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THE ELEMENTS OF
ORGANIC CHEMISTRY

BY

E. I. LEWIS, B.A., B.Sc.

ASSISTANT MASTER OF OUNDLE SCHOOL

Fourth Impression

LONDON: W. B. CLIVE
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1919

[1909]

PREFACE.

The course of Organic Chemistry in these pages is an extended form of one which has been followed in class for some years. It includes all that is commonly expected from Scholarship Candidates at Oxford and Cambridge, or from those about to study medicine or scientific farming: it deals with various typical substances, which are sufficient in number and importance to illustrate the commonest reactions, and from which a beginner may gain an intelligent appreciation of the fundamental theories of the science.

The method adopted is essentially practical: the leading principles of the Chemistry of Carbon Compounds are developed from and illustrated by a course of experiments mainly on the Ethyl, Methyl, Phenyl, and Benzyl compounds. Part I. is the most important and takes rather more than half the time of the course—with us nearly two terms. The most important substances—such as acetaldehyde, an alkyl-halide, aniline, and phenyl iodide—are prepared by everyone; the rest of the preparations are distributed amongst the class.

The order in which the subjects are taken is, in the main, imposed by the practical method, but in any case there are cogent reasons for altering the usual order. When pupils begin this branch of the subject with the doctrine of the tetravalency of the carbon atom and the use of graphic formulae, the majority of them acquire extremely crude conceptions of this great principle.

In this book the aliphatic and aromatic compounds are treated separately; experience has shown that it is most undesirable to treat them together.

Throughout the course the students' attention is frequently directed to helpful analogies or contrasts in inorganic chemistry; to do this in some cases would break the continuity of the argument, and references have accordingly been given to my *Inorganic Chemistry* (Cambridge University Press), and to the two volumes of the *Tutorial Chemistry* of this series. Many references are also given to *Systematic Practical Organic Chemistry*, the companion volume to this book, and to the practical works of Gattermann and Cohen. Those who are familiar with these books will recognise my indebtedness to them.

In conclusion I wish most warmly to thank my colleague Mr. H. O. Hale for very generous help, and my former pupil Mr. R. Dowson for many of the diagrams.

E. I. L.

OUNDLE,
January 1909.

CONTENTS.

PART I.

Typical Compounds.

PART II.

The Chief Classes of Aliphatic Compounds.

PART III.

SOME AROMATIC COMPOUNDS.

PART IV.

ANALYSES AND MOLECULAR WEIGHTS.

PART I.

TYPICAL COMPOUNDS.

CHAPTER I.

THE PREPARATION OF ALCOHOL.

Exp. 1.—Make some starch paste by grinding some starch with a little cold water, and adding this to a larger volume of water which is brought to the boiling point. To a part of the paste add a solution of malt, or some germinating barley; keep the paste at about 60° C. for half an hour. To another part of the starch paste add a little sulphuric acid and boil for some time; cool, and neutralise with calcium carbonate. Taste both solutions; add to a little of each a few drops of iodine solution; add to their boiling solutions a little alkaline solution of tartaric acid and copper sulphate.

Exp. 2.—Make a solution of cane sugar; add to it 50 c.c. of normal sulphuric or hydrochloric acid, and boil. Cool, neutralise with standard base. Treat some of the product, when boiling, with alkaline copper tartrate.

Exp. 3.—Dissolve about 50 grams of glucose (grape sugar) in 500 c.c. of water and place the solution in a large flask. Add to it some brewers' yeast. Warm the flask to 25°–30° C. and dip a delivery tube into lime-water. Keep the flask in a warm place for at least 24 hours. Observe what takes place. Filter the solution; taste it; treat a little of it, boiling, with alkaline copper tartrate. Keep the rest for Experiment 5.

Exp. 4.—Repeat Experiment 3 with a solution of cane sugar, and compare results.

1. Source of Alcohol.—Alcohol, or spirits of wine, is in some manner familiar to everyone. The pure, or "absolute," substance is used in large quantities by manufacturers and chemists. The dilute "rectified" spirit and the cheaper impure "methylated" spirit are in great demand for a variety of purposes, as solvents, cleansers, and fuel. In the more diluted condition alcohol is the essential part of many beverages.

For whatever purpose it is intended it is always obtained by the fermentation of sugars, and these are usually prepared from starch.

Starch is known to everybody as an indispensable article of diet; in flour, rice, or potatoes for instance. It is insoluble in cold water, but forms a clear jelly when heated with water. It is the most important and the commonest of the reserve foods of plants, and is usually stored by them in rhizomes, tubers, roots, and seeds. The spring brings conditions of moisture and temperature favourable for renewal of growth, but the insoluble starch is unsuitable for transmission and assimilation. It is accordingly converted into a soluble sugar. This appears to be accomplished, in some cases, by the influence of the living substance (protoplasm) itself; more commonly the protoplasm prepares special compounds, of complex composition and of somewhat unstable character which induce the desired changes. These bodies, which act catalytically,* are called *enzymes*. The enzyme of the barley grain is called *diastase*; it influences the starch to combine with water and become the sugar **Maltose**. On this maltose the embryo of the barley grain feeds until it is able to obtain food after the manner of green plants.

2. Brewing.—The brewer takes advantage of these changes. He supplies the favourable conditions of moisture and temperature on his malting floor, but when the diastase is well at work, and before the young plant can benefit by the sugar, he kills the latter at a higher

---

* See the author's *Inorganic Chemistry*, pp. 58 and 268; or *Tutorial Chemistry*, Part I., p. 116.

temperature. The maltose produced is extracted with hot water, and to the solution—the "wort"—bittered with hops, he adds yeast. At the temperature of 15°-20° C., which is maintained in the vats, the yeast flourishes exceedingly, while, at the same time, the sugar decreases in quantity, carbon dioxide is evolved, and a solution of alcohol remains.

Yeast is a very low plant organism, of microscopic size, nearly spherical in form. It is colourless—possesses no chlorophyll, and therefore is unable to make its own food.

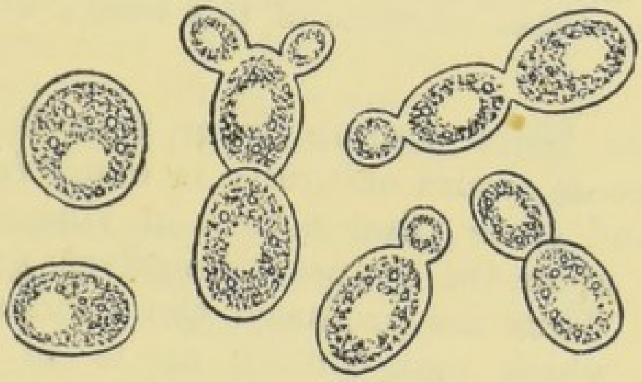

Fig. 1.—YEAST (BUDDING), VERY HIGHLY MAGNIFIED.

It lives upon sugar. To convert sugar into protoplasm demands the expenditure of energy, and this energy, it appears, the yeast obtains under the conditions occurring in the vats by the decomposition of more sugar into alcohol and carbon dioxide—an exothermic reaction.

Under favourable conditions the yeast increases rapidly; the growth of the individual plant is limited, for it is constantly reduced in size by giving rise to buds like itself, which soon become independent. The destruction of the sugar is altogether out of proportion to the needs of the yeast; moreover, when the concentration of the alcohol reaches 10 to 18 per cent. the yeast is itself destroyed.

Büchner has shown that, by pressure, an enzyme may be abstracted from the body of the yeast which ferments glucose. This he called *zymase*. But it seems that another enzyme first converts the maltose into glucose. Hence this enzyme is called *maltase*. Zymase does not influence cane sugar; but a third enzyme—*invertase*—always accompanies the yeast. This converts cane sugar, by hydrolysis (that is by reaction with the water in which it is dissolved), into two sugars, fructose and glucose, both of which are fermentable.

The Enzymes.—Some inorganic bodies, especially dilute mineral acids, will induce catalytically changes similar to those accomplished by the "organised" ferments. Thus starch is rapidly converted into glucose and dextrin when boiled with dilute acids, and cane sugar is under similar conditions converted into glucose and fructose. Similarly starch and cane sugar are digested by animals with the aid of the "organised" ferments of the saliva and other digestive juices. Other reactions of this nature will be given in later chapters.

The various beers contain from 2 to 6 per cent. of alcohol. Glucose occurs naturally in many fruits, notably the grape; and since yeast occurs in vineyard soil, and consequently upon the grapes themselves, grape juice is fermentable. Thus are produced the various clarets and other wines, which may contain up to 21 per cent. of alcohol. In fermentation about 5 per cent. of the product consists of glycerin, succinic acid, and a mixture of substances related to alcohol, called fusel oil. It has recently been shown that these are formed by the action of yeast on decomposition products of proteins (see *Nature*, October 8, 1908, p. 590).

3. Purification of Alcohol.—The starting point for alcohol which is used for industrial purposes is starch, especially potato starch. This is first submitted to the action of steam. To the starch thus treated some extract of malt is added. At 62° C. the diastase of the malt rapidly converts the starch into maltose. To this yeast is added, and the resulting solution, which may contain as much as 18 per cent. of alcohol, is then distilled. At first the distillate consists mainly of the more volatile alcohol, but as the distillation proceeds a larger and larger proportion of it is water. The distillation is stopped before the fusel oil is evolved in any quantity. By constantly changing the receivers the distillate is collected in fractions which are successively poorer in alcohol. These fractions can then be distilled again and new fractions collected. By this tedious process the greater part of the alcohol can be separated from the water. In practice the operation is facilitated by the use of fractionating still-heads. The "pear still-head" (Fig. 2) is one of the best for the laboratory. It is impossible completely to separate the alcohol and water by distillation only, for a solution which contains 96 per cent. of alcohol distils unchanged (see Walker's *Introduction to Physical Chemistry*, 4th edition, Chap. IX.).

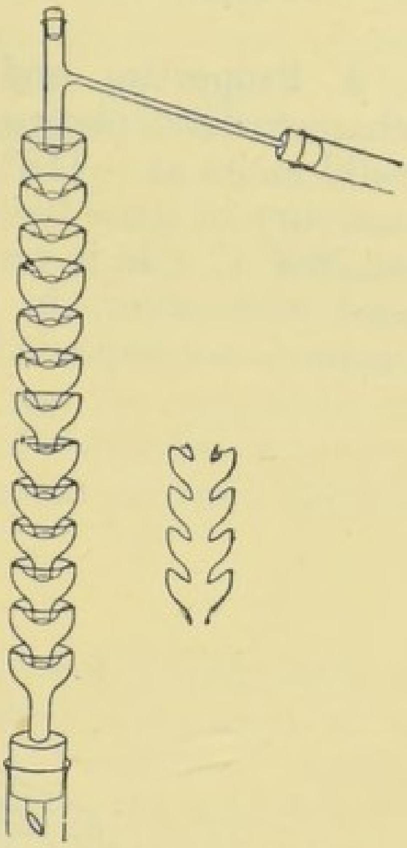

Fig. 2.—Young's "Pear Still-head. On the right four "Pears" in section.

For ordinary purposes no attempt is made to achieve complete separation: rectified spirit contains from 10 to 15 per cent. of water. When the purest spirit is required the rectified spirit is treated with quicklime, and is afterwards distilled from it. The operation may have to be repeated, and since the method is wasteful the purer product is correspondingly more expensive. The "absolute" alcohol so obtained still has from ·5 to 2 per cent. of water. This may be completely removed by treatment with sodium. The metal attacks the water in the usual manner, but some attacks the alcohol to form hydrogen and a non-vapourisable substance. From this and the accompanying caustic soda, the alcohol is completely separated by distillation.

Exp. 5.—Using a small flame, distil (Fig. 3) the product of Experiment 3; collect only the first 20 c.c. Add to this some solid potassium carbonate; this will cause a more concentrated solution of alcohol to rise to the top. Withdraw this by means of a pipette and place it in a small distilling flask (that is, a round flask with a side tube fused to the neck); add small pieces of quicklime until they rise above the solution;

allow to stand for a day or so, and then distil off the alcohol, again using a small flame. Its boiling point will be found to be nearly 79° C.

4. Properties and Uses of Alcohol.—Alcohol has a characteristic pleasant odour. It may be solidified; the solid melts at −112° C., hence the spirit is used instead of mercury in some low temperature thermometers. It boils at 78·3° C. It is very hygroscopic. It mixes with water, and with ether, in all proportions. The mixing with water is accompanied by contraction in volume.

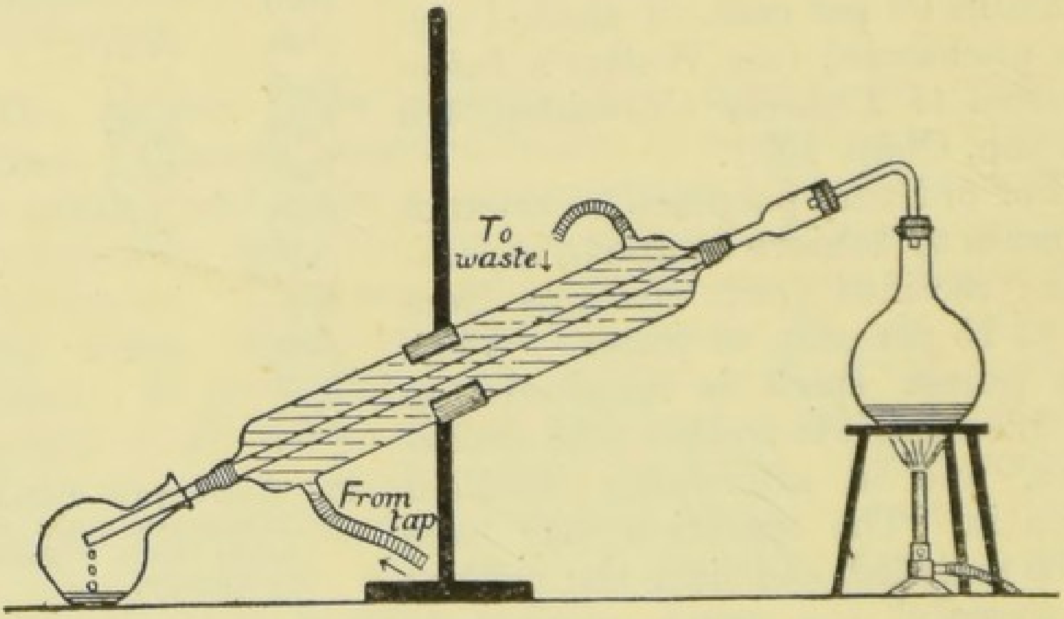

Fig. 3.—Distilling Apparatus.

It is particularly useful as a solvent for organic substances, as the following pages will show; it will also dissolve many inorganic bodies, and elements such as Hydrogen, Sulphur, Phosphorus, Iodine. On the other hand it is sometimes used to precipitate from solution substances which are more soluble in water, such as lead sulphate and potassium chloroplatinate. It preserves and hardens animal and plant specimens. It combines with certain anhydrous salts, for instance magnesium chloride and calcium chloride, to form compounds analogous to hydrates.

Alcohol is used in many beverages. Beers and wines have already been mentioned. By distillation "spirits" are obtained which may contain alcohol up to 51 per cent. Amongst these are whiskey and gin, obtained from malt, the latter flavoured with berries of juniper (Fr. Genévrier); real cognac, from grape juice; rum, from molasses; modern brandy, from potato spirit, etc. The effect of alcohol upon the pulse makes it at times a valuable drug; only a very small quantity can be oxidised in the body, and therefore it is of little value as a food. As a beverage it is condemned by physiologists on account of its toxic effects upon the nervous system and because its habitual use lessens the ability of the body to support physical and mental stress. It weakens the resistance of the system to zymotic diseases and impedes recovery therefrom. The student is recommended to read *Second Stage Hygiene*, Chapter IV.

5. Composition and Formula.—Alcohol burns with a hot, non-luminous, clear flame. Hence it is used as a fuel. For this purpose is sold the "rectified" spirit, which has been rendered unpalatable by the addition of paraffin and wood spirit; this is called methylated spirit.

The products of its burning are carbon dioxide and water only (for qualitative method of analysis see Section 214); hence it contains carbon and hydrogen. When a weighed quantity of alcohol is burned and the products are collected and weighed (for method see Section 220), it is found that the carbon dioxide corresponds to 52·17 per cent. of carbon (11 : 3) and the water to 13·04 per cent. of hydrogen (9 : 1); hence it must also contain 34·79 per cent. of oxygen. The ratio of atoms in the molecule must therefore be

$$\text{Carbon, } \frac{52{\cdot}17}{12} = 4{\cdot}35$$

$$\text{Hydrogen, } \frac{13{\cdot}04}{1} = 13{\cdot}04$$

$$\text{Oxygen, } \frac{34{\cdot}79}{16} = 2{\cdot}17.$$

Dividing these numbers by 2·17 we obtain the ratio in simple whole numbers, 2 : 6 : 1, wherefore the simplest, or "empirical," formula for alcohol is C_2H_6O. And since the vapour density of alcohol vapour is about 23, it follows, by Avogadro's theory, that the molecular weight is about 46; the simplest is therefore the true or "molecular" formula,

$$\mathbf{C_2H_6O.}$$

SUMMARY.

Alcohol is obtained by the fermentation of sugars, which are usually obtained from starch by hydrolysis. From solution the alcohol is separated by a process of fractional distillation and desiccation. Its composition is represented by the formula C_2H_6O.

QUESTIONS.—CHAPTER I.

1. A small amount of aqueous hydrochloric acid has been accidentally mixed with absolute alcohol. How would you obtain pure alcohol from the mixture, and how would you find out whether you had succeeded?

2. Determine the formula of a compound from the following data:—

0·1245 gram gave, on combustion, 0·1471 gram of water;
" " " 0·2374 " of carbon dioxide;

0·106 gram expelled air (Victor Meyer method) which occupied 51 c.c. at S.T.P.

3. Explain what is meant by "fermentation," illustrating your answer by reference to the various steps in the conversion either of starch or cane sugar into alcohol.

CHAPTER II.

THE CHEMICAL PROPERTIES OF ALCOHOL.

Exp. 6.—Add slowly small pieces of sodium to some absolute alcohol until the action becomes very slow; immerse a piece of red litmus paper in the solution. Carefully evaporate the solution to dryness. Treat some of the solid with water: notice its reaction towards litmus. Neutralise it with hydrochloric acid and identify the salt formed.

6. The Action of Sodium on Alcohol.—When Sodium (or Potassium) is added to alcohol a gentle reaction at once begins; hydrogen is liberated and a compound is formed which, on analysis, is found to correspond to the formula C_2H_5ONa. For a reason which will soon become evident, it is called **Sodium** (or Potassium) **Ethoxide.** It is soluble in water and in alcohol. In the former it is alkaline to litmus; this is due to its reaction with water to form sodium hydroxide and alcohol.

$$C_2H_5ONa + H_2O = C_2H_6O + NaOH.$$

The formation of the ethoxide and its hydrolysis* in solution seem to indicate that alcohol has acidic properties. For this reason the ethoxide has also been termed sodium *alcoholate*, but we need not regard this view as final without further evidence. In any case, since sodium will not react further with the ethoxide, we seem justified in concluding that in alcohol one equivalent of hydrogen has properties

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* *Inorganic Chemistry*, p. 165.

distinct from those of the remaining five. To indicate this conclusion and to recall the above reaction we may write the formula of alcohol $C_2H_5.H.O$.

7. The Action of the Haloid Acids on Alcohol.—When hydrogen chloride gas is passed into warmed alcohol, some gas escapes whose composition corresponds to the formula C_2H_5Cl. We can therefore represent the reaction as

$$C_2H_6O + HCl = C_2H_5Cl + H_2O.$$

The reaction proceeds better if some dehydrating agent, for instance anhydrous zinc chloride, is present. The gas is easily liquefied, the liquid boiling at 12·5° C. It is readily soluble in alcohol, but only very slightly so in water. When it is heated with water in a sealed tube to 100° C., it is hydrolysed into alcohol and hydrochloric acid; with potash the reaction proceeds more easily, alcohol and potassium chloride being formed. From these reactions, we may judge alcohol to have a basic nature.

$$C_2H_5Cl + KOH = KCl + C_2H_6O.$$

The reactions remind us of many familiar ones in inorganic chemistry, namely, the neutralisation of metallic hydroxides and the hydrolysis of salts generally, *e.g.*

$$Cu(OH)_2 + 2HCl = CuCl_2 + 2H_2O,$$

$$CuCl_2 + 2KOH = Cu(OH)_2 + 2KCl.$$

The chloride is also formed by the action of phosphorous chloride upon absolute alcohol.

$$3C_2H_6O + PCl_3 = H_3PO_3 + 3C_2H_5Cl.$$

Compare $3HOH + PCl_3 = H_3PO_3 + 3HCl.$

When absolute alcohol is treated with phosphorus halide, a considerable amount of the haloid acid escapes. Chemists account for its appearance by the formation of a derivative of phosphorous acid and alcohol.

Analogous compounds of bromine and iodine are more conveniently prepared, and since they have higher boiling points they are generally more useful. Their behaviour resembles that of the chloride.

