many cases that the scent of the part is due; many are prepared artificially for flavouring sweets, pastry, perfumes, &c.: amyl acetate, $CH_3{\cdot}COOC_5H_{11}$, for example, prepared from commercial amyl alcohol, has a strong smell of pears, and is known as 'pear-oil;' methyl butyrate, $C_3H_7{\cdot}COOCH_3$, is sold as 'pine-apple oil,' isoamyl isovalerate as 'apple-oil,' and so on.

CHAPTER XI.

SYNTHESIS OF KETONES AND FATTY ACIDS WITH THE AID OF ETHYL ACETOACETATE AND ETHYL MALONATE.

In the whole domain of organic chemistry probably no compounds have been more extensively used for synthetical purposes than ethyl acetoacetate and ethyl malonate, and certainly one of the most important uses to which these substances have been put is the synthesis of a great variety of ketones and fatty acids, many of which could have been prepared only with great difficulty by other methods.

Ethyl acetoacetate, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOC_2H_5$, the ethyl salt of **acetoacetic acid,** is formed when ethyl acetate is treated with sodium, and the product decomposed with dilute acids. The final result is that 2 molecules of ethyl acetate combine with loss of 1 molecule of alcohol, the following equation representing the reaction in its simplest form,

$$CH_3{\cdot}CO\boxed{OC_2H_5 + H}CH_2{\cdot}COOC_2H_5 = CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOC_2H_5 + C_2H_5{\cdot}OH.$$

In reality, however, the interaction is a complex one; the *sodium derivative* of ethyl acetoacetate is first formed,

$$2CH_3{\cdot}COOC_2H_5 + 2Na = CH_3{\cdot}CO{\cdot}CHNa{\cdot}COOC_2H_5 + C_2H_5{\cdot}ONa + H_2,$$

and this sodium derivative, when decomposed with dilute acids, yields ethyl acetoacetate,

$$CH_3{\cdot}CO{\cdot}CHNa{\cdot}COOC_2H_5 + HCl = CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOC_2H_5 + NaCl.$$

Preparation.—Sodium (30 grams), in the form of thin wire or shavings, is added to pure dry ethyl acetate (300 grams) contained in a flask connected with a reflux condenser. As soon as the vigorous action which sets in has subsided, the flask is heated on a water-bath, until bright particles of sodium are no longer visible on shaking.

The thick brownish semi-solid product, which consists of the sodium derivative of ethyl acetoacetate, is allowed to cool, and then treated with dilute (1 : 4) hydrochloric acid, until the solution is distinctly acid to test-paper. An equal volume of a saturated solution of salt is now added, and the oily layer separated from the aqueous solution, dried over calcium chloride, and fractionated. At first a quantity of unchanged ethyl acetate passes over; the thermometer then rises rapidly to about 160°, the fraction 170–185° consisting of nearly pure ethyl acetoacetate, and weighing 40–50 grams.

Ethyl acetoacetate is a colourless liquid, boiling at 180°, and having an agreeable fruity odour; it is sparingly soluble in water, but readily in alcohol and ether. The alcoholic solution assumes a beautiful violet colour on the addition of ferric chloride.

It is remarkable that, although neutral to test-paper, ethyl acetoacetate possesses acid properties. It dissolves in dilute potash or soda, and is reprecipitated on the addition of acids, but it is insoluble in alkali carbonates.

The **sodium derivative**, $CH_3{\cdot}CO{\cdot}CHNa{\cdot}COOC_2H_5$, which is so largely used for synthetical purposes, may be prepared by adding sodium to a solution of ethyl acetoacetate in ether or benzene,

$$2CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOC_2H_5 + 2Na = 2CH_3{\cdot}CO{\cdot}CHNa{\cdot}COOC_2H_5 + H_2,$$

or by mixing ethyl acetoacetate with an alcoholic solution of sodium ethoxide,

$$CH_3 \cdot CO \cdot CH_2 \cdot COOC_2H_5 + NaO \cdot C_2H_5 = CH_3 \cdot CO \cdot CHNa \cdot COOC_2H_5 + C_2H_5 \cdot OH.$$

On evaporating the solvent in a current of hydrogen, the sodium derivative is obtained as a white crystalline mass, which is readily soluble in water, alcohol, and ether ; it rapidly deliquesces in contact with moist air, and undergoes decomposition when its aqueous solution is boiled.

When shaken with a saturated solution of copper acetate, ethyl acetoacetate forms a green crystalline *copper derivative*, $(C_6H_9O_3)_2Cu$.

This property of forming metallic derivatives is due to the presence of the group $-CO-CH_2-CO-$; all substances which contain this, or the group $-CO-\underset{|}{C}H-CO-$, yield derivatives with sodium, frequently also with other metals.

The sodium derivative of ethyl acetoacetate interacts readily with alkyl halogen compounds with formation of a sodium halogen salt and a *mono-substitution derivative* of ethyl acetoacetate, the alkyl group taking the place previously occupied by the metal. Thus methyl iodide interacts with the sodium derivative of ethyl acetoacetate, forming ethyl *methyl*acetoacetate,

$$CH_3 \cdot CO \cdot CHNa \cdot COOC_2H_5 + CH_3I = CH_3 \cdot CO \cdot CH(CH_3) \cdot COOC_2H_5 + NaI,$$

whereas when propyl bromide is employed, ethyl *propyl*-acetoacetate, $CH_3 \cdot CO \cdot CH(C_3H_7) \cdot COOC_2H_5$, results, and so on.

All the alkyl mono-substitution derivatives of ethyl acetoacetate contain the group $-CO-\underset{|}{C}H-CO-$, and are therefore capable of forming sodium derivatives such as

$CH_3 \cdot CO \cdot CNa(CH_3) \cdot COOC_2H_5$, $CH_3 \cdot CO \cdot CNa(C_3H_7) \cdot COOC_2H_5$, &c., on treatment with sodium or sodium ethoxide, the metal taking the place of the hydrogen atom in the $-\underset{|}{C}H-$ group.

From these sodium derivatives, by the action of alkyl halogen compounds, *di-substitution derivatives* of ethyl acetoacetate are produced thus:

$$CH_3\cdot CO\cdot CNa(CH_3)\cdot COOC_2H_5 + C_2H_5Br = CH_3\cdot CO\cdot C(C_2H_5)(CH_3)\cdot COOC_2H_5 + NaBr.$$

Ethyl *Ethylmethyl*acetoacetate.

$$CH_3\cdot CO\cdot CNa(C_3H_7)\cdot COOC_2H_5 + C_3H_7I = CH_3\cdot CO\cdot C(C_3H_7)_2\cdot COOC_2H_5 + NaI.$$

Ethyl *Dipropyl*acetoacetate.

In order, then, to obtain a di-substituted ethyl acetoacetate, the mono-substitution derivative is first prepared and then treated with sodium ethoxide and the alkyl halogen compound; the introduction of both alkyl groups cannot be carried out in one operation, because ethyl acetoacetate is not sufficiently acid in properties to form a disodium derivative of the constitution $CH_3\cdot CO\cdot CNa_2\cdot COOC_2H_5$.

The synthesis of the alkyl substitution products of ethyl acetoacetate is usually carried out as follows: The theoretical quantity of sodium (1 atom) is dissolved in 10–12 times its weight of absolute alcohol, and the solution of sodium ethoxide is thoroughly cooled. The ethyl acetoacetate, or the mono-substituted ethyl acetoacetate, (1 mol.), and a slight excess of the alkyl halogen compound (1 mol.) are now gradually added, the whole being well cooled during the operation; the flask is then connected with a reflux condenser (p. 186), and the mixture heated to boiling until neutral to test-paper. In order to isolate the product, the alcohol is distilled from a water-bath, the residue mixed with water to dissolve the precipitated sodium salt, and the whole extracted with ether; the ethereal solution is dried with calcium chloride, the ether distilled off, and the residual oil purified by fractional distillation.

The following are some of the more important mono- and di-substitution products of ethyl acetoacetate, with their boiling-points:

		B.p.
Ethyl *methyl*acetoacetate,	$CH_3\cdot CO\cdot CH(CH_3)\cdot COOC_2H_5$..	187°
Ethyl *dimethyl*acetoacetate,	$CH_3\cdot CO\cdot C(CH_3)_2\cdot COOC_2H_5$....	184°
Ethyl *ethyl*acetoacetate,	$CH_3\cdot CO\cdot CH(C_2H_5)\cdot COOC_2H_5$.	198°
Ethyl *diethyl*acetoacetate,	$CH_3\cdot CO\cdot C(C_2H_5)_2\cdot COOC_2H_5$...	218°
Ethyl *propyl*acetoacetate,	$CH_3\cdot CO\cdot CH(C_3H_7)\cdot COOC_2H_5$.	209°
Ethyl *isopropyl*acetoacetate,	$CH_3\cdot CO\cdot CH(C_3H_7)\cdot COOC_2H_5$..	201°

The *mono*-substituted ethyl acetoacetates differ from ethyl acetoacetate in that they are insoluble in alkalies, and do not give copper derivatives, although they readily form sodium derivatives. The *di*-substituted ethyl acetoacetates do not contain a hydrogen atom displaceable by metals: both classes of compounds give a characteristic bluish-violet colouration with ferric chloride.

One of the most important reactions of ethyl acetoacetate and its derivatives is the decomposition which these substances undergo when treated with alkalies or mineral acids. Alkalies at ordinary temperatures simply hydrolyse the ethereal salts with formation of the alkali salts of the corresponding acids,

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOC_2H_5 + KOH = \underset{\text{Potassium Acetoacetate.}}{CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOK} + C_2H_5{\cdot}OH.$$

On acidifying the solution and extracting with ether, the free acids are obtained; these ketonic acids are, however, very unstable, decomposing in many cases at ordinary temperatures, and always very readily on warming, yielding carbon dioxide and a ketone,

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOH = CH_3{\cdot}CO{\cdot}CH_3 + CO_2$$
$$CH_3{\cdot}CO{\cdot}C(C_2H_5)_2{\cdot}COOH = CH_3{\cdot}CO{\cdot}CH(C_2H_5)_2 + CO_2.$$

When heated with alkalies, ethyl acetoacetate and its derivatives are decomposed in two ways, the course of the decomposition depending to a great extent on the strength of the alkali used.

Boiling *dilute* alcoholic potash converts these substances into *ketones*, with separation of potassium carbonate (**ketonic hydrolysis**),

$$CH_3{\cdot}CO{\cdot}CH_2 \vdots COOC_2H_5 + 2KOH = CH_3{\cdot}CO{\cdot}CH_3 + K_2CO_3 + C_2H_5{\cdot}OH$$

$$CH_3{\cdot}CO{\cdot}C(C_2H_5)_2 \vdots COOC_2H_5 + 2KOH = CH_3{\cdot}CO{\cdot}CH(C_2H_5)_2 + K_2CO_3 + C_2H_5{\cdot}OH.$$

Ketonic hydrolysis is also brought about by boiling with dilute mineral acids. If, however, *strong* alcoholic potash be employed, the decomposition takes place in quite a different manner, the potassium salt of a fatty acid being the principal product (**acid hydrolysis**),

$$CH_3{\cdot}CO \vdots CH_2{\cdot}COOC_2H_5 + 2KOH = 2CH_3{\cdot}COOK + C_2H_5{\cdot}OH$$

$$\begin{aligned} CH_3{\cdot}CO \vdots C(C_2H_5)_2{\cdot}COOC_2H_5 + 2KOH &= CH_3{\cdot}COOK \\ &+ \underset{\text{Potassium Diethylacetate.}}{(C_2H_5)_2CH{\cdot}COOK} + C_2H_5{\cdot}OH. \end{aligned}$$

Ethyl acetoacetate is therefore a very important compound, as with its aid any fatty acid, or any ketone (containing the group $CH_3{\cdot}CO{-}$) can be synthetically prepared, provided the requisite alkyl halogen compound can be obtained.

Example.—If an acid of the constitution $(C_2H_5)(C_3H_7)CH{\cdot}COOH$—namely, ethylpropylacetic acid—be required, ethyl *ethyl*acetoacetate, $CH_3{\cdot}CO{\cdot}CH(C_2H_5){\cdot}COOC_2H_5$, might be first prepared; on treating the sodium derivative of this substance with propyl iodide, ethyl *ethylpropyl*acetoacetate, $CH_3{\cdot}CO{\cdot}C(C_2H_5)(C_3H_7){\cdot}COOC_2H_5$, would be formed, and the latter, when heated with *strong* alcoholic potash, would yield the potassium salt of the acid required,

$$\begin{aligned} CH_3{\cdot}CO{\cdot}C(C_2H_5)(C_3H_7){\cdot}COOC_2H_5 + 2KOH &= \\ CH_3{\cdot}COOK + CH(C_2H_5)(C_3H_7){\cdot}COOK &+ C_2H_5{\cdot}OH. \end{aligned}$$

Example.—If a ketone of the constitution $CH_3{\cdot}CO{\cdot}CH_2{\cdot}C_4H_9$—namely, butyl acetone—be required, ethyl butylacetoacetate, $CH_3{\cdot}CO{\cdot}CH(C_4H_9){\cdot}COOC_2H_5$, would be prepared, by treating the sodium compound of ethyl acetoacetate with butyl iodide, and then decomposed by boiling with *dilute* alcoholic potash or dilute sulphuric acid,

$$\begin{aligned} CH_3{\cdot}CO{\cdot}CH(C_4H_9){\cdot}COOC_2H_5 + 2KOH &= \\ CH_3{\cdot}CO{\cdot}CH_2{\cdot}C_4H_9 + K_2CO_3 &+ C_2H_5{\cdot}OH. \end{aligned}$$

The acid and the ketonic hydrolysis of ethyl acetoacetate and its derivatives always take place to some extent side by side, whether weak or strong alkali be used. It is not possible, for instance, to decompose an ethyl acetoacetate derivative with strong alkali, without a small amount of ketone being formed, and when dilute alkali is used, a certain quantity of the salt of a fatty acid is invariably produced; nevertheless the relative quantities of the products depend very largely on the strength of the alkali employed.

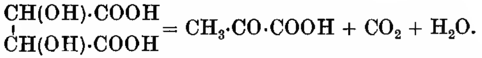
Constitution of Ethyl Acetoacetate.—On hydrolysis, ethyl acetoacetate is converted into acetoacetic acid, which when gently warmed is decomposed into acetone and carbon dioxide; this acid is therefore evidently the carboxylic acid of acetone, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOH$, and its ethereal salt, ethyl acetoacetate, must be represented by the formula $CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOC_2H_5$.

That ethyl acetoacetate contains a ketonic group $-CO-$ is shown by the fact that it combines with sodium bisulphite, hydroxylamine, phenylhydrazine, and hydrogen cyanide, and that on reduction it is converted into β-hydroxybutyric acid, $CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}COOH$, or its ethyl salt. In some of its reactions, however, ethyl acetoacetate behaves as if it contained a hydroxyl-group, and had the constitution represented by the formula $CH_3{\cdot}C(OH){:}CH{\cdot}COOC_2H_5$, and there are reasons for believing that other substances which contain the group $-CO-CH_2-$ or $-CO-C\underset{|}{H}-$ are also capable of existing in two forms; at all events, their behaviour is such that in some cases the assumption must be made that these groups, by intramolecular change (p. 290), are converted into $-C(OH){:}CH-$ and $-C(OH){:}\overset{|}{C}-$ respectively.

The constitution of the sodium derivative of ethyl acetoacetate may be expressed by the formula $CH_3{\cdot}CO{\cdot}CHNa{\cdot}COOC_2H_5$; the sodium atom is represented as directly combined with carbon, because when the sodium derivative is treated with alkyl halogen compounds, substitution products of ethyl acetoacetate are formed in which the alkyl group is certainly directly united with carbon, as is shown by their behaviour on hydrolysis.

Other Ketonic Acids.

Pyruvic acid, or acetylformic acid, $CH_3{\cdot}CO{\cdot}COOH$, is formed by the dry distillation of tartaric acid (p. 241),



$$\begin{array}{l}CH(OH){\cdot}COOH\\ |\\ CH(OH){\cdot}COOH\end{array} = CH_3{\cdot}CO{\cdot}COOH + CO_2 + H_2O.$$

It is an oily, sour-smelling liquid, distils at 165–170°, and is soluble in water in all proportions. It combines with hydroxylamine, and gives with phenylhydrazine in aqueous solution a very sparingly soluble phenylhydrazone, $CH_3{\cdot}C(N_2HC_6H_5){\cdot}COOH$, the formation of which serves as a ready means of detecting the acid, even when present in small quantity. When treated with sodium amalgam, pyruvic acid is reduced to lactic acid (p. 225),

$$CH_3{\cdot}CO{\cdot}COOH + 2H = CH_3{\cdot}CH(OH){\cdot}COOH.$$

Levulinic acid (β-acetylpropionic acid), $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, is produced when starch, cane-sugar, dextrose, levulose, and other carbohydrates containing 6, or a multiple of 6, carbon atoms are boiled with dilute hydrochloric acid.

Preparation.—Starch (3 kilos) is gradually added to hot hydrochloric acid of sp. gr. 1·1 (3 litres), and the thin syrup is then heated in a reflux apparatus for twenty hours on a water-bath. The solution is separated from the humus matter by pressure between cloths, and after concentration to a syrup, extracted with ether; the ethereal solution is evaporated, and the residual crude levulinic acid purified by distillation under reduced pressure.

Levulinic acid melts at 33·5° and distils at 250°; it is very soluble in water, combines readily with hydroxylamine and phenylhydrazine, and when reduced with sodium amalgam it yields γ-hydroxyvaleric acid, $CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}COOH$. Levulinic acid is isomeric with methylacetoacetic acid or α-acetylpropionic acid, $CH_3{\cdot}CO{\cdot}CH(CH_3){\cdot}COOH$.

Ethyl malonate, $CH_2(COOC_2H_5)_2$, does not belong to the same class of substances as ethyl acetoacetate, although, like the latter, it contains the group $-CO{\cdot}CH_2{\cdot}CO-$; it is, however, conveniently considered in this chapter on account of its employment in the synthesis of fatty acids.

When potassium chloracetate is digested with potassium cyanide in aqueous solution, potassium cyanacetate is produced,

$$CH_2Cl{\cdot}COOK + KCN = CH_2(CN){\cdot}COOK + KCl.$$

This salt, on hydrolysis with hydrochloric acid, yields malonic acid (p. 234),

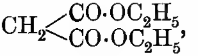
$$CH_2(CN){\cdot}COOK + 2HCl + 2H_2O = CH_2(COOH)_2 + KCl + NH_4Cl,$$

but if the dry potassium cyanacetate be mixed with alcohol and the mixture saturated with hydrogen chloride, ethyl malonate is produced,

$$CH_2(CN){\cdot}COOK + 2HCl + 2C_2H_5{\cdot}OH = CH_2(COOC_2H_5)_2 + KCl + NH_4Cl.$$

Preparation.—Chloracetic acid (100 grams) is dissolved in water (200 c.c.) and neutralised with potassium carbonate (76 grams);

potassium cyanide (75–80 grams) is then added, and the whole heated in a large porcelain basin until a vigorous reaction commences. As soon as this has subsided, the solution is evaporated on a sand-bath, the thick semi-solid residue being constantly stirred with a thermometer until the temperature reaches 135°; the solid cake of potassium chloride and cyanacetate is powdered, transferred to a flask, an equal weight of absolute alcohol added, and the boiling mixture saturated with dry hydrogen chloride (compare p. 187–8). When cold, the solution is poured into twice or thrice its volume of ice-water; the product is then extracted with ether, the ethereal solution washed with water, dried with calcium chloride, and the ether distilled off. The crude oil is purified by fractional distillation; the portion boiling at 195–200°, after two or three distillations, consists of practically pure ethyl malonate.

Ethyl malonate,  $CH_2<\begin{matrix}CO\cdot OC_2H_5\\CO\cdot OC_2H_5\end{matrix}$, like ethyl acetoacetate, contains the group $-CO\cdot CH_2\cdot CO-$, and is capable of forming a sodium derivative when treated with the metal or with sodium ethoxide,

$$2CH_2(COOC_2H_5)_2 + 2Na = 2CHNa(COOC_2H_5)_2 + H_2$$
$$CH_2(COOC_2H_5)_2 + NaO\cdot C_2H_5 = CHNa(COOC_2H_5)_2 + C_2H_5\cdot OH.$$

Unlike ethyl acetoacetate, it does not dissolve in aqueous alkalies, because its alkali derivatives are decomposed by water, and it does not give a colouration with ferric chloride. The sodium derivative of ethyl malonate interacts readily with alkyl halogen compounds, yielding homologues of ethyl malonate,

$$CHNa(COOC_2H_5)_2 + C_2H_5I = \underbrace{CH(C_2H_5)(COOC_2H_5)_2}_{\text{Ethyl } \textit{Ethyl}\text{malonate.}} + NaI;$$

these mono-substitution derivatives, like those of ethyl acetoacetate, are again capable of forming sodium derivatives, which, by further treatment with alkyl halogen compounds, yield di-substitution derivatives of ethyl malonate,

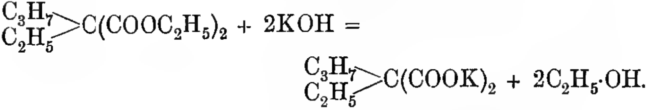
$$CH(C_2H_5)(COOC_2H_5)_2 + NaO\cdot C_2H_5 = CNa(C_2H_5)(COOC_2H_5)_2 + C_2H_5\cdot OH$$
$$CNa(C_2H_5)(COOC_2H_5)_2 + C_3H_7I = \underbrace{C(C_3H_7)(C_2H_5)(COOC_2H_5)_2}_{\text{Ethyl } \textit{Propylethyl}\text{malonate.}} + NaI.$$

In this way a great variety of derivatives may be obtained, the syntheses being carried out exactly as described in the case of the substitution products of ethyl acetoacetate.

Ethyl malonate and its derivatives are readily hydrolysed by boiling alcoholic potash with formation of the potassium salts of the corresponding acids,

$$C_2H_5{\cdot}CH(COOC_2H_5)_2 + 2KOH = C_2H_5{\cdot}CH(COOK)_2 + 2C_2H_5{\cdot}OH$$

Potassium Ethylmalonate.

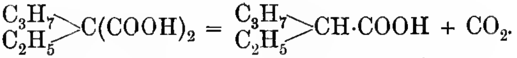


$$\begin{matrix}C_3H_7\\C_2H_5\end{matrix}\!>C(COOC_2H_5)_2 + 2KOH = \begin{matrix}C_3H_7\\C_2H_5\end{matrix}\!>C(COOK)_2 + 2C_2H_5{\cdot}OH.$$

Potassium Propylethylmalonate.

Malonic acid and the dicarboxylic acids derived from it are rapidly and quantitatively decomposed at about 200° with evolution of carbon dioxide and formation of fatty acids. This behaviour is shown by all acids which contain two carboxyl-groups directly combined with the *same* carbon atom (p. 234),

$$CH_2(COOH)_2 = CH_3{\cdot}COOH + CO_2$$



$$\begin{matrix}C_3H_7\\C_2H_5\end{matrix}\!>C(COOH)_2 = \begin{matrix}C_3H_7\\C_2H_5\end{matrix}\!>CH{\cdot}COOH + CO_2.$$

Propylethylmalonic Acid. Propylethylacetic Acid.

Ethyl malonate is, therefore, of the utmost service in the synthesis of fatty acids, and is indeed more used for this purpose than ethyl acetoacetate, because in the case of the latter, ketones are always formed on hydrolysis as bye-products. The value of both synthetical methods is also much enhanced by the fact that the constitution of the acid (or ketone) obtained is always known, which is very often not the case when other methods are employed.

Example.—Normal valeric acid, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, is to be prepared synthetically. In the first place the sodium derivative of ethyl malonate would be heated with propyl iodide, and the resulting ethyl propylmalonate, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH(COOC_2H_5)_2$, hydrolysed with boiling alcoholic potash. The propylmalonic acid obtained from the potassium salt is heated at about 200° or distilled, when it decomposes into normal valeric acid and carbon dioxide,

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH(COOH)_2 = CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOH + CO_2.$$

CHAPTER XII.

ALKYL COMPOUNDS OF NITROGEN, PHOSPHORUS, ARSENIC, SILICON, ZINC, MERCURY, AND OTHER ELEMENTS.

Amines.

Many of the compounds described in the preceding pages may be conveniently considered as having been derived from the hydrogen compounds of certain non-metals; the alcohols and ethers, for example, may be regarded as derivatives of water, the mercaptans and sulphides as derivatives of sulphuretted hydrogen,

$$\begin{array}{lll} H{\cdot}O{\cdot}H & C_2H_5{\cdot}OH & C_2H_5{\cdot}O{\cdot}C_2H_5 \\ H{\cdot}S{\cdot}H & C_2H_5{\cdot}SH & C_2H_5{\cdot}S{\cdot}C_2H_5. \end{array}$$

In a similar manner the hydrides of many other elements may be directly or indirectly converted into organic compounds by the substitution of one or more alkyl groups for an equivalent quantity of hydrogen; from ammonia, for example, a very important class of strongly basic substances, termed **amines,** may be obtained, these compounds being classed as *primary, secondary,* or *tertiary* amines, according as 1, 2, or 3 atoms of hydrogen in ammonia have been displaced by alkyl groups.

Primary.		*Secondary.*	
Methylamine,	$NH_2{\cdot}CH_3$	Dimethylamine,	$NH(CH_3)_2$
Ethylamine,	$NH_2{\cdot}C_2H_5$	Diethylamine,	$NH(C_2H_5)_2$
Propylamine,	$NH_2{\cdot}C_3H_7$	Dipropylamine,	$NH(C_3H_7)_2$

Tertiary.	
Trimethylamine,	$N(CH_3)_3$
Triethylamine,	$N(C_2H_5)_3$
Tripropylamine,	$N(C_3H_7)_3$.

The methods of formation and general character of the amines will, perhaps, be best understood from a description of the ethyl compounds.

Ethylamine, $NH_2{\cdot}C_2H_5$, was first obtained by Würtz, by distilling ethyl isocyanate (p. 287), with potash, the change being analogous to that which occurs in the case of hydrogen isocyanate (p. 286),

$$CO{:}N{\cdot}C_2H_5 + 2KOH = NH_2{\cdot}C_2H_5 + K_2CO_3$$
$$CO{:}NH + 2KOH = NH_3 + K_2CO_3.$$

It is formed when methyl cyanide (acetonitrile) is treated with nascent hydrogen, generated from zinc and sulphuric acid (Mendius' reaction), or from alcohol and sodium,

$$CH_3{\cdot}CN + 4H = CH_3{\cdot}CH_2{\cdot}NH_2.$$

It is also produced when ethyl chloride, bromide, or iodide is heated at about 100° in closed vessels with alcohol which has been saturated with ammonia (Hofmann); the halogen acid produced during the interaction combines with the amine, forming a salt,

$$C_2H_5I + NH_3 = NH_2{\cdot}C_2H_5, HI.$$

Ethylamine is prepared by mixing propionamide (1 mol.) with bromine (1 mol.), and then adding a 10 per cent. solution of potash until the colour of the bromine disappears: the solution of the bromamide which is thus produced,

$$C_2H_5{\cdot}CO{\cdot}NH_2 + Br_2 + KOH = C_2H_5{\cdot}CO{\cdot}NHBr + KBr + H_2O,$$

is now gently warmed with excess of potash, when the bromamide is converted into ethylamine,

$$C_2H_5{\cdot}CO{\cdot}NHBr + 3KOH = C_2H_5{\cdot}NH_2 + KBr + K_2CO_3 + H_2O.$$

In the conversion of propionamide into ethylamine one atom of carbon and one atom of oxygen are taken away, and a derivative of propionic acid is converted into what may be regarded as a derivative of acetic acid, since ethylamine is readily converted into ethyl alcohol and the latter into acetic acid; it is possible, therefore, to transform propionic into acetic acid,

$CH_3{\cdot}CH_2{\cdot}COOH$	$CH_3{\cdot}CH_2{\cdot}CO{\cdot}NH_2$	$CH_3{\cdot}CH_2{\cdot}NH_2$	$CH_3{\cdot}CH_2{\cdot}OH$
Propionic Acid.	Propionamide.	Ethylamine.	Ethyl Alcohol.

$$CH_3{\cdot}COOH.$$

Acetic Acid.

As, moreover, the amides of other fatty acids behave in this respect like propionamide, it is clear that a given fatty acid may be converted into the next lower homologue, and so on down the series.

Conversely, a given fatty acid may be transformed into the next higher homologue in the following manner: The calcium salt of the acid is distilled with calcium formate and the resulting aldehyde converted into the corresponding alcohol by reduction; the alcohol is then transformed into the chloride, the latter treated with potassium cyanide, and the resulting cyanide hydrolysed with alkalies or mineral acids,

$CH_3{\cdot}COOH$	$CH_3{\cdot}CHO$	$CH_3{\cdot}CH_2{\cdot}OH$	$CH_3{\cdot}CH_2Cl$	$CH_3{\cdot}CH_2{\cdot}CN$
Acetic Acid.	Acetaldehyde.	Ethyl Alcohol.	Ethyl Chloride.	Ethyl Cyanide.

$$CH_3{\cdot}CH_2{\cdot}COOH.$$

Propionic Acid.

The cyanide may be converted into the acid in another way; it is first reduced with sodium and alcohol, yielding an amine, from which the fatty acid is obtained in the manner already stated.

Primary amines may also be obtained by reducing the nitroparaffins,

$$CH_3{\cdot}NO_2 + 6H = CH_3{\cdot}NH_2 + 2H_2O,$$

and by heating the alkyl nitrates with alcoholic ammonia,

$$C_3H_7{\cdot}O{\cdot}NO_2 + NH_3 = C_3H_7{\cdot}NH_2, HNO_3.$$

Ethylamine is a colourless, mobile, inflammable liquid of sp. gr. 0·689 at 15°, and boils at 18·7°; it is soluble in water in all proportions, and the solution, like the liquid itself, has a pungent, slightly fish-like odour, distinguishable from that of ammonia only with difficulty. An aqueous solution of ethylamine might, in fact, be easily mistaken for a solution of ammonia, so closely do they resemble one another in properties; the former, like the latter, has a strongly alkaline reaction, and gives, especially on warming, a pungent-smelling gas, which fumes when brought into proximity with concentrated hydrochloric acid. It precipitates metallic hydroxides from solutions of their salts, and neutralises even the most powerful acids, forming salts, which are readily soluble in water. Ethylamine, therefore, is an organic *base*, and its basic properties are even more pronounced than those of ammonia, since it liberates ammonia from ammonium salts; the salts of ethylamine are, however, decomposed by the hydroxides and carbonates of sodium and potassium. In spite of the fact that ethylamine is so readily soluble in water, it separates from the solutions as an oil on the addition of a large quantity of solid potash or potassium carbonate; it is very hygroscopic, and readily absorbs carbon dioxide from the air, forming with it a salt.*

Although, speaking generally, ethylamine is very stable, it is rapidly converted into ethyl alcohol on treatment with nitrous acid in aqueous solution, nitrogen being liberated,

$$C_2H_5 \cdot NH_2 + HO \cdot NO = C_2H_5 \cdot OH + H_2O + N_2;$$

this reaction is exactly analogous to that which occurs when ammonia and nitrous acid (ammonium nitrite) are heated together,

$$NH_4NO_2 \text{ or } NH_3 + HO \cdot NO = 2H \cdot OH + N_2.$$

Ethylamine is also quickly changed when it is warmed with chloroform and alcoholic potash. The intensely disagreeable smell of the product (ethylcarbylamine, compare p. 285) is at once recognisable, and affords a sure indication of the presence of a primary amine (Hofmann's carbylamine reaction),

$$C_2H_5 \cdot NH_2 + CHCl_3 + 3KOH = C_2H_5 \cdot NC + 3KCl + 3H_2O.$$

The two reactions just mentioned are characteristic of *all primary amines*, and are of considerable practical importance; the first is employed for the conversion of the primary amines into hydroxy-compounds, the second for their detection.

Ethylamine is a monacid base, and, like ammonia, forms salts by direct combination, in virtue of the possible pentavalency of the nitrogen atom; these salts are all soluble in water, and some of them, like those of ammonia, readily sublime, even at ordinary temperatures; they usually differ from ammonium salts in being soluble in alcohol, a property which is frequently made use of in isolating the amine.

---

* **Probably not a carbonate, but a carbamate (p. 291),** $CO\!<\!\begin{smallmatrix}NH \cdot C_2H_5, \\ OH, C_2H_5 \cdot NH_2.\end{smallmatrix}$

Ethylamine hydrochloride, $C_2H_5{\cdot}NH_3Cl$, or $C_2H_5{\cdot}NH_2$, HCl, as usually written, crystallises in large plates, melts at about 80°, and is deliquescent. The *sulphate*, $2C_2H_5{\cdot}NH_2$, H_2SO_4, has similar properties. The halogen salts, like those of ammonia, form double salts with many other metallic halogen salts; of these compounds the *platinochlorides* and the *aurochlorides* are the most important; they correspond with the ammonium double salts of similar composition,

Ethylamine platinochloride, $(C_2H_5{\cdot}NH_2)_2$, H_2PtCl_6
Ammonium platinochloride, $(NH_3)_2$, H_2PtCl_6
Ethylamine aurochloride, $C_2H_5{\cdot}NH_2$, $HAuCl_4$
Ammonium aurochloride, NH_3, $HAuCl_4$.

These organic platinum and gold salts are usually yellow, orange, or red, and are generally much more sparingly soluble in water than the simple salts; for the latter reason they are very serviceable in detecting and isolating the amines; on ignition they give a residue of pure metal.

Diethylamine, $NH(C_2H_5)_2$, is formed when ethyl iodide is heated with alcoholic ammonia, just as described in the case of ethylamine; one molecule of the hydrogen iodide produced combines with the base to form a salt, the other uniting with the excess of ammonia,

$$2C_2H_5I + NH_3 = NH(C_2H_5)_2, HI + HI.$$

Diethylamine is a colourless, inflammable liquid, boiling at 56°; it is a stronger base than ethylamine, which it resembles very closely in smell, solubility, &c., and also in forming simple and double salts. It is readily distinguished from ethylamine inasmuch as it does not give the carbylamine reaction; its behaviour with nitrous acid is also totally different from that of ethylamine, since, instead of being converted into an alcohol, it yields *ethylnitrosamine*,

$$(C_2H_5)_2NH + HO{\cdot}NO = (C_2H_5)_2N{\cdot}NO + H_2O.$$

All secondary amines behave in this way; that is to say, on treatment with nitrous acid, they are converted into *nitrosamines* by the substitution of the monovalent nitroso-group

–NO for the atom of hydrogen which is directly united with nitrogen.

When a nitrosamine is mixed with phenol (part ii.) and concentrated sulphuric acid, it gives a dark-green solution which, after diluting with water, becomes red, and on adding excess of alkali, assumes a beautiful and intense blue or green colour; this reaction (Liebermann's, or the nitroso-reaction) affords a means, not only of detecting a nitrosamine, but also a secondary amine, as the latter is convertible into the former.

Diethylamine hydrochloride, $(C_2H_5)_2NH, HCl$, is colourless, and readily soluble in water; its *platinochloride*, $[(C_2H_5)_2NH]_2, H_2PtCl_6$, and *aurochloride*, $(C_2H_5)_2NH, HAuCl_4$, are orange, and less readily soluble.

Triethylamine, $N(C_2H_5)_3$, like the primary and secondary amines, is produced when ethyl iodide is heated with alcoholic ammonia,

$$3C_2H_5I + NH_3 = N(C_2H_5)_3, HI + 2HI.$$

It is a pleasant-smelling liquid, boiling at 89°, and except that it is more sparingly soluble in water, and is a stronger base even than diethylamine, it resembles the primary and secondary compounds in most ordinary properties. It does not give the carbylamine reaction, and is not acted on by nitrous acid at ordinary temperatures, so that it is readily distinguished from the primary and secondary amines; *other tertiary amines* resemble triethylamine in these respects. The salts of triethylamine correspond with those of the other bases.

Triethylamine, and other tertiary amines, combine directly with one molecule of the alkyl halogen compounds, yielding salts corresponding with those of ammonia,

$$N(C_2H_5)_3 + C_2H_5I = N(C_2H_5)_4I\,;\ NH_3 + HI = NH_4I.$$

These salts are more stable than those of the amines, and are either not acted on, or only very slowly attacked by potash or soda, even on boiling; when, however, their aqueous solutions are shaken with freshly precipitated silver oxide (which acts like a hydroxide), double decomposition results, and hydroxy-compounds, corresponding with ammonium hydroxide, are formed,

$$N(C_2H_5)_4I + Ag{\cdot}OH = N(C_2H_5)_4{\cdot}OH + AgI$$
$$NH_4I + Ag{\cdot}OH = NH_4{\cdot}OH + AgI.$$

The hydroxides obtained in this way are termed *quaternary ammonium bases*, or *tetralkylammonium hydroxides*; although, in constitution, they are similar to ammonium hydroxide, they differ from the latter in several important respects, and resemble rather the hydroxides of sodium and potassium.

Tetrethylammonium hydroxide, $N(C_2H_5)_4{\cdot}OH$, for example, is a crystalline, deliquescent substance, and has only a faint smell, like that of potash; it has a powerful alkaline reaction, absorbs carbon dioxide from the air, and is a stronger base even than potash or soda; when strongly heated, it is resolved into triethylamine and ethyl alcohol, or its decomposition products,

$$N(C_2H_5)_4{\cdot}OH = N(C_2H_5)_3 + C_2H_4 + H_2O.$$

The salts of tetrethylammonium hydroxide, such as the iodide (see above), may also be obtained by treating the hydroxide with acids; they are mostly crystalline.

The tetralkylammonium halogen salts undergo decomposition or dissociation on dry distillation, yielding a tertiary amine and an alkyl halogen salt, just as ammonium chloride is resolved into ammonia and hydrogen chloride,

$$N(C_2H_5)_4Cl = N(C_2H_5)_3 + C_2H_5Cl \qquad NH_4Cl = NH_3 + HCl.$$

Under ordinary circumstances the halogen ethereal salt, being much more volatile than the tertiary amine, can be separated from the latter before re-combination takes place.

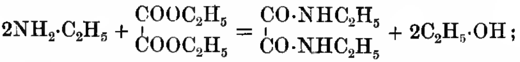
In a similar manner the halogen salts of *some* tertiary amines may be converted into secondary, and those of secondary into primary, amines,

$$N(CH_3)_3,\ HCl = N(CH_3)_2H + CH_3Cl$$
$$N(CH_3)_2H,\ HCl = N(CH_3)H_2 + CH_3Cl.$$

Separation of Amines.—Three of the general methods for the preparation of amines—namely, the decomposition of alkyl isocyanates, the reduction of nitriles, and the decomposition of amides of the fatty acids with bromine and potash, give the primary compounds only; when, however, an alkyl halogen compound is heated with alcoholic ammonia, not only are primary, secondary, and tertiary amines all produced at the same time, but the tertiary amine combines with the alkyl halogen compound to form a quaternary ammonium derivative; the product consists, therefore, of a mixture of four organic salts, and contains also ammonium salts. In order to separate and isolate the several compounds, the mixture is first evaporated to expel ammonia, alcohol, and any unchanged alkyl salt, and then distilled with excess of potash; the primary, secondary, and tertiary amines, which, together with ammonia, are thus liberated from their salts, collect in the receiver, and may be absorbed with hydrochloric acid, whilst the residue contains the stable salt of the tetralkylammonium base; the latter may usually be isolated by neutralising the solution with hydrochloric acid, evaporating to dryness, and extracting the powdered residue with alcohol.

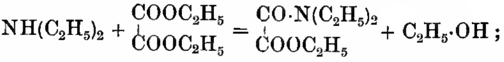
The acid solution of the three amine salts is evaporated almost to dryness and treated with solid potash, when a mixture of the bases rises to the surface as an oil and is separated with the aid of a funnel; the oil is dried by distilling it with lumps of potash and then treated with ethyl oxalate, when, in the case of the ethyl bases, for example, the following changes occur:

The primary amine is converted into ethyloxamide, a derivative of oxamide (p. 233),



$$2NH_2\cdot C_2H_5 + \begin{array}{l} COOC_2H_5 \\ | \\ COOC_2H_5 \end{array} = \begin{array}{l} CO\cdot NHC_2H_5 \\ | \\ CO\cdot NHC_2H_5 \end{array} + 2C_2H_5\cdot OH;$$

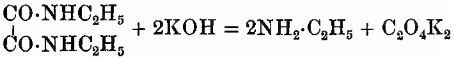
the secondary amine gives ethyl diethyloxamate, a derivative of oxamic acid (p. 234),



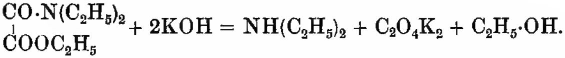
$$NH(C_2H_5)_2 + \begin{array}{l} COOC_2H_5 \\ | \\ COOC_2H_5 \end{array} = \begin{array}{l} CO\cdot N(C_2H_5)_2 \\ | \\ COOC_2H_5 \end{array} + C_2H_5\cdot OH;$$

the tertiary amine is not acted on, and is easily separated from the two less volatile products by heating the mixture as long as oil passes over.

The residue is allowed to cool, and the crystalline ethyloxamide separated from the liquid ethyl diethyloxamate by filtration or by treatment with water, in which the former alone is soluble; the two compounds are then separately distilled with potash, the bases being collected and isolated as described in the case of the mixture,



$$\begin{array}{l}CO\cdot NHC_2H_5\\ |\\ CO\cdot NHC_2H_5\end{array} + 2KOH = 2NH_2\cdot C_2H_5 + C_2O_4K_2$$



$$\begin{array}{l}CO\cdot N(C_2H_5)_2\\ |\\ COOC_2H_5\end{array} + 2KOH = NH(C_2H_5)_2 + C_2O_4K_2 + C_2H_5\cdot OH.$$

The three ethylamines and the tetrethylammonium compounds may be taken as typical examples of the several classes of alkyl derivatives of ammonia; the corresponding methyl bases, and those of the higher alkyl radicles, are prepared by methods so similar to those described in the case of the ethylamine compounds, and have properties so closely resembling those of the latter, that a detailed description would be of little value.

Methylamine, $NH_2\cdot CH_3$, *dimethylamine*, $NH(CH_3)_2$, and *trimethylamine*, $N(CH_3)_3$, are usually produced in small quantities during the decomposition of nitrogenous organic substances, and occur in herring brine, the last named especially in large relative proportions. Dimethylamine and trimethylamine are prepared on the large scale by distilling the waste-products obtained in refining beet-sugar, and are used in considerable quantities for various technical purposes; trimethylamine is employed in the manufacture of potassium carbonate, and its hydrochloride is used in the preparation of methyl chloride (p. 172).

The physical properties of the amines undergo a gradual change with increasing molecular weight, just as is the case in other series; the boiling-points of the four simplest primary amines may be taken as an illustration:

Methylamine, $CH_3\cdot NH_2$	Ethylamine, $C_2H_5\cdot NH_2$
B.p. − 6°	B.p. 19°
Propylamine, $C_3H_7\cdot NH_2$	Butylamine, $C_4H_9\cdot NH_2$
B.p. 49°	B.p. 76°.

The higher amines, like the higher ethers, ethereal salts, &c., exist in various metameric forms: there are, for example, three compounds of the molecular formula C_3H_9N (see below). The amines, like the ethers, may be classed into *simple* amines, such as propylamine, $C_3H_7\cdot NH_2$, diethylamine, $(C_2H_5)_2NH$, &c., and *mixed* amines, such as methylethylamine, $NH(CH_3)\cdot C_2H_5$, dimethylethylamine, $N(CH_3)_2\cdot C_2H_5$, according as they contain alkyl groups of the same or of different kinds.

Identification of Amines.—The most important methods by which a given amine may be recognised as a primary, secondary, or tertiary compound consist, as already stated, firstly, in applying the carbylamine reaction, and secondly, in treating the compound with nitrous acid. If a primary amine, it is converted by nitrous acid into a primary alcohol with evolution of nitrogen; if a secondary base, it yields a nitroso-compound, the presence of which is readily detected by Liebermann's reaction; if a tertiary amine, it is usually unchanged.

The experiment is made as follows: To a concentrated neutral solution of the hydrochloride of the base a small quantity of a solution of sodium nitrite is added; evolution of nitrogen, the separation of an oily nitrosamine (which is insoluble in water), or no visible change occurs, according to the nature of the base; further tests, which readily suggest themselves, are then made to confirm the results of the experiment.

As methylamine is a gas, and all the lower amines are volatile liquids, which are very difficult to characterise by ordinary tests, the nature of a given amine is usually ascertained by preparing and analysing its platinochloride or aurochloride; the percentage of metal in the salt, together with the behaviour of the base with nitrous acid, afford evidence sufficient, in most cases, to determine the identity of the compound.

Example.—A base produced by the destructive distillation of the molasses obtained in the preparation of beet-sugar gave a platinochloride, which, on analysis, was found to contain 37·2 per cent. of platinum; the probable molecular weight of the base is therefore 59 (see p. 40), so that it may be propylamine or isopropylamine, $C_3H_7{\cdot}NH_2$, methylethylamine, $CH_3(C_2H_5)NH$, or trimethylamine, $(CH_3)_3N$. On treatment with nitrous acid, it is found to be a tertiary amine; it is, therefore, trimethylamine.

Phosphines.

Since phosphorus and nitrogen belong to the same natural group of elements, it might be expected that phosphoretted hydrogen, PH_3, like ammonia, would be capable of yielding substitution products analogous to the amines. As a matter of fact, the **phosphines**, or alkyl substitution products of phosphorus trihydride, are readily obtained by heating the alkyl iodides with phosphonium iodide in presence of zinc oxide. In the case of ethyl iodide, for example, salts of *ethylphosphine* and *diethylphosphine*, corresponding with those of the primary and secondary amines respectively, are formed,

$$2PH_4I + 2C_2H_5I + ZnO = 2[PH_2{\cdot}C_2H_5, HI] + ZnI_2 + H_2O$$
$$PH_4I + 2C_2H_5I + ZnO = PH(C_2H_5)_2, HI + ZnI_2 + H_2O.$$

Tertiary phosphines, such as *triethylphosphine*, are *not* produced under the above conditions, but may be prepared by heating the alkyl iodides with phosphonium iodide alone; as in the case of the corresponding amines, the tertiary phosphines combine with alkyl iodides, forming salts of quaternary bases, such as *tetrethylphosphonium iodide*, so that the product is a mixture of two organic compounds,

$$PH_4I + 3C_2H_5I = P(C_2H_5)_3, HI + 3HI$$
$$P(C_2H_5)_3 + C_2H_5I = P(C_2H_5)_4I.$$

With the exception of *methylphosphine*, $PH_2{\cdot}CH_3$, which is a gas, the primary, secondary, and tertiary phosphines are colourless, volatile, highly refractive, very unpleasant-smelling liquids; they differ from the amines in smell, in being, as a rule, insoluble, or only sparingly soluble, in water (PH_3, unlike NH_3, is only sparingly soluble), and in readily undergoing oxidation on exposure to the air; in many cases, so much heat is developed during this process, that the compound takes fire—that is to say, many of the phosphines are spontaneously inflammable. When tertiary phosphines undergo slow oxidation in presence of air, they are converted into stable oxides, such as *triethylphosphine oxide*, $P(C_2H_5)_3O$.

Although phosphoretted hydrogen is only a feeble base compared with ammonia, and forms salts, such as phosphonium iodide, PH_4I, which are decomposed even by water, each successive substitution of an alkyl group for an atom of hydrogen is accompanied by an increase in basic properties, just as in the case of the amines. Salts of the primary phosphines, such as *ethylphosphine hydriodide*, $PH_2{\cdot}C_2H_5$, HI, are almost, if not quite, as unstable as those of hydrogen phosphide, and are decomposed into acid and base on treatment with water; they may thus be separated from the more stable salts of the secondary and tertiary phosphines, such as *diethylphosphine hydriodide*, $PH(C_2H_5)_2$, HI, and *triethylphosphine hydriodide*, $P(C_2H_5)_3$, HI, which are not acted on by water as a rule, but are readily decomposed by potash and soda. Salts of the tetralkylphosphonium compounds, such as *tetrethylphosphonium iodide*, $P(C_2H_5)_4I$, are not acted on by water or by alkalies, but, on treatment with moist silver oxide, they are converted into *quaternary phosphonium hydroxides*,

$$P(C_2H_5)_4I + Ag{\cdot}OH = P(C_2H_5)_4{\cdot}OH + AgI.$$

These compounds have a *strong* alkaline reaction, readily absorb carbon dioxide, and dissolve freely in water; they are, in fact, similar in properties to the hydroxides of the fixed alkalies, and their salts are much more stable than the phosphine salts, just as those of the corresponding tetralkylammonium bases are more stable than those of ammonia.

Arsines.

Arsenic, antimony, and bismuth, although belonging to the same natural group as nitrogen and phosphorus, differ from these two elements in many important particulars; although the two former give hydrides, the hydrogen atoms in which may be (indirectly) displaced by alkyl groups, substitution products corresponding with the *primary* and *secondary* amines and phosphines have not yet been prepared; in other words, the only known alkyl compounds theoretically derived from the trihydrides of arsenic, antimony, and bismuth correspond with the *tertiary* amines and phosphines, and have the composition AsR_3, SbR_3, and BiR_3 respectively.

The tertiary **arsines** are obtained by treating arsenious chloride with the zinc alkyl compounds (p. 215), or by heating the alkyl iodides with sodium arsenide,

$$2AsCl_3 + 3Zn(C_2H_5)_2 = 2As(C_2H_5)_3 + 3ZnCl_2$$
$$AsNa_3 + 3CH_3I = As(CH_3)_3 + 3NaI.$$

Triethylarsine, $As(C_2H_5)_3$, may be described as a typical arsine. It is a colourless, very unpleasant-smelling, highly poisonous liquid, and is only sparingly soluble in water; it fumes in the air, and takes fire when heated, but does not ignite spontaneously. It differs from the amines and phosphines in being a neutral compound, and, like arseniuretted hydrogen, it does not form salts with acids; it resembles the tertiary amines and phosphines in combining readily with alkyl iodides, forming salts of *quaternary arsonium hydroxides,*

$$As(C_2H_5)_3 + C_2H_5I = As(C_2H_5)_4I.$$

Tetrethylarsonium iodide, $As(C_2H_5)_4I$, for example, is a crystalline substance, and, like other quaternary organic salts, it is *not* decomposed by potash, although it interacts with silver hydroxide, giving **tetrethylarsonium hydroxide,**

$$As(C_2H_5)_4I + Ag{\cdot}OH = As(C_2H_5)_4{\cdot}OH + AgI.$$

This substance has a strong alkaline reaction, and neutralises even the most powerful acids; here, again, as in the case of nitrogen and phosphorus, the basic character increases with the number of alkyl groups in the molecule.

The tertiary arsines resemble the tertiary phosphines in readily undergoing oxidation on exposure to the air, forming oxides such as *triethylarsine oxide,* $As(C_2H_5)_3O$.

The tertiary *stibines,* the organic derivatives of antimony, are on the whole similar to those of arsenic, but have not been so carefully investigated; the tertiary bismuth compounds, such as $Bi(CH_3)_3$, cannot be converted into quaternary hydroxides, corresponding with those of arsenic and antimony, and owing to the more pronounced metallic character of bismuth, its compounds resemble rather those of the metals zinc, mercury, &c. (p. 214).

Derivatives of the Arsines.—Tertiary arsines combine directly with two atoms of a halogen, forming compounds, such as triethylarsine dichloride, $As(C_2H_5)_3Cl_2$, in which the arsenic atom is pentavalent; these substances are decomposed on heating, yielding an alkyl halogen compound and a *halogen derivative* of a secondary arsine,

$$As(C_2H_5)_3Cl_2 = As(C_2H_5)_2Cl + C_2H_5Cl.$$

Although, then, the secondary arsines are unknown, their halogen derivatives can be prepared; so, also, can those of primary arsines, since, when the derivatives of the secondary compounds are treated with halogens, direct union takes place,

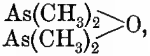
$$As(C_2H_5)_2Cl + Cl_2 = As(C_2H_5)_2Cl_3,$$

and the products, on heating, are decomposed into *dihalogen derivatives* of primary arsines,

$$As(C_2H_5)_2Cl_3 = As(C_2H_5)Cl_2 + C_2H_5Cl.$$

The derivatives of dimethylarsine are of considerable interest, and have been very carefully investigated by Bunsen.

Dimethylarsine oxide, or **cacodyl oxide**,



$\begin{matrix}As(CH_3)_2\\As(CH_3)_2\end{matrix}\!\!>\!O$, is formed when a mixture of equal parts of arsenic trioxide and potassium acetate is submitted to dry distillation; during the operation highly poisonous gases are evolved, and an oily liquid collects in the receiver,

$$As_2O_3 + 4CH_3{\cdot}COOK = As_2(CH_3)_4O + 2K_2CO_3 + 2CO_2.$$

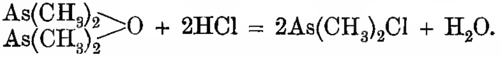
This liquid has an intensely obnoxious smell,* and is excessively poisonous, for which reasons its preparation, except in *minute* quantities, should not be attempted; its formation may, however, be used as a test for acetates if due care be taken, as the substance is readily recognisable by its smell.

Cacodyl oxide boils at 150°, and is insoluble in water; the substance prepared in the above-mentioned manner is spontaneously inflammable owing to the presence of cacodyl, but the pure compound is not. In chemical properties cacodyl oxide resembles the feebly basic metallic oxides; it has a neutral reaction, but interacts readily with acids,

---

* The name cacodyl is derived from the Greek κακώδης, 'stinking.'

forming salts, such as *cacodyl chloride* and *cacodyl cyanide*, $As(CH_3)_2 \cdot CN$,



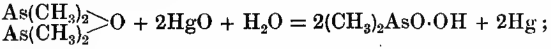
$$\begin{matrix} As(CH_3)_2 \\ As(CH_3)_2 \end{matrix}\!\!>O + 2HCl = 2As(CH_3)_2Cl + H_2O.$$

When cacodyl chloride is heated with zinc in an atmosphere of carbon dioxide, it yields **cacodyl** or diarsenic tetramethyl, a change which is analogous to the formation of ethane from methyl iodide,

$$2As(CH_3)_2Cl + Zn = As(CH_3)_2 - As(CH_3)_2 + ZnCl_2$$
$$2CH_3I + 2Na = CH_3 - CH_3 + 2NaI.$$

Cacodyl, like the oxide, is a colourless, excessively poisonous liquid, and has an intensely disagreeable smell; it takes fire on exposure to the air.

Cacodylic acid, $(CH_3)_2AsO \cdot OH$, is formed when cacodyl oxide is oxidised with mercuric oxide,



$$\begin{matrix} As(CH_3)_2 \\ As(CH_3)_2 \end{matrix}\!\!>O + 2HgO + H_2O = 2(CH_3)_2AsO \cdot OH + 2Hg;$$

it is a crystalline, odourless substance, and seems to be non-poisonous.

Organic Silicon Compounds.

The organic compounds of silicon are of exceptional interest, because their study exhibits in a very strong light the close relationship between silicon and carbon. Just as the paraffins may be considered as derived from the hydride, methane, CH_4, by the substitution of alkyl groups for hydrogen, so may the simplest silicon compounds be regarded as derivatives of silicon hydride, SiH_4. Up to the present, however, only those compounds containing four alkyl radicles have been prepared, as, for example, silicon tetramethyl, $Si(CH_3)_4$, corresponding with carbon tetramethyl or tetramethylmethane, $C(CH_3)_4$; substances such as $SiH(CH_3)_3$, $SiH_2(CH_3)_2$, &c., which would be analogous to the hydrocarbons $CH(CH_3)_3$, $CH_2(CH_3)_2$, &c., are not known.

Silicon tetramethyl, $Si(CH_3)_4$, is produced when silicon tetrachloride is heated with zinc methyl,

$$SiCl_4 + 2Zn(CH_3)_2 = Si(CH_3)_4 + 2ZnCl_2.$$

It is a colourless, mobile, volatile liquid, boiling at 30°, and has properties very similar to those of tetramethylmethane.

Silicon tetrethyl, $Si(C_2H_5)_4$, may be obtained from silicon tetrachloride and zinc ethyl in a similar manner, and closely resembles the normal paraffin, nonane, C_9H_{20}, in properties. It may, in fact, be regarded as derived from the as yet unknown isomeride of nonane, tetrethylmethane, $C(C_2H_5)_4$, by the substitution of one atom of silicon for one atom of carbon; for this reason it is sometimes named *siliconbackonane*.

The great similarity between silicononane and nonane is strikingly shown by the following facts: Silicononane, like nonane, is a colourless liquid, insoluble in, and specifically lighter than water; like nonane, it is a very stable substance, and is not acted on by nitric acid or caustic alkalies. On treatment with chlorine it behaves like a paraffin, and yields the substitution product *silicononyl chloride*, $Si(C_2H_5)_3{\cdot}C_2H_4Cl$, a colourless liquid, boiling at 185°; this chloride closely resembles the alkyl chlorides in properties, and, like the latter, interacts with silver acetate, giving *silicononyl acetate*,

$$Si(C_2H_5)_3{\cdot}C_2H_4Cl + C_2H_3O_2Ag = Si(C_2H_5)_3{\cdot}C_2H_4{\cdot}C_2H_3O_2 + AgCl.$$

This ethereal salt is readily hydrolysed by alkalies, yielding *silicononyl alcohol*, just as ethyl acetate gives ethyl alcohol,

$$Si(C_2H_5)_3{\cdot}C_2H_4{\cdot}C_2H_3O_2 + KOH = Si(C_2H_5)_3{\cdot}C_2H_4{\cdot}OH + C_2H_3O_2K;$$

this alcohol, again, is a colourless, neutral liquid, boiling at 190°, analogous in most respects to the higher alcohols of the general formula $C_nH_{2n+1}{\cdot}OH$.