B.P.
C_2H_5Cl 12·5° C. C_2H_5Br 38·5° C. C_2H_5I 72·3° C.

Exp. 7.—*Preparation of the Bromide.* In a round-bottomed ½-litre flask containing 100 grams of concentrated sulphuric acid, add quickly, without cooling, 45 grams of alcohol. Cool under the tap, and add carefully 38 grams of ice-cold water, and continue the cooling. Now add 50 grams of well-powdered potassium bromide. Distil fairly rapidly with a well-cooled long condenser and collect the distillate in water containing floating ice (Fig. 4). Take precautions against a back rush of the distillate. Separate the lower layer by decantation; wash it several times with distilled water and then with dilute sodium carbonate solution. Separate in a funnel and dry over fused calcium chloride. Distil again; collect and preserve in a stout bottle. [Suggest reasons for every precaution.]

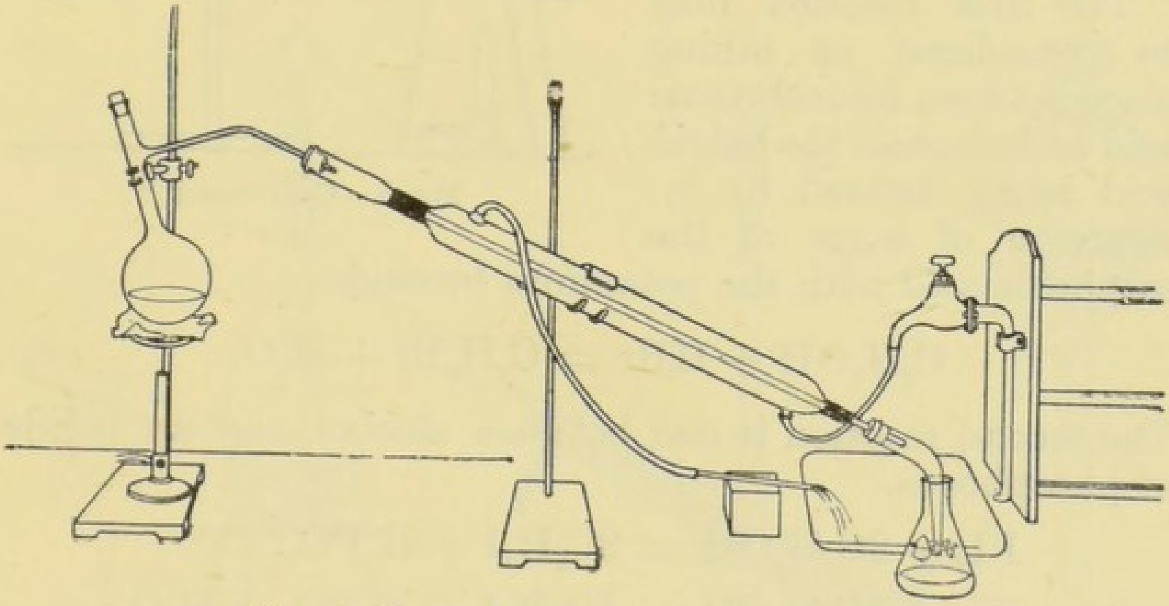

Fig. 4.—PREPARATION OF ETHYL BROMIDE.
(The side tube of flask need not be bent.)

Exp. 8.—*Preparation of the Iodide.* In a 200 c.c. flask place a mixture of 5 grams of red phosphorus and 40 grams of absolute alcohol. To this add gradually 50 grams of powdered iodine. Shake the flask and cool under the tap constantly. Attach an inverted condenser (no water) and allow the mixture to stand for several hours Now pass water through the condenser and heat the flask on the water bath for two hours (Fig. 5). Finally distil from a water bath. Wash the distillate with water and then with a little dilute caustic soda. Separate with funnel, dry with fused calcium chloride, and distil off. Keep in an opaque or red bottle to prevent decomposition by light.

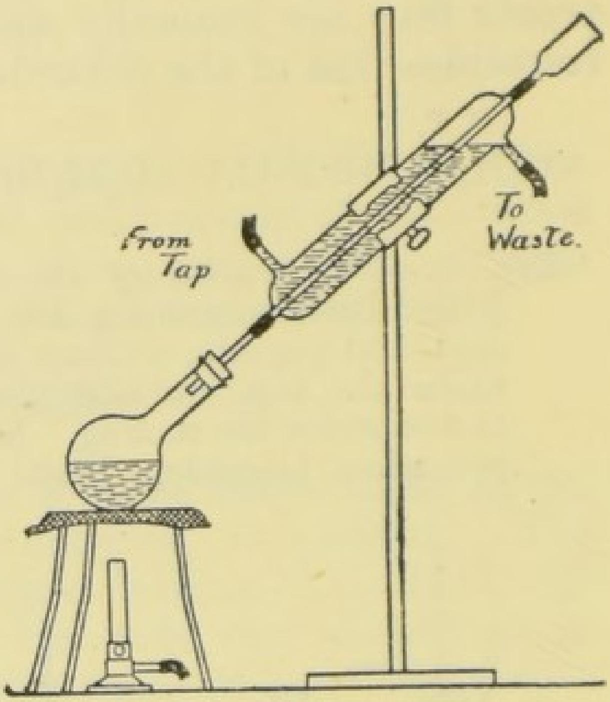

Fig. 5.—Condenser.

The first reaction may be considered as taking place between hydrobromic acid and alcohol: the haloid acid being formed by interaction of some of the sulphuric acid with the potassium bromide.

$$C_2H_5OH + HBr = C_2H_5Br + H_2O.$$

The second reaction is one between alcohol and an iodide of phosphorus.

$$PI_3 + 3C_2H_5OH = 3C_2H_5I + H_3PO_3,$$

and $$PI_5 + 5C_2H_5OH = 5C_2H_5I + H_3PO_4 + H_2O.$$

8. Sodium will act upon these halogen compounds also, but its action is quite different from that upon alcohol: it will not replace hydrogen. Hence we seem justified in concluding that the hydrogen which can be displaced by sodium from alcohol is also the hydrogen which, together with the oxygen, is replaced by the halogens. We can denote this conclusion by writing the formula of alcohol

$$C_2H_5 . OH.$$

That is, alcohol is an hydroxide.

The methods of analysis (qualitative and quantitative) of halogen compounds are given in Sections 216 and 219.

9. Analogous Compounds.—Alcohol is oxidised to carbon dioxide and water by fuming nitric acid, but with concentrated pure nitric acid it yields a **nitrate** (B.P. = 86°) $C_2H_5 . NO_3$. This body is explosive when heated quickly. It is soluble in water. Boiled with potash it yields potassium nitrate and alcohol.

When alcohol and concentrated acetic acid are mixed, a vapour of a pleasant fruity odour is evolved. This is the **acetate**. It is a colourless liquid, boiling at about the same temperature as alcohol, namely 78° C. When it is heated with water the reverse change takes place; when it is boiled with potash, potassium acetate and alcohol are formed.

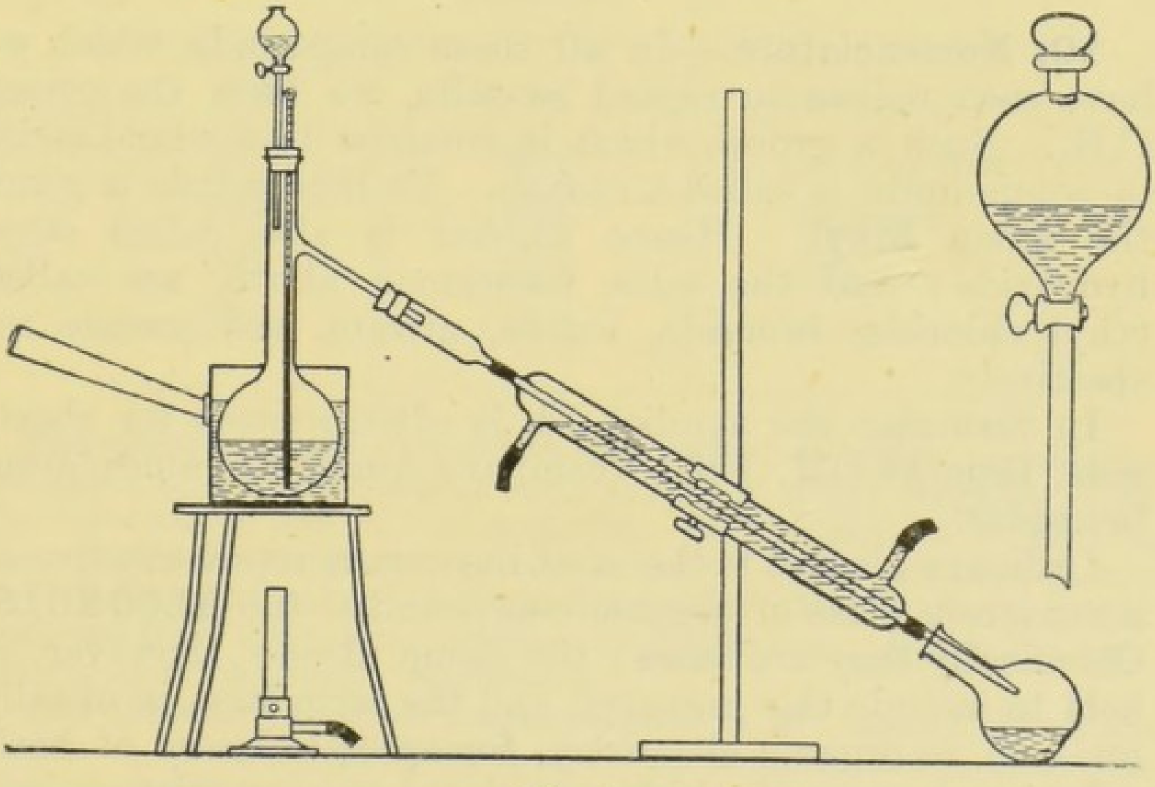

Fig. 6.

Exp. 9.—*Preparation of the Acetate.* Place a mixture of 50 c.c. of alcohol and 50 c.c. concentrated sulphuric acid in a 500 c.c. flask (Fig. 6) carrying a dropping funnel and connected with a long condenser. Heat the flask in an oil bath to 140° C., and then add a mixture of equal volumes of alcohol and glacial acetic acid through the funnel, drop by drop, at about the same rate as the acetate distils into the receiver. Treat the distillate with sodium carbonate until no further effervescence takes place and acidity is destroyed. Separate the layers in a funnel. Wash the upper one with a solution ot calcium chloride to remove alcohol. Again separate. Dry the upper layer with fused calcium chloride and distil over. [Explain the methods of purification.]

This method is called the "continuous" method, because the mixture of alcohol and acid may be continuously added. Some sulphuric acid is, however, constantly reduced to sulphurous acid (why ?), and therefore diminishes in quantity. In addition to this it is automatically diluted, and thus loses its activity. The reason of this is given in Section 11.

10. Nomenclature.—In all these compounds, which we have seen reason to regard as salts, we have the group C_2H_5. Such a group, which is common to a whole series of compounds, is called a *radicle.* To this radicle is given the name **Ethyl**. Hence alcohol is also called ethyl hydroxide; and the salts, mentioned above, are called ethyl chloride, bromide, iodide, nitrate, and acetate respectively.

In formulae the symbol *Et.* is often written for shortness, thus Et.OH, EtCl. (compare AmBr for ammonium bromide).

Ordinary alcohol is the most important representative of a numerous class of organic compounds—the **ALCOHOLS**. Chemically they are bases; the name alcohol, however, is held to include this meaning, and the term base is usually retained, in organic chemistry, for special classes of basic substances, some of which are related to ammonia.

The alcohol radicles are called "alkyl" radicles. The salt of an organic acid and an alcohol, ethyl acetate for instance, is termed an **ESTER**. The preparation of an ester from its alcohol and acid is called ***Esterification.*** The reverse processes, namely the hydrolysis of the ester by water or steam into the acid and the alcohol, and also its conversion by a caustic alkali into the mineral salt of the acid and the alcohol, are called ***Saponification.*** The origin of this term will be understood later (Chapter XV.).

11. The Esterification of Ethyl Acetate has provided some extremely interesting and important experiments. The reaction is non-thermal (that is, neither exo- nor endo-thermal), and, since it is reversible, it is written

$$C_2H_5OH + C_2H_4O_2 \rightleftarrows C_2H_5(C_2H_3O_2) + H_2O.$$

When the acid and alcohol are mixed together in equivalent proportions, it is found that the reaction balances* when two-thirds of the reagents have been converted into the ester and water.

The temperature does not affect the final result, a higher temperature merely hastens the reaction. The appended table is copied from Mellor's *Chemical Statics and Dynamics*.

Temp. °C.	Ethyl Acetate Formed. Percentage.	Time of Reaction.
10°	65·2	(16 years)
100°	65·6	a very long time
170°	66·5	42 hours
200°	67·3	24 hours
220°	66·5	38 hours

The reaction can be brought to completion, or nearly so, only by introducing a proportionally large excess of either reagent, or by the removal of one of the products. By the method of Exp. 9, the reaction is carried out so that, first of all, concentrated sulphuric acid removes the water formed, and, secondly, the ester is constantly removed from the sphere of action by distillation. Hence the reaction is for a long time "continuous."

The effect of excess of reagents—that is, of "mass" action—is shown in the accompanying table. The numbers are in molecular quantities (Nernst, *Theoretical Chemistry*).

Acid to Alcohol.	*Ester formed.*
1 : 0·05	0·05
1 : 0·33	0·3
1 : 0·5	0·42
1 : 1·0	0·667
1 : 2·0	0·86
1 : 8·0	0·966

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* See *Inorganic Chemistry*, pp. 255 and 264-269, and *Tutorial Chemistry*, Part II., Chapter VIII.

12. Ethyl Sulphates.—Another compound of great interest and importance is **Ethyl hydrogen sulphate** (or ethyl sulphuric acid). It is formed when the acid and alcohol are mixed together.

$$C_2H_5OH + H.HSO_4 = C_2H_5.H.SO_4 + H_2O.$$

Its existence may be proved by isolating it. A mixture of the two substances is kept at 100° C. for some time. The product is then poured into water and powdered barium carbonate is added: this reacts with the excess sulphuric acid to form insoluble barium sulphate, and carbonic acid which decomposes; with the ethyl hydrogen sulphate it forms barium ethyl sulphate $Ba(Et.SO_4)_2$ which, unlike barium sulphate, is soluble in water. The barium salt may be obtained from the filtered solution by crystallisation. If this substance is treated with the equational quantity (*i.e.* the quantity demanded by the equation) of sulphuric acid in solution, double decomposition takes place with formation of solution of pure ethyl hydrogen sulphate.

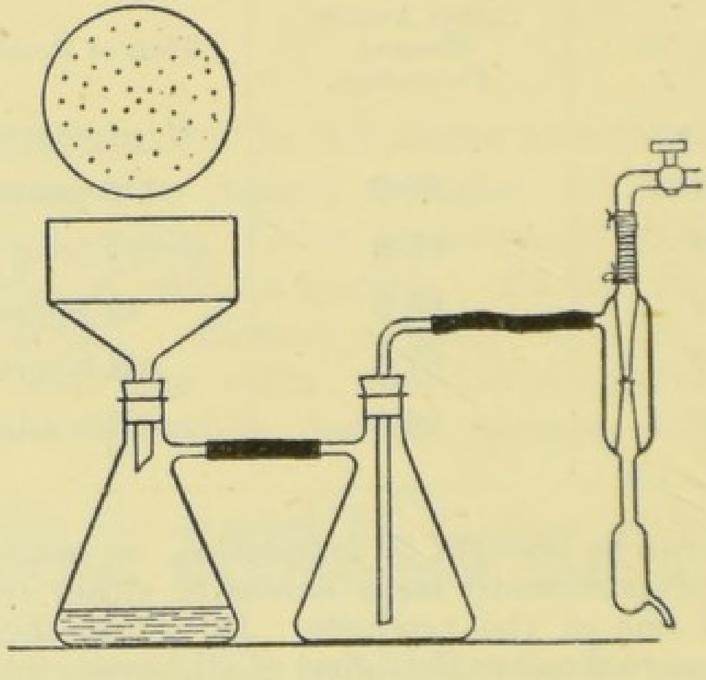

Fig. 7.

$$Ba(Et.SO_4)_2 + H_2SO_4 = BaSO_4 + 2Et.H.SO_4.$$

It is a strongly acid substance, for which reason it is sometimes called ethyl sulphuric acid. It is hydrolysed in dilute solution at high temperatures. It is analogous to potassium hydrogen sulphate ($K.H.SO_4$), and when treated with potassium carbonate the interesting potassium ethyl sulphate ($C_2H_5.K.SO_4$) is formed which may be isolated by crystallisation.

Exp. 10.—*Preparation of Potassium Ethyl sulphate.* Put about 100 c.c. of absolute alcohol in a round-bottomed flask, and add slowly 30 c.c. of concentrated sulphuric acid. Mix thoroughly. Fit the flask with an upright condenser and heat on the water bath for two or three hours. Cool, and pour the product into 500 c.c. cold water in a large basin or small trough. Stir thoroughly. Add pure finely divided calcium carbonate, ground into a paste with water. Filter hot through a Büchner suction filter (Fig. 7). Heat the filtrate on a water bath and add carefully a solution of potassium carbonate until the acidity is *just* removed. Do not let the solution be alkaline. Filter, and crystallise out the potassium salt. Redissolve this *carefully* in the smallest possible quantity of methylated spirit (flask and double surface upright condenser —Fig. 8—is best). Decant at once through a fluted filter and allow to cool.

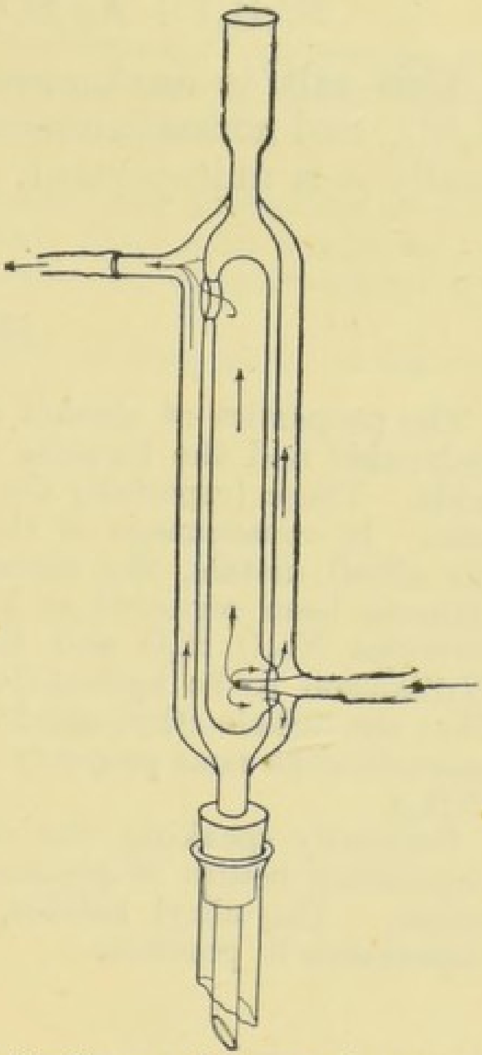

Fig. 8.—DOUBLE SURFACE CONDENSER (DAVIES').
Water current shown by arrows.

Ethyl hydrogen sulphate is valuable as a reagent; it is particularly reactive. The formation of ethyl bromide and acetate, as described above, is often represented as taking place according to the following equations.

$$C_2H_5HSO_4 + KBr = C_2H_5Br + KHSO_4,$$
$$EtHSO_4 + H.C_2H_3O_2 = EtC_2H_3O_2 + H_2SO_4.$$

The **normal ethyl sulphate** (di-ethyl sulphate) can be formed by a special reaction—by the double decomposition of silver sulphate and ethyl iodide.

$$2C_2H_5I + Ag_2SO_4 = (C_2H_5)_2SO_4 + 2AgI.$$

This salt is analogous to normal potassium sulphate, K_2SO_4, and normal ammonium sulphate $(NH_4)_2SO_4$. Practically it is unimportant.

SUMMARY.

The properties of alcohol are best epitomised by the name Ethyl hydroxide and the formula C_2H_5OH. It forms salts with many acids. These (especially the sulphates) show it to be a mon-acid base. In consequence of the analogy of these salts with those of the alkali metals, the corresponding hydrated bases, which had hitherto been regarded as hydrated oxides and represented by the formulae $Na_2O.H_2O$ and $K_2O.H_2O$, were, in 1852, asserted by Williamson to be hydroxides of the formulae NaOH and KOH. That the radicle ethyl should form salts is not surprising when we remember the same property is manifested by the radicle ammonium (NH_4).

Generally speaking, the ethyl halides and the esters are easily vapourised bodies of pleasant odour; quite or nearly insoluble in water. The alkyl halides, especially the iodides, are of great importance in practice.

QUESTIONS.—CHAPTER II.

1. Pure sodium ethoxide was prepared by both treating the alcohol with sodium and drying the compound in an atmosphere of hydrogen to prevent oxidation.