Organic silicon compounds, such as $Si_2(C_2H_5)_6$, corresponding with Si_2Cl_6, are known, but are of less importance.

Organo-Metallic Compounds.

Many of the metals, such as mercury, zinc, tin, and lead, form compounds with alkyl groups, although their hydrides are unknown. These alkyl compounds are named 'organo-metallic' compounds, but there is no sharp division between them and the alkyl compounds of other elements, just as there is none between the metals and non-metals. If, in fact, the alkyl compounds of elements belonging to the same natural group be considered, it will be evident that they show a *gradual* change in properties, just as do the elements themselves, and pass into organo-metallic compounds without any abrupt transition. The compounds of the elements of the fourth group, for example, such as

$$C(CH_3)_4 \qquad Si(CH_3)_4 \qquad Sn(CH_3)_4 \qquad Pb(CH_3)_4,$$

may be divided into two fairly distinct classes; but in the case of those of the elements of the fifth group,

$$N(CH_3)_3 \quad P(CH_3)_3 \quad As(CH_3)_3 \quad Sb(CH_3)_3 \quad Bi(CH_3)_3,$$

it is practically impossible to say which of them, if any, should be classed as organo-metallic compounds.

The zinc alkyl compounds are perhaps of the greatest importance, on account of their frequent employment in the synthesis of other organic substances, of which many examples have already been given; their properties, moreover, are in many respects typical of those of other organo-metallic compounds.

Zinc ethyl, $Zn(C_2H_5)_2$, is formed when ethyl bromide or iodide is digested with an alloy of sodium and zinc,

$$ZnNa_2 + 2C_2H_5I = Zn(C_2H_5)_2 + 2NaI.$$

It is usually prepared by heating zinc with ethyl iodide in an atmosphere of carbon dioxide; the first product is a colourless, solid substance (zinc ethiodide), containing iodine,

$$Zn + C_2H_5I = Zn{<}^{C_2H_5}_{I},$$

but on heating more strongly, a second change occurs, and zinc ethyl is formed,

$$2Zn{<}^{C_2H_5}_{I} = Zn(C_2H_5)_2 + ZnI_2.$$

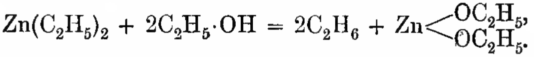
Zinc filings (100 grams) and an equal weight of ethyl iodide are placed in a flask connected with a reflux condenser, and the air is completely expelled from the apparatus by passing a stream of dry carbon dioxide through a narrow tube which runs through the condenser to the bottom of the flask. The condenser is then quickly fitted with a cork through which passes a tube, dipping under mercury, in order to prevent access of air; the materials and the apparatus must be perfectly dry.

The flask is now heated on a water-bath, when a rapid evolution of gas (butane) takes place, and the white intermediate product is gradually formed; after two to three hours' time the interaction is at an end. When cold, the flask is quickly fitted with a cork and glass tubes (just as in an ordinary wash-bottle), and the smaller tube is connected with a condenser; the flask is then heated in an oil-bath, and the zinc ethyl distilled, a stream of dry carbon dioxide being passed through the longer tube into the apparatus during the whole operation; the distillate is collected in a vessel which can be easily sealed.

Zinc ethyl is a colourless liquid, and boils at 118° without decomposition; it must be distilled in an atmosphere free from oxygen, since it inflames spontaneously on exposure to the air, burning with a luminous, greenish flame, and emitting clouds of zinc oxide. It decomposes water with great energy, yielding ethane and zinc hydroxide,

$$Zn(C_2H_5)_2 + 2H_2O = 2C_2H_6 + Zn(OH)_2,$$

and owing to its dehydrating action, it causes painful sores when brought into contact with the skin; it is also decomposed by alcohol, but not so quickly as by water,



$$Zn(C_2H_5)_2 + 2C_2H_5{\cdot}OH = 2C_2H_6 + Zn\begin{matrix}\diagup OC_2H_5, \\ \diagdown OC_2H_5.\end{matrix}$$

Zinc ethyl interacts readily with all substances containing the hydroxyl-group, and also with almost all halogen compounds, whether organic or inorganic, as, for example, with acid chlorides (pp. 107 and 136), alkyl halogen compounds (p. 69), and metallic chlorides; for these reasons it is extensively used in the synthesis of paraffins, ketones, tertiary alcohols, &c., as well as in the preparation of other organo-metallic compounds.

Zinc methyl, $Zn(CH_3)_2$, resembles zinc ethyl in most respects, and is prepared by heating methyl iodide with zinc, or, better, with the zinc-copper couple. It is a colourless liquid, boiling at 46°, and is decomposed by water, yielding methane and zinc hydroxide.

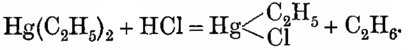
Mercuric ethyl, $Hg(C_2H_5)_2$, is formed when zinc ethyl is treated with mercuric chloride,

$$Zn(C_2H_5)_2 + HgCl_2 = Hg(C_2H_5)_2 + ZnCl_2,$$

but it is usually prepared by shaking ethyl iodide with sodium amalgam,

$$HgNa_2 + 2C_2H_5I = Hg(C_2H_5)_2 + 2NaI.$$

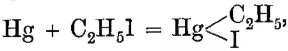
Mercuric ethyl is a colourless, very heavy liquid, of sp. gr. 2·44; it boils at 159° without decomposition, and is not spontaneously inflammable at ordinary temperatures, although it ignites readily when strongly heated. It is much less active than zinc ethyl, does not oxidise on exposure to the air, and is not decomposed by water, in which it is only sparingly soluble; both the liquid and its vapour are highly poisonous. On treatment with halogen acids, mercuric ethyl is converted into salts, analogous in some respects to the halogen salts of the alkali metals,



$$Hg(C_2H_5)_2 + HCl = Hg{<}\begin{matrix}C_2H_5\\Cl\end{matrix} + C_2H_6.$$

Mercuric Ethochloride.

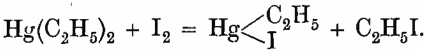
These salts are also formed by the direct union of mercury and alkyl halogen compounds at ordinary temperatures, especially in sunlight,



$$Hg + C_2H_5I = Hg{<}\begin{matrix}C_2H_5,\\I\end{matrix}$$

Mercuric Ethiodide.

and by treating di-alkyl mercury compounds with halogens,



$$Hg(C_2H_5)_2 + I_2 = Hg{<}\begin{matrix}C_2H_5\\I\end{matrix} + C_2H_5I.$$

They interact with moist silver oxide, being converted into *hydroxides*, just as sodium iodide, for example, gives sodium hydroxide,

$$Hg{<}\begin{matrix}C_2H_5\\I\end{matrix} + AgOH = Hg{<}\begin{matrix}C_2H_5\\OH\end{matrix} + AgI.$$

The hydroxides thus formed are thick, caustic liquids, readily soluble in water; they have an *alkaline* reaction, neutralise acids, liberate ammonia from its salts, and precipitate metallic hydroxides from their salts. Here, as in the case of nitrogen, phosphorus, arsenic, &c., the influence of alkyl groups in increasing the basic character of an element is very pronounced; mercuric oxide is a comparatively feeble base.

Of the other organo-metallic compounds those of tin, lead, and aluminium may be mentioned. Tin and lead form compounds, such as $Sn(C_2H_5)_4$ and $Sn_2(C_2H_5)_6$, $Pb(C_2H_5)_4$ and $Pb_2(C_2H_5)_6$, in which the metal is tetravalent; stannous ethyl, $Sn(C_2H_5)_2$, corresponding with stannous chloride, is also said to exist. Aluminium appears only to give alkyl compounds, such as $Al(CH_3)_3$ and $Al(C_2H_5)_3$, in which the metal is trivalent.

The organo-metallic compounds are of great service in determining the valency of metals, because, unlike the great majority of metallic compounds, most of them vaporise without decomposition; by ascertaining experimentally the density of the vapour, the molecular weight of the substance and the valency of the metal may be established.

CHAPTER XIII.

THE GLYCOLS AND THEIR OXIDATION PRODUCTS.

It may be assumed as a general rule that the changes which any particular group of atoms is capable of undergoing are independent of the nature of the groups with which it is combined; just as ethane, $CH_3{\cdot}CH_3$, for example, may be successively transformed into ethyl chloride, $CH_3{\cdot}CH_2Cl$, ethyl alcohol, $CH_3{\cdot}CH_2{\cdot}OH$, and acetic acid, $CH_3{\cdot}CO{\cdot}OH$, by changes in which only *one* of the methyl groups takes part, so also may it be converted into ethylene dichloride (dichlorethane), $CH_2Cl{\cdot}CH_2Cl$, dihydroxyethane, $OH{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, and oxalic acid, $HO{\cdot}CO{\cdot}CO{\cdot}OH$, by causing the *other* methyl group also to undergo the same modifications.

It follows, therefore, that, in many cases, a series of mono-substitution products of the paraffins may be directly or indirectly converted into a corresponding series of di-substitution products, between which there is, on the whole, a close relationship. The **glycols**, or dihydroxy-derivatives of the paraffins, discovered by Würtz in 1856, afford an example of this point; they form a homologous series of the general formula $C_nH_{2n}(OH)_2$, and are closely related to the monohydric alcohols.

Ethylene glycol, ethene glycol, or ethylene alcohol, $C_2H_4(OH)_2$, is the simplest glycol, and corresponds with ethyl alcohol, the compound, methylene glycol, $CH_2(OH)_2$, which would correspond with methyl alcohol, being unknown. Ethylene glycol is formed in small quantities when ethylene is oxidised with a dilute alkaline solution of potassium permanganate,

$$C_2H_4 + H_2O + O = C_2H_4(OH)_2.$$

It is prepared by heating ethylene dibromide, or ethylene dichloride, with dilute aqueous alkalies, or alkali carbonates, the change which occurs being similar to that which takes place in the formation of ethyl alcohol from ethyl chloride,

$$C_2H_4Br_2 + 2KOH = C_2H_4(OH)_2 + 2KBr.$$

For this purpose potassium carbonate (138 grams) is dissolved in water (1 litre), ethylene dibromide (188 grams) added, and the mixture boiled in a flask connected with a reflux condenser. As the insoluble oily dibromide is converted into ethylene glycol, it passes into solution, so that the change is known to be complete when globules of oil are no longer visible. The solution is then slowly evaporated on a water-bath* to expel most of the water, the semi-solid residue mixed with alcohol and ether (which precipitate potassium bromide, but dissolve the glycol), and the glycol isolated from the filtered solution by fractional distillation.

Ethylene glycol is a thick, colourless liquid, and has a rather sweet taste; it boils at 197·5°, and is miscible with water and alcohol in all proportions, but is only sparingly soluble in ether. Although it is a neutral substance, it dissolves sodium at ordinary temperatures with evolution of hydrogen, yielding *sodium glycol*, $C_2H_5O_2Na$, one atom of the metal

---

* If the solution be kept in rapid ebullition, a considerable quantity of the glycol escapes with the steam.

displacing one atom of hydrogen; if this substance be now heated with sodium, hydrogen is again evolved, and *disodium glycol*, $C_2H_4O_2Na_2$, is formed by a repetition of the substitution process. These sodium derivatives, like those of the monohydric alcohols, are colourless, crystalline, and hygroscopic, and are readily decomposed by water, being reconverted into glycol,

$$C_2H_4O_2Na_2 + 2H_2O = C_2H_6O_2 + 2NaOH.$$

From its behaviour with sodium it might be assumed that glycol contained hydroxyl-groups, and that the reason of its giving di-substitution products (whereas the monohydric alcohols yield only mono-substitution products) was due to the presence of *two* hydroxyl-groups. If this were so, it would be expected that glycol, like alcohol, would be readily attacked by the chlorides and bromides of phosphorus; this is indeed the case. When glycol is treated with phosphorus pentabromide, it is converted into ethylene dibromide, whereas with phosphorus pentachloride it yields the dichloride,

$$C_2H_4(OH)_2 + 2PBr_5 = C_2H_4Br_2 + 2POBr_3 + 2HBr.$$

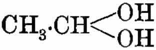
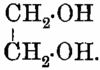
Again, it has been shown that ethyl alcohol and other hydroxy-compounds interact with acetic anhydride and with acetyl chloride, so that if glycol contain two hydroxyl-groups, it should be converted into a diacetyl-derivative; this, also, is the fact, since *glycol diacetate* is readily obtained on heating glycol with acetic anhydride,

$$C_2H_4(OH)_2 + 2(CH_3{\cdot}CO)_2O = C_2H_4(O{\cdot}CO{\cdot}CH_3)_2 + 2C_2H_4O_2.$$

Glycol diacetate is also formed when ethylene dibromide is digested with silver acetate,

$$C_2H_4Br_2 + 2C_2H_3O_2Ag = C_2H_4(C_2H_3O_2)_2 + 2AgBr;$$

this ethereal salt is decomposed by boiling alkalies, yielding ethylene glycol, which was first obtained by Würtz in this way.

Constitution of Glycol.—The facts already stated show clearly that glycol contains two hydroxyl-groups; the only matter requiring further attention is, therefore, whether these two groups are combined with the same, or with different carbon atoms—that is to say, whether glycol has the constitution  $CH_3{\cdot}CH{<}{OH \atop OH}$ or $OH{\cdot}CH_2{\cdot}CH_2{\cdot}OH$. This question is easily answered on considering the formation of glycol from ethylene dibromide; since the latter has the constitution $CH_2Br{\cdot}CH_2Br$, and its conversion into glycol is a simple process of substitution, glycol must be represented by the formula $OH{\cdot}CH_2{\cdot}CH_2{\cdot}OH$ or  $\begin{matrix}CH_2{\cdot}OH\\ | \\ CH_2{\cdot}OH.\end{matrix}$ This conclusion is confirmed by a study of the behaviour of glycol under other conditions, and of its relation to other compounds.

Homologues of Ethylene Glycol.—The higher glycols, or dihydroxy-derivatives of the paraffins, as, for example, *αβ-propylene glycol*, $CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$, and αγ-butylene glycol, $CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}OH$, are named after the unsaturated hydrocarbons of the olefine series, from which they may be regarded as derived. As they exist in isomeric forms, these are distinguished by employing α, β, γ, &c. to denote the positions of the hydroxyl-groups, commencing at the terminal carbon atom.

The glycols are neutral, thick liquids, similar to ethylene glycol in properties; they are usually prepared by treating the olefines with bromine, and decomposing the dibromo-additive products obtained in this way by boiling with alkali carbonates.

The great advantage of employing constitutional formulæ is well illustrated by the case of ethylene glycol. From a consideration of its method of formation and of one or two simple reactions, it is concluded that glycol has the constitution $OH{\cdot}CH_2{\cdot}CH_2{\cdot}OH$. Assuming this to be true, its behaviour under given conditions can be foretold with tolerable certainty from the facts established in the case of ethyl alcohol, because the constitutional formula of a compound is a summary of its most important reactions. Ethylene glycol contains two $-CH_2{\cdot}OH$ groups, each of which is similar to that in ethyl alcohol; it may be supposed, then, that any property of ethyl alcohol which is dependent on the presence of this group will also be exhibited by glycol. Since, for example, alcohol acts like a metallic hydroxide, and forms salts with one molecule of a monobasic acid, ethylene glycol, which contains two hydroxyl-groups, should behave as a diacid hydroxide, and form salts with two molecules of a monobasic acid.

When hydrogen chloride is passed into glycol heated at about 100°, *glycol chlorohydrin* is formed,

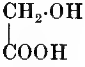
$$OH{\cdot}CH_2{\cdot}CH_2{\cdot}OH + HCl = CH_2Cl{\cdot}CH_2{\cdot}OH + H_2O,$$

and when this product is heated with hydrogen chloride at a higher temperature, glycol dichloride, or ethylene dichloride, is produced,

$$CH_2Cl{\cdot}CH_2{\cdot}OH + HCl = CH_2Cl{\cdot}CH_2Cl + H_2O,$$

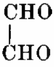
changes which are strictly analogous to the conversion of alcohol into ethyl chloride.

Again, when ethyl alcohol is carefully oxidised, it is first converted into aldehyde (the group $-CH_2{\cdot}OH$ being transformed into $-CHO$), and then into acetic acid (by the oxidation of the $-CHO$ group to $-COOH$). Since, therefore, glycol contains two $-CH_2{\cdot}OH$ groups, each of which may undergo these changes, it might be foretold that, on oxidation, glycol would probably yield several compounds, according as one or both the $-CH_2{\cdot}OH$ groups were attacked. This also is the fact; on oxidation with nitric acid glycol yields the following compounds:



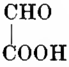
$$\begin{array}{l} CH_2{\cdot}OH \\ | \\ COOH \end{array}$$

Glycollic Acid.



$$\begin{array}{l} CHO \\ | \\ CHO \end{array}$$

Glyoxal.



$$\begin{array}{l} CHO \\ | \\ COOH \end{array}$$

Glyoxylic Acid.

$$\begin{array}{l} COOH \\ | \\ COOH \end{array}$$

Oxalic Acid.

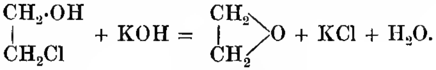
These examples show clearly that the constitution of any substance having been ascertained from a study of some of its reactions, its behaviour under given conditions may be foretold with tolerable certainty; in other words, the general reactions and the constitutional formulæ of organic compounds are the most important points to bear in mind.

When an olefine is treated with hypochlorous acid, direct combination ensues, and a *chlorohydrin* is formed,

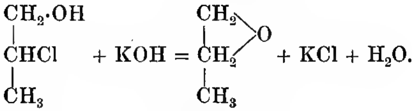
$$\underset{\text{Ethylene.}}{CH_2{:}CH_2} + HOCl = \underset{\text{Ethylene Chlorohydrin.}}{OH{\cdot}CH_2{\cdot}CH_2Cl}$$

$$\underset{\text{Propylene.}}{CH_3{\cdot}CH{:}CH_2} + HOCl = \underset{\text{Propylene Chlorohydrin.}}{CH_3{\cdot}CHCl{\cdot}CH_2{\cdot}OH.}$$

These chlorohydrins are usually readily acted on by alkalies, being converted into oxides by loss of one molecule of hydrogen chloride, a change which recalls the conversion of ethyl bromide into ethylene,



Ethylene Oxide.



Propylene Oxide.

Ethylene oxide is isomeric with aldehyde, C_2H_4O; it is a liquid, boils at 13·5°, and is slowly decomposed by water, being converted into glycol.

OXIDATION PRODUCTS OF THE GLYCOLS.

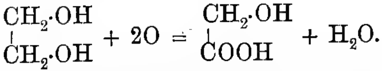
Glyoxal, CHO·CHO, is produced by the oxidation of glycol, but it is usually prepared by slowly oxidising alcohol or aldehyde with nitric acid,

$$CH_3{\cdot}CHO + 2O = CHO{\cdot}CHO + H_2O.$$

It is an amorphous substance, readily soluble in alcohol and ether; it shows all the properties of an aldehyde, reduces ammoniacal silver nitrate, and combines with sodium bisulphite to form a crystalline compound of the composition $C_2H_2O_2, 2NaHSO_3 + H_2O$. It also combines with hydroxylamine and with phenylhydrazine, giving the compounds $HON{:}CH{\cdot}CH{:}NOH$ and $C_6H_5N_2H{:}CH{\cdot}CH{:}N_2HC_6H_5$.

Hydroxycarboxylic Acids.

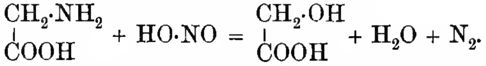
Glycollic acid, $OH{\cdot}CH_2{\cdot}COOH$, may be obtained by the oxidation of glycol, $OH{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, with nitric acid, just as acetic acid is produced by the oxidation of alcohol, $CH_3{\cdot}CH_2{\cdot}OH$,



$$\begin{matrix} CH_2{\cdot}OH \\ | \\ CH_2{\cdot}OH \end{matrix} + 2O = \begin{matrix} CH_2{\cdot}OH \\ | \\ COOH \end{matrix} + H_2O.$$

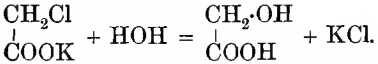
As, however, several other substances are formed, the isolation of the acid from the oxidation product is very troublesome.

It is also formed when amido-acetic acid (glycine, p. 292) is treated with nitrous acid, a reaction exactly analogous to the conversion of ethylamine into alcohol,



$$\begin{array}{l}\mathrm{CH_2{\cdot}NH_2}\\ |\\ \mathrm{COOH}\end{array} + \mathrm{HO{\cdot}NO} = \begin{array}{l}\mathrm{CH_2{\cdot}OH}\\ |\\ \mathrm{COOH}\end{array} + \mathrm{H_2O} + \mathrm{N_2}.$$

Glycollic acid is prepared by boiling the potassium salt of chloracetic acid with water, when the hydroxyl-group is substituted for one atom of chlorine, just as in the formation of alcohol from ethyl chloride,



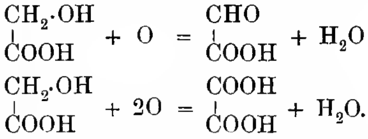
$$\begin{array}{l}\mathrm{CH_2Cl}\\ |\\ \mathrm{COOK}\end{array} + \mathrm{HOH} = \begin{array}{l}\mathrm{CH_2{\cdot}OH}\\ |\\ \mathrm{COOH}\end{array} + \mathrm{KCl}.$$

The solution is evaporated to dryness, and the residue extracted with acetone, which dissolves the glycollic acid, but not the potassium chloride.

Glycollic acid is a crystalline, hygroscopic substance, and melts at 80°; it is readily soluble in water, alcohol, and ether. Assuming that its constitution is correctly represented by the formula given above, and of this there can be little doubt when its methods of formation are carefully considered, it is almost unnecessary to describe at length the chemical behaviour of glycollic acid, because this is expressed by its constitutional formula.

Glycollic acid contains one carboxyl-group; therefore, like the fatty acids, it is a monobasic acid, neutralises carbonates, and forms salts with metallic hydroxides and with alcohols.

Glycollic acid also contains one $-CH_2{\cdot}OH$ group; therefore it behaves like a primary alcohol, as well as like an acid. On oxidation, for example, it yields glyoxylic acid and oxalic acid, just as alcohol gives aldehyde and acetic acid,



$$\begin{array}{l}\mathrm{CH_2{\cdot}OH}\\ |\\ \mathrm{COOH}\end{array} + \mathrm{O} = \begin{array}{l}\mathrm{CHO}\\ |\\ \mathrm{COOH}\end{array} + \mathrm{H_2O}$$

$$\begin{array}{l}\mathrm{CH_2{\cdot}OH}\\ |\\ \mathrm{COOH}\end{array} + 2\mathrm{O} = \begin{array}{l}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{array} + \mathrm{H_2O}.$$

Even when the hydrogen atom of the carboxyl-group has been displaced, glycollic acid still contains one atom of hydrogen, which, like that in alcohols, may be displaced by the alkali metals and by the acetyl-group; ethyl glycollate, for example, is readily converted into an acetyl-derivative on treatment with acetyl chloride,

$$\begin{array}{l} CH_2\cdot OH \\ | \\ COOC_2H_5 \end{array} + CH_3\cdot COCl = \begin{array}{l} CH_2\cdot O\cdot CO\cdot CH_3 \\ | \\ COOC_2H_5 \end{array} + HCl.$$

Homologues of Glycollic Acid.—Glycollic acid may be regarded as hydroxyacetic acid, or acetic acid in which a hydroxyl-group has been substituted for one atom of hydrogen; as, moreover, other fatty acids yield similar hydroxyl-derivatives, a homologous series of *hydroxycarboxylic acids* may be obtained.

The more important members of the series are :

Glycollic acid, or hydroxyacetic acid, $OH\cdot CH_2\cdot COOH$.
Lactic acid, or hydroxypropionic acid, $OH\cdot C_2H_4\cdot COOH$.

These compounds may also be regarded as oxidation products of the glycols; just as glycollic acid is formed on oxidising ethylene glycol, so the higher members of the series may be obtained from the corresponding glycols by oxidising a $-CH_2\cdot OH$ group to $-COOH$.

The lowest member of this series, carbonic acid or hydroxyformic acid, $OH\cdot COOH$, is not known in the free state, since, when liberated from its salts, it immediately loses water, and is converted into the anhydride, carbon dioxide.

The third member of the series exists in two isomeric forms—namely, as α- and β-hydroxypropionic acid; these isomerides are related to propionic acid, in the manner shown by the following formulæ :

$$CH_3\cdot CH_2\cdot COOH$$

Propionic Acid.

$$CH_3\cdot CH(OH)\cdot COOH \qquad CH_2(OH)\cdot CH_2\cdot COOH.$$

α-Hydroxypropionic or Lactic Acid. β-Hydroxypropionic or Hydracrylic Acid.

Lactic acid, or α-hydroxypropionic acid, $C_3H_6O_3$, or

$$CH_3\cdot CH(OH)\cdot COOH,$$

is formed during the lactic fermentation of sugar, starch, and other substances in presence of nitrogenous animal matter, and occurs in sour milk. It can be obtained by methods analogous to those given in the case of glycollic acid—namely, by oxidising $\alpha\beta$-propylene glycol with nitric acid,

$$\mathrm{CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}OH + 2O = CH_3{\cdot}CH(OH){\cdot}COOH + H_2O},$$

by heating α-chloro- or α-bromo-propionic acid with water, alkalies, or silver hydroxide,

$$\mathrm{CH_3{\cdot}CHBr{\cdot}COOH + H_2O = CH_3{\cdot}CH(OH){\cdot}COOH + HBr},$$

and by treating α-amido-propionic acid with nitrous acid,

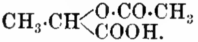
$$\mathrm{CH_3{\cdot}CH(NH_2){\cdot}COOH + HO{\cdot}NO = CH_3{\cdot}CH(OH){\cdot}COOH + N_2 + H_2O}.$$

It is prepared by the lactic fermentation of sugar (see butyric acid, p. 156), or simply by heating sugar with alkalies. Lactic acid is a thick, sour, hygroscopic liquid, miscible with water, alcohol, and ether in all proportions; it cannot be distilled as it undergoes decomposition into aldehyde, water, carbon monoxide, and other products. When heated with dilute sulphuric acid, it is decomposed into aldehyde and formic acid, a fact which shows that, compared with the fatty acids, lactic acid is very unstable,

$$\mathrm{CH_3{\cdot}CH(OH){\cdot}COOH = CH_3{\cdot}CHO + H{\cdot}COOH}.$$

Lactic acid is a monocarboxylic acid, and forms metallic and ethereal salts.

Calcium lactate, $\mathrm{[CH_3{\cdot}CH(OH){\cdot}COO]_2Ca + 5H_2O}$, and *zinc lactate*, $\mathrm{(C_3H_5O_3)_2Zn + 3H_2O}$, are crystalline, and readily soluble in hot water. *Ethyl lactate*, $\mathrm{CH_3{\cdot}CH(OH){\cdot}COOC_2H_5}$, is a neutral liquid, but, since it contains a $\mathrm{>CH(OH)}$ group, it yields metallic derivatives with potassium and sodium, and, like other hydroxyl-compounds, it interacts with acetyl chloride, giving *ethyl acetyl-lactate*, $\mathrm{CH_3{\cdot}CH(O{\cdot}C_2H_3O){\cdot}COOC_2H_5}$, an ethereal salt of acetyl-lactic acid,



$\mathrm{CH_3{\cdot}CH}\Big<\begin{matrix}\mathrm{O{\cdot}CO{\cdot}CH_3}\\ \mathrm{COOH}\end{matrix}.$

Lactic acid also contains the group $\mathrm{>CH{\cdot}OH}$, and shows, therefore, most of the reactions of a secondary alcohol. When, for example, it is heated with concentrated hydrobromic acid, it is converted into α-bromo-propionic acid, just as isopropyl alcohol gives isopropyl bromide,

$$CH_3{\cdot}CH(OH){\cdot}COOH + HBr = CH_3{\cdot}CHBr{\cdot}COOH + H_2O;$$

with concentrated hydriodic acid, however, it yields propionic acid, because the α-iodo-propionic acid which is first produced is reduced by the excess of hydriodic acid,

$$CH_3{\cdot}CHI{\cdot}COOH + HI = CH_3{\cdot}CH_2{\cdot}COOH + I_2.$$

On oxidation with potassium permanganate, lactic acid again behaves like a secondary alcohol, and is converted into pyruvic acid, just as isopropyl alcohol gives acetone,

$$CH_3{\cdot}CH(OH){\cdot}COOH + O = CH_3{\cdot}CO{\cdot}COOH + H_2O.$$

Sarcolactic acid, or *paralactic acid*, $C_3H_6O_3$, is the name given to an acid which occurs in animals, more especially in the muscle juices, and which is best prepared from extract of meat. It has the same constitution as lactic acid, because it undergoes the same chemical changes, and differs from it only in being optically active (part ii.).

Hydracrylic acid, or β-hydroxypropionic acid, $C_3H_6O_3$, or

$$CH_2(OH){\cdot}CH_2{\cdot}COOH,$$

is not formed during lactic fermentation, but may be obtained by reactions exactly similar to those which give the corresponding α-acid—namely, by oxidising αγ-propylene glycol, and by boiling β-chloro-, bromo-, or iodo-propionic acid, $CH_2X{\cdot}CH_2{\cdot}COOH$, with water or weak alkalies.

It is a thick, sour syrup, and, when heated alone or with moderately dilute sulphuric acid, it is converted into acrylic acid (p. 257), with loss of the elements of water, a change analogous to the conversion of ethyl alcohol into ethylene,

$$CH_2(OH){\cdot}CH_2{\cdot}COOH = CH_2{:}CH{\cdot}COOH + H_2O.$$

In most respects hydracrylic behaves like lactic acid; it is a monocarboxylic acid, but also contains a $-CH_2{\cdot}OH$ group, so that it shows most of the reactions of a primary alcohol as well as those of a monobasic acid; on oxidation with chromic acid, for example, it yields malonic acid,

$$CH_2(OH){\cdot}CH_2{\cdot}COOH + 2O = COOH{\cdot}CH_2{\cdot}COOH + H_2O.$$

Constitutions of the Hydroxypropionic Acids.—Since lactic acid and hydracrylic acid are both hydroxymonocarboxylic acids of the molecular composition $C_3H_6O_3$, and only two formulæ—namely,

$$\underset{\text{I.}}{CH_3{\cdot}CH(OH){\cdot}COOH} \quad \text{and} \quad \underset{\text{II.}}{CH_2(OH){\cdot}CH_2{\cdot}COOH}$$

—can be constructed, making the usual assumptions regarding valency, all that is necessary is to determine which represents the one and which the other acid. This point is, of course, already settled if the constitutions of the chloro-propionic or amido-propionic acids be taken as known; supposing, however, this were not the case, the following syntheses of the hydroxy-acids establish their constitutions.

When aldehyde is treated with hydrocyanic acid, direct combination occurs, and the product is converted into lactic acid on boiling it with hydrochloric acid,

$$CH_3{\cdot}CH(OH){\cdot}CN + 2H_2O = CH_3{\cdot}CH(OH){\cdot}COOH + NH_3.$$

Lactic acid, therefore, is represented by formula I., a conclusion which is fully borne out by all other facts.

When ethylene is treated with an aqueous solution of hypochlorous acid, glycol chlorohydrin is formed (p. 222); this compound interacts with potassium cyanide in dilute alcoholic solution, giving glycol cyanohydrin,

$$CH_2(OH){\cdot}CH_2Cl + KCN = CH_2(OH){\cdot}CH_2{\cdot}CN + KCl,$$

which, when boiled with mineral acids, is converted into hydracrylic acid,

$$CH_2(OH){\cdot}CH_2{\cdot}CN + 2H_2O = CH_2(OH){\cdot}CH_2{\cdot}COOH + NH_3.$$

Hydracrylic acid, therefore, is represented by formula II.

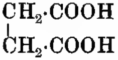
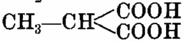
Since, moreover, aldehyde and ethylene may be prepared from their elements, this is also true as regards the two hydroxypropionic acids.

Lactic acid is sometimes called *ethylidenelactic acid*, hydracrylic acid being named *ethylenelactic acid;* these names serve to recall the facts that lactic acid contains the ethylidene group $CH_3 \cdot CH{<}$, hydracrylic acid the ethylene group $-CH_2 \cdot CH_2-$.

Dicarboxylic Acids.

Glycollic acid, $CH_2(OH) \cdot COOH$, being derived from ethylene glycol, $CH_2(OH) \cdot CH_2 \cdot OH$, by the oxidation of *one* of the $-CH_2 \cdot OH$ groups, it might be concluded that the *other* $-CH_2 \cdot OH$ group would be capable of undergoing a similar change; this is found to be so, since on further oxidation glycollic acid is converted into oxalic acid, $COOH \cdot COOH$. As, moreover, other glycols, such as $\alpha\gamma$-propylene glycol, $CH_2(OH) \cdot CH_2 \cdot CH_2 \cdot OH$, which contain two $-CH_2 \cdot OH$ groups, behave in the same way as ethylene glycol, it is possible to prepare a homologous series of *dicarboxylic* acids of the general formula $C_nH_{2n}(COOH)_2$. These compounds may also be considered as derived from the fatty acids by the substitution of the carboxyl-group for one atom of hydrogen, and, since they contain two such groups, they are dibasic acids.

The most important members of this series are:

Oxalic, or carboxyformic acid	$C_2H_2O_4$ or	 $\begin{array}{l} COOH \\ \vert \\ COOH \end{array}$
Malonic, or carboxyacetic acid	$C_3H_4O_4$ or	 $CH_2{<}\begin{array}{l} COOH \\ COOH \end{array}$
Succinic, or β-carboxypropionic acid	$C_4H_6O_4$ or	 $\begin{array}{l} CH_2 \cdot COOH \\ \vert \\ CH_2 \cdot COOH \end{array}$
Isosuccinic, or α-carboxypropionic acid	$C_4H_6O_4$ or	 $CH_3-CH{<}\begin{array}{l} COOH \\ COOH \end{array}$
Glutaric acid	$C_5H_8O_4$	
Adipic acid	$C_6H_{10}O_4$	

Oxalic acid, $C_2H_2O_4$, or  $\begin{array}{l} COOH \\ \vert \\ COOH \end{array}$, occurs in rhubarb (*rheum*), the dock (*rumex*), sorrel (*oxalis acetosella*), and other plants, usually in the form of its potassium hydrogen salt, or as calcium oxalate; it is formed when alcohol, glycol, sugar, fats, and a great many other organic substances are oxidised with nitric acid, and may be obtained by numerous reactions, of which the following are the most instructive:

It is formed when sodium is heated at about 350° in a stream of carbon dioxide,

$$2CO_2 + 2Na = \underset{\text{Sodium Oxalate.}}{C_2O_4Na_2},$$

and when sodium or potassium formate is quickly heated to about 440°,

$$2H{\cdot}COONa = C_2O_4Na_2 + H_2;$$

it is also produced, together with many other compounds, when an aqueous solution of cyanogen (p. 277) is kept for some time, a change which is analogous to the conversion of methyl cyanide into acetic acid,

$$(CN)_2 + 4H_2O = \underset{\text{Ammonium Oxalate.}}{C_2O_4(NH_4)_2}.$$

Each of these three reactions affords a means of synthesing oxalic acid from its elements, since carbon dioxide, formic acid, and cyanogen may be obtained from their elements.

Oxalic acid may be prepared by gently warming cane-sugar with about six times its weight of concentrated nitric acid.

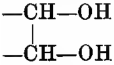
The operation is performed in a good draught cupboard, and as soon as brown fumes appear the heating is discontinued, in spite of which oxidation proceeds very vigorously; after some time, as the solution cools, crystals of oxalic acid are deposited. The solution is decanted or filtered through glass wool, and the oxalic acid purified by crystallisation from boiling water; further quantities may be obtained from the acid mother-liquors.

Oxalic acid is prepared on the large scale from sawdust, which contains organic compounds (cellulose, lignin, &c.) somewhat similar in composition to cane-sugar, and which, when heated with alkalies, undergo profound decomposition.

The sawdust is made into a paste with a concentrated solution of a mixture of equal parts of potash and soda, and then heated in iron pans at about 210°; afterwards the mass is treated with water, the solution of potassium and sodium oxalates boiled with lime, the precipitated calcium oxalate washed with water and decomposed with dilute sulphuric acid,

$$C_2O_4Ca + H_2SO_4 = C_2O_4H_2 + CaSO_4;$$

the solution of oxalic acid is then filtered from the calcium sulphate and evaporated to crystallisation. The acid obtained in this way contains small quantities of potassium and sodium hydrogen oxalates, from which it is separated only with great difficulty, so that on ignition it gives a residue of alkali carbonates; the pure acid is most conveniently prepared from cane-sugar. The formation of oxalic acid from sawdust and from sugar cannot be expressed by a simple equation; in both cases a complex molecule containing



$$\begin{array}{l}—CH—OH\\ \quad|\\ —CH—OH\end{array}$$

groups undergoes simultaneous decomposition and oxidation.

Oxalic acid crystallises in colourless prisms, which contain two molecules of water; it is readily soluble in alcohol and moderately so in water, but only sparingly in ether. When quickly heated, it melts at about 100° and loses its water; the anhydrous acid sublimes at about 150°, but, if heated too strongly, it decomposes into carbon dioxide and formic acid, or its decomposition products,

$$C_2O_4H_2 = H{\cdot}COOH + CO_2 = H_2O + CO + CO_2;$$

the anhydrous acid is very hygroscopic, and a powerful dehydrating agent.

Oxalic acid is decomposed by concentrated sulphuric acid, but only on heating moderately strongly (distinction from formic acid),

$$C_2O_4H_2 = CO_2 + CO + H_2O;$$

it is a feeble reducing agent, precipitates gold from its solutions, and is readily oxidised by warm potassium permanganate (or chlorine water), being converted into carbon dioxide and water, a reaction which is employed for the volumetric estimation of oxalic acid and also in standardising permanganate solutions,

$$C_2O_4H_2 + O = 2CO_2 + H_2O.$$

Oxalic acid is dibasic, and forms salts with two equivalents of a metallic hydroxide, and with two molecules of a monohydric alcohol; it has an acid reaction, decomposes carbonates, and dissolves certain metallic oxides. The salts of the alkalies are readily soluble in hot water, but most of the other salts are sparingly soluble or insoluble.

Ammonium oxalate, $C_2O_4(NH_4)_2$, is decomposed into oxamide when carefully heated, just as ammonium acetate yields acetamide,

$$\begin{matrix} COONH_4 \\ | \\ COONH_4 \end{matrix} = \begin{matrix} CO{\cdot}NH_2 \\ | \\ CO{\cdot}NH_2 \end{matrix} + 2H_2O.$$

Potassium oxalate, $C_2O_4K_2 + H_2O$, is readily soluble in water, but *potassium hydrogen oxalate*, C_2O_4KH, a salt which occurs in many plants, is more sparingly soluble; the latter forms with oxalic acid a crystalline compound of the composition $C_2O_4KH + C_2O_4H_2 + 2H_2O$, known as 'salts of sorrel,' or potassium quadroxalate; this salt is used in removing iron-mould and ink-stains, as it converts the iron into soluble iron potassium oxalate.

Silver oxalate, $C_2O_4Ag_2$, is obtained in crystals on adding silver nitrate to a neutral solution of an oxalate; it is only sparingly soluble in water, and explodes when quickly heated in the dry state, leaving a residue of silver.

Calcium oxalate, $C_2O_4Ca + H_2O$, occurs in crystals in the cells of various plants, and is obtained as a white precipitate on adding a solution of a calcium salt to a neutral or ammoniacal solution of an oxalate; it is insoluble in water, and also in acetic acid, whereas magnesium oxalate is soluble in the latter, a fact which is made use of in the separation of the two metals. Oxalic acid and its salts are used to a considerable extent in the manufacture of organic dyes, in calico-printing, in photography (as developers), and in analytical chemistry. The metallic salts of oxalic acid are all decomposed by dilute mineral acids, yielding oxalic acid, whereas, when heated with concentrated sulphuric acid, they give carbon dioxide, carbon monoxide, water, and a sulphate. Oxalic acid and its soluble salts are poisonous. The detection of oxalic acid or of an oxalate is chiefly based on (*a*) the behaviour of the neutral solution with calcium chloride, and the insolubility of the precipitate in acetic acid; (*b*) the behaviour of the dry substance with sulphuric acid.

Methyl oxalate, $C_2O_4(CH_3)_2$, is a colourless, crystalline compound, melting at 54°, and is easily prepared by boiling anhydrous oxalic acid with methyl alcohol; it is readily hydrolysed by alkalies and boiling water, and is sometimes employed in the preparation of pure methyl alcohol.

Ethyl oxalate, $C_2O_4(C_2H_5)_2$, can be obtained in a similar manner; it is a pleasant-smelling liquid, boiling at 181°, and sparingly soluble in water. It is a curious fact that the methyl salts of organic acids are frequently crystalline, even when the ethyl, propyl, butyl, &c., salts are liquid at ordinary temperatures.

The *constitution* of oxalic acid is determined by its formation from glycol, glycollic acid, and formates; it may be regarded as composed of two carboxyl-groups, and is for this reason sometimes called dicarboxyl.

Probably owing to the fact that oxalic acid is very rich in oxygen, it is a comparatively unstable compound; its *anhydride* is unknown, and, when treated with phosphorus pentachloride, instead of yielding the chloride, $\begin{array}{c}COCl\\ |\\ COCl\end{array}$, as might have been expected, oxalic acid is decomposed into the oxides of carbon and water.

Oxamide, $\begin{array}{c}CO{\cdot}NH_2\\ |\\ CO{\cdot}NH_2\end{array}$, is formed as an intermediate product in the conversion of cyanogen into ammonium oxalate (p. 278), also when ammonium oxalate is heated. It is prepared by shaking methyl or ethyl oxalate with concentrated ammonia, a method very generally employed in the preparation of amides from ethereal salts.

$$C_2O_4(C_2H_5)_2 + 2NH_3 = C_2O_2(NH_2)_2 + 2C_2H_5{\cdot}OH.$$

It is a colourless, crystalline powder, insoluble in water; when heated with water, alkalies, or mineral acids, it is converted into oxalic acid or an oxalate, a change exactly analogous to that undergone by acetamide (p. 162),

$$C_2O_2(NH_2)_2 + 2H_2O = C_2O_4H_2 + 2NH_3.$$

If methyl oxalate be treated with an aqueous solution of a primary or secondary amine instead of with ammonia, alkyl substitution products of oxamide or of oxamic acid, $NH_2{\cdot}CO{\cdot}COOH$, respectively are formed (compare amines, p. 206).

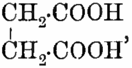
Malonic acid, $CH_2(COOH)_2$, the next homologue of oxalic acid, has already been mentioned, and the preparation of its ethyl salt from chloracetic acid has been described (p. 196).

If instead of the ethyl salt the free acid be required, the product of the action of potassium cyanide on potassium chloracetate is mixed with twice its volume of concentrated hydrochloric acid, and the solution saturated with hydrogen chloride; the clear liquid is then decanted from the precipitated potassium chloride, evaporated to dryness on a water-bath, and the malonic acid extracted from the residue by digesting with ether.

Malonic acid is a colourless, crystalline substance, readily soluble in water; it melts at 132°, and at higher temperatures undergoes decomposition into acetic acid and carbon dioxide,

$$CH_2(COOH)_2 = CH_3{\cdot}COOH + CO_2.$$

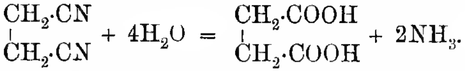
Other dicarboxylic acids, in which *both* the carboxyl-groups are united to one and the same carbon atom, are decomposed in a similar manner under the influence of heat.

Succinic acid, $C_4H_6O_4$, or  $\begin{array}{l}CH_2{\cdot}COOH\\ \vert\\ CH_2{\cdot}COOH\end{array}$, occurs in amber, and also in smaller quantities in lignite (fossil-wood), in many plants, and in certain animal secretions. It is formed during the alcoholic fermentation of sugar, and in several other fermentation processes; also when fats are oxidised with nitric acid.

It can be obtained from its elements in the following manner: acetylene, which can be prepared from carbon and hydrogen, is reduced to ethylene, the latter passed into bromine, and the ethylene dibromide thus produced boiled with potassium cyanide in aqueous alcoholic solution, when ethylene dicyanide is formed,

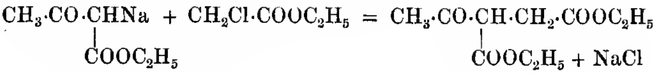
$$C_2H_4Br_2 + 2KCN = C_2H_4(CN)_2 + 2KBr;$$

this compound is decomposed by boiling it with alkalies or mineral acids, succinic acid and ammonia being obtained,

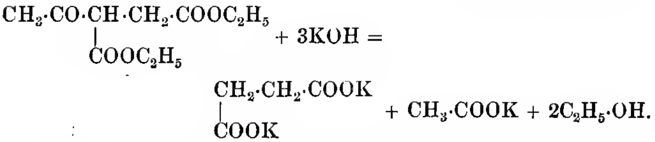


$$\begin{array}{l} CH_2\cdot CN \\ | \\ CH_2\cdot CN \end{array} + 4H_2O = \begin{array}{l} CH_2\cdot COOH \\ | \\ CH_2\cdot COOH \end{array} + 2NH_3.$$

It may also be prepared synthetically from ethyl acetoacetate (or ethyl malonate) and ethyl chloracetate,



$$\begin{array}{l} CH_3\cdot CO\cdot CHNa \\ \qquad\quad | \\ \qquad\quad COOC_2H_5 \end{array} + CH_2Cl\cdot COOC_2H_5 = \begin{array}{l} CH_3\cdot CO\cdot CH\cdot CH_2\cdot COOC_2H_5 \\ \qquad\quad | \\ \qquad\quad COOC_2H_5 + NaCl \end{array}$$



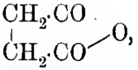
$$\begin{array}{l} CH_3\cdot CO\cdot CH\cdot CH_2\cdot COOC_2H_5 \\ \qquad\quad | \\ \qquad\quad COOC_2H_5 \end{array} + 3KOH = \begin{array}{l} CH_2\cdot CH_2\cdot COOK \\ | \\ COOK \end{array} + CH_3\cdot COOK + 2C_2H_5\cdot OH.$$

Succinic acid is usually prepared by distilling amber from iron retorts; the dark-brown oily distillate is evaporated, and the dirty-brown crystalline residue of succinic acid purified by recrystallisation from hot dilute nitric acid.

Succinic acid crystallises in colourless prisms, melts at 180°, and sublimes readily; it has an acid, unpleasant taste, and is only sparingly soluble in cold water, alcohol, and ether. It is a dibasic acid, and its salts, the **succinates,** with the exception of those of the alkalies, are sparingly soluble or insoluble in water.

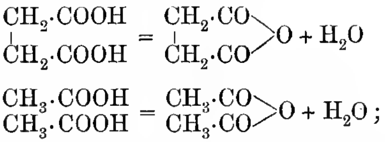
Ammonium succinate, $C_4H_4O_4(NH_4)_2$, is sometimes employed in the separation of iron from manganese, as, on adding a solution of a ferric salt to ammonium succinate, the whole of the iron is converted into an insoluble basic salt, which is obtained as a buff precipitate.

The *constitution* of succinic acid is determined by its formation from ethylene dibromide, and by the fact that the only alternative formula for a dicarboxylic acid of the molecular composition $C_4H_6O_4$ must be assigned to isosuccinic acid (see below).

Succinic anhydride,  $\left.\begin{matrix}CH_2\cdot CO\\ |\\ CH_2\cdot CO\end{matrix}\right>O$, is formed when succinic acid is distilled, $C_4H_6O_4 = C_4H_4O_3 + H_2O$, but a large proportion of the acid passes over unchanged. It is prepared by heating the acid with phosphorus oxychloride for some time and then distilling, the oxychloride combining with the water which is produced, and thus preventing the reconversion of the anhydride into the acid; phosphorus pentoxide, acetyl chloride, or some other dehydrating agent may be used in the place of the oxychloride.

Succinic anhydride is a colourless, crystalline substance, and melts at 120°; it resembles the anhydrides of the fatty acids in chemical properties, and when boiled with water or alkalies, it is reconverted into succinic acid or a succinate.

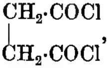
Succinic anhydride differs from the anhydrides of fatty acids in this, that it is formed from *one* molecule of the acid with elimination of one molecule of water, whereas the anhydride of a fatty acid is produced from *two* molecules of the acid in a similar manner,

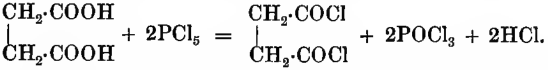


$$\begin{matrix}CH_2\cdot COOH\\ |\\ CH_2\cdot COOH\end{matrix} = \left.\begin{matrix}CH_2\cdot CO\\ |\\ CH_2\cdot CO\end{matrix}\right>O + H_2O$$

$$\begin{matrix}CH_3\cdot COOH\\ CH_3\cdot COOH\end{matrix} = \left.\begin{matrix}CH_3\cdot CO\\ CH_3\cdot CO\end{matrix}\right>O + H_2O\,;$$

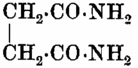
the constitution of succinic anhydride is therefore expressed by the above formula, which recalls the fact that *both* the carboxyl-groups take part in the change, as is shown by the neutral character of the anhydride. Many other dicarboxylic acids are converted into their anhydrides in a similar manner.

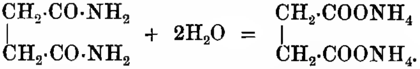
Succinyl chloride,*  $\begin{array}{l}CH_2\cdot COCl\\ |\\ CH_2\cdot COCl\end{array}$, is formed when succinic acid is treated with two molecules of phosphorus pentachloride, the interaction recalling that which occurs in the formation of acetyl chloride,



$$\begin{array}{l}CH_2\cdot COOH\\ |\\ CH_2\cdot COOH\end{array} + 2PCl_5 = \begin{array}{l}CH_2\cdot COCl\\ |\\ CH_2\cdot COCl\end{array} + 2POCl_3 + 2HCl.$$

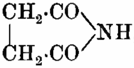
It is a colourless liquid, boils at 190°, and resembles acetyl chloride in chemical properties; like the latter, it is decomposed by water, alkalies, and hydroxy-compounds, yielding succinic acid or a succinate.

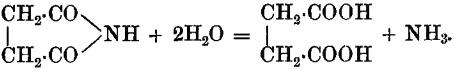
Succinamide,  $\begin{array}{l}CH_2\cdot CO\cdot NH_2\\ |\\ CH_2\cdot CO\cdot NH_2\end{array}$, is prepared by shaking ethyl succinate with concentrated ammonia; it is a crystalline substance, melts at 242–243°, and is only very sparingly soluble in cold water. When heated with water, it is slowly converted into ammonium succinate, just as oxamide is converted into ammonium oxalate,



$$\begin{array}{l}CH_2\cdot CO\cdot NH_2\\ |\\ CH_2\cdot CO\cdot NH_2\end{array} + 2H_2O = \begin{array}{l}CH_2\cdot COONH_4\\ |\\ CH_2\cdot COONH_4.\end{array}$$

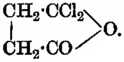
Succinamide cannot be obtained by distilling ammonium succinate, although oxamide and acetamide are produced by the distillation of the corresponding ammonium salts; this fact shows that it is not always safe to judge by analogy, since compounds very closely related in constitution may, in certain respects, behave very differently. When, in fact, ammonium succinate or succinamide is heated, it is converted into succinimide.

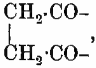
Succinimide,  $\left.\begin{array}{l}CH_2\cdot CO\\ |\\ CH_2\cdot CO\end{array}\right>NH$, is also formed when succinic anhydride is heated in a stream of dry ammonia; it is readily soluble in water, from which it crystallises with one molecule of water, the anhydrous substance melting at 126°. When boiled with water, alkalies, or mineral acids, it is converted into succinic acid,

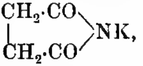


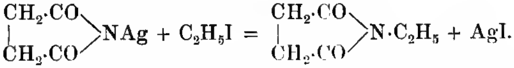
$$\left.\begin{array}{l}CH_2\cdot CO\\ |\\ CH_2\cdot CO\end{array}\right>NH + 2H_2O = \begin{array}{l}CH_2\cdot COOH\\ |\\ CH_2\cdot COOH\end{array} + NH_3.$$

---

* The constitution of succinyl chloride is not definitely established, certain facts pointing to the formula  $\left.\begin{array}{l}CH_2\cdot CCl_2\\ |\\ CH_2\cdot CO\end{array}\right>O$.

The constitution of succinimide, as expressed by the above formula, is based principally on its methods of formation; it may be regarded as a di-substitution product of ammonia—that is to say, as ammonia in which two atoms of hydrogen have been displaced by the divalent *succinyl*-group  $\begin{matrix}CH_2\cdot CO-\\ |\\ CH_2\cdot CO-\end{matrix}$, just as an amide is a mono-substitution product of ammonia. Many other dicarboxylic acids yield *imides* similar in constitution to succinimide.

Although succinimide is not an acid in the ordinary sense of the word, has a neutral reaction, and does not decompose carbonates, it contains one atom of hydrogen displaceable by metals. When, for example, a solution of potash in alcohol is added to an alcoholic solution of succinimide, a crystalline derivative, *potassium succinimide*,  $\begin{matrix}CH_2\cdot CO\\ |\\ CH_2\cdot CO\end{matrix}\!\!>\!NK$, is produced; this compound interacts with silver nitrate, giving *silver succinimide*, and the latter, on treatment with ethyl iodide, yields *ethyl succinimide*,



$$\begin{matrix}CH_2\cdot CO\\ |\\ CH_2\cdot CO\end{matrix}\!\!>\!NAg + C_2H_5I = \begin{matrix}CH_2\cdot CO\\ |\\ CH_2\cdot CO\end{matrix}\!\!>\!N\cdot C_2H_5 + AgI.$$

It has already been pointed out, that hydrogen in combination with *carbon* becomes displaceable by metals when the carbon atom is directly united with two $>CO$ groups, as in ethyl acetoacetate and ethyl malonate. From the behaviour of succinimide, and of other imides, it is found that the hydrogen atom of an imido-group $>NH$ is also displaceable by metals when the imido-group is directly united with two $>CO$ groups.

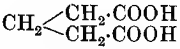
Isosuccinic acid, $CH_3\cdot CH(COOH)_2$, is isomeric with succinic acid; it may be prepared by treating an alcoholic solution of the sodium derivative of ethyl malonate with methyl iodide, and hydrolysing the product, a reaction which shows that isosuccinic acid is methylmalonic acid,

$$CHNa(COOC_2H_5)_2 + CH_3I = CH_3\cdot CH(COOC_2H_5)_2 + NaI.$$

It is a crystalline substance, sublimes readily, and melts at 130°; it does not form an anhydride, and when heated alone, or with water, it is decomposed into propionic acid and carbon dioxide, just as malonic acid gives acetic acid and carbon dioxide,

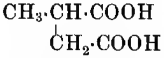
$$CH_3\cdot CH(COOH)_2 = CH_3\cdot CH_2\cdot COOH + CO_2.$$

The higher members of this series of dicarboxylic acids exist in several isomeric forms; four acids of the composition $C_5H_8O_4$, for example, are theoretically possible, and four are actually known—namely,



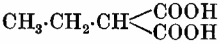
$$CH_2<\begin{matrix}CH_2\cdot COOH\\ CH_2\cdot COOH\end{matrix}$$

Normal Glutaric Acid.



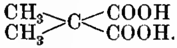
$$\begin{matrix}CH_3\cdot CH\cdot COOH\\ |\\ CH_2\cdot COOH\end{matrix}$$

Pyrotartaric Acid or
Methylsuccinic Acid.



$$CH_3\cdot CH_2\cdot CH<\begin{matrix}COOH\\ COOH\end{matrix}$$

Ethylmalonic Acid.



$$\begin{matrix}CH_3\\ CH_3\end{matrix}>C<\begin{matrix}COOH\\ COOH.\end{matrix}$$

Dimethylmalonic Acid.

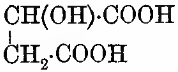
Adipic acid, $C_6H_{10}O_4$, is of some importance, as it is often obtained on oxidising fats with nitric acid; it may be produced synthetically by heating β-iodo-propionic acid with finely divided silver, the reaction being analogous to the production of ethane by the action of sodium or zinc on methyl iodide,

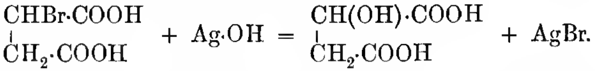
$$2CH_2I\cdot CH_2\cdot COOH + 2Ag = COOH\cdot[CH_2]_4\cdot COOH + 2AgI;$$

it is a crystalline substance, melting at 148°.

Hydroxydicarboxylic Acids.