5·2 grams of it were dissolved in pure water; and it was found that 38·2 c.c. of $\frac{N}{10}$ hydrochloric acid were needed to neutralise one-twentieth of the solution. Does this result agree with the formula adopted in the text?

2. Find the simplest formula of a compound,

0·1836 gram of which yielded 0·1934 gram of carbon dioxide;
0·0693 ,, ,, water;

and 0·3212 gram of which when oxidised by nitric acid in presence of silver nitrate yielded 0·3616 gram of silver bromide.

3. Draw a figure of the apparatus you would use in saponifying ethyl acetate completely by caustic potash (the volatile original substance and the volatile product must be constantly returned to the sphere of action).

4. What do you understand by a "continuous" process for preparing chemical substances? Illustrate your answer by one example drawn from inorganic and one from organic chemistry.

5. What is "HYDROLYSIS"? Illustrate your answer by as many as possible types of hydrolysis drawn from both inorganic and organic chemistry. How have the phenomena been accounted for?

6. Try the effect of adding a piece of calcium metal to absolute alcohol.

CHAPTER III.

FURTHER REACTIONS OF SULPHURIC ACID WITH ALCOHOL.

In the previous chapter we have seen that by the interaction of concentrated sulphuric acid and alcohol, at about 100° C., ethyl hydrogen sulphate is produced. We will here discuss the effect of altering the conditions.

ETHER.

Exp. 11.—*Preparation of Ether.* Fit a flask to a long condenser, and bore the cork to carry a thermometer and a dropping funnel also. Place the receiver in ice, or a mixture of pounded ice and salt. Introduce into the flask a cold mixture of 100 grams of alcohol and 180 grams of concentrated sulphuric acid. Raise the temperature to about 130°-140° C. As the ether distils over add more alcohol through the funnel, which must reach below the mixture. When about 150 c.c. have passed over, shake it with a very dilute solution of caustic soda, and then with a solution of calcium chloride—this will remove sulphurous acid, alcohol, and some ether. Treat the rest of the ether with fused calcium chloride for some time, pour it into a dry flask, and distil cautiously on a water bath.

13. Properties of Ether.—It is by no means easy to obtain ether free from alcohol and water. To remove the last traces of water, it must be treated with sodium, and distilled again. Ether boils at 35° C., and since it forms a very explosive mixture with air, the greatest care must be taken, when using it, that no flame is near. It is employed as a solvent by chemists; surgeons use it as an anaesthetic. When it evaporates a considerable amount of heat is absorbed (try one drop on the hand); it is occasionally utilised to produce local insensibility. It mixes with alcohol in all proportions, but is only partially miscible with water. It is less dense than water.

14. Formula and Reactions of Ether.—By analysis its empirical formula is found to be $C_4H_{10}O$; its vapour density shows this to be the true molecular formula.

Its *chemical behaviour* is peculiar; as a rule, when treated with reagents, it yields several substances at one time; most of the products can be obtained more easily and purer by corresponding reactions with alcohol. When it is heated with acidified water to 150° C. in a sealed tube, alcohol is formed,

$$C_4H_{10}O + H_2O = 2C_2H_5OH,$$

hence we need not be surprised that, at one time, ether was regarded as a dehydration product of alcohol.

When ether is heated with concentrated sulphuric acid at 120° C., ethyl hydrogen sulphate and alcohol are formed. This appears to be the reverse action of Exp. 11, in which case we have the key to its formation.

$$C_4H_{10}O + HHSO_4 \rightleftarrows C_2H_5.H.SO_4 + C_2H_5OH.$$

We owe this view, and also the accepted idea concerning the "structure" of ether, to Williamson. He obtained ether by the interaction of sodium ethoxide and ethyl iodide. (The preparation may easily be carried out in a distilling flask. The ether comes over at about 60° C.) Since these compounds, whose formulae may be considered as well established, are both ethyl compounds, ether must be regarded as a di-ethyl compound.

$$C_2H_5O \boxed{Na + I} C_2H_5 = NaI + \mathbf{C_2H_5O.C_2H_5}.$$

We may now rewrite the equations for the first method of preparation

$$C_2H_5OH + HHSO_4 = C_2H_5.HSO_4 + H_2O,$$
$$C_2H_5.H.SO_4 + C_2H_5OH = C_2H_5.O.C_2H_5. + H_2SO_4.$$

The equation would lead us to expect that as the sulphuric acid is continuously regenerated a small amount of the acid would suffice for the preparation of unlimited quantities of ether. This is not the case, however, for by secondary reaction part of the acid is reduced, and moreover, as water is continuously accumulating, the ethyl hydrogen sulphate undergoes hydrolysis at the high temperature of the reaction. In practice the reaction ceases after a time.

The preparation of ether from the ethoxide and iodide indicates that ether should be regarded as the oxide of ethyl, corresponding to the hydroxide alcohol and analogous to potassium oxide.

$$\begin{array}{ll} KOH & (C_2H_5)OH \\ K_2O & (C_2H_5)_2O. \end{array}$$

Two interesting reactions contribute to this view.

When ethyl iodide is treated with *dry* silver oxide, ether and silver iodide are formed.

$$Ag_2O + 2C_2H_5I = 2AgI + (C_2H_5)_2O.$$

When sulphur trioxide is passed into well-cooled ether di-ethyl sulphate is formed.

$$(C_2H_5)_2O + SO_3 = (C_2H_5)_2SO_4.$$

Compare $BaO + SO_3 = BaSO_4.$

In many of its reactions, however, ether differs considerably from alcohol, notably in its attitude towards oxidising substances, and to chlorine. It is the type of a large class of substances, named after it, the **ETHERS**.

ETHYLENE.

When a mixture of concentrated sulphuric acid and alcohol is heated to 160° C., a colourless inflammable gas called Ethylene is evolved. It is but slightly soluble in water.

Exp. 12.—*Preparation of Ethylene.* A mixture of 25 grams of alcohol and 150 grams of concentrated sulphuric acid is heated in a round-bottomed litre flask fitted with a delivery tube on a sand bath (Fig. 9). As soon as an active evolution of ethylene occurs, a cold mixture of alcohol and sulphuric acid (1 : 2 by weight) is run in slowly until sufficient gas has been prepared. It may be collected over water. Great care must be taken to prevent frothing. Some charring of the materials will be observed. The flask and its contents will be used for Exp. 13.

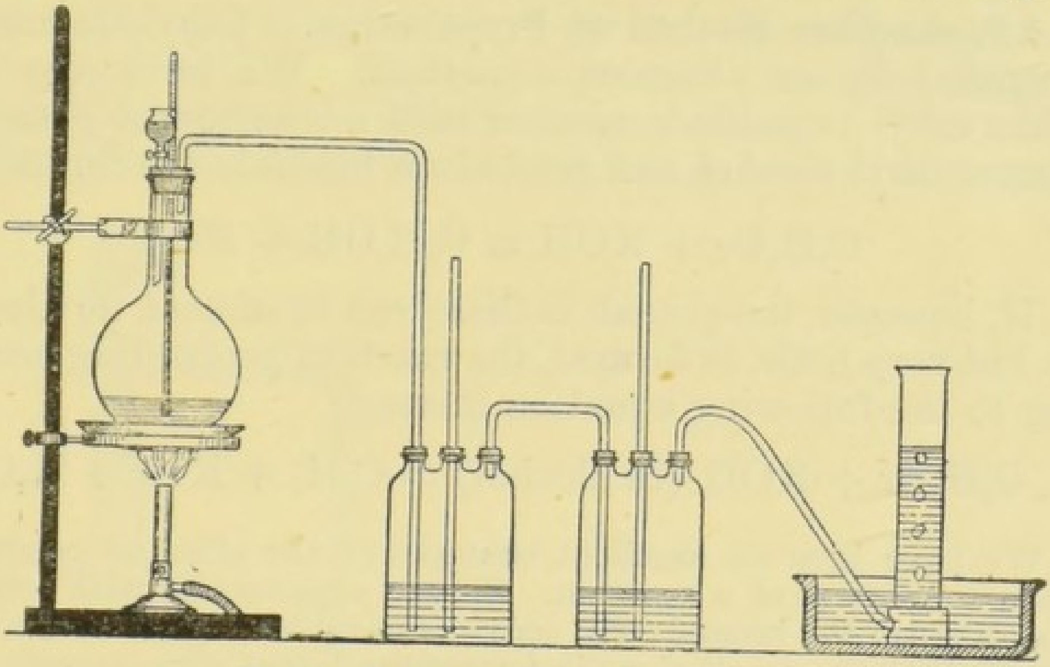

Fig. 9.—PREPARATION OF ETHYLENE.
(The gas is washed with dilute soda.)

15. Properties and Formula.—Ethylene burns with a very brilliant and slightly smoky flame. It is 14 times as heavy as hydrogen, hence its molecular weight is about 28.

By burning it in oxygen its simplest formula is found to be CH_2, therefore from the density determination its true formula is C_2H_4. This formula may be deduced independently from the volume relations. When exploded with oxygen, three volumes of the element react with one volume of ethylene to produce two volumes of carbon dioxide besides water,

$$C_xH_y + 3O_2 = 2CO_2 + \frac{y}{2} H_2O.$$

Whence x and y must be 2 and 4 respectively—$\mathbf{C_2H_4}$.

The preparation of ethylene may be regarded as the dehydration of alcohol; but since we know that ethyl hydrogen sulphate is formed at 100° C., this compound is probably concerned in the formation of ethylene. The following reactions support this view. A concentrated solution of the salt when heated above 140° C. yields ethylene and sulphuric acid. When ethylene is shaken with concentrated H_2SO_4 at ordinary temperatures, combination occurs with formation of ethyl hydrogen sulphate.

16. Another Method of Preparation.—Ethylene may be prepared by an alternative method. We have seen that when ethyl bromide is treated with a solution of potash in water, ethyl alcohol and potassium bromide are formed.

$$C_2H_5Br + KOH = C_2H_5OH + KBr.$$

If, however, the potash is dissolved in *alcohol*, no alcohol, or but very little, is formed, the reaction proceeding according to the following equation instead.

$$C_2H_5Br + KOH \text{ (in alcohol)} = C_2H_4 + KBr + H_2O.$$

We have here an excellent example of the effect of conditions upon the course of a reaction. Simple experiments with weighed quantities of the bromide will convince the student that with watery potash little or no ethylene is formed, and that with concentrated alcoholic potash nearly the quantitative yield of ethylene is obtained. [In the latter case a little ether is formed ; why ?]

17. Reactions of Ethylene.—Ethylene is remarkable for the ease with which it will combine with other substances. Such reactions are called "additive."

(i) With SULPHURIC ACID—see Section 15.

(ii) With HYDROGEN.

When ethylene and hydrogen are passed together over spongy platinum heated below 300° C., combination takes place to form a gas of the formula C_2H_6. Neither more nor less hydrogen is taken up. The gas is called **Ethane**: it will be considered in a later chapter.

(iii) With HALOID ACIDS.

Ethylene combines with hydriodic or hydrobromic acid to form the corresponding ethyl halide. It will not combine with a greater proportion of acid. The reaction proceeds most readily with hydriodic acid, least so with hydrochloric acid.

$$C_2H_4 + HI = C_2H_5I.$$

(iv) With HALOGENS.

When ethylene is treated with chlorine or bromine, combination takes place to form oily compounds (hence the name *Olefiant gas* for Ethylene) of the formulae $C_2H_4Cl_2$ and $C_2H_4Br_2$. No greater proportion of halogen will enter into combination. These compounds are called Ethylene (di-)chloride and (di-)bromide respectively. The reaction takes place most readily with chlorine, least so with iodine.

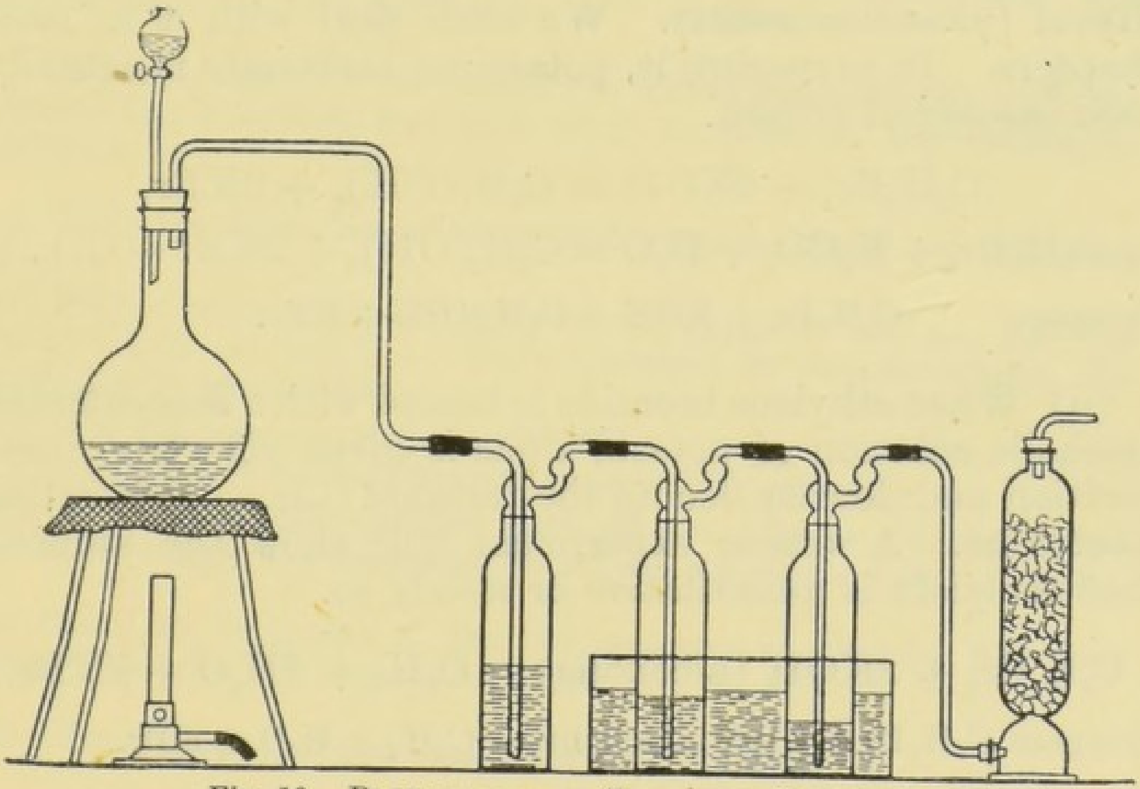

Fig. 10.—PREPARATION OF ETHYLENE DI-BROMIDE.
(The first absorption tube contains potash; the second and third contain bromine; the tower contains lime.)

Exp. 13.—*Preparation of Ethylene di-bromide.* Prepare ethylene as in Experiment 12, but instead of collecting it, pass it through the apparatus of Figure 10. If the mixture in the flask foams badly the heating has been too severe. The reaction is finished as soon as the bromine colour has disappeared. The apparatus must be disconnected at once. The ethylene bromide is washed repeatedly with water in a separating funnel and finally with dilute caustic soda (why?). It is dried over calcium chloride and then distilled.

18. Ethylene di-bromide is an oily colourless liquid, boiling at 131° C. Its behaviour towards caustic potash is exactly analogous to that of ethyl bromide. The substances formed, as well as the reactions, are important. The student may easily verify for himself part of the following statements.

(i) When ethylene bromide is heated with a watery solution of potash no gas is evolved, but there remains in solution a substance with alcoholic (basic) properties which is sweet to the taste. (In order to taste this, neutralise the excess potash with dilute acetic acid.) Its composition corresponds to the formula $C_2H_4(OH)_2$. It is called **Glycol** (γλυκυς = sweet). We shall deal with it in later chapters. In preparing it, potassium carbonate is actually used instead of potash.

$$C_2H_4Br_2 + 2KOH = C_2H_4(OH)_2 + 2KBr,$$

$$\text{or } C_2H_4Br_2 + K_2CO_3 + H_2O = C_2H_4(OH)_2 + 2KBr + CO_2.$$

$$\text{Compare} \quad C_2H_5Br + KOH = C_2H_5(OH) + KBr.$$

(ii) When ethylene bromide is heated with a concentrated alcoholic solution of potash, a gas is given off whose composition and density denote the formula C_2H_2. It is called **Acetylene.** A simple experiment will show the student that the yield is quantitative or nearly so.

$$C_2H_4Br_2 + 2KOH \text{ (alcoholic)} = C_2H_2 + 2H_2O + 2KBr.$$

$$\text{Compare } C_2H_5Br + KOH \text{ (alcoholic)} = C_2H_4 + H_2O + KBr.$$

Acetylene burns with a very brilliant flame. Its properties recall those of ethylene. It will be discussed in a later chapter.

SUMMARY.

When sulphuric acid reacts with alcohol, ethyl hydrogen sulphate is formed. This is stable up to 120° C., but at a higher temperature, in the presence of excess of alcohol, it reacts with this to yield ether and sulphuric acid. Above 140° C. ethyl hydrogen sulphate is unstable, particularly with excess of sulphuric acid; it breaks up into ethylene and sulphuric acid.

Ether seems to be related to alcohol in a manner analogous to that of a metallic oxide to the corresponding hydroxide.

Ethylene is a hydrocarbon—that is, a substance which contains only hydrogen and carbon—which is noteworthy for its "additive" reactions.

QUESTIONS.—CHAPTER III.

1. Under what conditions is ether obtained from alcohol by the action of sulphuric acid? Make a sketch of the apparatus which you would use for the preparation, and describe how the crude product might be purified.

2. What is an "ethereal salt" or ester? Explain fully why ethyl acetate was formerly known as "acetic ether."

3. Mention some of the substances which unite directly with the hydrocarbon ethylene, and give short accounts of the substances produced.

4. Find the formulae of three hydrocarbons from the following data :—

(i) 6·4 c.c. were exploded with 20 c.c. oxygen ; 13·5 c.c. gas was left of which all but 7 c.c. were absorbed by caustic potash, the remainder by pyrogallol.

(ii) 5·3 c.c. were exploded with 21 c.c. oxygen ; of the residual 15·7 c.c. gas only 5·1 c.c. were unabsorbed by potash.

(iii) 5·7 c.c. were exploded with 18 c.c. oxygen ; 15·2 c.c. gas remained, which was decreased to 3·7 c.c. by shaking with potash.

5. Give the formulae of the two acetates of glycol. Are they comparable with the acetates of lead?

6. Give two methods of preparing ethyl iodide.

CHAPTER IV.

SOME PRODUCTS OF THE OXIDATION OF ALCOHOL.

19. Alcohol burns to carbon dioxide and water: it is evident that oxidation can go no further. Oxidation can, however, be carried out in a gentler manner. Thus, if a mixture of alcohol vapour and air is driven slowly over warmed platinum black, the platinum will continue to glow even though the heating is discontinued; a reaction is progressing, and at the opposite end of the tube the presence of new substances can be detected by their characteristic odours. Or, the alcohol may be treated in a beaker with moderately dilute solutions of potassium permanganate: according to the conditions—temperature, concentration, acidity—varying proportions of three substances can be recognised. One of them is acetic acid, hence this acid is an oxidation product of alcohol; the smell of ethyl acetate is pronounced: its formation is readily understood.

ALDEHYDE.

20. In addition there is formed more or less of a volatile substance which has a very pungent and peculiar odour. This is called **Aldehyde**.

By combustion its simplest formula is found to be C_2H_4O. Since its vapour density is 22 ($H = 1$), this also must be its true molecular formula. Evidently it is formed from alcohol by the removal of hydrogen, hence its name ***Alcohol dehydrogenatus.***

$$2C_2H_6O + O_2 = 2C_2H_4O + 2H_2O \text{ [platinum as catalyser].}$$

$$2KMnO_4 + 3H_2SO_4 + 5C_2H_6O$$
$$= 5C_2H_4O + 8H_2O + K_2SO_4 + 2MnSO_4.$$

The reaction is more easily controlled when an oxidiser less active than permanganate is used. For instance, a dichromate. The preparation is an extremely fine exercise, and should not be passed over.

Exp. 14.—*Preparation of Aldehyde.* A 1½-litre flask containing 110 grams of concentrated sulphuric acid and 200 grams of water is fitted with a dropping funnel and connected with a long condenser, the end of which is fitted into a receiver by means of an adaptor (Fig. 11). The receiver is immersed in a freezing mixture. A solution of 200 grams of *sodium* dichromate in 200 grams of water is prepared, and to this 100 grams of alcohol are added. From the dropping funnel the dichromate alcohol solution is admitted in a fine stream to the acid in the flask until the latter is just boiling. The end of the funnel tube should be about 1 inch from the liquid. During the addition of the oxidation mixture the reaction should be such as to keep the liquid boiling. When all has been added, continue the boiling for a short time, then disconnect and stopper the receiver. The aldehyde will contain some water and alcohol, and a third substance called Acetal (formed by reaction between some aldehyde and alcohol).