With the exception of oxalic acid, the dicarboxylic acids just considered are capable of yielding substitution products in exactly the same way as the fatty acids; malonic acid, for example, may be converted into chloromalonic acid, $CHCl(COOH)_2$, hydroxymalonic acid, $HO\cdot CH(COOH)_2$, &c.; succinic acid into bromosuccinic acid, $COOH\cdot CHBr\cdot CH_2\cdot COOH$, dibromosuccinic acid, $COOH\cdot CHBr\cdot CHBr\cdot COOH$, hydroxysuccinic acid, $COOH\cdot CH(OH)\cdot CH_2\cdot COOH$, dihydroxysuccinic acid, $COOH\cdot CH(OH)\cdot CH(OH)\cdot COOH$, and so on. Some of these compounds—namely, the hydroxy-derivatives—occur in nature, and for this and other reasons are of considerable importance.

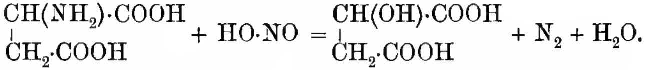
Malic acid,  $\begin{matrix}CH(OH)\cdot COOH\\ |\\ CH_2\cdot COOH\end{matrix}$ or $C_4H_6O_5$, a monohydroxy-derivative of succinic acid, occurs, not only in the free state, but also in the form of salts, in many plants, more specially in (unripe) apples, from which it derives its name (*acidum malicum*), in grapes, and in the berries of the mountain ash. It may be obtained by boiling bromosuccinic acid with water and silver hydroxide, a reaction analogous to the formation of lactic acid from α-bromo-propionic acid,



$$\begin{array}{l}\mathrm{CHBr{\cdot}COOH}\\ \vert\\ \mathrm{CH_2{\cdot}COOH}\end{array} + \mathrm{Ag{\cdot}OH} = \begin{array}{l}\mathrm{CH(OH){\cdot}COOH}\\ \vert\\ \mathrm{CH_2{\cdot}COOH}\end{array} + \mathrm{AgBr}.$$

As, therefore, bromosuccinic acid is easily prepared by heating succinic acid with bromine and water, and succinic acid may be synthesised in the manner already described (pp. 234–5), it is possible to obtain malic acid from its elements.

Malic acid is produced on treating amidosuccinic acid, or aspartic acid (a compound which may be obtained indirectly from asparagus*), with nitrous acid, just as lactic acid may be prepared from α-amido-propionic acid,



$$\begin{array}{l}\mathrm{CH(NH_2){\cdot}COOH}\\ \vert\\ \mathrm{CH_2{\cdot}COOH}\end{array} + \mathrm{HO{\cdot}NO} = \begin{array}{l}\mathrm{CH(OH){\cdot}COOH}\\ \vert\\ \mathrm{CH_2{\cdot}COOH}\end{array} + \mathrm{N_2} + \mathrm{H_2O}.$$

It is usually prepared from the juice of unripe berries of the mountain ash.

The expressed juice is boiled with milk of lime and the crystalline, sparingly soluble calcium salt, $C_4H_4O_5Ca + H_2O$, which is precipitated, dissolved in hot dilute nitric acid; the calcium hydrogen malate, $(C_4H_5O_5)_2Ca + 6H_2O$, which separates in crystals, is then decomposed with the theoretical quantity of oxalic acid, and the filtered solution evaporated.

Malic acid is a crystalline, deliquescent substance, melts at 100°, and is readily soluble in water and alcohol, but only sparingly in ether; its metallic and ethereal salts are of little importance.

Many of the reactions of malic acid may be foretold from a consideration of its constitution, which is established by its methods of formation. Since, for example, it is a hydroxy-derivative of succinic acid, it is to be expected that, on reduction with hydriodic acid at a high temperature, it will be

---

* ***Asparagine***, $COOH{\cdot}CH(NH_2){\cdot}CH_2{\cdot}CO{\cdot}NH_2$, the amide of aspartic acid occurs, in asparagus; when boiled with acids or alkalies, it is converted into aspartic acid, $COOH{\cdot}CH(NH)_2{\cdot}CH_2{\cdot}COOH$.

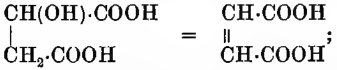
converted into succinic acid, just as lactic acid is converted into propionic acid; also that, when heated with hydrobromic acid, it will yield bromosuccinic acid, a change which would be analogous to the conversion of lactic into bromopropionic acid. Both these changes actually take place,

$$COOH\cdot CH(OH)\cdot CH_2\cdot COOH + 2HI = COOH\cdot CH_2\cdot CH_2\cdot COOH + H_2O + I_2$$

$$COOH\cdot CH(OH)\cdot CH_2\cdot COOH + HBr = COOH\cdot CHBr\cdot CH_2\cdot COOH + H_2O.$$

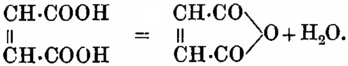
Although the malic acid obtained from plants undergoes exactly the same chemical changes as that prepared from bromosuccinic acid, and that obtained from aspartic acid, the three acids are not identical in all respects; they differ principally in their action on polarised light, a point which is referred to later (part ii.).

When malic acid is heated for a long time at 130°, it does not form malic anhydride, as might have been expected from the behaviour of succinic acid, but is slowly converted into *fumaric acid* and water,



$$\begin{array}{l}CH(OH)\cdot COOH\\ |\\ CH_2\cdot COOH\end{array} = \begin{array}{l}CH\cdot COOH\\ \|\\ CH\cdot COOH\end{array};$$

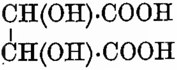
if now the fumaric acid be distilled, part passes over unchanged, the rest being converted into *maleïc anhydride* and water,



$$\begin{array}{l}CH\cdot COOH\\ \|\\ CH\cdot COOH\end{array} = \begin{array}{l}CH\cdot CO\\ \|\\ CH\cdot CO\end{array}\!\!>O + H_2O.$$

Maleïc anhydride is decomposed by boiling water, giving *maleïc acid*, which has the same constitution as fumaric acid—that is to say, both compounds are unsaturated dicarboxylic acids of the constitution $COOH\cdot CH{:}CH\cdot COOH$; the existence of these two isomerides, and other cases of isomerism of a similar kind, are accounted for by the theory of stereochemical isomerism proposed by Van't Hoff and Wislicenus, for an account of which other works must be consulted.

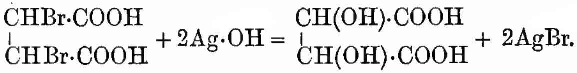
Tartaric acid, or dihydroxysuccinic acid, $C_4H_6O_6$ or



$$\begin{array}{l}CH(OH)\cdot COOH\\ |\\ CH(OH)\cdot COOH\end{array}$$

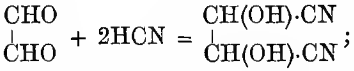
is one of the most commonly occurring vegetable acids, and is contained in grapes, in the berries of the mountain ash, and in other fruits; during the (secondary) fermentation of grape-juice, which takes place in the casks, a considerable quantity of 'argol,' or impure potassium hydrogen tartrate, is deposited, and it is from this salt that the tartaric acid of commerce is obtained.

Tartaric acid can be obtained from succinic acid, and, therefore, from its elements, by reactions similar to those employed in the synthesis of malic acid; dibromosuccinic acid is first prepared by heating succinic acid with bromine (2 mols.) and water, and two hydroxyl-groups are then substituted for the two atoms of bromine in the usual way—namely, by heating the dibromo-derivative with water and silver hydroxide,*



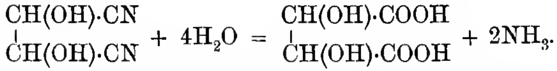
$$\begin{array}{l}\mathrm{CHBr{\cdot}COOH}\\ |\\ \mathrm{CHBr{\cdot}COOH}\end{array} + 2\mathrm{Ag{\cdot}OH} = \begin{array}{l}\mathrm{CH(OH){\cdot}COOH}\\ |\\ \mathrm{CH(OH){\cdot}COOH}\end{array} + 2\mathrm{AgBr}.$$

Tartaric acid may also be obtained synthetically from glyoxal (p. 223), which, like other aldehydes, combines directly with hydrocyanic acid,



$$\begin{array}{l}\mathrm{CHO}\\ |\\ \mathrm{CHO}\end{array} + 2\mathrm{HCN} = \begin{array}{l}\mathrm{CH(OH){\cdot}CN}\\ |\\ \mathrm{CH(OH){\cdot}CN}\end{array};$$

the dicyanohydrin thus produced is decomposed by mineral acids, giving tartaric acid,† just as cyanoacetic acid yields malonic acid,



$$\begin{array}{l}\mathrm{CH(OH){\cdot}CN}\\ |\\ \mathrm{CH(OH){\cdot}CN}\end{array} + 4\mathrm{H_2O} = \begin{array}{l}\mathrm{CH(OH){\cdot}COOH}\\ |\\ \mathrm{CH(OH){\cdot}COOH}\end{array} + 2\mathrm{NH_3}.$$

Tartaric acid is prepared on the large scale from argol. This crude, dark-red deposit is partially purified by recrystallisation from hot water, and its aqueous solution is then boiled with chalk, when insoluble calcium tartrate is precipitated, neutral potassium tartrate remaining in solution,

$$2\mathrm{C_4H_5O_6K} + \mathrm{CaCO_3} = \mathrm{C_4H_4O_6Ca} + \mathrm{C_4H_4O_6K_2} + \mathrm{CO_2} + \mathrm{H_2O};$$

the calcium salt is separated, and the solution treated with

---

* The tartaric acid obtained in this way is optically inactive (part ii.), and is a mixture of racemic acid and mesotartaric acid.

† This product is also optically inactive, and consists of racemic acid only.

calcium chloride, when a second precipitate of calcium tartrate is obtained,

$$C_4H_4O_6K_2 + CaCl_2 = C_4H_4O_6Ca + 2KCl.$$

The calcium tartrate from these two operations is washed with water, and decomposed with the theoretical quantity of dilute sulphuric acid; finally, the filtered solution of the tartaric acid is evaporated to crystallisation.

Tartaric acid forms large transparent crystals, and is readily soluble in water and alcohol, but insoluble in ether; it melts at about 167°, but not sharply, owing to decomposition taking place. When heated for a long time at about 150°, it is converted into tartaric anhydride, $C_4H_4O_5$, and several other compounds, and on dry distillation it yields a variety of products, among others, pyruvic acid and pyrotartaric acid.

Tartaric acid, like other dicarboxylic acids, forms both neutral and acid salts, some of which are of considerable importance.

Normal *potassium tartrate*, $C_4H_4O_6K_2 + \frac{1}{2}H_2O$, is readily prepared by neutralising the acid, or the acid potassium salt, with potash; it is readily soluble in cold water, in which respect it differs from *potassium hydrogen tartrate*, $C_4H_5O_6K$, which is only sparingly soluble. The latter is precipitated* on adding excess of tartaric acid to a concentrated neutral solution of a potassium salt (test for potassium), and also on treating an aqueous solution of normal potassium tartrate with one equivalent of a mineral acid,

$$C_4H_4O_6K_2 + HCl = C_4H_5O_6K + KCl;$$

it is known in commerce as 'argol' or 'cream of tartar.'

Potassium sodium tartrate, or 'Rochelle salt,' $C_4H_4O_6KNa + 4H_2O$, is obtained when potassium hydrogen tartrate is neutralised with sodium carbonate and then concentrated; it forms large transparent crystals, and is employed in the preparation of Fehling's solution (p. 263).

---

* The precipitation is much hastened by shaking or stirring with a glass rod.

Calcium tartrate, $C_4H_4O_6Ca + 4H_2O$, being insoluble in water, is precipitated on adding a soluble calcium salt to a neutral solution of a tartrate; it is readily soluble in potash, but is reprecipitated on boiling the solution, a behaviour which is made use of in testing for tartaric acid.

Tartar emetic, or potassium antimonyl tartrate,

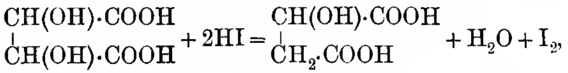
$$C_4H_4O_6K(SbO) + \tfrac{1}{2}H_2O,$$

is prepared by boiling potassium hydrogen tartrate with antimonious oxide and water; it is readily soluble in water, and is used in medicine as an emetic, and in calico-printing as a mordant.

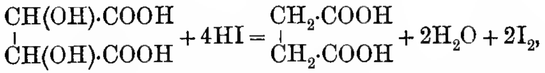
The detection of tartaric acid or of a tartrate is based (*a*) on the behaviour of the neutral solution with calcium chloride (in the cold), and on the solubility of the precipitate in potash; (*b*) on the behaviour of the neutral solution with an ammoniacal solution of silver nitrate, from which a mirror of silver is deposited on warming; (*c*) on the fact that the solid compound rapidly chars when heated alone, giving an odour of burnt sugar; it also chars when heated with concentrated sulphuric acid, sulphur dioxide and the two oxides of carbon being evolved.

That the *constitution* of tartaric acid is expressed by the formula given above is shown by the methods of formation of the acid; it is a dihydroxy-derivative of succinic acid, just as malic acid is a monohydroxy-derivative of the same compound.

On reduction with hydriodic acid, tartaric acid is converted first into malic, then into succinic acid,



$$\begin{array}{l} CH(OH){\cdot}COOH \\ \vert \\ CH(OH){\cdot}COOH \end{array} + 2HI = \begin{array}{l} CH(OH){\cdot}COOH \\ \vert \\ CH_2{\cdot}COOH \end{array} + H_2O + I_2,$$



$$\begin{array}{l} CH(OH){\cdot}COOH \\ \vert \\ CH(OH){\cdot}COOH \end{array} + 4HI = \begin{array}{l} CH_2{\cdot}COOH \\ \vert \\ CH_2{\cdot}COOH \end{array} + 2H_2O + 2I_2,$$

whereas, when heated with concentrated hydrobromic acid, it yields dibromosuccinic acid, as was to be expected,

$$\begin{array}{l} CH(OH)\cdot COOH \\ | \\ CH(OH)\cdot COOH \end{array} + 2HBr = \begin{array}{l} CHBr\cdot COOH \\ | \\ CHBr\cdot COOH \end{array} + 2H_2O.$$

It is a remarkable fact that four distinct modifications of tartaric acid are known—namely, dextrotartaric acid (the compound just described), levotartaric acid, racemic acid, and mesotartaric acid. These four compounds have the same constitution—that is to say, they are all dihydroxy-derivatives of succinic acid, as represented by the formula

$$COOH\cdot CH(OH)\cdot CH(OH)\cdot COOH\,;$$

they differ, however, in certain physical properties, as, for example, in crystalline form, solubility, &c., but more especially in their behaviour towards polarised light; the salts of the four acids exhibit similar differences. This point is referred to later (part ii.).

Dextrotartaric acid rotates the plane of polarisation to the right, *levotartaric acid* to an equal extent to the left.

Racemic acid is optically inactive; it is produced when equal quantities of the dextro- and levo-acids are dissolved in water, and the solution of the mixture allowed to crystallise. It may be obtained synthetically by heating an aqueous solution of dibromosuccinic acid with silver hydroxide, as described above; also from glyoxal. Racemic acid may be resolved into dextro- and levotartaric acids.

Mesotartaric acid, like racemic acid, is optically inactive, but it cannot be resolved into the two optically active modifications; it is formed, together with racemic acid, when dextrotartaric acid is heated for a long time with a small quantity of water at about 165°, and when dibromosuccinic acid is heated with silver hydroxide.

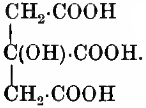
Hydroxytricarboxylic Acids.

Citric acid, $C_6H_8O_7$, like tartaric acid, occurs in the free state in the juice of many fruits; it is found in comparatively large quantities in lemons, in smaller quantities in currants, gooseberries, raspberries, and other sour fruit. It is prepared on the large scale from lemon-juice, which is first boiled, in order to coagulate and precipitate albuminoid matter, and then neutralised with calcium carbonate; the calcium salt, which is precipitated from the hot solution, is washed with water, decomposed with the theoretical quantity of dilute sulphuric acid, and the filtrate from the calcium sulphate evaporated to crystallisation.

Citric acid forms large transparent crystals which contain one molecule of water and melt at 100°, but do not lose their water until about 130°; it is readily soluble in water and fairly so in alcohol, but insoluble in ether. Like tartaric acid, and several other organic acids, it has the property of preventing the precipitation of certain metallic hydroxides from solutions of their salts. Solutions of ferric chloride and of zinc sulphate, for example, give no precipitate with potash or ammonia, if citric acid be present; on account of this property, citric acid and tartaric acid are employed in analytical chemistry and in calico-printing.

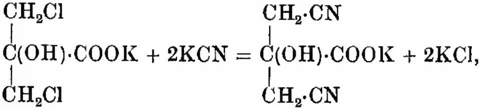
Citric acid is a tricarboxylic acid, and like phosphoric acid forms three classes of salts, as, for example, the three potassium salts, $C_6H_5O_7K_3$, $C_6H_6O_7K_2$, and $C_6H_7O_7K$, all of which are readily soluble in water. *Calcium citrate*, $(C_6H_5O_7)_2Ca_3 + 4H_2O$, is not precipitated on adding a solution of a calcium salt to a neutral solution of a citrate, because it is readily soluble in cold water; on heating, however, a crystalline precipitate is produced, as the salt is less soluble in hot than in cold water. This behaviour, and the fact that the precipitate is insoluble in potash, distinguishes citric from tartaric acid. When heated alone, citric acid chars and gives irritating vapours, but no smell of burnt sugar is noticed; it also differs from tartaric acid, inasmuch as it does not char when gently heated with concentrated sulphuric acid until after some time.

Citric acid may be obtained synthetically by a series of reactions which show it to be a hydroxytricarboxylic acid of the constitution



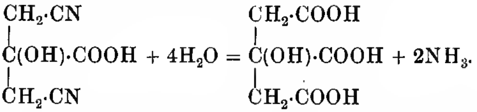
$$\begin{array}{l} CH_2\cdot COOH \\ | \\ C(OH)\cdot COOH. \\ | \\ CH_2\cdot COOH \end{array}$$

Symmetrical dichloracetone, $CH_2Cl\cdot CO\cdot CH_2Cl$, which may be obtained by oxidising *αα*-dichlorohydrin (p. 252) with chromic acid, like other ketones, combines with hydrogen cyanide, forming the cyanohydrin, $(CH_2Cl)_2C{<}\begin{smallmatrix}OH\\CN\end{smallmatrix}$; this product, like other compounds containing the –CN group, is converted into a carboxylic acid, $(CH_2Cl)_2C{<}\begin{smallmatrix}OH\\COOH\end{smallmatrix}$, by boiling mineral acids. The two atoms of chlorine in this acid may now be displaced by –CN groups by treating the potassium salt of the acid with potassium cyanide,



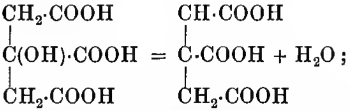
$$\begin{array}{l}CH_2Cl\\ |\\ C(OH){\cdot}COOK\\ |\\ CH_2Cl\end{array} + 2KCN = \begin{array}{l}CH_2{\cdot}CN\\ |\\ C(OH){\cdot}COOK\\ |\\ CH_2{\cdot}CN\end{array} + 2KCl,$$

and this dicyano-derivative may then be converted into citric acid by boiling it with hydrochloric acid,



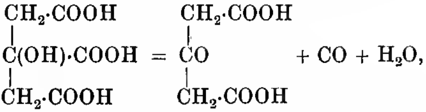
$$\begin{array}{l}CH_2{\cdot}CN\\ |\\ C(OH){\cdot}COOH\\ |\\ CH_2{\cdot}CN\end{array} + 4H_2O = \begin{array}{l}CH_2{\cdot}COOH\\ |\\ C(OH){\cdot}COOH\\ |\\ CH_2{\cdot}COOH\end{array} + 2NH_3.$$

This view of the constitution of citric acid is borne out by all the reactions of the compound; it is shown to contain one hydroxyl-group by the fact that ethyl citrate, $C_3H_4(OH)(COOC_2H_5)_3$, yields a monacetyl-derivative with acetyl chloride. When heated alone at 175°, citric acid is converted into *aconitic acid*, just as malic is converted into fumaric acid,



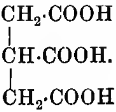
$$\begin{array}{l}CH_2{\cdot}COOH\\ |\\ C(OH){\cdot}COOH\\ |\\ CH_2{\cdot}COOH\end{array} = \begin{array}{l}CH{\cdot}COOH\\ |\\ C{\cdot}COOH\\ |\\ CH_2{\cdot}COOH\end{array} + H_2O;$$

when carefully warmed with sulphuric acid, it yields *acetone-dicarboxylic* acid, with evolution of carbon monoxide,



$$\begin{array}{l}CH_2{\cdot}COOH\\ |\\ C(OH){\cdot}COOH\\ |\\ CH_2{\cdot}COOH\end{array} = \begin{array}{l}CH_2{\cdot}COOH\\ |\\ CO\\ |\\ CH_2{\cdot}COOH\end{array} + CO + H_2O,$$

and on reduction with hydriodic acid, it is converted into *tricarballylic acid*,



$$\begin{array}{l}CH_2{\cdot}COOH\\ |\\ CH{\cdot}COOH.\\ |\\ CH_2{\cdot}COOH\end{array}$$

CHAPTER XIV.

TRIHYDRIC AND POLYHYDRIC ALCOHOLS.

In the preceding chapter it has been shown that it is possible to convert a paraffin first into a monohydric alcohol, and then into a dihydric alcohol, or glycol, by the substitution of hydroxyl-groups for atoms of hydrogen; ethane, for example, may be converted into ethyl alcohol and ethylene glycol, propane into propyl alcohol and propylene glycol.

In a similar manner those paraffins containing three or more carbon atoms may be converted into **trihydric alcohols**, compounds which stand in the same relation to the glycols as the latter to the monohydric alcohols,

Propyl Alcohol. $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}OH$

Propylene Alcohol. $CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$

Propenyl Alcohol.

$$CH_2(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}OH.$$

As, however, the preparation of such trihydric alcohols from the paraffins is a matter of very considerable difficulty, their study has necessarily been very limited except in the case of glycerol, which, from its occurrence in such large quantities in natural fats and oils, has offered exceptional opportunities for investigation.

Glycerol, glycerin, propenyl alcohol, or trihydroxypropane, $C_3H_5(OH)_3$, or $CH_2(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}OH$, has been previously referred to as one of the unimportant products of the alcoholic fermentation of sugar, and its preparation from fats and oils, which consist essentially of tripalmitin, tristearin, and trioleïn (ethereal salts of which glycerol is the base) has been described.

The concentrated glycerol obtained on evaporating its aqueous solution (p. 167) may be further purified and freed from water by distillation under reduced pressure, the first fractions, which contain the water, being collected separately.

Glycerol may be obtained from propane, and therefore from its elements, by treating the hydrocarbon with bromine, and then heating the tribromopropane which is thus formed with water at 170°,

$$CH_2Br{\cdot}CHBr{\cdot}CH_2Br + 3H_2O = CH_2(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}OH + 3HBr.$$

Pure glycerol is a colourless, crystalline substance, melting at 17°; as ordinarily prepared, however, it is a thick syrup of sp. gr. 1·265 at 15°, and does not solidify readily owing to the presence of water and traces of other impurities. It boils at 290° under ordinary atmospheric pressure, without decomposition; if however, it contain even traces of salts, it undergoes slight decomposition, so that in such cases it must first be distilled in a current of steam. Glycerol is very hygroscopic, and rapidly absorbs water from the air, mixing with it and also with alcohol in all proportions; it is insoluble in ether, a property which is common to most substances which contain many hydroxyl-groups. It has a distinctly sweet taste; this property also seems to be connected with the presence of hydroxyl-groups, as is shown by the fact that other trihydric alcohols, and to an even greater extent the tetra-, penta-, and hexa-hydric alcohols, are sweet, sugar-like compounds.

Glycerol readily undergoes decomposition into acroleïn (p. 256) and water,

$$C_3H_5(OH)_3 = C_3H_4O + 2H_2O;$$

this change takes place to a slight extent when impure glycerol is distilled, but much more readily and completely when glycerol is heated with potassium hydrogen sulphate, sulphuric acid, phosphorus pentoxide, or other dehydrating agents.

Glycerol, like glycol, yields a variety of oxidation products according to the conditions under which it is treated; when carefully oxidised with dilute nitric acid, it is converted into glyceric acid, a change analogous to the formation of glycollic acid from glycol,

$$CH_2(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}OH + 2O = CH_2(OH){\cdot}CH(OH){\cdot}COOH + H_2O;$$

under other conditions, however, it is usually oxidised to a mixture of oxalic, glycollic, and carbonic acids,

$$CH_2(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}OH + 4O = CH_2(OH){\cdot}COOH + CO_2 + 2H_2O$$

$$CH_2(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}OH + 6O = COOH{\cdot}COOH + CO_2 + 3H_2O.$$

Glycerol is extensively used in the preparation of nitroglycerin (p. 252) and toilet-soaps, also for filling gas-meters; it is used in smaller quantities in medicine and as an antiputrescent in preserving food materials.

Derivatives of Glycerol.—Assuming that glycerol is a trihydric alcohol of the constitution given above, its behaviour under various conditions may be foretold with a good prospect of success, if that of ethyl alcohol and of glycol be borne in mind. The fact, for example, that glycerol contains hydrogen displaceable by sodium, was only to be expected, and, just as in the case of glycol, only one atom of hydrogen is displaced at ordinary temperatures; the product, $C_3H_5(OH)_2{\cdot}ONa$, is hygroscopic, and is immediately decomposed by water.

Again, the behaviour of glycerol with acids is analogous to that of alcohol and of glycol; when treated with acetic acid, for example, it yields the ethereal salt, *triacetin*, or *glyceryl acetate*, and water,

$$C_3H_5(OH)_3 + 3CH_3{\cdot}COOH = C_3H_5(O{\cdot}CO{\cdot}CH_3)_3 + 3H_2O.$$

It is obvious, however, that triacetin is not the only ethereal salt which may be produced by the interaction of glycerol and acetic acid, because, being a *triacid* base, glycerol may yield compounds, such as *monacetin* and *diacetin*, by the displacement of only one or of two atoms of hydrogen,

$$C_3H_5(OH)_3 + CH_3{\cdot}COOH = C_3H_5(OH)_2{\cdot}O{\cdot}CO{\cdot}CH_3 + H_2O$$
$$C_3H_5(OH)_3 + 2CH_3{\cdot}COOH = C_3H_5(O{\cdot}CO{\cdot}CH_3)_2{\cdot}OH + 2H_2O.$$

These three compounds may all be prepared by heating glycerol with acetic acid, the higher the temperature and the larger the relative quantity of acetic acid employed, the larger the proportion of triacetin produced. Acetic anhydride acts more readily than acetic acid, but gives the same three products.

Chlorohydrins.—The action of concentrated hydrochloric acid on glycerol is similar to that of acetic acid; at moderately high temperatures, and employing only the theoretical quantity of the acid, one atom of chlorine is substituted for one hydroxyl-group, and *glycerol chlorohydrin* is formed, just as ethylene glycol is converted into glycol chlorohydrin,

$$C_3H_5(OH)_3 + HCl = C_3H_5Cl(OH)_2 + H_2O;$$

with excess of hydrochloric acid, however, *glycerol dichlorohydrin* is produced,

$$C_3H_5(OH)_3 + 2HCl = C_3H_5Cl_2{\cdot}OH + 2H_2O.$$

Glyceryl trichloride, or propenyl trichloride,

$$CH_2Cl{\cdot}CHCl{\cdot}CH_2Cl,$$

cannot easily be obtained by heating glycerol with hydrochloric acid, but may be prepared by treating the dichlorohydrin with phosphorus pentachloride,

$$C_3H_5Cl_2{\cdot}OH + PCl_5 = C_3H_5Cl_3 + POCl_3 + HCl;$$

it is a colourless liquid, boiling at 158°, and smells like chloroform. The name '*glyceryl*,' or *propenyl*, is sometimes given to the group of atoms $-CH_2-\overset{|}{C}H-CH_2-$, which may be regarded as a trivalent radicle.

Glycerol chlorohydrin and the dichlorohydrin exist in two isomeric forms,

$CH_2(OH){\cdot}CH(OH){\cdot}CH_2Cl$
α-Chlorohydrin.

$CH_2(OH){\cdot}CHCl{\cdot}CH_2{\cdot}OH$
β-Chlorohydrin.

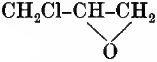
$CH_2Cl{\cdot}CH(OH){\cdot}CH_2Cl$
αα-Dichlorohydrin.

$CH_2Cl{\cdot}CHCl{\cdot}CH_2{\cdot}OH.$
αβ-Dichlorohydrin.

Glycerol α-chlorohydrin is formed, together with small quantities of the β-compound, when glycerol is heated at 100° with hydrochloric acid; it is an oily liquid, soluble in water. *Glycerol β-chlorohydrin* can be obtained by treating allyl alcohol (p. 254) with hypochlorous acid.

Glycerol αα-dichlorohydrin is produced when glycerol is heated with a solution of hydrogen chloride in glacial acetic acid; it is a mobile liquid, only sparingly soluble in water, and on oxidation with chromic acid it yields symmetrical dichloracetone, $CH_2Cl{\cdot}CO{\cdot}CH_2Cl$.

Glycerol αβ-dichlorohydrin is obtained on treating allyl alcohol (p. 254) with chlorine; on oxidation with nitric acid it gives αβ-dichloropropionic acid, $CH_2Cl{\cdot}CHCl{\cdot}COOH$. When treated with potash, both αα- and αβ-chlorohydrin yield *epichlorhydrin*,



$$CH_2Cl{-}\underbrace{CH{-}CH_2}_{O}$$

(compare ethylene oxide, p. 223).

When glycerol is treated with acetyl chloride, it does not yield triacetin, as might have been expected, but *diacetylchlorohydrin*,

$$C_3H_5(OH)_3 + 2CH_3{\cdot}COCl = C_3H_5Cl(O{\cdot}CO{\cdot}CH_3)_2 + H_2O + HCl.$$

This behaviour, although apparently abnormal, is not really so; in the first place, the glycerol is converted into a *diacetyl*-derivative in the usual manner,

$$C_3H_5(OH)_3 + 2CH_3{\cdot}COCl = C_3H_5(O{\cdot}CO{\cdot}CH_3)_2{\cdot}OH + 2HCl,$$

and the hydrogen chloride produced during the reaction then acts on the diacetyl-derivative just as it does on other monohydric alcohols,

$$C_3H_5(O{\cdot}CO{\cdot}CH_3)_2{\cdot}OH + HCl = C_3H_5(O{\cdot}CO{\cdot}CH_3)_2Cl + H_2O.$$

Ethylene glycol and other di- and poly-hydric alcohols show a similar behaviour.

Nitro-glycerin, glyceryl trinitrate, or propenyl trinitrate, $C_3H_5(O{\cdot}NO_2)_3$, is an ethereal salt of glycerol and nitric acid. It is prepared by slowly adding pure glycerol drop by drop, or in a fine stream, to a *well-cooled* mixture of concentrated sulphuric acid (4 parts) and nitric acid of sp. gr. 1·52 (1 part); the solution is run into cold water, and the nitro-glycerin, which is precipitated as a heavy oil, washed well with water and dried.

It is a colourless oil of sp. gr. 1·6, has a sweetish taste, and is poisonous; although readily soluble in ether, it is only sparingly soluble in alcohol, and insoluble in water, so that, as regards solubility, its behaviour is almost the exact opposite of that of glycerol, a fact which shows the influence of hydroxyl-groups in a very distinct manner. It explodes violently when suddenly heated, or when subjected to percussion, but when ignited with a flame it burns without explosion, and is even rather difficult to ignite.

Nitro-glycerin is readily hydrolysed by boiling alkalies, being converted into glycerol and a nitrate,*

$$C_3H_5(O{\cdot}NO_2)_3 + 3KOH = C_3H_5(OH)_3 + 3KNO_3;$$

on reduction with ammonium sulphide (p. 94) it yields glycerol and ammonia,

$$C_3H_5(O{\cdot}NO_2)_3 + 12H_2S = C_3H_5(OH)_3 + 3NH_3 + 6H_2O + 12S.$$

In these two reactions the behaviour of nitro-glycerin is exactly analogous to that of ethyl nitrate, $CH_3{\cdot}CH_2{\cdot}O{\cdot}NO_2$, but quite different from that of nitro-ethane, $CH_3{\cdot}CH_2{\cdot}NO_2$, which, as previously stated, is not decomposed by alkalies, and on reduction yields amido-ethane or ethylamine; since, moreover, groups of atoms in a similar state of combination show a similar behaviour, it is clear that nitro-glycerol, like ethyl nitrate, is an ethereal salt, and not a nitro-derivative; in other words, the nitro groups ($-NO_2$) in nitro-glycerin are directly combined with oxygen, and not with carbon. The name nitro-glycerin is, therefore, misleading, but, being so well known, it is usually employed instead of the more correct names, glyceryl trinitrate, or propenyl trinitrate.

Nitro-glycerin is extensively employed as an explosive, sometimes alone, sometimes in the form of *dynamite*, which is simply a mixture of nitro-glycerin and kieselguhr, a porous, earthy powder, consisting of the siliceous remains of small marine animals; the object of absorbing the nitro-glycerin with kieselguhr is to render it less liable to explode, and, consequently, safer to handle and to transport. The presence of acids in nitro-glycerin make it liable to undergo spontaneous decomposition and explosion; great care must, therefore, be taken in washing it thoroughly. Nitro-glycerin

---

* An alkali nitrite is also formed owing to reduction, the glycerol undergoing partial oxidation.

is also employed, mixed with gun-cotton (p. 274), as blasting-gelatine, and in the preparation of smokeless gunpowder; it is used in medicine in cases of heart disease.

Unsaturated Compounds related to Glycerol.

Allyl alcohol, $CH_2{:}CH{\cdot}CH_2{\cdot}OH$, is formed when anhydrous glycerol is slowly heated with crystallised oxalic acid until the temperature rises to about 260°, and the mixture then distilled; in the first place, the glycerol is converted into monoformin, with evolution of carbon dioxide, water, and a little formic acid (p. 144),

$$C_3H_5(OH)_3 + C_2H_2O_4 = C_3H_5(OH)_2{\cdot}O{\cdot}CHO + CO_2 + H_2O$$
$$C_3H_5(OH)_2{\cdot}O{\cdot}CHO + H_2O = C_3H_5(OH)_3 + H{\cdot}COOH,$$

but, on further heating, the rest of the monoformin undergoes decomposition, and allyl alcohol collects in the receiver,

$$CH_2(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}O{\cdot}CHO = CH_2(OH){\cdot}CH{:}CH_2 + CO_2 + H_2O.$$

Allyl alcohol is also produced when acroleïn (acraldehyde, p. 256) is treated with nascent hydrogen, a change which is exactly analogous to the formation of alcohol from aldehyde,

$$CH_2{:}CH{\cdot}CHO + 2H = CH_2{:}CH{\cdot}CH_2{\cdot}OH.$$

It is a colourless, neutral liquid, boils at 96–97°, and has a very irritating smell; it is miscible with water, alcohol, and ether in all proportions.

Allyl alcohol is an unsaturated compound, and has, therefore, not only the properties of a primary alcohol, but also those of unsaturated compounds in general. Its alcoholic character is shown by the following facts: it dissolves sodium with evolution of hydrogen,

$$2CH_2{:}CH{\cdot}CH_2{\cdot}OH + 2Na = 2CH_2{:}CH{\cdot}CH_2{\cdot}ONa + H_2,$$

forms ethereal salts with acids,

$$CH_2{:}CH{\cdot}CH_2{\cdot}OH + HCl = CH_2{:}CH{\cdot}CH_2Cl + H_2O,$$

and on oxidation is converted, first into acroleïn, then into acrylic acid,

$$CH_2{:}CH{\cdot}CH_2{\cdot}OH + O = CH_2{:}CH{\cdot}CHO + H_2O$$
$$CH_2{:}CH{\cdot}CH_2{\cdot}OH + 2O = CH_2{:}CH{\cdot}COOH + H_2O.$$

In all these reactions its behaviour is so closely analogous to that of ethyl alcohol and other primary alcohols, that it must be concluded that allyl alcohol contains the group $-CH_2{\cdot}OH$. That it is an unsaturated compound is shown by its behaviour with chlorine and bromine, with which it combines directly, forming a dichloro- or dibromohydrin, isomeric with the corresponding compounds obtained by treating glycerol with halogen acids,

$$CH_2{:}CH{\cdot}CH_2{\cdot}OH + Br_2 = CH_2Br{\cdot}CHBr{\cdot}CH_2{\cdot}OH.$$

Allyl iodide, $CH_2{:}CH{\cdot}CH_2I$, is an unsaturated ethereal salt, related to allyl alcohol in the same way as ethyl iodide to ethyl alcohol. It may be obtained by treating allyl alcohol with iodine and phosphorus, but is more conveniently prepared directly from glycerol.

For this purpose iodine (10 parts) is dissolved in glycerol (15 parts), and small pieces of dry phosphorus (6 parts) added from time to time, the mixture being very gently warmed at first to start the reaction; the operation is conducted in a large retort connected with a condenser, a stream of carbon dioxide being passed through the apparatus during the experiment. It is probable that the glycerol is first converted into the tri-iodide, $CH_2I{\cdot}CHI{\cdot}CH_2I$, which then undergoes decomposition into iodine and allyl iodide; if excess of phosphorus and iodine be employed, isopropyl iodide is formed,

$$CH_2{:}CH{\cdot}CH_2I + HI = CH_2{:}CH{\cdot}CH_3 + I_2.$$
$$CH_2{:}CH{\cdot}CH_3 + HI = CH_3{\cdot}CHI{\cdot}CH_3.$$

Allyl iodide is a colourless liquid, boiling at 101°, and has an odour of garlic; it resembles ethyl iodide in many respects, but has also the properties of an unsaturated compound. When heated with potassium sulphide in alcoholic solution, it is converted into allyl sulphide (see below), just as ethyl iodide gives ethyl sulphide,

$$2CH_2{:}CH{\cdot}CH_2I + K_2S = (CH_2{:}CH{\cdot}CH_2)_2S + 2KI.$$

Allyl bromide, $CH_2{:}CH{\cdot}CH_2Br$, may be obtained by treating allyl alcohol with phosphorus tribromide; it is a heavy liquid, and boils at 70–71°.

Allyl sulphide occurs in nature in many Cruciferæ, but is especially abundant in garlic (*Allium sativum*), from which it is obtained by distilling the macerated plant with water; it is therefore known as *oil of garlic.* It is a colourless, very unpleasant-smelling liquid, boiling at 140°. Another allyl derivative—namely, allyl isothiocyanate, occurs in nature in considerable quantities in black mustard seeds, and is known as *oil of mustard* (p. 289).

Acroleïn, or acraldehyde, $CH_2{:}CH{\cdot}CHO$, is formed during the partial combustion of fats, and when impure glycerol is distilled under ordinary pressure; also when allyl alcohol undergoes oxidation. It is prepared by distilling glycerol with some dehydrating agent, potassium hydrogen sulphate being usually employed,

$$C_3H_5(OH)_3 = C_3H_4O + 2H_2O.$$

Acroleïn is an aldehyde, and is related to allyl alcohol in the same way as aldehyde to ethyl alcohol; it is a colourless liquid, boils at 52°, and has an exceedingly irritating and disagreeable odour, like that of partially burnt fat; it produces sores when brought on to the skin, and its vapours cause a copious flow of tears. Like other aldehydes, it reduces ammoniacal solutions of silver oxide with formation of a mirror, and readily undergoes polymerisation into an amorphous, brittle substance named *disacryl;* it also gives the aldehyde reaction with rosaniline, but, on the other hand, it does not combine with sodium hydrogen sulphite. On reduction it yields allyl alcohol; on exposure to the air, or on treatment with silver oxide, it readily undergoes oxidation, yielding acrylic acid. That it is an unsaturated compound is shown by the fact that it combines directly with bromine, forming an additive-product of the composition

$$CH_2Br{\cdot}CHBr{\cdot}CHO.$$

Crotonaldehyde, $CH_3{\cdot}CH{:}CH{\cdot}CHO$ is a homologue of acraldehyde; it is obtained on heating acetaldehyde with dilute hydrochloric acid, or with a solution of zinc chloride, aldol being formed as an intermediate product (p. 124),

$$2CH_3{\cdot}CHO = CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CHO$$
$$CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CHO = CH_3{\cdot}CH{:}CH{\cdot}CHO + H_2O.$$

It boils at 104–105°, and closely resembles acraldehyde in properties; on reduction it yields, first, crotonalcohol, $CH_3{\cdot}CH{:}CH{\cdot}CH_2{\cdot}OH$, and then butyl alcohol, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$; on oxidation it gives crotonic acid, $CH_3{\cdot}CH{:}CH{\cdot}COOH$.

Acrylic acid, $CH_2{:}CH{\cdot}COOH$, the oxidation product of allyl alcohol and of acroleïn, may also be obtained from hydracrylic acid (p. 227), which on distillation loses the elements of water,

$$CH_2(OH){\cdot}CH_2{\cdot}COOH = CH_2{:}CH{\cdot}COOH + H_2O,$$

a change analogous to the formation of ethylene from alcohol; acrylic acid is also produced when β-bromopropionic acid is treated with alcoholic potash, just as ethylene is formed from ethyl bromide,

$$CH_2Br{\cdot}CH_2{\cdot}COOH = CH_2{:}CH{\cdot}COOH + HBr.$$

Acrylic acid is a liquid at ordinary temperatures, and boils at 139–140°; it smells like acetic acid, is miscible with water in all proportions, and its solutions have an acid reaction. It is a monocarboxylic acid, and forms metallic and ethereal salts just as do the fatty acids; it differs from the latter, however, in being an unsaturated compound, as is shown by its forming additive-products. It combines directly with bromine, giving dibromopropionic acid,

$$CH_2{:}CH{\cdot}COOH + Br_2 = CH_2Br{\cdot}CHBr{\cdot}COOH;$$

with halogen acids, yielding β-halogen derivatives* of propionic acid,

$$CH_2{:}CH{\cdot}COOH + HCl = CH_2Cl{\cdot}CH_2{\cdot}COOH,$$

and with nascent hydrogen, giving propionic acid,

$$CH_2{:}CH{\cdot}COOH + 2H = CH_3{\cdot}CH_2{\cdot}COOH.$$

---

* This behaviour is abnormal, as usually the halogen combines with that carbon atom which is combined with the *least* number of hydrogen atoms (p. 80).

Crotonic acid, $CH_3{\cdot}CH{:}CH{\cdot}COOH$, the next homologue of acrylic acid, may be obtained by methods similar to those mentioned in the case of acrylic acid—namely, by the oxidation of crotonalcohol or of crotonaldehyde, by the distillation of β-hydroxybutyric acid, $CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}COOH$, and by treating α-bromobutyric acid with alcoholic potash. It melts at 72°, and resembles acrylic acid in general behaviour.

Oleïc acid, $C_{18}H_{34}O_2$, one of the higher members of the acrylic series, has been previously mentioned (p. 168).

Polyhydric Alcohols.

The existence of tetra-, penta-, and hexa-hydric alcohols, which theoretically should be obtained from the higher paraffins by the substitution of four, five, or six hydroxyl-groups for an equivalent quantity of hydrogen, just as glycerol is derived from propane, was of course to be expected; nevertheless, owing to the difficulties which would be met with in the actual synthesis of such complex compounds from the paraffins, or by other methods, it is highly probable that they might still have been unknown, were it not that many of them occur in nature, and may also be prepared from products of the vegetable kingdom by simple processes.

Erythritol, $CH_2(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}OH$, for example, is a tetrahydric alcohol which occurs in many lichens, and in certain seaweeds. *Arabitol* and *xylitol* are pentahydric alcohols of the constitution

$$CH_2(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}OH;$$

they may be respectively prepared by reducing *arabinose* and *xylose*, two sugar-like compounds which occur in various vegetable products, with sodium amalgam. Hexahydric alcohols, such as *mannitol* and *dulcitol*, also occur in nature.

Mannitol,

$$CH_2(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}OH,$$

is found in manna, the dried sap of a species of ash, from which it may be extracted with boiling alcohol; it may also be obtained by reducing levulose, mannose, or dextrose (p. 264) with sodium amalgam. It is a colourless, crystalline substance, has a very sweet taste, and is readily soluble in water and hot alcohol, but insoluble in ether. When carefully oxidised with nitric acid it yields the aldehyde, mannose, and the ketone, levulose (p. 265); on reduction with hydriodic acid it is converted into (secondary) hexyl iodide, a derivative of normal hexane,

$$CH_2(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH_2\cdot OH + 11HI =$$
$$CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CHI\cdot CH_3 + 6H_2O + 5I_2.$$

This conversion of mannitol into a derivative of *normal* hexane is a fact of great importance, as it throws much light on the constitution, not only of mannitol, but also of mannose, levulose, and dextrose; since these compounds yield mannitol on reduction, it is proved that they also are derivatives of *normal* hexane, and not of some secondary or tertiary paraffin, isomeric with hexane.

The constitution of mannitol is further established by the usual methods; that it contains six hydroxyl-groups is shown by the fact that it yields a hexacetyl-derivative, $C_6H_8(O\cdot CO\cdot CH_3)_6$, and a hexanitrate, $C_6H_8(O\cdot NO_2)_6$. As, moreover, it is known from experience that in all stable hydroxy-compounds one carbon atom does not unite with more than one hydroxyl-group, each of the six hydroxyl-groups in mannitol must be combined with a different carbon atom.

Mannitol, like tartaric acid, exists in several modifications, which differ principally in their optical properties.

CHAPTER XV.

THE CARBOHYDRATES.

The compounds usually known as the carbohydrates do not form a well-defined group, inasmuch as the term is applied to substances widely different both in properties and in constitution; they may, however, be roughly described as naturally occurring substances, composed of carbon, hydrogen, and oxygen, in which the ratio of hydrogen to oxygen is the same as in water. The word carbohydrate was originally given to such compounds because they might be represented as composed of carbon and water in different proportions: grape-sugar, $C_6H_{12}O_6$, for example, might be represented as $6C + 6H_2O$; cane-sugar, $C_{12}H_{22}O_{11}$, as $12C + 11H_2O$; and starch, $C_6H_{10}O_5$, as $6C + 5H_2O$.

The carbohydrate group is one of the most important in organic chemistry, as it includes all the principal constituents of plants, except water. To this group belong (*a*) the *sugars*, substances which are of great value as food-stuffs and as sources of alcohol, and to which the sweetness of fruits is due; (*b*) the *starches*, the most abundant of all foods; and (*c*) the *celluloses*, substances of which the cell membranes and tissues of plants are principally composed.

The Sugars.

Cane-sugar, or saccharose, $C_{12}H_{22}O_{11}$, is very widely distributed in nature; it occurs in large quantities in the sugar-cane (15–20 per cent.) and in beetroot (some kinds of which contain as much as 16 per cent.), in smaller quantities in strawberries, pine-apples, and other fruits.

The sugar-cane and beetroot are the raw materials from which practically the whole of the sugar of commerce is manufactured, the processes of extraction being much the same in both cases, and requiring expensive apparatus in order to obtain the largest possible yield of crystallised sugar.

The material is crushed in hydraulic presses, and the expressed juice boiled with about 1 per cent. of milk of lime, in order to neutralise acids present, and to coagulate the vegetable albumin which is always contained in the extract. The solution is treated with carbon dioxide, in order to precipitate any excess of lime, decolourised as far as possible by boiling with animal charcoal, and filtered; it is then evaporated under reduced pressure in an apparatus heated with steam, until the syrup is of such a consistency that it deposits crystals on cooling. These crystals are separated from the brown mother-liquor (*molasses*, or treacle) in a centrifugal machine, and purified by recrystallisation from water.

The molasses still contains about 50 per cent. of sugar which does not crystallise from the syrup even on further evaporation, owing to the presence of impurities; nearly the whole of this sugar, however, can be profitably extracted, by adding strontium hydroxide, and separating the insoluble strontium saccharosate (see below) from the dark mother-liquor by filtration. This precipitate is suspended in water, decomposed by passing carbon dioxide, and the filtrate from the strontium carbonate evaporated to a syrup; the impurities having now been removed, the cane-sugar separates in the crystalline form. The annual production of cane-sugar is about 5–6 million tons.

Cane-sugar crystallises from water in hard four-sided prisms, and is soluble in one-third of its weight of water at ordinary temperatures, but only sparingly soluble in alcohol. It melts at about 160–161°, and on cooling does not immediately crystallise, but solidifies to a pale-yellow, glassy mass, called *barley-sugar*, which, however, on long standing, gradually becomes opaque and crystalline. At about 200–210° cane-sugar loses water, and is gradually converted into a brown mass called *caramel*, which is largely used for colouring liqueurs, soups, gravies, &c.

Warm concentrated sulphuric acid chars cane-sugar; if a strong aqueous solution of sugar be mixed with an equal volume of concentrated sulphuric acid, the sugar blackens and the carbonaceous product swells up enormously, owing to the evolution of steam, carbon dioxide, sulphur dioxide, and other gases.

Cane-sugar is *dextrorotatory*—that is, its solutions have the property of rotating the plane of polarisation of light to the *right*,* and the strength of a solution of sugar may be estimated by determining the amount of rotation which it causes. The apparatus used for this purpose is called a *saccharimeter*, and the operation itself, *saccharimetry*.

If a trace of a mineral acid be added to a solution of cane-sugar, and the liquid warmed or simply allowed to stand, the

---

* $[\alpha]_D = +66{\cdot}5°$. For a description of the action of sugar solutions on polarised light, works on physics must be consulted.

cane-sugar is hydrolysed, with formation of equal quantities of dextrose (see below) and levulose (p. 265),

$$\underset{}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Levulose.}}{C_6H_{12}O_6}.$$

This process is usually called *inversion*, and the mixture of dextrose and levulose is called *invert sugar.* Invert sugar comes into the market as a somewhat brownish-coloured mass, and is extensively used in the manufacture of preserves, confectionery, &c., as well as for the preparation of alcohol. Prolonged boiling with hydrochloric acid (sp. gr. 1·1) converts cane-sugar into levulinic acid (p. 196).

Cane-sugar does not reduce Fehling's solution (p. 263), and it does not directly undergo alcoholic fermentation with yeast; when, however, it is left for some time in contact with yeast, a ferment, *invertase*, which is present in the yeast converts it into dextrose and levulose, and then alcoholic fermentation sets in. When boiled with acetic anhydride and sodium acetate, cane-sugar is converted into *octacetylsaccharose*, $C_{12}H_{14}O_3(C_2H_3O_2)_8$, and therefore contains eight hydroxyl-groups; its constitution, however, has not yet been clearly established.

Cane-sugar combines readily with certain hydroxides, such as those of calcium, barium, and strontium, with formation of metallic compounds called *saccharosates*, in which one or more of the hydroxyl-groups in the sugar is displaced by the metal or hydroxide. These saccharosates are produced by simply mixing the sugar solution with the metallic hydroxide. They are readily decomposed by much water and by carbon dioxide into sugar and the hydroxide or carbonate of the metal.

Strontium saccharosate, $C_{12}H_{20}(SrOH)_2O_{11}$, is a granular substance of great commercial importance, owing to its use in separating sugar from molasses (p. 261).

Dextrose, $C_6H_{12}O_6$, or $CH_2(OH)\cdot[CH\cdot OH]^*_4\cdot CHO$, also known as **glucose**, or **grape-sugar**, is found in large quantities in grapes—hence its name, grape-sugar; when the grapes are dried in the sun, in the preparation of raisins, the dextrose

---

* Compare foot-note, p. 134.

in the juice is deposited in hard, brownish-coloured nodules. Dextrose is more frequently met with associated with levulose as invert sugar, mixtures of these sugars occurring in the juice of a great many sweet fruits, and also in the roots and leaves of plants, and in honey. Pure dextrose may be prepared from cane-sugar by inversion with acids, and recrystallisation of the product (invert sugar) from alcohol, when the more readily soluble levulose remains in solution.

Alcohol (1 litre, 90 per cent.) is mixed with concentrated hydrochloric acid (40 c.c.), heated at about 50°, and powdered cane-sugar (350 grams) added in small portions, the whole being well stirred during the operation. The mixture is now kept for two hours at this temperature, then allowed to cool, and crystallisation promoted by stirring, or, better, by the addition of a crystal of dextrose. After some days the crystals are collected and purified by recrystallisation from 80 per cent. alcohol.

Dextrose crystallises with 1 mol., H_2O, in warty masses which melt at 86°, the anhydrous substance melting at 146°; it is almost insoluble in absolute alcohol, but soluble in about its own weight of water at ordinary temperatures, the solution being less sweet than that of cane-sugar. It is not carbonised when gently warmed with sulphuric acid (distinction from cane-sugar); its solutions are dextrorotatory,* hence the name dextrose.

Dextrose is a strong reducing agent, and quickly precipitates gold, silver, and platinum from solutions of their salts on warming. If a solution of dextrose be mixed with potash, and then copper sulphate added, a deep blue solution is obtained, and on gently warming, a bright red precipitate of cuprous oxide, Cu_2O, is deposited, the solution becoming colourless if sufficient dextrose be added; as, moreover, a given quantity (1 molecule) of dextrose always reduces exactly the same quantity (approximately 5 molecules) of cupric to cuprous oxide, this behaviour affords a method of estimating sugar by simple titration.

The solution used for this purpose is known as *Fehling's solution*, and as it decomposes on keeping, it is best prepared as required by

---

* $[\alpha]_D = +52{\cdot}5°$.

mixing equal quantities of the following solutions: (1) 34·6 grams of crystallised copper sulphate, made up to 500 c.c. with water; (2) 173 grams of Rochelle salt, and 60 grams of sodium hydrate, made up to 500 c.c. with water. 10 c.c. of the deep blue solution thus obtained are completely reduced—that is, the colour discharged—by 0·05 gram of dextrose, or by 0·0475 gram of cane-sugar (after inversion).

Dextrose ferments readily with yeast in dilute aqueous solution at a temperature of about 20–30°, yielding principally alcohol and carbon dioxide,

$$C_6H_{12}O_6 = 2C_2H_6O + 2CO_2,$$

but at the same time fusel-oil and small quantities of glycerol, succinic acid, and other substances are formed.

Like cane-sugar, dextrose readily combines with certain metallic hydroxides, forming *glucosates*, such as calcium glucosate, $C_6H_{11}(CaOH)O_6$, and barium glucosate, $C_6H_{11}(BaOH)O_6$; these compounds are readily soluble in water, and are decomposed by carbonic acid, with regeneration of the sugar.

Dextrose has the properties of an *aldehyde*, and at the same time those of a *polyhydric alcohol;* its constitution may be expressed by the formula

$$CH_2(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CHO,$$

which is based on a number of facts, only a few of which can be given here.

On reduction with sodium amalgam in aqueous solution, it is converted into the primary alcohol, mannitol,

$$CH_2(OH)\cdot[CH\cdot OH]_4\cdot CHO + 2H = CH_2(OH)\cdot[CH\cdot OH]_4\cdot CH_2\cdot OH;$$

whereas, when oxidised with bromine water, it yields *gluconic acid*, $CH_2(OH)\cdot[CH\cdot OH]_4\cdot COOH$. These changes are clearly analogous to those undergone by acetaldehyde, and the fact that gluconic acid contains the same number of carbon atoms as dextrose, shows that the latter is an aldehyde and not a ketone (p. 139). Powerful oxidising agents, such as nitric acid, convert dextrose into *saccharic acid*,

$COOH\cdot[CH\cdot OH]_4\cdot COOH$, the $-CH_2\cdot OH$ group, as well as the $-CHO$ group, undergoing oxidation; ultimately it is resolved into oxalic acid. Dextrose, like other aldehydes, interacts readily with hydroxylamine and with phenylhydrazine, with formation of the oxime, $CH_2(OH)\cdot[CH\cdot OH]_4\cdot CH{:}NOH$, and the hydrazone (p. 133),

$$CH_2(OH)\cdot[CH\cdot OH]_4\cdot CH{:}N_2H\cdot C_6H_5.$$

Dextrose gives a pentacetyl derivative, $C_5H_6(C_2H_3O_2)_5\cdot CHO$, when warmed with acetic anhydride and a little zinc chloride, showing that it contains five hydroxyl-groups.

Levulose, $C_6H_{12}O_6$, or $CH_2(OH)\cdot[CH\cdot OH]_3\cdot CO\cdot CH_2\cdot OH$, also called **fructose,** or fruit-sugar, occurs, together with dextrose, in most sweet fruits and in honey; it may be prepared from invert sugar by taking advantage of the fact that its lime compound is sparingly soluble in water, whereas that of dextrose is readily soluble.

Invert sugar (10 grams) is dissolved in water (50 c.c.), the solution well cooled with ice, and slaked lime (6 grams) added in small quantities at a time, with constant stirring. The sparingly soluble lime compound of levulose is collected on a filter, washed with a little water, well pressed, and then decomposed by suspending it in water, and passing carbon dioxide; the filtrate yields, on evaporation, nearly pure fructose as a transparent, uncrystallisable syrup.

Pure crystallised levulose is prepared from *inulin*, $(C_6H_{10}O_5)_n$, a starch which occurs in many plants, and especially in dahlia tubers; for this purpose the inulin is simply boiled with dilute sulphuric acid,

$$(C_6H_{10}O_5)_n + nH_2O = nC_6H_{12}O_6.$$

An aqueous solution of inulin is heated on a water-bath for one hour, with a few drops of sulphuric acid; the sulphuric acid is then removed by precipitation with barium hydroxide, and the solution evaporated at 80°. On the addition of a crystal of levulose the syrup slowly solidifies, and the crystals may then be purified by recrystallisation from alcohol.