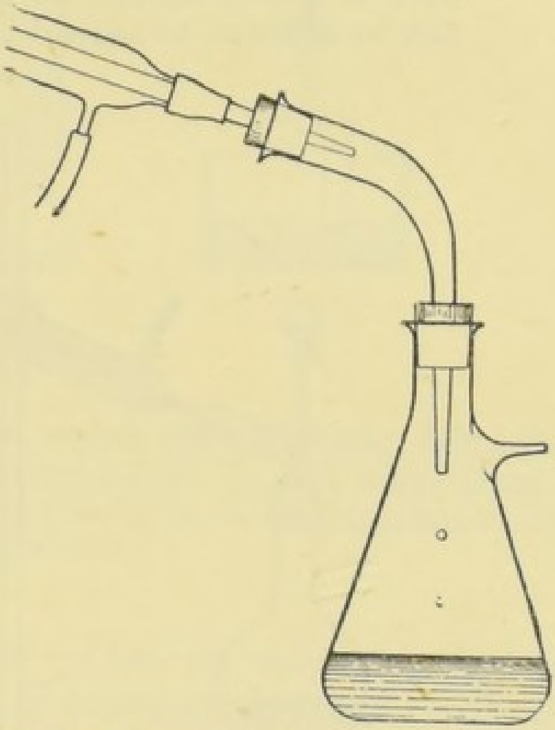

Fig. 11.—Preparation of Aldehyde

(Receiver should be in freezing mixture.)

$$Na_2Cr_2O_7 + 4H_2SO_4 + 3C_2H_6O$$
$$= 3C_2H_4O + Na_2SO_4 + Cr_2(SO_4)_3 + 7H_2O.$$

Chemically, aldehyde is remarkable for its tendency to form "addition" products (see Section 17). Advantage is taken of its reaction with ammonia to form a crystalline body, **aldehyde-ammonia**, in order to separate it from impurities.

Exp. 15.—*Purification of Crude Aldehyde.*

Process I. To prepare the ether solution.

Place the aldehyde in a flask to which is fitted a reflux condenser (that is, one sloping upwards). The condenser communicates by a *long* tube with two wash-bottles, each containing 50 c.c. of dried ether (Fig. 12). The condenser is filled with water at 30° C. (aldehyde boils at 21° C.), and the mixture is gently boiled for about 10 minutes. The ether must not be allowed to ascend the connecting tube.

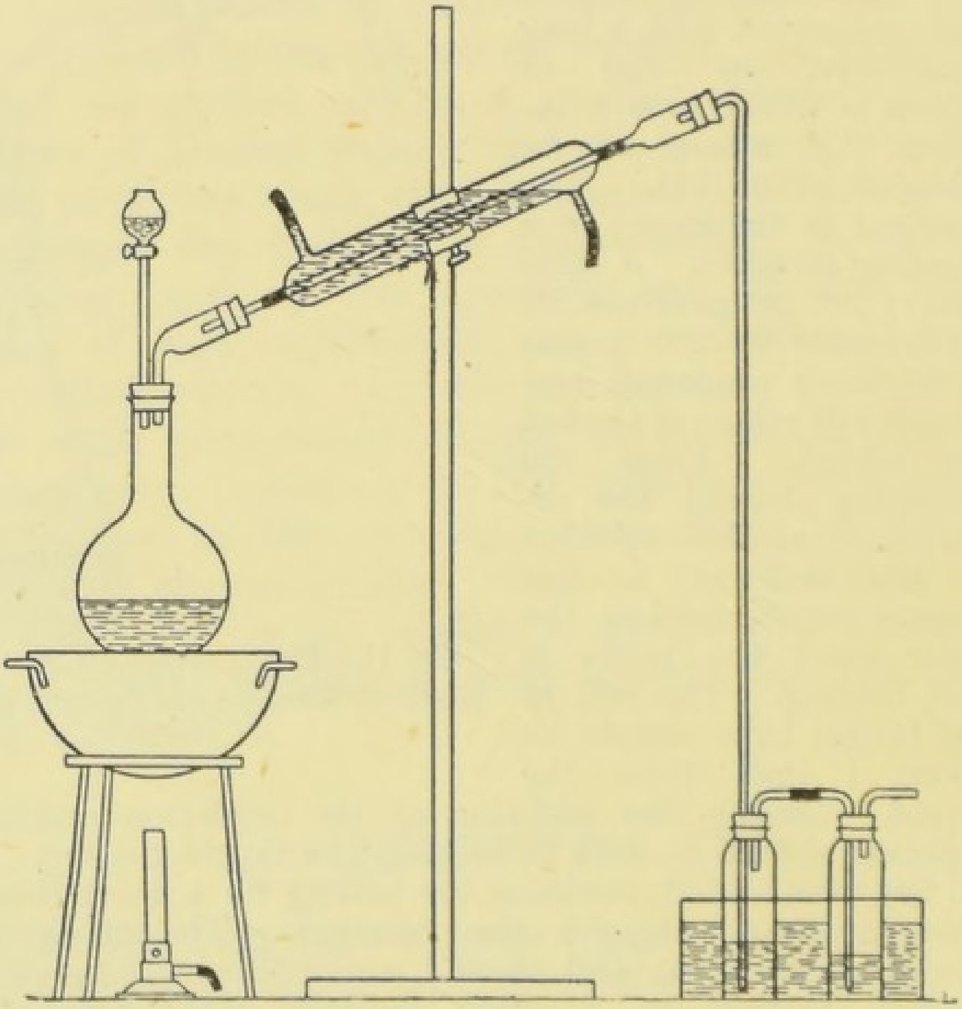

Fig. 12.

Process II. To obtain aldehyde-ammonia.

The ether solution of aldehyde is placed in a beaker surrounded with a freezing mixture. Ammonia, well dried by passage over quicklime, is passed into it by an inverted funnel or wide adaptor, until the solution smells strongly of ammonia (Fig. 13). Leave the solution in the freezing mixture for an hour or more, and then scrape out the crystals, filter by suction pump, washing with a little ether. Dry in a desiccator. [The aldehyde-ammonia may have a smell of mice. This is due to slight oxidation.]

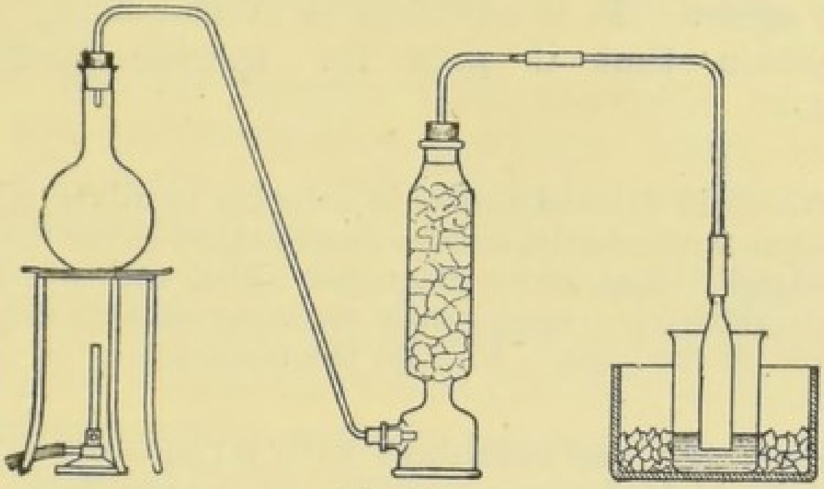

Fig. 13.

Process III.

Dissolve the crystals in an equal mass of water, treat the solution with dilute sulphuric acid (3 in 7), and distil from a water bath, collecting the pure aldehyde as in Experiment 14. Dry by calcium chloride and redistil.

21. Properties of Aldehyde.—Just as ethyl alcohol is the type of an important series of compounds—the alcohols, so also aldehyde is the type of a hardly less important series—the **ALDEHYDES.**

Aldehyde combines with many substances; only a few of these will be mentioned here. In general, these reactions are common to all aldehydes.

(i) With AMMONIA (see Exp. 15).

(ii) With the HYDROGEN SULPHITE OF SODIUM or potassium.

Exp. 16.—To 5 c.c. of a cooled, saturated solution of the hydrogen sulphite add 1 c.c. of aldehyde. Shake the mixture. Crystals of aldehyde sodium hydrogen sulphite, $C_2H_4O.NaHSO_3$, separate out.

(iii) When aldehyde is subjected to the action of "nascent" HYDROGEN, this element is taken up with formation of alcohol.

$$C_2H_4O \longrightarrow C_2H_6O.$$

(iv) When aldehyde is exposed to the air, or to a gentle oxidising agent, it takes up OXYGEN; hence it is a good reducing agent. It is oxidised to Acetic acid; it is from this reaction that it gets its specific name, Acetic aldehyde.

Exp. 17.—Add diluted ammonia solution to dilute silver nitrate solution until nearly all the precipitated silver (hydr)oxide is dissolved; filter into a clean test tube, and to it add a little dilute aldehyde; upon gentle warming silver is deposited as a mirror on the glass. Explain the reaction.

(v) Aldehyde also combines with HYDROGEN CYANIDE to form aldehyde hydrogen cyanide, or cyanhydrin,

$$C_2H_4O.\,HCN.$$

This reaction is of great importance, for when the cyanide is treated with mineral acid it is converted into lactic acid, a reaction which helps us to a formula for the latter compound.

(vi) When aldehyde stands for some time, especially if it contains certain impurities, it acquires new properties. It is found to have the same percentage composition, but its molecular weight is trebled. It is said to *polymerise.* When polymerisation takes place at ordinary temperatures **paraldehyde** is formed: at 0° C. **metaldehyde** is formed. Both bodies are converted into ordinary aldehyde when they are warmed with moderately dilute sulphuric acid; the acid undergoes no change. Paraldehyde does not react with ammonia or with a hydrogen sulphite.

Aldehyde, readily soluble in water, B.P. = 21° C.

Paraldehyde, $C_6H_{12}O_3$, slightly soluble in water, B.P. = 124° C., M.P. = 10°.

Metaldehyde $(C_2H_4O)_3$, a solid insoluble in water, sublimes at 100° C.

Exp. 18.—To prepare paraldehyde, add one drop concentrated sulphuric acid to 1 c.c. aldehyde.

To prepare metaldehyde. To aldehyde cooled to 0° add sulphuric acid; or, at ordinary temperature, pass into it gaseous hydrochloric acid or sulphur dioxide.

When aldehyde is treated with caustic alkalis, it is transformed into **aldehyde-resin**, a substance of which little is known.

It must not be thought that aldehyde forms only addition and polymerisation products, many important reactions take place in which aldehyde "condenses" with some other compound, the condensation being accompanied by the elimination of the elements of water. Thus "**acetal**" is formed by the interaction of aldehyde and alcohol.

$$C_2H_4O + 2C_2H_5OH = C_2H_4(OC_2H_5)_2 + H_2O.$$

Still another reaction must be mentioned here, a reaction which is important for its bearing upon the

22. Formula of Aldehyde.—We have seen that the chlorides of phosphorus act readily with alcohol to replace the hydroxyl group by an equivalent of chlorine. This reaction is so common with bodies which contain the hydroxyl group, that its occurrence is accepted as a proof of the existence of that group in the molecule of the substance concerned.

$$3X'OH + PCl_3 = 3X'Cl + H_3PO_3.$$

Now phosphorus *tri*chloride will not react with aldehyde, hence we conclude that aldehyde does not possess the hydroxyl group, and, generally speaking, its other reactions support this conclusion. Phosphorus *penta*chloride will indeed attack aldehyde, but in quite a different manner, for the oxygen alone is removed, and in its place two equivalents of chlorine are introduced.

$$C_2H_4O + PCl_5 = C_2H_4Cl_2 + POCl_3.$$

This product, however, whose formula is identical with that of ethylene chloride, has properties, both chemical and physical, which differ entirely from those of ethylene chloride. For example, it boils at 57° C., while the latter compound boils at 84° C.

Also, when this new chloride is heated with caustic potash it is reconverted into aldehyde, whereas ethylene chloride yields glycol.

$$C_2H_4Cl_2 + 2KOH = C_2H_4O + 2KCl + H_2O.$$

Hence aldehyde cannot be regarded as the oxide of ethylene. It is evident that there is a fundamental difference between the two chlorides To distinguish them, the chloride related to aldehyde is called **Ethylidene chloride**.

23. Isomerism.—Many pairs of substances are known the individuals of which share one molecular formula, but have quite distinct properties, and the term "***Isomerism***" is used to indicate this. One such pair of "isomers" is par- and met-aldehyde; another is ethylene and ethylidene chlorides.

To give a name to the phenomenon does not explain it, and the student will experience a growing need of some explanation. We shall defer it until we have material for the purpose.

Although ethylene and ethylidene chlorides are so unlike, yet they are not altogether unrelated, since both are converted into Ethane (C_2H_6) by "nascent" hydrogen. Moreover, when ethyl chloride is treated with chlorine in diffused light, besides other products ethylidene chloride is formed, and, in favourable circumstances such as in the presence of iron, ethylene chloride is produced.

ACETIC ACID.

24. We have seen that acetic acid is produced by the guarded oxidation of Alcohol. Large quantities of the dilute acid are prepared by oxidation of wine and malt alcohol.

Preparation by aid of Bacteria.—When alcohol is exposed to the air it is slowly oxidised, but the oxidation is immensely hastened by bacterial agency, especially by "mother of vinegar" or *Mycoderma aceti* and *Bacillus xylinum*. The most favourable temperature is 35° C. The souring of beer and light wines is a good example of this action. Commercially, the oxidation is hastened by exposing large surfaces of the dilute alcohol to the air and the bacilli, by causing the liquid to trickle through a perforated cask filled with beech shavings which have previously been treated with infected vinegar in order to induce a growth of the bacteria. Vinegar contains less than 10 per cent. of acetic acid.

Preparation from Wood Distillation.—The ordinary acetic acid may be prepared from vinegar; most of it, however, is obtained from the liquid products of the dry (destructive) distillation of wood. This liquid, which contains water, wood spirit, and acetone also, is treated with quicklime; the calcium acetate formed is separated, freed from adhering impurities, and then heated with hydrochloric acid. The distillate (pyroligneous acid) contains about 50 per cent. of real acid. Purification is accomplished by distillation in contact with dichromates. The product is treated with sodium carbonate. The hydrated sodium acetate which crystallises out is heated strongly but cautiously, and the anhydrous salt so obtained is heated with concentrated sulphuric acid. The pure substance, which distils over, solidifies as **Glacial Acetic acid.**

A shorter method is to treat the calcium acetate with the equational quantity of concentrated sulphuric acid and distil. The distillate is concentrated acetic acid. This can be rendered anhydrous by the freezing method. The acid is cooled until solid separates out; this is nearly pure acetic acid, the water with some dissolved acid remains liquid and is poured off. The solid is melted and again frozen, and so on until the residue melts at 16·7° C. It is then perfectly pure.

25. The Molecular Formula of Acetic Acid.—As determined by combustion, the simplest (or empirical) formula of acetic acid is CH_2O. Its vapour density at about 130° C. (it boils at 119°) corresponds to the molecular formula $C_4H_8O_4$. As the temperature rises the vapour density falls until at 200° C. it is halved. We might consider this as due to the dissociation* of the acetic acid molecule were it not that other evidence supports the formula $C_2H_4O_2$. That it cannot be simpler than $C_2H_4O_2$ is proved by analysis of the silver salt—the normal salt will be formed.

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* See *Inorganic Chemistry*, pp. 217 and 289, and *Tutorial Chemistry*, pp. 276 and 202.

Exp. 19.—Prepare some silver (hydr)oxide from silver nitrate solution (1 in 10) by precipitation with caustic soda. Wash the precipitate very thoroughly, and then boil it with dilute acetic acid. Filter hot, recrystallise from hot water, and then evaporate to dryness on a water bath. Heat a weighed quantity to redness in a weighed porcelain crucible and weigh the silver.

It will be found by calculation that 108 grams of silver are combined with 59 grams of acid radicle. Therefore the lowest value for the molecular weight must be $59 + 1 = 60$, which corresponds to the formula $\mathbf{C_2H_4O_2}$. The vapour densities of some of its esters show that this is also the true formula.

26. Properties.—Acetic acid melts at 16·7° C. and boils at 119° C. It is hygroscopic, and miscible in all proportions with water. It is used as a solvent in chemical works. It is comparatively stable towards oxidising agents, although in certain circumstances it yields oxalic acid, and finally carbon dioxide and water.

It is a monobasic acid, hence its acid radicle is $(C_2H_3O_2)$.

The acetate radicle $(C_2H_3O_2)$ is often written shortly as $\bar{A}$. For ethyl acetate, $C_2H_5 . C_2H_3O_2$, the shortened form $Et.\bar{A}$ is used in writing.

It is a comparatively weak acid, and phenol-phthalein should be used as indicator when titrating it. It reacts energetically with several metals, for instance with iron, and the reaction is occasionally useful for preparing "nascent" hydrogen. It acts readily upon carbonates to displace carbonic acid and form acetates.

27. Salts and Esters.—**Sodium acetate** is often used instead of the acid itself in preparing other substances. It crystallises from solution as $C_2H_3O_2Na . 3H_2O$. The water of hydration is detached by heating. **Ammonium acetate** is well known; we shall deal with it later. The acetates of the heavy metals are usually soluble, and crystallise well. As a rule they are readily hydrolysed, and therefore find use as mordants. The basic acetates formed are insoluble: advantage is taken of this in analysis of metallic substances. "Sugar of Lead" is the normal lead salt. "Verdigris" is the basic copper salt.

The esters of acetic acid are insoluble or only moderately soluble in water. The preparation of ethyl acetate has been considered above. $C_2H_3O_2 . C_2H_5$. Acetic acid forms two esters with glycol, since this is a di-acid alcohol. $C_2H_4(OH).C_2H_3O_2$ and $C_2H_4(C_2H_3O_2)_2$. They are best prepared by the action of potassium or, better, silver acetate upon ethylene bromide (see Sect. 18). Many other acetic esters are known, some of which are used as "essences" for flavouring purposes.

SUMMARY.

By gentle oxidising agents alcohol is oxidised by loss of hydrogen to aldehyde, a substance which is particularly noteworthy for its additive reactions. By addition of oxygen aldehyde is oxidised to acetic acid.

$$C_2H_5OH \longrightarrow C_2H_4O \longrightarrow C_2H_4O_2.$$

In this book acetic aldehyde and acetic acid are chosen to represent the classes of aldehydes and organic acids respectively.

QUESTIONS.—CHAPTER IV.

1. Write the formulae for the normal acetates of lead, aluminium, and ferric iron.

2. Give reasons for accepting or rejecting anhydrous calcium chloride, concentrated sulphuric acid, phosphorus pentoxide, and quicklime as desiccating agents for ethyl alcohol, ethyl ether, ethyl acetate, and ethyl bromide.

3. To samples of pure water, tap water, and brine add some absolute alcohol, rectified spirit, methylated spirit, ethyl ether and ethyl acetate. Describe, and if possible explain, what takes place in each of the fifteen cases.

4. How would you obtain pure ethyl alcohol from methylated spirit? What is the greatest difficulty to overcome? Give carefully the details of the fractional distillation.

5. Devise a method (draw the apparatus you would use) for reducing aldehyde to alcohol. See if the polymerides of aldehyde will react similarly.

CHAPTER V.

SIMILAR REACTIONS WITH METHYL ALCOHOL.

METHYL ALCOHOL.

28. One of the products of the distillation of wood is a substance whose behaviour towards sodium and the haloid and other acids is entirely analogous to that of ethyl alcohol. Hence its molecular formula, CH_4O, is written $\mathbf{CH_3.OH}$. The group CH_3 is called "Methyl" (sometimes written Me), and the alcohol "methyl alcohol." The alcohol is also called "wood spirit," because it was discovered by heating wood without access to the air. It is separated from the acetic acid formed in the same operation, when the latter is treated with lime; and from the other bodies present by fractional distillation over quicklime. Like ethyl alcohol it combines with some salts, notably calcium chloride, as "alcohol of crystallisation." It may be recovered from the combination by heating: these reactions are also made use of in its purification.

It boils at 66° C. It readily burns. It is used in the preparation of formalin; for making "methylated spirit" nauseous; and as a solvent.

By the oxidation of methyl alcohol, compounds are produced analogous to acetaldehyde and acetic acid: they are called form-aldehyde, CH_2O, and formic acid, CH_2O_2, respectively.

FORMALDEHYDE.

29. *Preparation.*—The aldehyde is prepared by the very gentle oxidation of methyl alcohol in air. Air charged with the alcohol vapour is drawn over warmed finely divided platinum (even a spiral will serve) or a piece of warmed copper gauze. The aldehyde is collected in cooled water (Fig. 14).

$$2CH_4O + O_2 = 2CH_2O + 2H_2O.$$

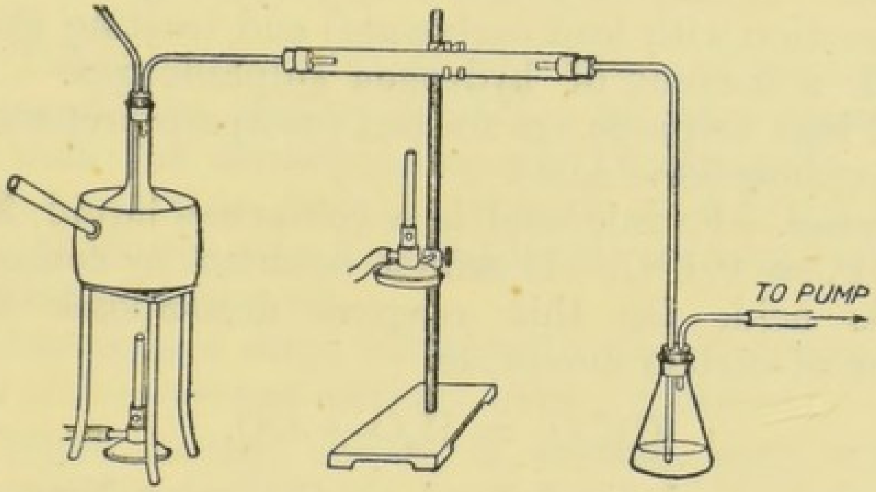

Fig. 14.—Oxidation of Methyl Alcohol to Formaldehyde.

Properties.—Formaldehyde is a gas (B.P. = $-21°$ C.), soluble in water and in methyl alcohol. It has remarkable antiseptic properties; the merest trace is said to be fatal to most bacteria and infusoria. In 40 per cent. solution it is sold as a germicide called "**formalin.**"* Its reactions are, with but few exceptions, analogous to those of acetic aldehyde. It polymerises to the solid **para-formaldehyde,** $C_2H_4O_2$, and to some other bodies. One is of special importance, namely "**Formose,**" $C_6H_{12}O_6$, obtained by the action of lime water: it is a mixture of sugars resembling glucose. Formaldehyde also differs rather widely from acetic aldehyde in its action with ammonia; it will indeed react, but it does not form an aldehyde-ammonia. Almost any oxidising agent converts it into formic acid.

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* Formalin is also the active principle in the disinfectant lozenges, the use of which is said to have lessened the incidence of infectious diseases among elementary school children in London.

FORMIC ACID.

30. This acid owes its name to its occurrence in red ants (*Formica rufa*). It occurs in many plants, for instance, the stinging hairs of the true nettle. It causes wounds on the skin.

Preparation.—It is usually prepared by distilling a mixture of oxalic acid and glycerine at 120° to 130° C. This reaction will not be understood until oxalic acid itself is studied. It may be purified by preparing the lead salt (by interaction with lead carbonate) and treating this when dry with a current of hydrogen sulphide gas. Formic acid and lead sulphide are formed (compare preparation of pure pyrophosphoric acid).

Properties.—Formic acid is a colourless liquid, M.P. = 8° C., B.P. = 101° C. It cannot be dried by concentrated sulphuric acid, for this reagent decomposes it with liberation of carbon monoxide.

$$CH_2O_2 = H_2O + CO.$$

Since water only is formed at the same time, carbon monoxide is sometimes regarded as formic anhydride. Carbon monoxide does not dissolve in water to form formic acid, but some colour is given to the view by the fact that the oxide is absorbed by heated caustic soda (soda-lime at 210° C. is used) with formation of sodium formate.

$$CO + NaOH = CHO_2Na.$$

In laboratories sodium formate is sometimes used as a source of pure carbon monoxide: in commerce, carbon monoxide is used as the source of some formic acid.

Formic acid is a much stronger acid than acetic acid. Its dilute solution resembles vinegar. Its metallic salts resemble the acetates in appearance and properties. Its esters are formed in the same manner as the acetic esters, and are hydrolysed and saponified in the same manner. **Methyl formate,** $CHO_2 . CH_3$ (or shortly $Me\overline{F}$), and **Ethyl formate,** $CHO_2 . C_2H_5$, boil at 32° C. and 54° C. respectively. Both have the pleasant odours characteristic of most esters.

Formic acid differs considerably from acetic acid in that it is very easily oxidised to carbonic acid,

$$2CH_2O_2 + O_2 = 2CO_2 + 2H_2O,$$

for which reason it, or its salts, are not uncommonly used as reducing agents. Its power in this direction may be illustrated by treating a warm ammoniacal solution of silver nitrate with a little sodium formate.

HALIDES, ETC.

31. The chloride, bromide, and iodide of methyl may all be prepared from methyl alcohol. All have lower boiling points than the corresponding ethyl compounds. Methyl chloride boils at $-24°$ C.; bromide at $4{\cdot}5°$ C.; iodide at $43°$ C. It will be seen that the iodide is usually the most convenient as a reagent.

The reactions of ethyl iodide with which we are familiar find an almost perfect analogy here. Thus—

(i) When methyl iodide is treated with "nascent" hydrogen, the halogen is replaced by an equivalent of hydrogen.

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

Compare $C_2H_5I + 2H = C_2H_6 + HI.$

This hydrocarbon is called **Methane.** It is the simplest of the hydrocarbons; we shall consider it in later chapters. Like Ethane, C_2H_6, it is a colourless, insoluble gas, difficult to liquefy.

(ii) When methyl iodide is treated with aqueous caustic potash methyl alcohol is formed.

$$CH_3I + KOH = CH_3OH + KI.$$

Compare $C_2H_5I + KOH = C_2H_5OH + KI.$

When, however, the potash is dissolved in ethyl alcohol, *Ethylene* is formed together with methyl alcohol. By analogy with the ethyl alcohol reaction we might have expected a substance of the formula CH_2, which we might have named Methylene. Such a substance is unknown.

$$2CH_3I + 2KOH \text{ (alcoholic)} = C_2H_4 + 2KI + 2H_2O.$$

Contrast $C_2H_5I + KOH \text{ (,,)} = C_2H_4 + KI + H_2O.$

The formation of ethylene instead of methylene is of importance in the theory of chemistry.

It is stated that if the potash is dissolved in methyl alcohol, ethylene is not formed, but only methyl ether. (Explain the reaction after reading Section 32.)

Methyl alcohol forms salts with other mineral acids; such are methyl nitrate, methyl hydrogen sulphate, and methyl sulphate. Similarly it forms esters with organic acids.

ETHERS.

32. When methyl alcohol is heated with concentrated sulphuric acid, methyl ether, $(CH_3)_2O$, is formed. We can represent its formation thus:—

$$CH_3 . HSO_4 + CH_3OH = (CH_3)_2O + H_2SO_4.$$

It is a gas which boils at about −20° C.

It may also be prepared by the Williamson method.

$$CH_3I + NaOCH_3 = CH_3O . CH_3 + NaI.$$

This method is of peculiar interest, for Williamson also determined what happens when the iodide and sodium compounds possess *different* radicles. Thus he mixed together ethyl iodide and sodium methoxide and obtained some ethyl ether, some methyl ether, and also some of a third ether (B.P. = 11° C.) of the empirical formula C_3H_8O. He obtained the same three products when he started with methyl iodide and sodium ethoxide. It is evident that the third is **methyl-ethyl ether**.

$$CH_3I + NaOC_2H_5 = CH_3OC_2H_5 + NaI,$$

$$C_2H_5I + NaOCH_3 = C_2H_5OCH_3 + NaI.$$

Methyl-ethyl ether corresponds to no known alcohol; and since the radicles are unlike, it is called a MIXED ETHER to distinguish it from the SIMPLE ETHERS already described.

ISOMERISM AND POLYMERISM.

33. This chapter has added to our list of isomers.

The molecular formula $C_2H_4O_2$ stands for acetic acid and for methyl formate, and there is no great difficulty in understanding why these two substances should have properties so different. They belong to different classes of bodies, namely acids and esters respectively; and, in addition, one possesses the radicle of acetic, the other the radicle of formic acid.

Another pair of isomers, ethyl formate (B.P. 54° C.) and methyl acetate (B.P. = 57·4° C.), however, are both esters, but again we can attribute their differences to their different radicles. They may be distinguished by their boiling points, or by saponifying them and isolating the respective acid and alcohol. Still another pair of isomers is methyl ether and ethyl alcohol. These compounds also possess different radicles and belong to different classes.

That the above pairs should differ is easily understood, but we have, as yet, had no reason for the differences between ethylene and ethylidene chlorides. Again, metaldehyde and paraldehyde are isomerides, convertible, via aldehyde, one into the other, and we are entirely at a loss to explain why they should differ so considerably. In nearly all cases where isomers differ widely in their chemical properties, the differences may be attributed to the possession of different "radicles."

By some writers the term ***Metamerism*** is used to denote isomerism between compounds of different classes (Richter); by others, however, it is used to denote isomerism between members of the same class which possess different radicles, such as the esters mentioned above (see Cohen). These two kinds of isomers do not exhaust the list of all that are known. The student must be on his guard against some confusion in the nomenclature of this subject.

The instances of ***Polymerisation*** are also interesting. Aldehyde and paraldehyde are a pair of substances easily convertible one into the other, but the cause of the change is not obvious. A second instance is the conversion of acetylene into benzene. When acetylene is heated in a closed space, a part of it becomes thrice as dense and acquires new properties. It has been converted into benzene, C_6H_6. It is said that at still higher temperatures some benzene vapour is decomposed to form acetylene. If we define polymers as substances having the same percentage composition but different molecular weights, we must include formaldehyde, CH_2O, and acetic acid, $C_2H_4O_2$, as a third pair. These are, in the ordinary sense, unrelated.

HOMOLOGY.

34. Methyl and ethyl alcohols, with their respective derivatives, are two series of compounds which exhibit perfect parallelism of properties. In addition to these methyl and ethyl compounds, there are compounds of the radicles *Propyl* (C_3H_7') and *Butyl* (C_4H_9') : and the properties of the corresponding members of all four series are similar; they differ only in degree. The student will see that each radicle differs from the next simpler by an additional atom of carbon and two additional atoms of hydrogen. And these four radicles are but the simplest of a long series whose general formula may be written

$$C_nH_{(2n+1)}.$$

The regular increase in molecular weight in any one series of compounds, such as the alcohols, ethers, aldehydes, etc., is accompanied by a regular change in the physical properties, such as boiling point, etc., and in the intensity of chemical reaction. Such series are called **Homologous.** The members have the same general formula, are homologous in their composition, and are analogous in their reactions. As an instance of a physical property we may take the case of the boiling point in two homologous series :—

	B.P.		B.P.
CH_3OH	66° C.	CH_3I	43° C.
C_2H_5OH	78°	C_2H_5I	72°
C_3H_7OH	97°	C_3H_7I	102°
C_4H_9OH	117°	C_4H_9I	130°

When we look for a similar group in Inorganic Chemistry we find nothing so striking, yet we are not entirely without examples, for the members of the odd and even series in the Periodic Classification of the elements may be cited as an example of homology.

It may be contemplated that later discoveries will so elucidate the underlying cause of these similarities amongst the elements that the analogy will be seen to be still closer.

SUMMARY.

Methyl alcohol on oxidation yields formaldehyde and formic acid, which are analogous to acetaldehyde and acetic acid. Similarly the methyl halides, esters and ethers are analogous to those of ethyl. The alcohols, halides, etc., of these two alkyl radicles are the two simplest members of the corresponding homologous series.

EXERCISES.

1. Can you suggest a volumetric method for finding the formulae of $CaCl_2, xC_2H_5OH$ and $CaCl_2, xCH_3OH$?

2. Arrange an experiment to find if formalin is formed when methyl alcohol and air are passed over a heated incandescent light mantle.

3. Prepare a crystalline specimen of copper acetate.

CHAPTER VI.

THE IMPORTANCE OF THE HALIDES.

We are now in the position to understand the great importance of the alkyl halides. A knowledge of the chief reactions to which they are disposed enables us to get a bird's-eye view of a large part of the domain of "organic" chemistry.

35. (i) **Substitution of the Halogen by Hydrogen.**—The action of "nascent" hydrogen upon the iodide of methyl (Section 31) is a particular case of a general reaction for alkyl halides.

$$R'I + 2H = R'H + HI.$$

The hydrocarbons Methane, CH_4, Ethane, C_2H_6, Propane, C_3H_8, and Butane, C_4H_{10}, which are formed from the corresponding alkyl halides, are but the simplest hydrocarbons of a numerous series called the "**PARAFFINS**." They owe this name to their resistance to the attack of most reagents; very few substances will affect them except the halogens. Since their molecular formulae differ successively by an additional CH_2, their general formula is

$$C_nH_{2n+2}$$

Pure methane can readily be prepared by this method. Gladstone and Tribe used the action of the zinc-copper couple on a mixture of alcohol and water as the source of hydrogen. We will give here Cohen's method.

Exp. 20.—*Reduction of Methyl Iodide.* The zinc-copper couple is made by immersing thin pieces of granulated zinc in dilute solution of blue vitriol, until a coating of copper is deposited upon them. They are washed thoroughly, first in distilled water and then in dry methyl alcohol. Instead of a flask, a U-tube is used. A dropping funnel, reaching to the bend, is fitted into one limb, the other is filled with the couple and fitted with a delivery tube. The bend of the U-tube is placed in cold water, and a mixture of equal volumes of methyl alcohol and methyl iodide is dropped from the funnel. The methane is collected over water as soon as the air is displaced (Fig. 15). The reaction proceeds according to the following equation:—

$$CH_3OH + CH_3I + Zn = CH_4 + ZnI(OCH_3).$$

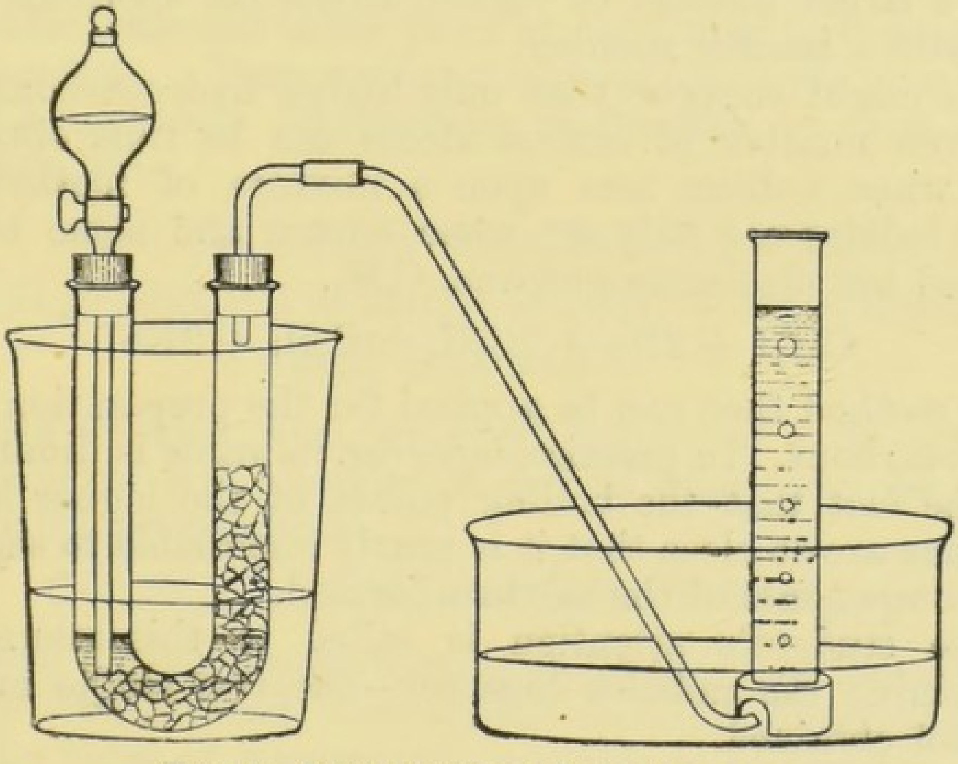

Fig. 15.—Preparation of Pure Methane.

36. (ii) **The Action of Sodium** (**Wurtz' reaction**).—When a piece of sodium is placed in a small flask containing methyl iodide, a reaction takes place in which sodium iodide is formed and a gas escapes. This gas can be shown to be ethane. Ethyl bromide under the same conditions yields butane.

Exp. 21.—*Preparation of Butane from Ethyl Bromide.* For the experiment sodium amalgam is generally used instead of sodium shavings, but the reaction is not violent as a rule, and with some halides warming is necessary. An upright double surface condenser should be fitted to the flask. The gas can be collected over water.

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

$$2C_2H_5Br + 2Na = C_4H_{10} + 2NaBr.$$

The reaction discovered by Wurtz is important for two reasons.

Firstly.—It gives a new idea of ethane, namely as **di-methyl**; similarly butane is di-ethyl. This view we shall find very helpful.

Secondly.—It enables us to obtain a higher hydrocarbon from a lower, or in other words, to obtain a hydrocarbon with a larger number of carbon atoms per molecule from one with a smaller number.

We might suppose that only higher hydrocarbons with an even number of carbon atoms can be thus obtained. But when sodium acts upon a mixture of methyl and ethyl iodides not only are some ethane and some butane formed but also some propane, C_3H_8.

$$CH_3I + 2Na + IC_2H_5 = C_3H_8 + 2NaI.$$

This method then can be applied for the preparation of all hydrocarbons. In practice, however, its value is diminished by the fact that the boiling points of the higher hydrocarbons are so close that it is nearly impossible to separate the components of the mixture formed.

The student's attention is called to this manner of combining the radicles together—the free single radicles are not obtained.

37. (iii) **The Metal-alkyl Compounds.**—When zinc dust is treated with certain alkyl iodides remarkable compounds are formed. With methyl iodide and zinc, zinc iodide and a volatile liquid of the formula $Zn(CH_3)_2$ are formed. The latter is called **Zinc Methyl.** With ethyl iodide, zinc ethyl is formed. These and other **ORGANO-METALLIC COMPOUNDS**, as they are called, have been, and still are, of the greatest assistance in introducing alkyl radicles into carbon compounds. The lower ones are spontaneously inflammable. Magnesium, in somewhat similar circumstances, forms a compound which is not spontaneously inflammable and which is easily prepared. It is more reactive than the zinc alkyls.

Exp. 22.—Drop a known mass of well-scraped pieces of magnesium ribbon into a flask containing well-dried ether. The flask must be fitted with a double surface condenser in order to prevent loss of ether. Add to the flask the equational quantity of methyl iodide dissolved in ether. Reaction begins at once. Afterwards the product may be freed from excess of ether by gentle evaporation. It is **ether-magnesium methiodide.** Keep it in a well-stoppered bottle. It is called *Grignard's reagent.*

$$C_4H_{10}O + Mg + CH_3I = C_4H_{10}O . Mg . CH_3I.$$

Reaction.—(i) When zinc alkyl is brought into contact with water, reaction takes place at once with formation of a hydrocarbon. Pure methane may be obtained from the methyl compound. Magnesium methiodide is more convenient to use.

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

$$2(C_4H_{10}O)MgCH_3I + 2HOH = 2CH_4 + Mg(OH)_2 + MgI_2 + 2C_4H_{10}O.$$

(ii) By reaction with an alkyl halide, a hydrocarbon containing an odd number of carbon atoms can be prepared in a pure condition.

$$Zn(CH_3)_2 + 2C_2H_5Br = ZnBr_2 + 2C_3H_8.$$

These two reactions represent probably the least important types of those which the organo-metallic compounds—especially those of magnesium—are able to accomplish.

38. (iv) **The Action of Potash.**—The action of potash upon the alkyl halides, in the formation of methyl and ethyl alcohols and glycol, and also for the preparation of ethylene and acetylene, have already been given in Sections 7, 16, 18, and 31. This action is of wide application.

39. (v) **The Action of Ammonia.**—When an alkyl halide is heated in a sealed tube with an alcoholic solution of ammonia several reactions take place with the production of a number of substances related to each other and to ammonia. By carefully attending to the conditions, the reaction can be biassed to some extent. We shall study the reaction more fully in Chapter XVII. The substances can be separated, but the methods adopted are not simple to understand. We shall here speak only of the simplest of the substances formed. When methyl iodide is taken, the simplest substance formed has the formula CH_6NI. It is a salt. When it is treated with potash a gas is evolved which smells like ammonia with a suggestion of decaying fish. It is soluble in water, and its solution has an alkaline reaction. In almost every way it behaves like ammonia itself. Hence its formula (CH_5N) is written **CH_3NH_2** and it is called an **AMINE**, **Methylamine.** It differs from ammonia in the replacement of one hydrogen equivalent of the latter by an equivalent of the radicle methyl. Its formation can be represented by the equation

$$CH_3I + NH_3 = CH_3NH_2 . HI,$$

$$CH_3NH_2HI + KOH = CH_3NH_2 + KI + H_2O.$$

Reaction with Nitrous Acid.—Like ammonia it forms salts with acids by combination. It will be remembered that ammonium nitrite is difficult to obtain, and that in solution it is readily decomposed by warming into water and nitrogen. The substituted ammonium nitrite behaves in an analogous manner, for when sodium nitrite solution is added to acidified methylammonium chloride solution, and the mixture is warmed, nitrogen is evolved, and water and methyl alcohol remain.

$$CH_3NH_2HNO_2 = CH_3OH + HOH + N_2.$$

Compare $HNH_2 . HNO_2 = HOH + HOH + N_2.$

The reactions given above are fairly general, and this method for obtaining an alcohol from an amine is, in some cases, the most convenient. The group NH'_2 is called the *amido* group.