Levulose separates from alcohol in small hard crystals, and melts at 95°; it is more soluble in water and alcohol than dextrose, and its taste is just about as sweet as that of the latter. Levulose is *levorotatory**—hence its name; it rotates the plane of polarisation to the left to a somewhat greater extent than dextrose to the right—hence invert sugar, which consists of equal parts of dextrose and levulose, is slightly levorotatory. When, therefore, a solution of cane-sugar, which is dextrorotatory, is boiled with acids, the resulting solution of invert sugar is levorotatory—that is to say, the direction of the rotation has been reversed or 'inverted.'

Levulose ferments with yeast, but less rapidly than dextrose, consequently, in fermenting a solution of invert sugar, the dextrose is decomposed first, and the operation can be stopped at a point when the solution contains only levulose; by the further action of yeast, however, the levulose also undergoes fermentation, yielding the same products as dextrose (p. 264).

Levulose has even stronger reducing powers than dextrose, and reduces Fehling's solution more rapidly, although to exactly the same extent as dextrose; this behaviour is due to the presence of the group $-CO\cdot CH_2\cdot OH$, as all substances (ketonic alcohols) which contain this group are strong reducing agents.

Levulose has the properties of a *ketone*, as well as those of a *polyhydric alcohol*, and its constitution may be expressed by the formula

$$CH_2(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CO\cdot CH_2\cdot OH.$$

It is reduced by sodium amalgam in aqueous solution more readily than dextrose, mannitol being formed,

$$CH_2(OH)\cdot[CH\cdot OH]_3\cdot CO\cdot CH_2\cdot OH + 2H = \\ CH_2(OH)\cdot[CH\cdot OH]_3\cdot CH(OH)\cdot CH_2\cdot OH,$$

just as acetone, under similar treatment, yields isopropyl alcohol. When oxidised with nitric acid or bromine water, it yields tartaric acid and glycollic acid,

$$CH_2(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot \vdots\, CO\cdot CH_2\cdot OH + 4O = \\ COOH\cdot CH(OH)\cdot CH(OH)\cdot COOH + COOH\cdot CH_2\cdot OH + H_2O;$$

---

* $[\alpha]_D = -93^\circ$.

whereas, when boiled with mercuric oxide in aqueous solution, it is oxidised to trihydroxybutyric acid and glycollic acid,

$$\begin{aligned} &CH_2(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}\vdots CO{\cdot}CH_2{\cdot}OH + 2O = \\ &\quad CH_2(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}COOH + COOH{\cdot}CH_2{\cdot}OH. \end{aligned}$$

This behaviour shows that levulose is a ketone, and not an aldehyde; it does not, like dextrose, yield, on oxidation, an acid containing the same number of carbon atoms, but is decomposed in a variety of ways which throw considerable light on its constitution.

Levulose, like other ketones, interacts with hydroxylamine (yielding the oxime, $CH_2(OH){\cdot}[CH{\cdot}OH]_3{\cdot}C(NOH){\cdot}CH_2{\cdot}OH$), and with phenylhydrazine; it also combines directly with hydrocyanic acid. When digested with acetic anhydride and zinc chloride, levulose yields a pentacetyl derivative, $C_6H_7O(C_2H_3O_2)_5$, a fact which shows that it contains five hydroxyl-groups.

Dextrose and levulose have recently been prepared synthetically from formaldehyde and also from glycerol. When an aqueous solution of formaldehyde is treated with milk of lime at ordinary temperatures, a sugar-like substance called *formose* (or methylenitan) is produced. Formose consists of a mixture of various sugars of the composition $C_6H_{12}O_6$, produced by the polymerisation of formaldehyde,

$$6CH_2O = C_6H_{12}O_6.$$

From this mixture E. Fischer isolated a sugar which he called α-acrose, and from which, by a series of operations, too numerous to discuss here, he succeeded in preparing both dextrose and levulose.

Action of Phenylhydrazine on Dextrose (Glucose) and Levulose (Fructose).

When the sugars glucose and fructose are treated with phenylhydrazine (1 mol.), they yield hydrazones, just as do other aldehydes and ketones,

$$\underset{\text{Glucose.}}{{}^{*}M\cdot CH(OH)\cdot CHO} + C_6H_5\cdot NH\cdot NH_2 = \underset{\text{Glucosephenylhydrazone.}}{M\cdot CH(OH)\cdot CH{:}N_2HC_6H_5} + H_2O.$$

$$\underset{\text{Fructose.}}{M\cdot CO\cdot CH_2\cdot OH} + C_6H_5\cdot NH\cdot NH_2 = \underset{\text{Fructosephenylhydrazone.}}{M\cdot C(N_2HC_6H_5)\cdot CH_2\cdot OH} + H_2O.$$

These hydrazones, when heated with excess of phenylhydrazine, undergo oxidation, the —CH·OH group of the one and the $—CH_2·OH$ group of the other being transformed into —CO and —CHO respectively by loss of hydrogen, some of the phenylhydrazine being reduced to aniline (part ii.) and ammonia,

$$C_6H_5\cdot NH\cdot NH_2 + 2H = C_6H_5\cdot NH_2 + NH_3.$$

These oxidation products of the hydrazones then combine with a second molecule of phenylhydrazine, with formation of *osazones*,

$$\underset{\textit{Hydrazones.}}{\begin{array}{l} M\cdot CH(OH)\cdot CH{:}N_2HC_6H_5 \\ M\cdot C(N_2HC_6H_5)\cdot CH_2\cdot OH \end{array}} \qquad \underset{\textit{Intermediate Oxidation Products.}}{\begin{array}{l} M\cdot CO\cdot CH{:}N_2HC_6H_5 \\ M\cdot C(N_2HC_6H_5)\cdot CHO \end{array}}$$

$$\underset{\textit{Osazone.}}{M\cdot C(N_2HC_6H_5)\cdot CH{:}N_2HC_6H_5.}$$

Although the hydrazones of glucose and fructose are quite distinct substances, they yield one and the same osazone; this fact proves that the two sugars differ in constitution only as regards the two terminal groups.

Many other sugars show a similar behaviour, and yield hydrazones and osazones according as 1 mol. or excess of phenylhydrazine is employed. The hydrazones are usually readily soluble in water, but the osazones are only sparingly soluble; the latter are therefore of the greatest service, not only in the detection and identification of a sugar, but also as offering a means of isolating it from a mixture.

When treated with strong hydrochloric acid, the osazones are decomposed with separation of phenylhydrazine hydrochloride, and formation of *osones*, substances which contain the group —CO·CHO, and which are therefore both ketones and aldehydes,

$$\underset{\text{Glucosazone.}}{M\cdot C(N_2HC_6H_5)\cdot CH{:}N_2HC_6H_5} + 2HCl + 2H_2O =$$
$$\underset{\text{Glucosone.}}{M\cdot CO\cdot CHO} + 2C_6H_5NH\cdot NH_2,\ HCl.$$

As, moreover, osones may be reduced to sugars with the aid of zinc dust and acetic acid, the sugars may be prepared indirectly

---

* The group $CH_2(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)$–, which takes no part in the reaction, is represented by M, for the sake of clearness.

from the osazones. A given osazone does not, however, necessarily yield the sugar from which it was derived; glucosazone, for example, yields first glucosone and then fructose (the group $—CO·CHO$ in the osone being converted into $—CO·CH_2·OH$),

$$\underset{\text{Glucosone.}}{M·CO·CHO} + 2H = \underset{\text{Fructose.}}{M·CO·CH_2·OH}.$$

This series of reactions affords, therefore, a means of converting glucose into fructose.

Maltose, $C_{12}H_{22}O_{11}$, is produced, together with dextrin (p. 272), by the action of malt on starch; this change may be roughly represented by the equation

$$3(C_6H_{10}O_5)_n + nH_2O = nC_{12}H_{22}O_{11} + nC_6H_{10}O_5,$$

and, as already stated in describing the manufacture of alcohol and spirituous liquors, it is brought about by an unorganised ferment, *diastase*, which is contained in the malt.

Preparation of Maltose.—Potato starch (1 kilo) is heated with water (4 litres) on a water-bath until it forms a paste, and after cooling to 60°, malt (60 grams) is added, the mixture being kept at this temperature for an hour. The solution is then heated to boiling, filtered, and evaporated to a syrup, which crystallises on the addition of a crystal of maltose; the crude substance is purified by washing with alcohol, and then recrystallising from this solvent.

Maltose crystallises with one molecule of water in needles, and is very soluble in water, the solution being strongly dextrorotatory;* it reduces Fehling's solution, but only about two-thirds as much as the same weight of dextrose, and ferments readily with yeast. When boiled with dilute sulphuric acid, it is *completely* converted into glucose,

$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6,$$

a change which indicates that maltose is an anhydride of the latter.

Maltose combines with phenylhydrazine, yielding *phenylmaltosazone*, $C_{12}H_{20}O_9(N_2HC_6H_5)_2$, and gives with acetic anhydride *octacetylmaltose*, $C_{12}H_{14}(C_2H_3O_2)_8O_3$.

Milk-sugar, or lactose, $C_{12}H_{22}O_{11}$, has so far only been

---

* $[\alpha]_D = +140·6°$.

found in the animal kingdom. It occurs in the milk of all mammals to the extent of about 4 per cent., and is obtained as a bye-product in the manufacture of cheese.

When milk is treated with rennet, the *caseïn* separates, and milk-sugar remains in solution; on evaporation, the crude sugar is deposited in crystals, which are readily purified by recrystallisation from water.

Milk-sugar forms large, hard, colourless crystals, which contain one molecule of water of crystallisation. It dissolves in six parts of water at ordinary temperatures, and is very much less sweet than cane-sugar; it is dextrorotatory.* It reduces Fehling's solution on boiling, but much more slowly than dextrose. Like cane-sugar, it does not ferment with pure yeast, but ordinary yeast decomposes it into alcohol and lactic acid. When oxidised with nitric acid, it yields a mixture of saccharic and mucic acids, both of which have the constitution $COOH\cdot[CH\cdot OH]_4\cdot COOH$, and which differ from one another, like the tartaric acids, in their action on polarised light (part ii.). Milk-sugar is decomposed, by boiling with dilute sulphuric acid, into *dextrose* and *galactose*,

$$C_{12}H_{22}O_{11} + H_2O = \underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Galactose.}}{C_6H_{12}O_6}.$$

Galactose, $C_6H_{12}O_6$, or $CH_2(OH)\cdot[CH\cdot OH]_4\cdot CHO$, is formed by the hydrolysis of milk-sugar (see above), together with dextrose, from which it may be separated by crystallisation from water. It is also formed by boiling gum-arabic and other gums with dilute sulphuric acid.

It is less soluble than dextrose, and crystallises from water in prisms, which melt at 168°. Its solutions are strongly dextrorotatory,† and ferment readily with yeast. When oxidised with nitric acid, it yields *mucic acid*, $COOH\cdot[CH\cdot OH]_4\cdot COOH$. It combines with phenylhydrazine, yielding galactosazone,

$$CH_2(OH)\cdot[CH\cdot OH]_3\cdot C(N_2HC_6H_5)\cdot CH : N_2HC_6H_5;$$

and on reduction with sodium amalgam it is converted into the corresponding alcohol, *dulcitol*, $CH_2(OH)\cdot[CH\cdot OH]_4\cdot CH_2\cdot OH$, which is isomeric with mannitol, as explained later (part ii.).

---

* $[\alpha]_D = +52{\cdot}53°$.

† $[\alpha]_D = +80{\cdot}3°$.

Starch, or amylum, $(C_6H_{10}O_5)_n$, is widely disseminated throughout the vegetable world, and is found in almost all the organs of plants in the form of nodules.

It occurs in large quantities in all kinds of grain, as, for example, rice, barley, and wheat, and also in tubers, such as potatoes and arrowroot. In Europe, starch is manufactured principally from potatoes, but sometimes also from wheat, maize, and rice.

The potatoes are well washed, crushed, and macerated with water in fine sieves, when the starch passes through with the water, leaving a pulp, consisting of gluten, cellulose, and other substances. The milky liquid, on standing, deposits the starch as a paste, which is repeatedly washed by decantation, and then slowly dried.

The grain is first softened by soaking in warm water, then ground in a mill, and the product run into a large vat, where it is allowed to undergo lactic fermentation. During this process the sugar in the grain is converted into lactic, butyric, and acetic acids, and the gluten (see below) is brought into a less tenacious condition, which favours the subsequent washing of the starch, an operation which is carried out in the manner described above, the crude starch being washed by decantation, and dried.

Starch is a white powder, which, when examined under the microscope, is seen to be made up of peculiarly striated granules, having a definite shape and structure. These granules vary very much in appearance and in size, those composing potato starch being comparatively large, those of wheaten starch considerably smaller.

Starch is insoluble in cold water, but when heated with water, the granules swell up and then burst. The contents of the cells, or the *granulose*, dissolve, but the cell-wall, or *starch cellulose*, is insoluble, and remains in suspension.

The homogeneous, gelatinous mass obtained in this way is called *starch paste*, and is largely used for stiffening linen and calico goods, and also as a substitute for gum. It is best prepared by rubbing starch into a thin paste with cold water, and then adding a considerable quantity of boiling water.

Characteristic of starch is the brilliant blue colour which is produced when a solution of iodine is added to starch paste, or to its solution in water; this colour disappears on heating, but reappears on cooling.

When boiled with dilute acids, starch is first converted into *dextrin* $(C_6H_{10}O_5)^n$, and then into *dextrose*,

$$(C_6H_{10}O_5)_n + nH_2O = nC_6H_{12}O_6.$$

Malt extract, containing the ferment, *diastase*, decomposes starch at 60–70°, with formation of *dextrin* and *maltose*,

$$3C_6H_{10}O_5 + H_2O = C_6H_{10}O_5 + C_{12}H_{22}O_{11},$$

a process which, as already mentioned (p. 98), is of the utmost importance in the manufacture of alcohol and spirituous liquors from grain.

The empirical formula of starch is $C_6H_{10}O_5$; the actual molecular formula has not as yet been determined, but it is undoubtedly many times that represented by the empirical formula, and, therefore, the composition of starch is usually expressed as $(C_6H_{10}O_5)_n$.

Gluten.—Wheaten flour contains about 70 per cent. of starch and 10 per cent. of a sticky, nitrogenous substance called *gluten*. An approximate separation of these two constituents may be brought about by kneading flour in a thin calico bag under water, when the starch passes through with the water, forming a milky liquid, from which it is deposited on standing. The gluten remains in the bag as a tenacious, sticky, gray mass, which soon decomposes and smells disagreeably.

Both starch and gluten are very valuable food-stuffs.

Dextrin, $(C_6H_{10}O_5)_n$, is the name given to the substance, or mixture of substances, obtained as an intermediate product in the conversion of starch into dextrose (see above). It is produced on heating starch to about 210°, or on treating it with dilute acids or infusion of malt.

Dextrin is a colourless, amorphous substance, soluble in water, and is largely used as a cheap substitute for gum; when boiled with dilute acids, it is converted into *dextrose*. It is probably a mixture of various isomeric substances of the empirical formula $C_6H_{10}O_5$.

Cellulose, $(C_6H_{10}O_5)_n$, like starch, occurs very widely distributed throughout the vegetable kingdom. It is the principal constituent of cell membrane and of wood, and constitutes indeed the framework of all vegetable tissues.

Linen, cotton-wool, hemp, and flax, which have been freed from inorganic matter by repeated extraction with acids, consist of almost pure cellulose; an even purer form may be obtained by extracting Swedish filter-paper with hydrofluoric acid, in order to remove traces of silica, washing well with water, and drying at 100°.

Cellulose is insoluble in all the ordinary solvents, but it dissolves in an ammoniacal solution of cupric oxide (Schweitzer's reagent). It is reprecipitated from this solution on the addition of acids, in the form of a jelly, which, when washed with water and dried, is obtained in the form of a grayish powder.

Concentrated sulphuric acid gradually dissolves cellulose, and if the solution be diluted with water and boiled, dextrin and ultimately dextrose are produced. It is thus possible to convert wood into sugar, and indirectly into alcohol.

If unsized paper be subjected to the action of sulphuric acid for a few seconds, then washed with water and dilute ammonia, and again with water, it is converted into a tough substance called *parchment paper* on account of its resemblance to parchment. Such paper serves as a convenient substitute for animal membrane, and is used for a variety of purposes.

Cellulose gives on analysis results agreeing with the formula $C_6H_{10}O_5$, but its molecular weight is certainly very much greater than that expressed by this formula, and probably very much higher than that of starch. Its formula is, therefore, generally written $(C_6H_{10}O_5)_n$, or, more frequently, $(C_{12}H_{20}O_{10})_n$.

It contains ten hydroxyl-groups, because when heated with acetic anhydride and a trace of zinc chloride, it yields cellulose decacetate, $C_{12}H_{10}(C_2H_3O_2)_{10}$, a white flocculent mass, which is reconverted into cellulose by alkalies.

Gun-cotton and Collodion.—When cotton-wool is treated with nitric acid, or, better, with a mixture of nitric and sulphuric acids, nitrates of cellulose of variable composition are produced, according to the amount and concentration of the acids employed, and the length of time during which they are allowed to act.

If cotton-wool be soaked in ten parts of a mixture of one part of nitric acid (sp. gr. 1·5) and three parts of concentrated sulphuric acid for twenty-four hours, the resulting mass, after thoroughly washing and drying, constitutes *gun-cotton.* This substance has, approximately, the composition $C_{12}H_{14}(NO_3)_6O_4$, and is, therefore, cellulose hexa-nitrate. It is insoluble in a mixture of alcohol and ether.

When treated with nitric and sulphuric acids for a short time only, cellulose is converted principally into *tetra-nitrate,* $C_{12}H_{16}(NO_3)_4O_6$, and *penta-nitrate,* $C_{12}H_{15}(NO_3)_5O_5$, both of which dissolve in a mixture of alcohol and ether; a solution of 14 grams of the mixed nitrates in 450 c.c. of alcohol and 550 c.c. of ether constitutes *collodion,* which is largely used for photographic and other purposes.

The nitrates of cellulose are decomposed by alkalies, yielding nitrates of the alkalies and cellulose; they are, therefore, true ethereal salts.

SUMMARY AND EXTENSION.

The carbohydrates are usually subdivided into the following groups:

The saccharoses or monoses.
The disaccharoses or bioses.
The polysaccharoses or polyoses.

The saccharoses, as, for example, dextrose, levulose, and galactose, have the composition $C_6H_{12}O_6$. They all resemble dextrose more or less closely in ordinary physical properties, reduce Fehling's solution, and usually undergo alcoholic fermentation with yeast; they are not resolved into simpler substances on treatment with dilute acids.

The disaccharoses, such as cane-sugar, milk-sugar, and maltose, have the composition $C_{12}H_{22}O_{11}$. From their behaviour under various conditions, more especially with dilute mineral acids, they must be regarded as composed of 2 mols. of identical or of different saccharoses, less 1 mol. of water—that is to say, they are anhydride or ether-like derivatives of the saccharoses. Cane-sugar, for example, is an anhydride or ether-like substance formed from 1 mol. of dextrose and 1 mol. of levulose, whereas milk-sugar is derived from dextrose and galactose in a similar manner. With the exception of maltose, the disaccharoses are not, as a rule, directly fermentable with yeast (compare cane-sugar), nor do they immediately reduce Fehling's solution, as in both cases they must first be converted into saccharoses by hydrolysis.

The polysaccharoses, such as starch and cellulose, have the composition $(C_6H_{10}O_5)_n$, and are much more complex than the disaccharoses, as is shown by their behaviour on hydrolysis; starch, for example, yields, under certain conditions, not only maltose, $C_{12}H_{22}O_{11}$, but also dextrin, a compound which has itself a very high molecular weight, so that the molecule of starch must be highly complex. The high molecular weight of the polysaccharoses, compared with the saccharoses and disaccharoses, is also indicated by their general physical properties, as, for example, their insolubility and their non-crystalline character. The polysaccharoses do not ferment with yeast, and do not reduce Fehling's solution.

The constitutions of the members of the carbohydrate group have been ascertained only in the case of some of the saccharoses, and even here the facts are sometimes not quite conclusive. That the saccharoses are either aldehydes (aldoses) or ketones (ketoses), is shown by their behaviour on oxidation and reduction, and also by the fact that they interact with phenylhydrazine, hydroxylamine, &c.; that they contain hydroxyl-groups is proved by their conversion into acetyl-derivatives (and in the case of the polysaccharose, cellulose, by its conversion into various nitrates).

The constitutions of the saccharoses are further determined by a method which was worked out by Kiliani, and which is based on the following reactions: The saccharoses, like the simpler aldehydes and ketones, combine directly with hydrocyanic acid, forming cyanohydrins (p. 139),

$$\mathrm{M{\cdot}CHO + HCN = M{\cdot}CH(OH){\cdot}CN}$$
$$\mathrm{M{\cdot}CO{\cdot}CH_2{\cdot}OH + HCN = M{\cdot}C(OH)(CN){\cdot}CH_2{\cdot}OH,}$$

and these products are converted into polyhydric acids on hydrolysis with a mineral acid,

$$\mathrm{M{\cdot}CH(OH){\cdot}CN + 2H_2O = M{\cdot}CH(OH){\cdot}COOH + NH_3}$$
$$\mathrm{M{\cdot}C(OH)(CN){\cdot}CH_2{\cdot}OH + 2H_2O = M{\cdot}C(OH)(COOH){\cdot}CH_2{\cdot}OH + NH_3.}$$

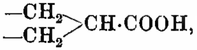
When these polyhydric acids are heated at a high temperature with a large excess of hydriodic acid and a little amorphous phosphorus, all the hydroxyl-groups in the molecule are displaced by hydrogen atoms—that is to say, complete reduction of all the $>CH\cdot OH$ and $—CH_2\cdot OH$ groups is effected, and a fatty acid is obtained. In the case of the polyhydric acid prepared from glucose cyanohydrin, this change is represented by the equation

$$CH_2(OH)\cdot[CH\cdot OH]_4\cdot CH(OH)\cdot COOH + 12HI = CH_3\cdot[CH_2]_4\cdot CH_2\cdot COOH + 6H_2O + 6I_2,$$

and *normal* heptylic acid is obtained; whereas on reducing the corresponding polyhydric acid prepared from levulose cyanohydrin, methylbutylacetic acid, an isomeride of normal heptylic acid, is formed,

$$CH_2(OH)\cdot[CH\cdot OH]_3\cdot C(OH)(COOH)\cdot CH_2\cdot OH + 12HI = CH_3\cdot[CH_2]_3\cdot CH(COOH)\cdot CH_3 + 6H_2O + 6I_2.$$

These facts show that dextrose is an aldehyde and a derivative of *normal* hexane. Had it been a ketone, the polyhydric acid produced from it could not have contained the group $—CH(OH)\cdot COOH$, but must have contained the group $\begin{array}{l}—CH(OH)\\—CH(OH)\end{array}\!\!>C(OH)\cdot COOH$; this, on reduction, would have been transformed into



$$\begin{array}{l}—CH_2\\—CH_2\end{array}\!\!>CH\cdot COOH,$$

and consequently the fatty acid finally produced would not have been normal heptylic acid, but one of its isomerides. In a similar manner, the conversion of levulose into methylbutylacetic acid, taken in conjunction with other facts, shows that this sugar is a ketone and not an aldehyde, and that its constitution is expressed by the formula already given (p. 265). In addition to this evidence, the fact that dextrose and levulose may be converted into mannitol, shows them to be derivatives of normal hexane.

CHAPTER XVI.

CYANOGEN COMPOUNDS.

The cyanogen compounds, like the carbohydrates, do not form a natural group or series, such as that of the paraffins, alcohols, fatty acids, &c.; nevertheless (with the exception of urea and uric acid) they may all be considered as derived from cyanogen, $(CN)_2$, just as the chlorides, hypochlorites, &c., may be regarded as derivatives of chlorine, Cl_2. In many cases the cyanogen compounds are closely related to the compounds of chlorine in properties, although they differ from the latter in composition, and contain the monovalent *group of atoms* –CN in the place of a *single atom* of chlorine, –Cl, as shown by the following examples:

$$\begin{array}{lllllll} Cl_2, & HCl, & KCl, & AgCl, & HgCl_2, & HOCl, & C_2H_5Cl \\ (CN)_2, & HCN, & KCN, & AgCN, & Hg(CN)_2, & HO{\cdot}CN, & C_2H_5{\cdot}CN. \end{array}$$

This fact brings out very clearly the meaning of the term 'radicle,' the monovalent group –CN* playing much the same part as the atom of chlorine, just as the radicle ammonium may play the part of a single atom of an alkali metal.

Cyanogen, dicyanogen, C_2N_2, or Cy_2, or $N{\equiv}C{-}C{\equiv}N$, is produced in small quantities when the electric arc passes between carbon poles in an atmosphere of nitrogen,

$$2C + N_2 = C_2N_2;$$

also when ammonium oxalate is strongly heated,

$$NH_4OOC{\cdot}COONH_4 = N{\equiv}C{-}C{\equiv}N + 4H_2O,$$

a reaction of considerable interest, as it shows that cyanogen is the nitrile (p. 280) of oxalic acid.

Cyanogen is prepared by heating silver cyanide or mercuric cyanide (p. 282) in a hard glass tube, the gas being collected over mercury,

$$Hg(CN)_2 = Hg + C_2N_2.$$

During the operation a considerable quantity of a brown amorphous substance called *paracyanogen*, $(CN)_n$, is produced; this compound is a polymeride of cyanogen, and when heated at a high temperature it is completely resolved into cyanogen gas, just as paraformaldehyde is converted into formaldehyde under like conditions.

Cyanogen is a colourless gas, which condenses to a liquid

---

* The cyanogen radicle –CN is often written Cy.

at ordinary temperatures under a pressure of four atmospheres; it has a peculiar smell, is excessively poisonous, and burns with a characteristic purple or peach-coloured flame, yielding carbon dioxide and nitrogen.

It is moderately soluble in water, readily in alcohol, but its aqueous solution soon decomposes, a brown amorphous precipitate ('azulmic acid') being deposited; the solution then contains ammonium oxalate and other substances.

When an aqueous solution of cyanogen is treated with acids or with alkalies, oxalic acid or an oxalate is produced,

$$NC{\equiv}C{-}C{\equiv}N + 4H_2O = NH_4OOC{\cdot}COONH_4,$$

this change being the reverse of that which occurs when ammonium oxalate is heated alone.

All substances which contain the cyanogen group $-C{\equiv}N$ behave in a similar manner, and are converted on hydrolysis into carboxylic acids or their salts, amides being formed as intermediate products.

Cyanogen is readily absorbed by potash, potassium cyanide and cyanate being produced,

$$C_2N_2 + 2KOH = KCN + KOCN + H_2O,$$

just as potassium chloride and hypochlorite are formed when chlorine is led into potash,

$$Cl_2 + 2KOH = KCl + KOCl + H_2O.$$

Derivatives of Cyanogen.—Cyanogen chloride, $CNCl$, is formed by the action of chlorine on a solution of hydrocyanic acid,

$$HCN + Cl_2 = CNCl + HCl.$$

It is a colourless, very poisonous liquid, boils at 15·5°, and readily undergoes spontaneous polymerisation, yielding *cyanuric chloride*, $C_3N_3Cl_3$, a solid substance which melts at 146°, and is decomposed by alkalies, yielding cyanuric acid,

$$C_3N_3Cl_3 + 3H_2O = C_3N_3(OH)_3 + 3HCl.$$

The corresponding bromo- and iodo- derivatives of cyanogen, $CNBr$ and CNI, are also known.

Hydrocyanic acid (prussic acid), $H{-}C{\equiv}N$, is found in the free state in plants, sometimes in considerable quantities;

more frequently it occurs in combination with glucose and benzaldehyde in the form of the glucoside *amygdalin* (part ii.). Bitter almonds and cherry kernels contain this glucoside; when macerated and kept in contact with water, fermentation soon sets in, due to the presence of a ferment, *emulsin*, and the amygdalin is decomposed into hydrocyanic acid, benzaldehyde (part ii.), and glucose,

$$\underset{\text{Amygdalin.}}{C_{20}H_{27}NO_{11}} + 2H_2O = \underset{\text{Benzaldehyde.}}{C_7H_6O} + HCN + \underset{\text{Glucose.}}{2C_6H_{12}O_6}.$$

Hydrocyanic acid is formed when the silent electric discharge passes through a mixture of hydrogen and cyanogen,

$$H_2 + C_2N_2 = 2HCN;$$

and also when ammonium formate is heated, a change which is analogous to the formation of cyanogen from ammonium oxalate,

$$H{\cdot}COONH_4 = HCN + 2H_2O.$$

Hydrocyanic acid is prepared by distilling potassium cyanide, or, more usually, potassium ferrocyanide, with dilute sulphuric acid,

$$KCN + H_2SO_4 = KHSO_4 + HCN$$

$$\underset{\text{Potassium Ferrocyanide.}}{2K_4Fe(CN)_6} + 3H_2SO_4 = 6HCN + \underset{\text{Ferric Potassioferrocyanide.}}{FeKFe(CN)_6} + 3K_2SO_4;$$

in the latter reaction, only half of the potassium ferrocyanide yields hydrocyanic acid.