40. (vi) **Reaction with Potassium Cyanide.**—When an alkyl halide is treated with potassium cyanide in alcoholic solution, double decomposition takes place.

$$CH_3I + KCN = CH_3CN + KI.$$

The experiment can be carried out in a flask fitted with a reflux condenser (draught chamber). If methyl cyanide is prepared this cannot nicely be separated from the methyl alcohol since a mixture of constant boiling point is formed. This mixture is quite suitable for some experiments however.

It is a liquid of pleasant odour boiling at 81·6° C.

Alkyl cyanides are not always prepared by this method, indeed, **methyl cyanide** is much more easily prepared by a method to be described in Chapter IX.

The cyanides are capable of two extremely important reactions, with which we shall now deal.

(*a*) *Reduction of the Cyanide.*—When sodium is added to the alcoholic solution of a cyanide, the nascent hydrogen produced by interaction between the metal and the alcohol reduces the cyanide to an amine. Thus *methyl* cyanide is converted into *ethyl*amine.

$$CH_3CN + 4H = C_2H_5NH_2.$$

This reaction is of great importance practically; theoretically it helps us to understand the nature of the methyl and ethyl radicles, and, taken with the reaction now to be described, it helps us to understand well the cyanide group also.

(*b*) *Hydrolysis of the Cyanide.*—When an alkyl cyanide is heated with a solution of potash or of a mineral acid, a change of great theoretical interest and practical importance takes place.

With a base, ammonia is expelled and the metallic salt of an organic acid remains.

Thus from methyl cyanide, potassium acetate is formed,

$$HOH + KOH + CH_3CN = (C_2H_3O_2)K + NH_3.$$

With hydrochloric acid,

$$CH_3CN + 2H_2O + HCl = C_2H_4O_2 + NH_4Cl.$$

Even when there is neither acid nor base present in the aqueous solution, practically the same change occurs, the ammonium salt of the organic acid being formed.

$$CH_3CN + 2H_2O = C_2H_3O_2 . NH_4.$$

It will be seen that the reaction is a remarkable case of hydrolysis of a salt—that is a reaction between a salt and the water in which it is dissolved to produce free base and free acid—unique in that the salt, on hydrolysis, yields an acid and a base which are not even remotely related to the acid and base proper to the original salt.

Since the reaction is general, the alkyl cyanides are also named after the acids to which they give rise. In this case they are called **NITRILES.**

Hence methyl cyanide is also known as **aceto nitrile.** The great importance of this hydrolysis to us is that it gives us a new insight into the chemistry of acetic acid.

SUMMARY.

The reactions described above—which are by no means exhaustive—will show the student that organic chemists can, by appropriate methods, obtain a needed substance from another which, at first thought, may seem a most unlikely source. The reactions by which a compound higher in a series may be obtained from one lower in the series, or a compound of a higher radicle from one of a lower, are of special importance. Many of these reactions owe much of their interest to the clues they afford in a search for clear conceptions of the nature of organic substances.

QUESTIONS.—CHAPTER VI.

1. By what general methods may the number of carbon atoms in a molecule be increased?

2. How can methane be obtained from ethyl alcohol as a starting point?

3. Explain how the following "ethereal compounds" are formed from the corresponding alcohol: ethyl chloride, methyl chloride, ethyl acetate, ethylene di-bromide. Describe the action of potash and ammonia upon these bodies.

4. Explain the meaning—in its widest sense—of the term "hydrolysis." Illustrate your answer by giving as many types of hydrolysis as you can.

5. Account for the application of the terms ethyl, ethylene, ethane, "ethereal salt." (Gk. *aithō* = to blaze.)

6. Give an equation for the action of "nascent" hydrogen upon propyl bromide.

7. What hydrocarbons are formed by the action of sodium upon a mixture of ethyl and butyl bromides?

8. By what methods would you attempt to obtain Nonane, C_9H_{20}, from methyl iodide as a starting point?

9. Give the formula of the paraffin whose molecule contains 31 atoms of carbon.

10. How would you obtain ethylamine from ethyl alcohol; and *vice versa*?

11. How would you obtain propyl amine from ethyl bromide?

12. How would you obtain propionic acid from ethyl alcohol as a starting point?

13. Give the formulae of the products which you would expect to obtain by the oxidation of glycol.

14. Give the formula of the organic base whose analysis gave:—

Carbon, 60·8 per cent.; *Hydrogen*, 15·3 per cent.; *Nitrogen*, 23·8 per cent.; vapour density = 30.

Does this formula conform with its reaction with nitrous acid to give an alcohol of the formula C_3H_8O?

15. Add silver nitrate in solution to solutions of methyl and ethyl halides; notice if silver chloride is precipitated or not.

16. Write the formulae of the ethers, esters (acetates and formates), and "alcoholates" of propyl and butyl.

17. What formulae would you give to the oxidation products of propyl and butyl alcohols?

CHAPTER VII.

THE ACETIC ACIDS.

41. In Chapter IV. we arrived at $C_2H_4O_2$ as the molecular formula for acetic acid. This formula may be modified to $C_2H_3O_2.H$ to denote that the acid is monobasic. But since acetic acid may be prepared by the hydrolysis of methyl cyanide, of which the nitrogen is detached to form ammonia and to give place for its equivalent of oxygen and hydrogen, we are fairly justified in concluding that acetic acid is a *methyl* compound, and in further modifying its formula to

$$CH_3.CO_2.H.$$

The Action of Chlorine on Acetic Acid.

Exp. 23.—A flask whose weight is known approximately is fitted with a tube reaching to the bottom for the admission of chlorine, and with an inverted[*] condenser which is connected by a long tube with a Volhard trap containing caustic potash solution for the absorption of hydrogen chloride and excess chlorine (Fig. 16). The flask is heated on a rapidly boiling water bath and placed in bright sunshine. If the experiment is to be finished in a reasonable time the sunshine is essential. A mixture of 100 grams of glacial acetic acid and 8 grams of red phosphorus is placed in the flask. Chlorine, prepared by dropping hydrochloric acid on heated manganese dioxide, and dried by concentrated sulphuric acid, is passed through the mixture. The reaction is finished (it will take the best part of a day

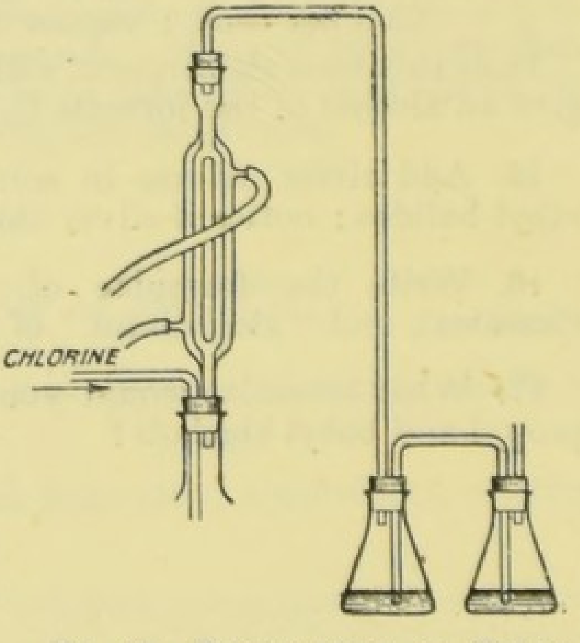

Fig. 16.—Preparation of Chloracetic Acid.

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[*] A double surface condenser can be employed in most experiments. It makes the apparatus more compact and easier to manage.

even in favourable circumstances) when a little of the product in a test-tube, cooled with ice, deposits crystals on the wall of the tube when this is rubbed with a glass rod. By this time the acetic acid should have gained about 50 grams in weight. The product is then distilled in a flask connected with a long air-condenser (a wide glass tube). The fraction which comes over from 150° to 200° C. contains the product sought. This is cooled in ice water, when the part which solidifies (rub the walls with a glass rod) is the substance required. Pour off the still liquid portion. Take great care that the substance does not touch the skin. Redistil the solid. It should come over at about 186° C.

42. When chlorine is passed into glacial acetic acid in sunlight—better when a chlorine carrier, such as phosphorus, iodine, or sulphur, is present—hydrochloric acid is liberated and the acetic acid increases in weight. If the reaction is not allowed to proceed too far, a product is obtained in which one equivalent of hydrogen in the acid is replaced by chlorine, and yet which behaves in every way similarly to acetic acid itself, which is indeed even stronger as an acid. Therefore it is called monochloracetic acid, and its formula is written $CH_2Cl.CO_2H$.

$$CH_3CO_2H + Cl_2 = CH_2Cl.CO_2H + HCl.$$

If the reaction is allowed to proceed further another hydrogen equivalent is replaced by chlorine, and even a third, with formation of dichloracetic acid, $CHCl_2.CO_2H$, and trichloracetic acid, $CCl_3.CO_2H$, progressively.

As each hydrogen is substituted, the acid formed is stronger than that from which it was obtained: trichloracetic acid is almost as strong as sulphuric acid.

Chlorine itself has no further action on the tri-chlor acid. The chloracetic acids behave with reagents in the same way as acetic acid itself, the products are analogous.

	M.P.	B.P.	Relative strength* shown by K.
Acetic acid ...	16·7°	119°	·0018
Monochlor ,, ,, ...	63°	185°	·155
Di ,, ,, ,, ...	−4°	190°	5·14
Tri ,, ,, ,, ...	52°	195°	121·

* See Walker's *Physical Chemistry*.

The corresponding bromine and iodine acetic acids are known.

Monochloracetic acid is prepared in the manner given above, but trichloracetic and dichloracetic acids, which can be formed in the same manner, are, in practice, prepared from a substance called chloral, with which we shall become acquainted later.

When the assertion was first made by Laurent and Dumas (1834-1840) that the replacement of the electro-positive hydrogen by the electro-negative chlorine does not change essentially the chemical character of the acetic acid, the fact came as a surprise to other famous chemists, and provoked somewhat scornful criticism from Berzelius and Liebig in particular.

43. Replacement of the Halogen by other Groups.—*The Amino-acid.* When ammonia solution is intimately mixed with monochloracetic acid, a reaction occurs quite similar to that described in Section 39. As in that case, the reaction proceeds with formation of more than one product, but the simplest of them may be separated fairly easily (see Cohen's *Practical Organic Chemistry*, p. 82). It is the *Amino-acetic Acid.*

$$CH_2Cl . CO_2 . H + 2NH_3 = CH_2(NH_2) . CO_2 . H + NH_4Cl.$$

This acid is also called **Glycine** and **Glycocoll**, because it is a sweet substance and was first obtained from glue (κολλα = glue). It may be obtained more easily from a natural product called Hippuric acid. Glycine is both an amine—a base—and an acid. In solution it is almost neutral. If the conditions are proper it will, as an acid, react with bases to form salts, that is glycine salts. The copper salt is especially easily formed. On the other hand it will combine with nitric acid as a substituted ammonia should.

44. The Hydroxy-acid.—When glycine is treated with nitrous acid, it behaves like an alkyl amine (Section 39), nitrogen is evolved, and a hydroxide is formed.

$$CH_2(NH_2)CO_2H + HNO_2$$
$$= CH_2(OH) . CO_2H + N_2 + HOH.$$

The product is hydroxy-acetic acid, usually called **Glycollic acid**. The same product is formed by boiling together potassium monochloracetate and caustic potash for some time.

$$CH_2ClCO_2K + KOH = CH_2OH . CO_2K + KCl.$$

It is also formed when acetic acid is gently oxidised with dilute nitric acid.

Glycollic acid is, at the same time, an alcohol and an acid. As an acid it forms salts and esters by the replacement of acid hydrogen by metals and radicles: it is stronger than acetic acid, but not as strong as monochloracetic acid. As an alcohol it can form esters with other acids, and like alcohol can be oxidised to an aldehyde and another acid. The products of oxidation we shall mention again.

45. The Cyan-acetic Acid.—When potassium chloracetate is heated with potassium cyanide, the expected reaction (§ 40) occurs and potassium cyanacetate is formed.

$$CH_2ClCO_2K + KCN = CH_2 . CN . CO_2K + KCl.$$

The *cyan*-acetic acid is stronger than the *chlor*-acetic acid. When the potassium salt is heated with potash hydrolysis takes place with the evolution of ammonia and the formation of a new acid, which of course is dibasic.

$$CH_2CN . CO_2H + 2H_2O = CH_2 . (CO_2H)_2 + NH_3.$$

The di-basic acid so formed is called Malonic acid. It is of great importance in the synthesis of other substances. When it is heated it loses carbon dioxide and is reconverted into acetic acid.

$$CH_2(CO_2H)_2 = CH_3CO_2H + CO_2.$$

SUMMARY.

Acetic acid has many derivatives which still are acids. By substitution the halide acetic acids are produced. The halogen is exchanged for other groups—amino, hydroxyl, cyanide—as in the case of an alkyl halide. The products have both the properties of acetic acid and those arising from the new group.

CHAPTER VIII.

THE ACETYL COMPOUNDS.

46. When glacial acetic acid is warmed with phosphorus trichloride, an energetic reaction takes place. We have learnt to regard this as good evidence of the presence of an hydroxide group (Section 22). In this case a substance is formed which reacts readily with water to yield acetic acid and hydrochloric acid. Since the chloracetic acids behave similarly with phosphorus trichloride to yield similar products, we may write the formula of this substance $CH_3CO.Cl$. It is called **Acetyl chloride**. Consequently we can make a still more discriminative formula for acetic acid:

$$\mathbf{CH_3CO.OH.}$$

The equation for the preparation of acetyl chloride is written differently by different authorities. Hydrochloric acid is always evolved: some people regard this as due to a secondary reaction, and write the equation

$$3CH_3CO.OH + PCl_3 = P(OH)_3 + 3CH_3CO.Cl,$$

others regard the formation of the hydrochloric acid as part of the ordinary reaction, and write the equation

$$3CH_3CO.OH + 2PCl_3 = 3CH_3CO.Cl + 3HCl + P_2O_3.$$

Exp. 24.—*Preparation of Acetyl Chloride.* Fit up the apparatus of Figure 17. Place 50 grams of glacial acetic acid in the flask and immerse this in cold water. Run in slowly from the funnel 40 grams of phosphorous chloride. Now change the water in the bath for some at 40° to 50°, and keep it at that temperature until the rush of hydrochloric acid is nearly over and until the product separates into two layers. Now heat the water bath to boiling until no more distillate collects in the receiver. This is the acetyl chloride ; it can be redistilled from a similar apparatus, without the dropping funnel. Collect that which comes over at 50° to 56° C. The apparatus must always be protected from the moisture of the air by the calcium chloride tube.

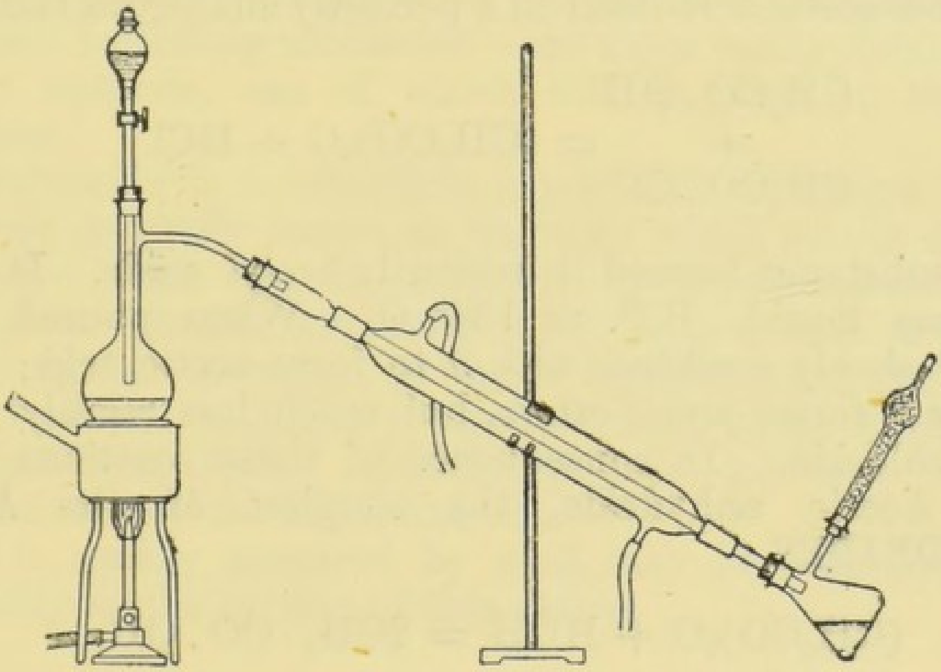


Fig. 17.

Acetyl chloride is a colourless liquid, B.P. 51° C., very hygroscopic. It is very reactive, and is used in large quantities by chemists. It is hydrolysed at once by water, as we have said. It is a typical **ACID CHLORIDE**.

It may be compared with the acid chlorides of the mineral acids, for instance—

$$SO_3H.Cl \rightarrow SO_3H.OH, \qquad CrO_2Cl_2 \rightarrow CrO_2(OH)_2,$$
$$POCl_3 \rightarrow PO(OH)_3.$$

Similarly it reacts with other hydroxides, such as alcohols, and this is one of the easiest ways of preparing esters.

$$CH_3CO.Cl + HO.C_2H_5 = CH_3CO.OC_2H_5 + HCl.$$

Since the associations of the group CH_3CO can be changed in this way, it follows that it is a radicle. It is called *Acetyl.*

47. Reaction with Acetic Acid.—Acetyl chloride will react with acetic acid itself in a perfectly analogous manner.

$$\begin{array}{c} CH_3CO.OH \\ + \\ CH_3CO.Cl \end{array} = (CH_3CO)_2O + HCl.$$

The substance formed is evidently *acetyl oxide.* It is a colourless liquid, B.P. = 138° C. When poured into water it slowly combines with it to form acetic acid; with alcohols it forms acetic esters, but much less readily than acetyl chloride. In consequence of these reactions it is called **Acetic anhydride,** the simplest of the **ACID ANHYDRIDES.**

$$(CH_3CO)_2O + HOH = 2CH_3.CO.OH.$$

It cannot be formed by the dehydration of acetic acid.

It may perhaps be likened to nitrogen pentoxide,

$$N_2O_5 + HOH = 2HNO_3,$$

but it does not bear the same relationship to its acid as carbon monoxide does to formic acid.

In making the compound in quantity the starting point is perfectly anhydrous sodium acetate. It is not so easy to prepare successfully as it might appear.

(For the method see Cohen, *Practical Organic Chemistry*, p. 68, or Gattermann, p. 127.)

48. Reaction of Acetyl Chloride and Ammonia.—The chlorine of acetyl chloride reacts with reagents in the same way as does the chlorine of the alkyl chlorides. When acetyl chloride is treated with ammonia, an amide is formed.

$$CH_3CO \,.\, Cl + NH_3 = CH_3CO \,.\, NH_2 + HCl.$$

This compound is called **Acetamide**; it is the type of the **ACID AMIDES**. This term is chosen in place of amine in order to distinguish these bodies from the alkylamines and amino-acids, from which they differ considerably. Many acid amides are prepared in the manner given above, but others—including acetamide—are more easily obtained by other methods, one of which will be given in the next chapter.

Acetamide is a colourless crystalline substance. With it there generally occurs an impurity which smells strongly of mice; this can be removed by crystallisation from Benzene. Acetamide melts at 82° C., and boils at 222° C. It is soluble in water, giving a neutral solution; yet it will form an additive compound with hydrochloric acid $(CH_3CONH_2)_2HCl$. Caustic potash converts it into potassium acetate and ammonia.

It is readily prepared by what may be regarded theoretically as the reverse of this action.

Exp. 25.—*Preparation of Acetamide from Ethyl Acetate.* Bring together in a corked distilling flask 25 c.c. of ethyl acetate with an equal volume of concentrated ammonia solution, shake occasionally until there is no surface of separation; if this stage is not reached in two days, the mixture is not in a sufficiently warm place. Now distil; excess of ammonia will come first, and then ammonia and alcohol. Finally acetamide, as an oily liquid, will come over and will solidify. Use a short tube as condenser. Purify by fractional crystallisation. Take care that none gets on your clothes.

$$CH_3CO.OC_2H_5 + NH_3 = CH_3CO.NH_2 + C_2H_5OH.$$

When acetamide is treated with bromine and caustic potash (see Section 129) methylamine is produced.

49. When acetamide is heated with phosphorus pentoxide **methyl cyanide** is formed by the loss of the elements of water.

$$2CH_3CONH_2 + P_4O_{10} = 2CH_3CN + 4HPO_3.$$

Exp. 26.—*Preparation of Methyl Cyanide from Acetamide.* Fix a short condenser to a small distilling flask which carries a thermometer. Place 15 grams of phosphorus pentoxide in the flask *quickly*, and then add 10 grams of well-powdered acetamide; shake well. The mixture is gently heated with a luminous flame kept in motion. To the distillate add half its volume of water and then solid potassium carbonate until no more is dissolved. The upper layer is separated off with a syringe and redistilled from a little phosphoric oxide. It should boil at 82° C.

50. A Reaction with Organic-metallic Compounds.—One more reaction of acetyl chloride will be mentioned in this chapter because it will give the student a better idea of the possibilities of the reagent, and of its importance in deciding the formulae of substances. Incidentally, we here meet with Acetone, the most important member of a new class of organic bodies—the **KETONES.** It is chiefly prepared by another method to be given in the next chapter.

Acetone is formed together with acetic acid and methyl alcohol when wood is destructively distilled. Some of it is obtained from this source. It is a liquid of pleasant odour, boiling at 57° C. In many of its reactions it resembles aldehyde, particularly in that it forms additive products with hydrogen cyanide, and potassium hydrogen sulphite.

By combustion and vapour density determination its molecular formula is found to be C_3H_6O. Like aldehyde it will not react with phosphorus trichloride, hence it has no hydroxide group; but, like aldehyde, it reacts with phosphorus pentachloride to exchange the atom of oxygen for two of chlorine. The resulting product is capable of a reaction of great importance which will be referred to in a later chapter.

But acetone is isomeric with propion-aldehyde, which is obtained by the oxidation of propyl alcohol, C_3H_7OH.

Propion-aldehyde is readily oxidised to propionic acid, $C_2H_5CO.OH$. Acetone on oxidation yields, on the contrary, acetic acid and carbon dioxide.

Acetyl chloride forms with zinc methyl different compounds according to the time allowed for reaction; when the time is restricted acetone and zinc chloride are formed. Hence acetone is an acetyl compound, and the foregoing method for its preparation leads to the formula $\mathbf{CH_3CO.CH_3}$.

$$2CH_3CO.Cl + Zn(CH_3)_2 = 2CH_3CO.CH_3 + ZnCl_2.$$

The reaction with phosphorus pentachloride is represented,

$$CH_3.CO.CH_3 + PCl_5 = CH_3CCl_2CH_3 + POCl_3.$$

SUMMARY.

The formula of acetic acid may be written $CH_3.CO.OH$. The group CH_3CO' occurs in a number of compounds, and therefore is called the acetyl radicle. Acetyl chloride reacts in much the same manner as the alkyl chlorides. It is a very valuable reagent, both for testing in other compounds for the existence of alcohol hydroxyl, and in syntheses.

CHAPTER IX.

THE CHEMICAL BEHAVIOUR OF SOME METALLIC ACETATES.

51. Effect of Distilling Calcium Acetate.

Exp. 27.—Place some well-dried calcium acetate in a hard glass boiling tube, connect this horizontally to a long condenser (Fig. 18). Then heat until a distillate is evolved, and continue heating at about that temperature. Shake the distillate with a saturated solution of sodium hydrogen sulphite (made by passing sulphur dioxide into a saturated solution of the normal sulphite). Dry the solid on a porous plate. Distil the dried solid with saturated solution of sodium carbonate. Dry the distillate with calcium chloride and redistil. *Acetone,* B.P. 57° C., comes over.

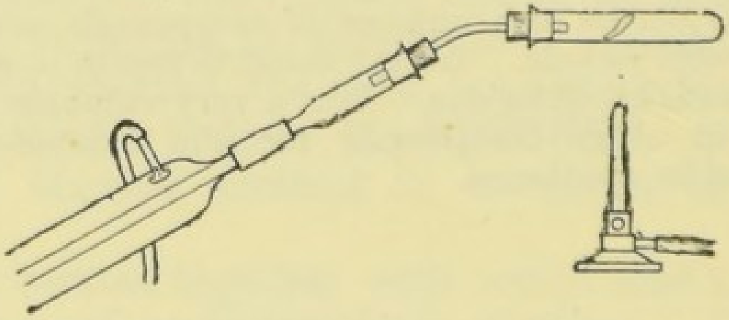


Fig. 18.—Destructive Distillation of Calcium Acetate.

When anhydrous barium or calcium acetate is destructively distilled **acetone** is evolved, while the bye-product is barium (or calcium) carbonate.

$$(CH_3CO.O)_2Ba = (CH_3)_2CO + BaCO_3.$$

The distillation of calcium salts is a general method for the preparation of ketones.

52. When instead of heating calcium acetate alone we distil a mixture of this salt and calcium formate, calcium carbonate and **Acetaldehyde** are formed. The reaction is general, and some aldehydes are commonly prepared from the mixture of calcium formate and the calcium salt of the acid corresponding to the aldehyde required.

$$(CH_3CO.O)_2Ca + (H.CO.O)_2Ca = 2CaCO_3 + 2C_2H_4O.$$

From this reaction it is clear that the aldehyde is also a methyl compound. $\mathbf{CH_3CHO}$.

53. Effect of Distilling Ammonium Acetate.—We are accustomed to the peculiar effects of heating some of the ammonium salts of mineral acids, for instance the nitrate, nitrite, and dichromate. The same treatment of the ammonium salts of organic acids gives an important result. Each yields an acid-amide and water. This is the best way to prepare many acid amides. (See also § 48.)

$$CH_3CO.ONH_4 = CH_3CO.NH_2 + H_2O.$$

The ammonium salt is prepared from glacial acetic acid and ammonium carbonate. The melted salt is run into hard glass tubes, which are then sealed and heated in a bomb furnace to 220° C. (for details see Gattermann, p. 131; also Norman, *Systematic Practical Organic Chemistry*, p. 9, for a simpler but less productive method).

54. Effect of Heating Sodium Acetate with Caustic Soda.—When dry sodium acetate and caustic soda are heated together, **methane**, mixed with some hydrogen and other hydrocarbons, is evolved, and sodium carbonate remains.

$$CH_3.CO.ONa + NaOH = CH_4 + Na_2CO_3.$$

In practice soda lime is used instead of caustic soda (it is less hygroscopic and does not melt so readily). If the two substances are also mixed with iron filings the reaction may be more easily controlled. The drier every substance is made the more successful the experiment.

Exp. 28.—*Preparation of Methane* (*impure*). Place a mixture of 6 grams of well powdered perfectly anhydrous sodium acetate, 12 grams of soda lime, and 4 grams of clean iron filings in a hard glass boiling tube, and heat. Collect the gas over water. To avoid breakage of the retort due to condensation of water, slant the tube downwards, and heat from the upper and closed end forwards, keeping the front of tube fairly hot.

The reaction is general. Many acids, particularly the more complex ones, will lose carbon dioxide when heated alone. Thus malonic acid is easily converted into acetic acid. Although acetic acid is not so easily decomposed the general equation can be written

$$X'CO.OH = X'H + CO_2.$$

The formation of methane from sodium acetate is also taken as good evidence that the acid possesses the methyl group, and, generally, the decomposition of an acid in this way is resorted to as a means of discovering its relationship to other substances.

55. The Electrolysis of Sodium Acetate.—When a solution of sodium acetate (preferably acidified with acetic acid) is electrolysed, between platinum electrodes in a divided cell, hydrogen escapes at the cathode, and a mixture of **ethane** and carbon dioxide at the anode.

In order to obtain a good yield of ethane the electrolysis must be carried out carefully (full details are given in F. Mollwo Perkin's *Practical Methods of Electro-Chemistry*).

Assuming that the true molecular formula of acetic acid is $C_2H_4O_2$, we may regard the formation of the cathode products as due to the decomposition of the acetate radicle ($C_2H_3O_2$). The decomposition is both helpful and suggestive. We have already had occasion to regard ethane as di-methyl; therefore its formation here confirms our belief that acetic acid is a methyl compound. It also shows us that even in what are apparently most favourable circumstances free methyl is not formed. Taking into consideration also those other reactions in which ethane is formed instead of methyl (Section 36), we conclude that methyl is incapable of free existence, except for the exceedingly short time which passes between the disengagement of the discharged radicle and the formation of ethane.

Moreover, the liberation of carbon dioxide by the decomposition of the radicle, points to the close relation of the second carbon atom with both atoms of oxygen, a conclusion which agrees well with the formation of sodium carbonate in Exp. 28. This does not mean that carbon dioxide exists as such in the acetic acid molecule; such a view would clash with our idea of the acid as acetyl-hydroxide. On the other hand some acids can be prepared by the combination of certain substances with carbon dioxide (Section 198). On the whole we may say that the electrolysis of its sodium salt may alone lead us to the formula, $CH_3 . CO_2H$, for acetic acid.

$$\begin{matrix} - \\ + \end{matrix}\left\{\begin{matrix} 2CH_3CO.O = C_2H_6 + 2CO_2 \\ 2HOH + 2Na = 2NaOH + H_2 \end{matrix}\right.$$

QUESTIONS.—CHAPTER IX.

1. Give the formula of the ketone you would expect to obtain by heating calcium propionate $Ca(C_3H_5O_2)_2$; what would be the aldehyde formed when this salt is heated with calcium formate?

2. Give the formulae of the substances which should be formed when soda lime is heated with trichlor, dichlor, and monochlor-acetates of sodium respectively.

3. What formula would you assign to the aldehyde which on oxidation yields trichloracetic acid?

4. How would you separate methyl alcohol and acetone from wood spirit?

5. Compare the properties of acetyl chloride and chloracetic acid.

6. Give as many methods as you can for the preparation of esters.

7. The word "acetic" has the sanction of antiquity. Can you justify the terms acetyl, acetone, and acetylene in their respective uses?

8. How would you obtain from acetic acid specimens of acetyl chloride, acetamide, methane, and ethane?

9. With methyl iodide as starting point, how would you obtain methyl alcohol, formaldehyde, formic acid, and acetone?

10. When sodium tri-chlor-acetate is electrolysed the tri-chlor-methyl ester of tri-chloracetic acid is formed in the anode chamber, and only the merest trace of hexachlor-ethane (C_2Cl_6). How does this affect the argument concerning the methyl group in acetic acid?

CHAPTER X.

RATIONAL FORMULAE.

56. We can define a rational formula as that formula which represents most clearly the greatest number of reactions of which the substance considered is capable and by which it is produced.

Thus chemists unanimously adopt $CH_3.CO.OH$ for acetic acid. We will here collect the evidence we have met which favours this formula. It has been shown :—

(i) That one hydrogen atom has properties different from those of the other three.

Acetic acid is monobasic. Three of the hydrogen atoms may be successively replaced by a halogen with formation of substances whose characters do not differ essentially from those of acetic acid; and, further, the acidic hydrogen cannot be so replaced.

(ii) That the acidic hydrogen is peculiarly related to one of the oxygen atoms to form the hydroxyl group.

Phosphorus chloride reacts with the acid to replace one atom of hydrogen together with one of oxygen by one of chlorine per molecule; from the compound formed the chlorine is readily displaced by other groups, and in no case is the product an acid. Moreover the substituted acetic acids undergo the same changes.

(iii) That acetic acid possesses the Methyl group.

The acid may be formed by the hydrolysis of methyl cyanide.

By heating sodium acetate with caustic soda, methyl hydride (methane) is formed.

By electrolysing sodium acetate, di-methyl (ethane) is formed.

(iv) That the second carbon atom is closely related to both oxygen atoms.

Caustic soda is converted into carbonate when heated with sodium acetate. Carbon dioxide is eliminated during the electrolysis of sodium acetate.

57. A rational formula therefore is constructed by rearranging the molecular formula in such a manner that the established radicles are clearly indicated. Scientific chemical nomenclature is almost entirely a system of "radicle" terms. Thus $(C_2H_3O_2).H$ is to us hydrogen acetate; it reminds us of the acidic nature of the substance: by a slight alteration, $C_2H_3O.OH$, we get acetyl hydroxide, and now we think also of the acetyl compounds. Expanded to $CH_3.CO.OH$ it reminds us of a larger number of possibilities; we may read the formula as methyl carboxyl. The name **Carboxyl** is given to the group $(CO.OH)$; all substances in whose rational formula it appears are found to be acids, and nearly all organic substances having an acid reaction may be regarded as carboxyl compounds. Thus Formic acid is hydrogen carboxyl, $H.CO.OH$.

58. Formulae for Aldehyde and Alcohol.—By the aid of the accepted formula of acetic acid we can arrive at rational formulae for the compounds from which it may be prepared.

The acid is formed by the oxidation of aldehyde, C_2H_4O, by the addition of one atom of oxygen per molecule; hence we may regard aldehyde as a methyl compound also, and, since it appears not to possess the hydroxyl group, its rational formula may be written $\mathbf{CH_3.C.H.O}$. This has been found most appropriate (compare Section 52). Now aldehyde is formed from alcohol, C_2H_5OH, by the removal of two hydrogen equivalents. By reducing aldehyde the reverse action takes place, and, since alcohol possesses the hydroxyl group, we can write its formula as $\mathbf{CH_3CH_2.OH}$: this also expresses well the reactions of alcohol.

We may arrive at the last by an independent argument. We have seen that ethane, by its formation from methyl iodide, may be regarded as di-methyl, CH_3CH_3. When ethane is mixed with its own volume of chlorine, reaction takes place with formation of ethyl chloride, C_2H_5Cl. We must regard this as a reaction in which one methyl group remains intact and the other suffers change, CH_3CH_2Cl. Caustic potash converts ethyl chloride into alcohol—$CH_3.CH_2OH$.

The group $\mathbf{CH_2OH}$ has been found to be common to all alcohols which may be converted into aldehydes, and all aldehydes are found to possess the group $\mathbf{C.H.O}$.

We may thus write for the methyl and ethyl series

$$H.CH_3 \rightarrow H.CH_2Cl \rightarrow H.CH_2OH \rightarrow H.C.H.O \rightarrow H.CO.OH.$$

$$CH_3.CH_3 \rightarrow CH_3.CH_2Cl \rightarrow CH_3.CH_2OH \rightarrow CH_3.C.H.O \rightarrow CH_3.CO.OH.$$

Notice that the above scheme of reactions expresses clearly that the groups $CH_2.Cl$, CH_2OH, $C.H.O$, and $CO.OH$ are all derived from the methyl group by oxidation; that each is a substitution product of methyl; and that each may be regarded as equivalent to a methyl group.

59. Formulae of Ethylidene and Ethylene Chlorides.—From the formula of acetaldehyde we can deduce that of ethylidene chloride, for this body is obtained from the former by the substitution of Cl_2 for O, and reversely, it is converted into aldehyde by the action of potash.

$$CH_3C.H.O + PCl_5 = CH_3CHCl_2 + POCl_3.$$

The formation of aldehyde by the reverse action may be attributed to loss of water.

$$CH_3CHCl_2 + 2KOH = [CH_3CH(OH)_2] \\ H_2O + CH_3C.H.O + 2KCl.$$

Hence ethylidene chloride should be a *methyl* compound.

Now we have seen that ethylidene chloride is isomeric with ethylene chloride, from which it differs considerably. We may make the suggestion that ethylene chloride is not a methyl compound but di-methylene chloride (CH_2 is called the "methylene" group), $CH_2Cl.CH_2Cl$, which would at once account for the differences; and we have previously mentioned that, in certain circumstances, ethylene dichloride is formed by the action of chlorine on ethyl chloride (Section 23).

$$CH_3CH_2Cl + Cl_2 = CH_3CHCl_2 + HCl$$

and $$CH_3CH_2Cl + Cl_2 = CH_2Cl . CH_2Cl + HCl.$$

If this assumption be true we should obtain a diacid alcohol by the reaction of potash on ethylene dichloride: as we know **Glycol** is such a substance. $CH_2OH . CH_2OH$.

From this formula also that of **Ethylene** follows as di-methylene, CH_2CH_2. The formation of acetylene from ethylene bromide can easily be interpreted.

There is not wanting some contradictory evidence for this formula, since ethylidene bromide when treated with sodium yields ethylene. However, the bulk of evidence is strongly favourable.

60. Uses of Rational Formulae.—To the trained chemist a rational formula not only tells the tale of reactions achieved, but indicates to him others which he has not hitherto effected. Thus we write the formula of glycol $C_2H_4(OH)_2$, since glycol may be prepared from ethylene bromide, $C_2H_4Br_2$; and from it we can conclude very little more than that glycol is a di-acid alcohol. But if we write the formula $CH_2OH . CH_2OH$, we recognise that it contains two alcoholic groups of CH_2OH, and we can with considerable confidence predict the preparation of oxidation products of glycol, as represented by the formulae

$CHO . CH_2OH$, (an aldehyde alcohol)	$CHO . CHO$, (a di-aldehyde)	$CH_2OH . COOH$, (an alcohol acid)
$CHO . COOH$, (an aldehyde acid)	$COOH . COOH$. (a di-basic acid)	

When we attempt to prepare the substances we may not choose at once the most favourable conditions, nor even the correct oxidising agents, but with care and patience we may be pretty sure eventually of hitting upon the most suitable method for obtaining each substance. Every one of the substances represented above is known; the first is **glycollic aldehyde**, an important substance related to the sugars; the second is called **glyoxal**; the third we are already acquainted with as **glycollic acid**; the fourth is **glyoxalic acid**; and the last is the well-known **oxalic acid**. The three acids and glyoxal are formed when glycol is cautiously oxidised with nitric acid; glycollic aldehyde is obtained from glycol by the action of hydrogen peroxide in the presence of ferrous sulphate, and several have been obtained by reducing oxalic acid, or by oxidising alcohol.

But in some cases experienced chemists have made wider use of the methods exemplified above: by reflecting upon the established formulae of many substances they have predicted possibilities hitherto unforeseen, and thus have discovered ways of preparing compounds by new methods, or of preparing substances of a totally new character.

61. When we said that a rational formula is primarily the epitome of the chemical properties of the substance so represented, we said all that is necessary. At the same time it can hardly be doubted that these formulae give us some clue as to the method of arrangement of the atoms in the molecule. For this arrangement must have the most important influence upon the reactions of the substance; and the rational formula, while it does not pretend to give even the vaguest picture of the molecule itself, is the picture of its commonest reactions. Two other syntheses are interesting in this context.

(i) Phosgene gas (which can be formed by the combination of carbon monoxide and chlorine) when treated, for not too long, with zinc methyl yields acetyl chloride; we can represent these changes by the following:

$$\mathrm{CO} \xrightarrow{\mathrm{Cl_2}} \mathrm{CO.Cl_2} \xrightarrow{\mathrm{Zn(CH_3)_2}} \mathrm{COCl.CH_3} \xrightarrow{\mathrm{H_2O}} \mathrm{CO.OH.CH_3}.$$

(ii) Sodium acetate has been prepared by heating together sodium methoxide and carbon monoxide.

This last synthesis raises the question of the interrelation of the constituent radicles. In the next chapter we shall see how, by means of the doctrine of valency, together with an important assumption concerning the carbon atom, chemists have been able to suggest very precise relations between the constituent atoms of the molecule.

PART II.

THE CHIEF CLASSES OF ALIPHATIC COMPOUNDS.

CHAPTER XI.

THE SATURATED HYDROCARBONS.

62. In Chapter VI. we described Methane, Ethane, Propane, and Butane as the simplest members of the homologous series of hydrocarbons called the "**PARAFFINS.**" Their general formula is $C_nH_{(2n+2)}$. Each member differs from the one simpler by the group CH_2, and this regular difference in chemical composition is accompanied by a less regular difference in physical properties, such as the boiling point, and also by a change in degree of chemical activity. The members of this series are very numerous. Those which contain more than four carbon atoms in the molecule are named according to the number they contain. Thus pentane, C_5H_{12}, hexane, C_6H_{14}, and so on up to pentatriacontane, $C_{35}H_{72}$, and beyond it. Patience alone seems to set the limit to their preparation.

		B.P.		Heat of Combustion.	
Methane	CH_4	−164°	>80	2119K	>1585
Ethane	C_2H_6	−84°	>47	3704K	>1588
Propane	C_3H_8	−37°	>38	5292K	>1580
Butane	C_4H_{10}	+1°	>35	6872K	>1599
Pentane	C_5H_{12}	36°	>33	8471K	>1521
Hexane	C_6H_{14}	69°	>29	9992K	
Heptane	C_7H_{16}	98°	>27		
Octane	C_8H_{18}	125°			

63. Consider the methods of preparing them. Methyl chloride when treated with sodium yields ethane, $CH_3.CH_3$. Chlorine converts this into ethyl chloride, CH_3CH_2Cl. By treatment with zinc methyl, another methyl group replaces the chlorine, $CH_3.CH_2.CH_3$. Surely the new methyl group is related to the CH_2 group in the same manner as was the chlorine atom; that is to say, the method of the reaction seems to show that the formula $CH_3CH_2CH_3$ not only indicates the radicles but represents their relative positions also.

$$CH_3Cl \rightarrow CH_3.CH_3 \rightarrow CH_3CH_2Cl \rightarrow CH_3CH_2CH_3.$$

64. Isomerism of the Hydrocarbons.—Just as we have isomerides amongst the halides, esters, ethers, etc., so also we have them amongst the hydrocarbons. Thus there are two paraffins of the formula C_4H_{10}. That one which boils at 1° C. is formed by the action of sodium upon ethyl bromide: we must give it the formula $CH_3CH_2.CH_2CH_3$. It is called *normal*-butane. The other is called *iso*-butane. Its boiling point is $-17°$ C. By its method of synthesis it appears to contain three methyl groups, $(CH_3)_3CH$.