Powdered potassium ferrocyanide (10 parts) is mixed with concentrated sulphuric acid (7 parts) previously diluted with water (10–40 parts, according to the desired strength of the hydrocyanic acid), and the mixture distilled from a retort connected with a condenser. The anhydrous acid may be prepared from the aqueous solution thus obtained by fractional distillation and dehydration over calcium chloride.

Anhydrous hydrocyanic acid is a colourless liquid; it boils at 26°, and solidifies in a freezing mixture to colourless crystals, which melt at -14°; it has an odour similar to that of oil of bitter almonds, and burns with a pale blue flame, with formation of carbon dioxide, water, and nitrogen. It is a terrible poison, very small quantities being sufficient to cause death.

Hydrocyanic acid dissolves readily in water, but the solution rapidly decomposes, with separation of a brown substance, and the liquid then contains ammonium formate and other compounds,

$$HCN + 2H_2O = H{\cdot}COONH_4.$$

This hydrolysis takes place only slowly if a trace of some mineral acid be present, more quickly if the solution be heated with mineral acids or alkalies.

The facts that hydrocyanic acid is formed on heating ammonium formate, and is reconverted into this substance on hydrolysis, show that it is the nitrile of formic acid. On reduction with nascent hydrogen, hydrocyanic acid is converted into methylamine,

$$HCN + 4H = CH_3{\cdot}NH_2.$$

The constitution of hydrocyanic acid is expressed by the formula $H{\cdot}C{\vdots}N$ for the following reasons: The acid is produced from ammonium formate, by a change similar to that by which acetonitrile is formed from ammonium acetate,

$$H{\cdot}COONH_4 = H{\cdot}CN + 2H_2O$$
$$CH_3{\cdot}COONH_4 = CH_3{\cdot}CN + 2H_2O;$$

when heated with mineral acids, it is converted into formic acid, just as methyl cyanide is converted into acetic acid,

$$H{\cdot}CN + 2H_2O = H{\cdot}COOH + NH_3$$
$$CH_3{\cdot}CN + 2H_2O = CH_3{\cdot}COOH + NH_3.$$

As, moreover, many facts show that the methyl group in methyl cyanide and in acetic acid is directly united with carbon, it is very probable that the hydrogen atom in hydrocyanic acid is in a similar state of combination (p. 286).

Hydrocyanic acid is the nitrile of formic acid, or rather of ammonium formate, the name nitrile being given to those compounds which are derived from ammonium salts by the elimination of 2 mols. of water. The fact that the hydrogen atom in hydrocyanic acid, like that in hydrochloric acid, is displaceable by metals, although it is directly united with carbon (and not with oxygen, as in the case of the carboxylic acids), is accounted for by the close similarity between —CN and —Cl, both of which have acid-forming or electro-negative properties.

Hydrocyanic acid is a feeble acid, and scarcely reddens blue litmus. It forms salts with the hydroxides (but not with the carbonates) of potassium, sodium, and many other metals; the alkali salts are decomposed by carbon dioxide with liberation of the acid, and this is the reason why potassium cyanide, for example, in contact with moist air, always smells of hydrocyanic acid.

Potassium cyanide, KCN, may be obtained synthetically by passing nitrogen into a mixture of carbon and fused potash, and by burning potassium in cyanogen. It is prepared on a large scale by strongly heating potassium ferrocyanide,

$$K_4Fe(CN)_6 = 4KCN + FeC_2 + N_2;$$

the fused product is filtered through hot, porous crucibles, to free it from finely-divided iron carbide, and then cast into sticks. The pure salt may be prepared by neutralising hydrocyanic acid with pure potash, and evaporating the solution out of contact with air.

Potassium cyanide crystallises in colourless plates, and is very readily soluble in water, but nearly insoluble in absolute alcohol; it is excessively poisonous.

Fused potassium cyanide is a powerful reducing agent; it liberates the metals from many metallic oxides, being itself converted into potassium cyanate,

$$KCN + PbO = KCNO + Pb,$$

hence its use in analytical chemistry and in some metallurgical operations.

The aqueous solution of potassium cyanide gives, with silver nitrate, a curdy white precipitate of *silver cyanide*, $AgCN$, which is insoluble in dilute acids, but soluble in ammonia and potassium cyanide; in the latter case, with formation of the soluble double salt, $KAg(CN)_2$, which is used in electroplating. Silver cyanide is thus very similar in its properties to silver chloride, from which, however, it differs in this, that when heated, it is decomposed completely into silver and cyanogen,

$$2AgCN = 2Ag + C_2N_2.$$

Mercuric cyanide, $Hg(CN)_2$, is prepared by dissolving mercuric oxide in hydrocyanic acid,

$$HgO + 2HCN = Hg(CN)_2 + H_2O.$$

The solution, on evaporation, deposits the salt in colourless crystals, which are moderately soluble in water; when strongly heated, the salt is decomposed into mercury and cyanogen.

The detection of hydrocyanic acid or of a cyanide is usually based on the following tests: (*a*) The aqueous solution is made strongly alkaline with potash, a few drops of ferrous sulphate added, and the liquid warmed; potassium ferrocyanide is thus formed, and on acidifying and adding ferric chloride, a blue colouration or precipitate of Prussian blue is produced. (*b*) The solution is mixed with a few drops of ammonium sulphide, and evaporated to dryness on a water-bath; the residue contains ammonium thiocyanate, and on the addition of ferric chloride, an intense blood-red colouration is produced.

The cyanides of many of the metals, like many of the metallic chlorides, are capable of forming 'double salts' with the compounds of other metals. Silver cyanide, for instance, is soluble in potassium cyanide, with which it forms a double salt of the composition $AgK(CN)_2$; the compound $KAu(CN)_4$ may be obtained in a similar manner by dissolving auric cyanide, $Au(CN)_3$, in potassium cyanide. These 'double salts' crystallise unchanged from water, but are decomposed by mineral acids in the cold, with evolution of hydrocyanic acid. Like the soluble simple cyanides, they are excessively poisonous.

In addition to these double salts, complex metallic cyanides of a different class are known, the most important of which are potassium ferrocyanide, $K_4Fe(CN)_6$, and potassium ferricyanide, $K_3Fe(CN)_6$. These salts are not poisonous, and are more stable than the double salts just referred to. On treatment with mineral acids, in the cold, they do not yield hydrocyanic acid, but hydrogen is substituted for one of the metals only, and an acid, such as hydroferrocyanic acid, is liberated,

$$K_4Fe(CN)_6 + 4HCl = H_4Fe(CN)_6 + 4KCl.$$

Potassium ferrocyanide, or yellow prussiate of potash, $K_4Fe(CN)_6$, is formed when ferrous hydrate is dissolved in potassium cyanide,

$$6KCN + Fe(OH)_2 = K_4Fe(CN)_6 + 2KOH.$$

It is manufactured by fusing together in an iron pot nitrogenous animal refuse (horn-shavings, hair, blood, &c.), crude potashes (containing potassium carbonate), and scrap-iron. The product is extracted with hot water, the solution filtered, and evaporated to crystallisation.

Potassium ferrocyanide cannot be present in the melted mass, because it is decomposed at a high temperature; it must, therefore, be formed when the product is extracted with water.

Probably the melt contains iron, potassium cyanide, and ferrous sulphide (the latter having been produced by the action of the sulphur in the animal refuse on the scrap-iron); these substances would interact in the presence of water, yielding potassium ferrocyanide,

$$6KCN + FeS = K_4Fe(CN)_6 + K_2S$$
$$2KCN + Fe + 2H_2O = Fe(CN)_2 + 2KOH + H_2$$
$$Fe(CN)_2 + 4KCN = K_4Fe(CN)_6.$$

Potassium ferrocyanide crystallises in lemon-yellow prisms, which contain 3 mols. of water of crystallisation; it is soluble in about 4 parts of water. When ignited it decomposes, yielding potassium cyanide, nitrogen, and a compound of iron and carbon (iron carbide),

$$K_4Fe(CN)_6 = 4KCN + N_2 + FeC_2,$$

a reaction which is made use of in the preparation of potassium cyanide. When warmed with strong (90 per cent.) sulphuric acid, it gives carbon monoxide,

$$K_4Fe(CN)_6 + 6H_2O^* + 6H_2SO_4 = 6CO + 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4,$$

but when boiled with dilute sulphuric acid, hydrocyanic acid is produced.

Solutions of ferric salts in excess give with potassium ferrocyanide a precipitate of 'Prussian blue,' or ferric ferrocyanide,

$$Fe_4[Fe(CN)_6]_3.$$

Potassium ferricyanide, or red prussiate of potash, $K_3Fe(CN)_6$, is prepared by passing chlorine into a solution of potassium ferrocyanide until the liquid ceases to give a blue precipitate with ferric salts; on evaporation, potassium ferricyanide separates out in dark-red crystals.

The transformation of potassium ferrocyanide into ferricyanide is simply a process of oxidation, as other oxidising agents, such as nitric acid, produce the same result; this change is easily understood if it be assumed that potassium ferrocyanide is a compound of potassium cyanide and *ferrous* cyanide, $(4KCN + Fe(CN)_2)$. On oxidation, the ferrous is converted into ferric cyanide, and potassium ferricyanide, which may be regarded as a compound of potassium cyanide and *ferric* cyanide, $(3KCN + Fe(CN)_3)$, is formed.

Potassium ferricyanide gives, with ferrous salts, a precipitate of Turnbull's blue, or ferrous ferricyanide, $Fe_3[Fe(CN)_6]_2$; it is employed as a mild oxidising agent, as in alkaline solution, in presence of an oxidisable substance, it is converted into potassium ferrocyanide,

$$3K_3Fe(CN)_6 + 2KOH = 2K_4Fe(CN)_6 + H_2O + O.$$

The **nitriles,** or alkyl cyanides, as the *ethereal salts* of *hydrocyanic acid* are termed, may be prepared by heating the alkyl halogen compounds with *potassium* cyanide,

$$KCN + C_2H_5I = C_2H_5{\cdot}CN + KI,$$

or by distilling the ammonium salts, or the amides, of the fatty acids either alone or with some dehydrating agent, such as phosphorus pentoxide,

---

* The water necessary for this decomposition is partly derived from the crystals of the salt, partly from the acid, which is not anhydrous.

$$CH_3{\cdot}COONH_4 = CH_3{\cdot}CN + 2H_2O$$
$$C_2H_5{\cdot}CO{\cdot}NH_2 = C_2H_5{\cdot}CN + H_2O.$$

The lower members of the series, such as methyl cyanide (b.p. 81°) and ethyl cyanide (b.p. 97°), are colourless liquids, possessing a strong, but not disagreeable smell, and are readily soluble in water; the higher members, as, for example, octyl cyanide, $C_8H_{17}{\cdot}CN$, are almost insoluble in water.

When boiled with acids or alkalies, they are decomposed, with formation of fatty acids, the –CN group being converted into the –COOH group,

$$CH_3{\cdot}CN + KOH + H_2O = CH_3{\cdot}COOK + NH_3$$
$$C_2H_5{\cdot}CN + HCl + 2H_2O = C_2H_5{\cdot}COOH + NH_4Cl.$$

For this reason, and also because they may be obtained from the ammonium salts of the fatty acids, the nitriles are named after the acids which they yield on hydrolysis: methyl cyanide, $CH_3{\cdot}CN$, for example, is called *acetonitrile;* ethyl cyanide, $C_2H_5{\cdot}CN$, *propionitrile*, and so on.

On reduction with zinc and sulphuric acid, or, better, with sodium and alcohol, the alkyl cyanides are converted into primary amines, a fact which shows that the alkyl group is directly united with carbon,

$$CH_3{\cdot}CN + 4H = CH_3{\cdot}CH_2{\cdot}NH_2.$$

The *isonitriles*, carbylamines or isocyanides, are isomeric with the nitriles: they may be prepared by heating the alkyl halogen compounds with *silver* cyanide,

$$C_2H_5I + Ag{\cdot}N{\equiv}C = C_2H_5{\cdot}N{\equiv}C + AgI,$$

and by treating primary amines with chloroform and potash,

$$CH_3{\cdot}NH_2 + 3KOH + CHCl_3 = CH_3{\cdot}N{\equiv}C + 3KCl + 3H_2O.$$

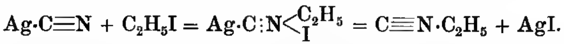
The isonitriles or carbylamines are colourless liquids, sparingly soluble in water; they have an almost unbearable odour and poisonous properties.

They boil at lower temperatures than the isomeric cyanides; methyl isonitrile, $CH_3{\cdot}NC$, for example, boils at 58°; ethyl isonitrile, $C_2H_5{\cdot}NC$, at 82°. They differ from the nitriles, inasmuch as they are not decomposed by boiling alkalies; they are, however, readily decomposed by dilute mineral acids, yielding formic acid and an amine,

$$C_2H_5\cdot NC + 2H_2O = H\cdot COOH + C_2H_5\cdot NH_2.$$

This behaviour is also totally different from that of the nitriles, and shows that the alkyl group in the isonitriles is united with nitrogen and not with carbon—that is to say, the nitriles are ethereal salts of hydrocyanic acid, $H\cdot C\vdots N$, whereas the isonitriles may be regarded as derivatives of an isomeric modification of hydrocyanic acid, $H\cdot N\equiv C$.

In order to explain the difference in the constitution of the products produced by the action of alkyl halogen compounds on potassium and silver cyanide respectively, it is necessary to assume either that in the formation of silver cyanide from potassium cyanide by precipitation, *intramolecular change* (p. 290) has taken place, $K\cdot C\equiv N$ yielding $Ag\cdot N\equiv C$, or that silver cyanide, $Ag\cdot C\equiv N$, first yields, with the alkyl halogen compound, an additive product, which is then decomposed, yielding the isonitrile,



$$Ag\cdot C\equiv N + C_2H_5I = Ag\cdot C\vdots N{<}^{C_2H_5}_{I} = C\equiv N\cdot C_2H_5 + AgI.$$

Cyanic acid, $HO\cdot CN$, is produced when cyanuric acid (see below) is heated, and the vapours condensed in a receiver cooled in a freezing mixture,

$$C_3N_3(OH)_3 = 3HO\cdot CN.$$

It is a strongly acid, unstable liquid, and at temperatures above 0° rapidly undergoes polymerisation into an opaque, porcelain-like mass called cyamelide. Its aqueous solution decomposes very rapidly into carbon dioxide and ammonia,

$$HO\cdot CN + H_2O = CO_2 + NH_3,$$

and therefore the acid cannot be prepared by the decomposition of its salts with mineral acids.

Potassium cyanate, $KO\cdot CN$, is produced when potassium cyanide slowly oxidises in the air; it is usually prepared by heating potassium cyanide (or ferrocyanide) with some readily reducible metallic oxide, such as litharge or red-lead, and then extracting the product with dilute alcohol,

$$KCN + PbO = KO\cdot CN + Pb.$$

It is a colourless, crystalline powder, readily soluble in water and dilute alcohol, but insoluble in absolute alcohol; its aqueous solution rapidly decomposes with formation of ammonia and potassium bicarbonate,

$$KO{\cdot}CN + 2H_2O = NH_3 + KHCO_3.$$

When a solution of this salt is mixed with ammonium sulphate and evaporated, *urea* is formed, ammonium cyanate, $NH_4O{\cdot}CN$, being the intermediate product (p. 289).

Ethereal Salts of Cyanic Acid.—Cyanic acid, like hydrocyanic acid, yields two series of ethereal salts—namely, the normal cyanates, such as $C_2H_5O{\cdot}CN$, derived from $HO{\cdot}CN$; and the isocyanates, such as $C_2H_5{\cdot}N{:}CO$, derived from $H{\cdot}N{:}CO$.

The *alkyl* (*normal*) *cyanates* are produced by the action of cyanogen chloride on the sodium compounds of the alcohols,

$$NaO{\cdot}C_2H_5 + Cl{\cdot}CN = C_2H_5O{\cdot}CN + NaCl;$$

they are colourless, ethereal-smelling liquids, and are decomposed by alkalies into alkali carbonates, ammonia, and alcohols; this fact shows that the alkyl group is united with oxygen and not with nitrogen.

The *alkyl isocyanates* are obtained by the action of the alkyl halogen compounds on silver isocyanate (obtained as a white precipitate on adding silver nitrate to an aqueous solution of potassium cyanate),

$$AgN{:}CO + CH_3I = CH_3N{:}CO + AgI.$$

They are very unpleasant-smelling, volatile liquids; when heated with alkalies, they are decomposed into alkali carbonates and *primary amines* (Würtz), a reaction which shows that the alkyl group is united with nitrogen,

$$CH_3N{:}CO + 2KOH = CH_3{\cdot}NH_2 + K_2CO_3.$$

Cyanuric acid, $N_3C_3O_3H_3$, is produced by the action of water on cyanuric chloride (p. 278),

$$N_3C_3Cl_3 + 3H_2O = N_3C_3(OH)_3 + 3HCl.$$

It is a crystalline, tribasic acid, forming well-defined salts, of which the crystalline trisodium salt, $N_3C_3(ONa)_3$, is the most characteristic. On distillation, the acid is converted into cyanic acid.

Thiocyanic acid, or sulphocyanic acid, $HS{\cdot}CN$, is obtained in the form of its salts when the alkali cyanides are heated with sulphur,

$$KCN + S = KS{\cdot}CN,$$

the change being analogous to the formation of cyanates by the oxidation of cyanides.

Thiocyanic acid may be obtained by distilling potassium thiocyanate with dilute sulphuric acid; it is a liquid, solidifies at 12·5°, and has a very penetrating odour. It is decomposed by moderately concentrated sulphuric acid, with evolution of carbon oxysulphide,

$$HS{\cdot}CN + H_2O = COS + NH_3.$$

Potassium thiocyanate, $KS{\cdot}CN$, is prepared by fusing potassium cyanide (or ferrocyanide) with sulphur, and extracting the mass with alcohol. On concentrating the alcoholic solution, the salt is deposited in colourless, very deliquescent needles. The *ammonium salt*, $NH_4S{\cdot}CN$, is most conveniently prepared by agitating strong ammonia with carbon bisulphide,

$$4NH_3 + CS_2 = NH_4S{\cdot}CN + (NH_4)_2S.$$

The thiocyanates are used in inorganic analysis, as reagents for ferric salts, with which they give an intense blood-red colouration, caused by the formation of a double salt. Thiocyanates are also employed in dyeing and calico-printing as mordants, and are known commercially as 'rhodanates.'

Thiocyanic acid, like cyanic acid, forms two series of ethereal salts—namely, the normal thiocyanates, such as $C_2H_5S{\cdot}CN$, derived from $HS{\cdot}C{:}N$, and the isothiocyanates, such as $C_2H_5N{:}CS$, derived from $HN{:}C{:}S$. The *alkyl* (*normal*) *thiocyanates* are produced by the action of the alkyl iodides on potassium thiocyanate, or from the mercaptides (especially lead mercaptide), by the action of cyanogen chloride,

$$(C_2H_5S)_2Pb + 2ClCN = 2C_2H_5S{\cdot}CN + PbCl_2,$$

a reaction which is exactly similar to the formation of ethyl cyanate by the action of cyanogen chloride on sodium ethoxide (see above).

The normal thiocyanates are volatile liquids possessing a slight though not penetrating smell of garlic; when oxidised with nitric acid they are converted into alkyl sulphonic acids, $C_2H_5S{\cdot}CN$, for example, yielding $C_2H_5{\cdot}SO_3H$, a reaction which shows that the alkyl group is united with sulphur.

The *alkyl isothiocyanates*, or *mustard-oils*, are produced by heating the normal thiocyanates at 180°, or by simply repeatedly distilling them, intramolecular change (p. 290) taking place; the alkyl group in these compounds is combined with nitrogen, because when heated with hydrochloric acid they are decomposed into primary amines, carbon dioxide, and sulphuretted hydrogen,

$$C_2H_5N{:}CS + 2H_2O = C_2H_5{\cdot}NH_2 + CO_2 + SH_2.$$

Allyl isothiocyanate, or '**mustard-oil**,' $CH_2{:}CH{\cdot}CH_2{\cdot}N{:}CS$, is prepared by distilling macerated black mustard seeds with steam. Mustard seeds contain a glucoside, 'potassium myronate,' $C_{10}H_{18}NS_2O_{10}K$, which is soluble in water; its solution gradually undergoes fermentation, owing to the presence of a ferment, 'myrosin,' mustard-oil, glucose, and potassium hydrogen sulphate being produced,

$$C_{10}H_{18}NS_2O_{10}K = C_3H_5{\cdot}N{:}CS + C_6H_{12}O_6 + KHSO_4.$$

Allyl isothiocyanate is a colourless, pungent-smelling liquid, which boils at 151°; when dropped on the skin, it produces blisters.

Urea,* or carbamide, CH_4N_2O or $CO(NH_2)_2$, is a compound of great physiological importance. It occurs in the urine of mammals and of carnivorous birds and reptiles, and is one of the principal nitrogenous constituents of human urine, of which it forms about 3 per cent.

It was discovered in urine in 1773, and was first artificially produced in 1828 by Wöhler, who found that on warming an aqueous solution of ammonium cyanate the salt was converted into urea,

$$NH_4{\cdot}O{\cdot}CN = CO(NH_2)_2,$$

a discovery which, being the first synthetical production of an animal product, was of fundamental importance (compare p. 10).

---

* Although urea, uric acid, and glycine are not derivatives of cyanogen, they are in many ways related to the cyanogen compounds, and for this reason may be conveniently considered in this chapter.

When one substance is converted into another which has the same molecular formula, the change is spoken of as 'intramolecular.' Ammonium cyanate, NH_4OCN, has the same molecular formula as urea, $CO(NH_2)_2$; but the atoms in the molecules of the two compounds are arranged differently—that is to say, their constitutions are different. Many cases of intramolecular change are met with in organic chemistry.

Urea may be prepared from urine by evaporating to a small bulk and adding strong nitric acid. The precipitate of crude urea nitrate (see below) is recrystallised from nitric acid, dissolved in boiling water, and decomposed with barium carbonate; the solution is then evaporated to dryness, and the urea extracted with alcohol, in which barium nitrate is insoluble.

It is more commonly prepared by mixing a solution of potassium cyanate (2 mols.) with an equivalent quantity of ammonium sulphate (1 mol.), evaporating to dryness, and extracting with alcohol. In both cases the crude urea is purified by recrystallisation from water or alcohol.

Urea may be also synthetically obtained by treating ethyl carbonate, or phosgene gas* (carbonyl chloride), with ammonia,

$$CO(OC_2H_5)_2 + 2NH_3 = CO(NH_2)_2 + 2C_2H_5{\cdot}OH$$
$$COCl_2 + 4NH_3 = CO(NH_2)_2 + 2NH_4Cl.$$

It crystallises in colourless needles, melts at 132°, and is readily soluble in water and alcohol, but almost insoluble in ether; when heated with water at 120°, or boiled with dilute acids, it is decomposed into carbon dioxide and ammonia (or one of its salts),

$$CO(NH_2)_2 + H_2O + 2HCl = CO_2\ 2N + H_4Cl,$$

but when heated alone it yields ammonia, cyanuric acid, and complex cyanogen compounds,

$$3CO(NH_2)_2 = H_3C_3N_3O_3 + 3NH_3.$$

Urea is decomposed by nitrous acid into nitrogen and carbon dioxide,

---

[*] *Ethyl carbonate* is formed when silver carbonate is treated with ethyl iodide: it is an agreeably-smelling, neutral liquid, which boils at 126°. *Carbonyl chloride* is obtained by the direct combination of carbon monoxide and chlorine in sunlight; it is a gas which decomposes rapidly in contact with water, into carbon dioxide and hydrochloric acid.

$$CO(NH_2)_2 + 2HNO_2 = CO_2 + N_2 + 2H_2O,$$

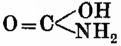
a similar change taking place when it is mixed with solutions of hypochlorites or hypobromites,

$$CO(NH_2)_2 + 3NaOCl = CO_2 + N_2 + 2H_2O + 3NaCl;$$

by measuring the volume of nitrogen given off, on treating a solution of urea with nitrous acid, the quantity in solution can be readily estimated.

Urea possesses basic properties, and combines with *one* equivalent of acids to form salts, most of which are soluble in water. The most characteristic salt is *urea nitrate*, $CO(NH_2)_2,HNO_3$, which crystallises in glistening plates, and is sparingly soluble in nitric acid.

Constitution.—The formation of urea from the ethyl salt and from the chloride of carbonic acid is exactly analogous to the formation of acetamide from ethyl acetate and from acetyl chloride; urea is therefore the diamide of carbonic acid—hence the name carbamide—and its constitution is represented by the formula  $O=C\begin{matrix}\diagup NH_2\\ \diagdown NH_2\end{matrix}$.

The monamide of carbonic acid,  $O=C\begin{matrix}\diagup OH\\ \diagdown NH_2\end{matrix}$ (carbamic acid), is not known in a free state. Ammonium carbamate is formed by the action of carbon dioxide on ammonia,

$$CO_2 + 2NH_3 = CO(NH_2)\cdot ONH_4,$$

and is one of the constituents of commercial ammonium carbonate, which is frequently prepared by this method.

Uric acid, $C_5H_4N_4O_3$, occurs in small quantities in human urine, from which it separates on exposure to the air in the form of a light yellow powder; it also occurs in the excrements of birds and reptiles, and is present in large quantities in *guano*. The excrements of serpents consist almost entirely of ammonium urate: from this source uric acid is conveniently prepared by boiling the excrement with caustic soda until all the ammonia has been expelled, and pouring the hot filtered liquid into hydrochloric acid; on cooling, uric acid separates as a fine crystalline powder.

Uric acid is insoluble in alcohol and ether, and very sparingly soluble in water (1 part dissolves in 1800 parts of water at 100°). If uric acid be moistened with nitric acid in a porcelain basin, and the mixture then evaporated to dryness on a water-bath, a yellow stain is left, which, on the addition of ammonia, becomes intensely violet (murexide reaction).

Uric acid is a weak dibasic acid; when dissolved in sodium carbonate, it yields an acid sodium salt, $C_5H_3N_4O_3Na + \frac{1}{2}H_2O$; the neutral sodium salt, $C_5H_2N_4O_3Na_2 + H_2O$, is formed when uric acid is dissolved in caustic soda. The salts, like the acid itself, are all sparingly soluble in water.

Uric acid has been prepared synthetically by heating glycine with urea at 200–230°.

Glycine, glycocoll, or amido-acetic acid, $CH_2(NH_2)\cdot COOH$, like urea and uric acid, is found in animal secretions, but usually in combination. As *hippuric acid*, or benzoylglycine, $C_6H_5\cdot CO\cdot NH\cdot CH_2\cdot COOH$ (part ii.), it occurs in considerable quantities in the urine of horses, and it is best prepared from this substance by treatment with hydrochloric or sulphuric acid,

$$C_6H_5\cdot CO\cdot NH\cdot CH_2\cdot COOH + H_2O + HCl = \underset{\text{Benzoic Acid.}}{C_6H_5\cdot COOH} + \underset{\text{Glycine Hydrochloride.}}{NH_2\cdot CH_2\cdot COOH, HCl.}$$

It may also be conveniently prepared by treating monochloracetic acid with ammonia,

$$CH_2Cl\cdot COOH + 3NH_3 = CH_2(NH_2)\cdot COONH_4 + NH_4Cl.$$

Glycine crystallises from water in colourless prisms, and melts at 235°. It is readily soluble in water; the aqueous solution gives with ferric chloride a red colouration, and with phenol and sodium hypochlorite an intense blue colouration.

Glycine contains an amido-group and a carboxyl-group, and is therefore capable of forming salts both with acids and bases.

The most characteristic metallic salt is the *copper salt*,

$(C_2H_4NO_2)_2Cu$, which is readily formed by dissolving cupric hydrate in a hot, strong, aqueous solution of glycine; on cooling, the salt crystallises in deep blue needles.

Glycine hydrochloride, $C_2H_5NO_2$, HCl, is produced by dissolving glycine in hydrochloric acid, or by decomposing hippuric acid with hydrochloric acid; it crystallises in colourless needles, is readily soluble in water, and is decomposed by alkalies or alkali carbonates, with liberation of glycine.

When treated with nitrous acid, glycine is converted into glycollic acid (p. 223),

$$CH_2(NH_2){\cdot}COOH + NO_2H = CH_2(OH){\cdot}COOH + N_2 + H_2O.$$

Other *amido-acids* such as *alanine* or α-amidopropionic acid,

$$CH_3{\cdot}CH(NH_2){\cdot}COOH,$$

may be prepared from the corresponding halogen acids by the action of ammonia; in their properties they are very similar to glycine.

INDEX.

[Where more than one reference is given, and one of them is in heavy type, the latter refers to the systematic description of the substance.]

THE END.