There are three hydrocarbons of the formula C_5H_{12}. That one which boils at 36° C. is called *normal*-pentane. That which boils at 28° C. is called *iso*-pentane. The third boils at 10°, it is called *neo*-pentane. Neo-pentane is formed by the action of zinc methyl on acetone chloride, $CH_3CCl_2.CH_3$, hence it must be a tetra-methyl compound, $(CH_3)_4C$. Iso-pentane has three methyl groups; normal-pentane has two.

65. Tetravalency of Carbon.—As we rise in the series, the number of isomers increases and the phenomenon becomes bewildering; yet two assumptions with regard to the carbon atom, not difficult to grant, have accounted in a simple manner for this phenomenon and many others.

Before we state the theory we will collect some of the truths which are to be co-ordinated by it.

(i) The paraffins never form additive products, directly or indirectly.

(ii) The substituted products are formed by the substitution of hydrogen by its equivalent of another element or radicle.

(iii) Hydrocarbons like ethylene and acetylene form additive products, but the products correspond to the substituted paraffins; addition never goes further.

(iv) Only one methyl chloride is known, only one methyl alcohol, and so on. Only one ethyl alcohol and only one ethyl chloride are known. But *two* propyl chlorides are known.

(v) All the paraffins correspond to the formula C_nH_{2n+2}. These are very stable, even when comparatively high in the series.

(vi) When experiments seem to favour the formation of free methyl, ethane is formed.

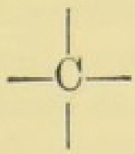
The theory says:

(i) The carbon atom is tetravalent, that is, it can combine with 4 and not more than 4 atoms of hydrogen.

(ii) The four valencies are of equal value.

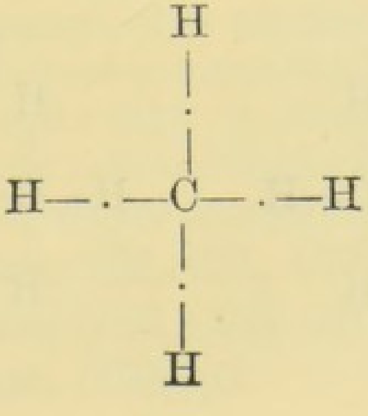
(iii) Combination between radicles takes place as a consequence of the power of the carbon atoms of "satisfying" mutually one or more valencies each.

66. **Graphic (or structural) formulae** will make this clearer. The valency of an atom of hydrogen is represented by one short line H—. The divalency of oxygen by two short lines O= or —O—. The tetravalency of a carbon atom by four straight lines



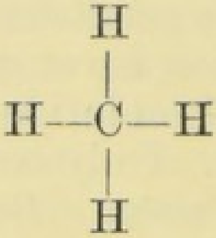
$$\begin{array}{ccc} & | & \\ \text{—} & C & \text{—} \\ & | & \end{array}$$

Methane therefore is represented by the formula



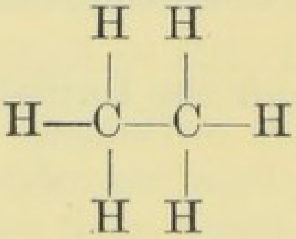
$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ & & \cdot & & \\ & & | & & \\ H & \text{—}\cdot\text{—} & C & \text{—}\cdot\text{—} & H \\ & & | & & \\ & & \cdot & & \\ & & | & & \\ & & H & & \end{array}$$

but the —·— sign is simplified in all cases to ——



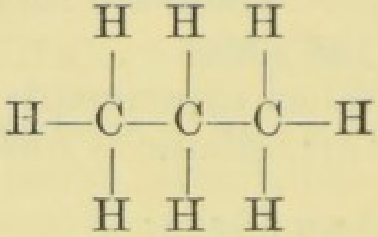
$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ & & H & & \end{array}$$

Ethane is written



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

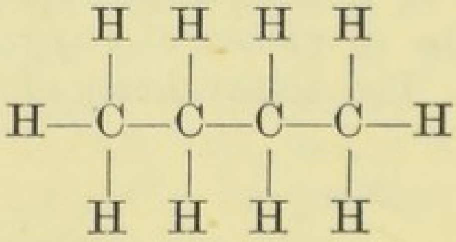
Propane as



$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$

and so on. All these diagrams represent the four valencies attributed to the carbon atom as satisfied either mutually or by atoms of hydrogen.

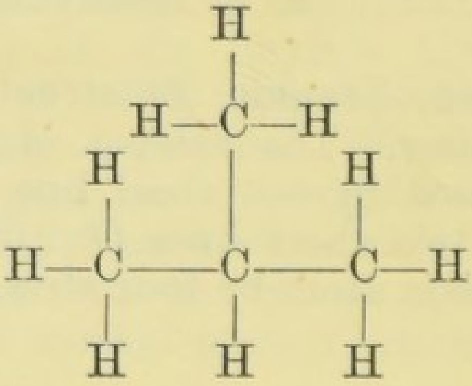
The two *Butanes* are written—



$$\begin{array}{ccccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array}$$

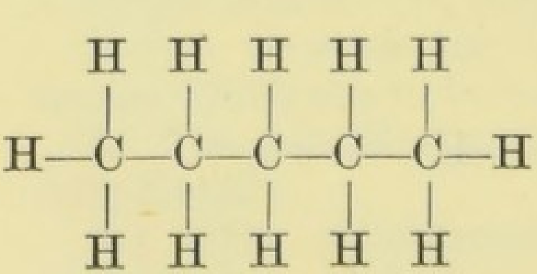
(normal)

and



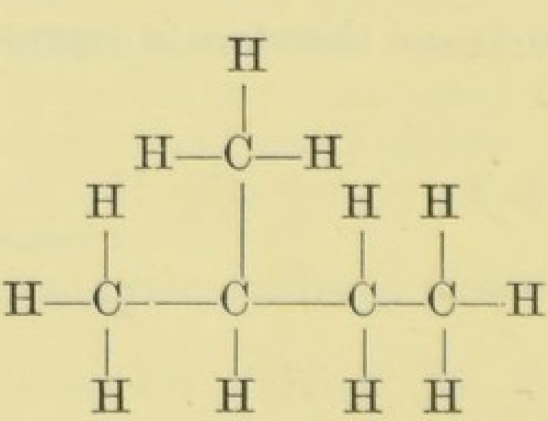
(iso)

and the three *Pentanes*—

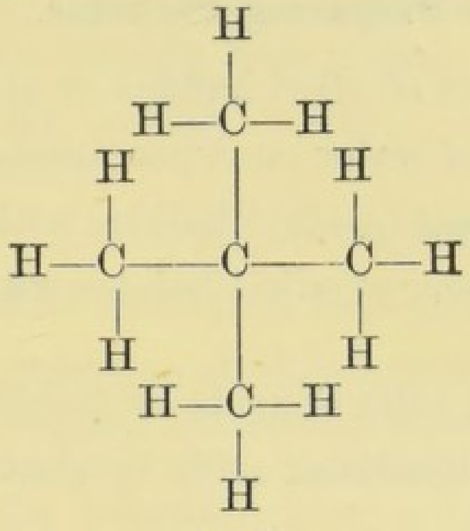


$$\begin{array}{ccccccccccccc} & & H & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & H & & \end{array}$$

(normal)



(iso)



(neo)

The "normal" paraffins can always be represented by an unbranched chain of linked carbon atoms, made up of two methyl groups at the ends connected by methylene groups; an iso-paraffin has a branched chain and contains at least three methyl groups and at least one C.H group; a neo-paraffin contains a carbon atom not directly linked to hydrogen. The student will see that we can rename iso-butane as tri-methyl methane, iso-pentane as trimethyl-ethyl methane, and neo-pentane as tetra-methyl methane. This is the nomenclature adopted for the non-normal paraffins.

This theory, so simple and yet so comprehensive, has been found to agree with the facts; no paraffins have been discovered which it cannot represent; and many have been prepared, and more still will probably be prepared, as the result of its adoption. There can be no better justification for a theory. Rational formulae represent the groups only, structural formulae represent their relative positions. At the same time they must not be considered as pictures of molecules. For example they are flat formulae: but they represent in a simple graphic manner all that chemists need.

Since graphic formulae take up considerable space, it is usual to write them like rational formulae, indicating linked carbon atoms by a dot where convenient. Thus

normal pentane, $CH_3.CH_2.CH_2.CH_2.CH_3$;
iso-pentane, $(CH_3)_2CH.CH_2.CH_3$;
neo-pentane, $(CH_3)_4C$.

67. Methods of Preparing Paraffins.

(i) By reduction of alkyl halides or alcohols.

(ii) By action of water on organo-metallic bodies.

(iii) By treatment of alkyl halides with sodium or zinc.

(iv) By treatment of alkyl halides with organo-metallic bodies.

(v) From alkali salts of acids by distillation with alkali.

(vi) From alkali salts of acids by electrolysis.

68. Petroleum.—The mineral oils of America consist chiefly of paraffins. They are usually obtained by boring to the reservoirs. The lower gaseous paraffins are often evolved from these in large volume. The Russian oils are hydrocarbons of another kind, called naphthenes, polymers of ethylene. Since the hydrocarbons are freely miscible it is extremely difficult to separate them, and the commercial products are mixtures. They are subjected to distillation. That fraction which boils at about 150°-300° is called Kerosene, it is most suitable for lamps. Mixtures of lower boiling point are used for solvent or sparking purposes (benzine, petrol, benzoline). Those of higher boiling point for lubricating purposes. The solid paraffins are used for insulating, for making candles, and for a variety of other purposes.

Their origin is doubtful. Some suggest that they are the final products of decomposition of animal and vegetable remains: others that they are formed from natural carbides.

For illuminating purposes it is extremely dangerous to use an oil of low boiling point: thousands of people have lost their lives from the explosion of paraffin oil. Protective regulations governing the "flash point" of oils in common use are in force in every country. The "flash point" is the lowest temperature at which the vapours of the oil form an explosive mixture with air. In England it is 73° F., which is dangerously low.

69. Methane.—The preparation of methane by methods (i), (ii), and (iv) has already been given.

$$CH_3I + \underset{\text{(nascent)}}{2H} = CH_4 + HI,$$

$$Zn(CH_3)_2 + 2HOH = 2CH_4 + Zn(OH)_2 \text{ (Section 37)},$$

$$CH_3COONa + NaOH = CH_4 + Na_2CO_3 \text{ (Exp. 28)}.$$

At one time the attention of chemists was concentrated in efforts to obtain organic substances directly or indirectly from their elements, and, since methane may be made a starting point in the preparation of a large number of organic substances, its complete synthesis was especially valued. These are special methods :—

(i) Direct union. Pure sugar carbon, freed from hydrogen by ignition in chlorine, was heated in a current of dry hydrogen, the issuing gas contained 1 per cent. methane (Bone 1901).

(ii) Sabatier and Sanderens synthesised methane from the oxides of carbon and hydrogen, by passing these over reduced nickel.

$$CO + 3H_2 = CH_4 + H_2O \text{ (at 200° C.-250° C.)},$$

$$CO_2 + 4H_2 = CH_4 + 2H_2O \text{ (at 230° C.-300° C.)}.$$

(iii) One of the most famous, because the earliest, is due to Berthelot. He passed a mixture of hydrogen sulphide and carbon disulphide over red-hot copper.

$$2H_2S + CS_2 + 8Cu = 4Cu_2S + CH_4.$$

(iv) Pure methane may be obtained from pure aluminium carbide (formed in the electric furnace).

$$Al_4C_3 + 12HOH = 4Al(OH)_3 + 3CH_4.$$

These methods are not practically important; methane is formed naturally in sufficient quantities. It is constantly being evolved from decaying vegetation: this is due apparently to the action of bacteria on cellulose. The bubbles of gas which may be seen rising from stagnant water consist largely of methane; hence the name "Marsh gas." Ford Madox Brown has preserved to fame how

Dalton, when he was at work on his Law of Combination, obtained the gas from this source. Methane is produced during the formation of coal. It is often pent up in reservoirs, and when it escapes into the mines it forms dangerously explosive mixtures with the mine air. For this reason the miners call it "firedamp" (damp = gas); the carbon dioxide formed by its combustion they call "Black damp." The mine air mixed with black-damp they call "After-damp." When coal is distilled in retorts the gases evolved often contain 40 per cent. of methane or more, and to this, together with the free hydrogen it contains, coal gas owes its value as a fuel. Methane is evolved in large quantities with other gaseous hydrocarbons from some petroleum springs.

QUESTIONS.—CHAPTER XI.

1. Organic chemistry has sometimes been defined as the chemistry of the hydrocarbons and their derivatives, and the hydrocarbons and hydrocarbon radicles have been stated to correspond to the metals. Criticise these statements, illustrating your judgment with examples.

2. Explain by reference to the paraffins the meaning of the terms "homology" and "isomerism."

3. How can ethane be obtained in the pure state, and distinguished from methane?

4. From the theoretical consideration given in this chapter, suggest structural formulae for the isomeric hexanes.

CHAPTER XII.

THE UNSATURATED HYDROCARBONS.

70. The paraffins are called "saturated" because they cannot be induced to form addition products. Ethylene, and Acetylene are distinguished from them as "Unsaturated" hydrocarbons. Their reactions are characteristically combinations. **Ethylene** is also called "Olefiant gas." It is the simplest member of the **OLEFINES**, a series of hydrocarbons whose properties resemble those of Ethylene, of which they are the homologues and polymers. Their general formula is C_nH_{2n}. In this, and only this, they resemble the "Naphthenes." **Acetylene** is also the simplest member of an homologous series, of the general formula $C_nH_{(2n-2)}$. They are called the **ACETYLENES**. The Paraffins, Olefines, and Acetylenes are distinguished from the other series of hydrocarbons by the name **ALIPHATIC HYDROCARBONS**. This name has reference to their relationship to fats.

ETHYLENE.

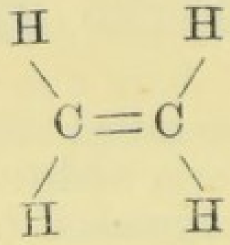
71. The preparation of Ethylene by several methods has already been mentioned. (See Sections 15 and 16.)

$$C_2H_5I + KOH \text{ (alcoholic)} = C_2H_4 + KI + H_2O,$$
$$C_2H_5OH = C_2H_4 + H_2O.$$

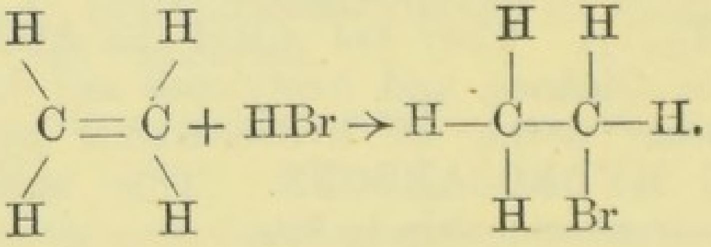
It may be obtained from alcohol without the usual charring if phosphoric is used instead of sulphuric acid.

The reactions of Ethylene have been given in Section 17. In addition we must mention that with dilute alkaline permanganate it is oxidised readily to glycol.

Graphic Formula.—The rational formula of ethylene is CH_2CH_2. It will be seen that, from the point of view of the tetravalency of carbon, this formula is not perfect. Much argument has been expended upon the subject, and as a concession to the idea of immutable valency, the formula is written



The carbon atoms are represented as satisfying two mutual valencies. It has, at any rate, this advantage over a formula with but a single connecting linkage, that it draws attention to the propensity of ethylene to form very definite additive products.



Its only disadvantage is that beginners are inclined to regard the doubly linked formula as an indication of special stability of the compound, whereas the opposite is true. They need only remember that formulae are pictures of reactions, not of molecules. The formula is written shortly $H_2C : CH_2$.

Ethylene burns with a brilliant and somewhat smoky flame. Its presence in coal gas to the extent of about 4 per cent. is the chief cause of the luminosity of the latter. It is also formed by the action of water upon some of the rarer carbides.

72. Homologues of Ethylene.—We need only give the shortened formulae of some other olefines. The next highest is **Propylene**, $CH_3.CH{:}CH_2$. There are three **Butylenes** (C_4H_8); they are represented by

$$CH_3.CH_2.CH{:}CH_2 (\text{B.P.} = -5°),$$

$$CH_3CH{:}CH.CH_3 (\text{B.P.} = +1°),$$

and

$$(CH_3)_2C{:}CH_2 (\text{B.P.} = -6°)$$

respectively. The derivatives of propylene are called **Allyl** compounds, thus $CH_2{:}CH.CH_2OH$ is allyl alcohol.

ACETYLENE.

73. The preparation of Acetylene from Ethylene bromide has already been given. Its rational formula is CHCH. Here the difficulty of the valency of carbon is aggravated. The structural formula is generally written

$$H—C \equiv C—H \text{ or } HC \vdots CH.$$

Acetylene surpasses Ethylene in the variety of its reactions.

(i) When a mixture of acetylene and hydrogen is passed over platinum black, Ethylene and Ethane are successively formed.

(ii) Acetylene rapidly combines with the halogens

$$\underset{}{CH \vdots CH} \longrightarrow \underset{\text{(acetylene dibromide)}}{CHBr : CHBr} \longrightarrow \underset{\text{(acetylene tetrabromide)}}{CHBr_2 . CHBr_2}.$$

(iii) When acetylene is treated with a haloid acid, two molecular quantities of the acid are added in succession. The final product is an *ethylidene* halide.

$$HC \vdots CH \longrightarrow H_2C : CHI \longrightarrow H_3C . CHI_2.$$

(iv) Acetylene reacts with an ammoniacal solution of cuprous chloride (or oxide) to form Copper acetylide which is usually represented by the formula $Cu_2C_2.H_2O$

This is a red solid, which is extremely explosive when dry. When treated with mineral acids it yields pure acetylene, hence this reaction is used both as a test for the gas and as a means of purifying it. Thus its formation when a bunsen has struck back can be proved by aspirating the gases through the cuprous chloride solution. A similar carbide is formed with silver; it is even more unstable.

(v) Acetylene is oxidised by alkaline permanganate to an oxalate.

Syntheses.

(i) Acetylene was synthesised by Berthelot by submitting hydrogen to electric discharge between carbon poles. This also was at one time regarded as of great importance.

(ii) Another synthetical method is actually of commercial importance. When calcium carbide—which is made by heating lime and carbon in the electric furnace—is treated with water, acetylene is immediately disengaged.

$$CaC_2 + 2HOH = Ca(OH)_2 + C_2H_2.$$

Properties and Uses.—Since the carbide is comparatively cheap, and may be transported safely, it is used as a source of illuminating gas in country houses, and even in towns where coal gas and the electric current are not available. Acetylene burns with an intensely luminous and hot flame. To prevent smoking, special burners with very fine emission pores are necessary. Great attention has been bestowed upon the improvement of the plant, so that with the newest generators its use is almost without danger.

Acetylene is a colourless gas, which, when quite pure, is said to have but little odour; ordinarily, however, it has a very unpleasant smell. Since it is also very poisonous, it is perhaps just as well for those who use it that its odour should be so penetrating. It is fairly soluble in water.

Effect of Heat.—It is an endo-thermic substance; violent concussion will cause violent decomposition. When heated strongly it is also decomposed; at the highest temperatures it is reformed. At moderate temperatures it polymerises into **Benzene**, C_6H_6, and some other substances. The properties of Benzene differ entirely from those of Acetylene.

Homologues of Acetylene.—Of the homologues of Acetylene, **Allylene**, $HC \vdots C.CH_3$, is the most important.

74. Di-propargyl.—One other unsaturated hydrocarbon will be mentioned here for the sake of future reference. This is di-propargyl, an isomeride of Benzene. It is prepared from di-allyl tetrabromide by the usual method.

$$CH_2Br.CHBr.CH_2.CH_2.CHBr.CH_2Br \xrightarrow{KOH(alc)} HC \vdots C.CH_2.CH_2.C \vdots CH.$$

It is a liquid which boils at 85° C., four degrees higher than Benzene. It combines with *eight* equivalents of a monovalent element to form derivatives of the paraffin hexane.

QUESTIONS.—CHAPTER XII.

1. Describe the preparation and properties of ethylene, and explain carefully the reasons for assigning to it the formula $H_2C:CH_2$.

2. Explain the use of the terms *saturated* and *unsaturated* in organic chemistry. Can you give instances of a similar use in inorganic chemistry?

3. On what evidence is carbon said to be tetravalent?

4. Give descriptive names to the three butylenes.

5. The combustion of 0·246 gram of a liquid hydrocarbon yielded 0·792 gram carbon dioxide, and 0·27 gram of water. The hydrocarbon absorbed a large quantity of bromine, forming a compound containing 79·6 per cent. of bromine. What conclusions can you draw as to the formula of the hydrocarbon?

CHAPTER XIII.

THE HALIDES.

75. Preparation.—The halides are prepared:

(i) By direct substitution of hydrogen.

(ii) By substitution of the hydroxyl of alcohols; or of oxygen of aldehydes and ketones.

(iii) From unsaturated hydrocarbons by direct addition.

(iv) By special methods (chloroform).

76. Direct Substitution.—When the halogens act upon the paraffins, one or more equivalents, even all, of the hydrogen may be replaced by the halogen according to the conditions of the reaction. The greatest control is exercised if the hydrocarbon is vapourised. The reaction proceeds more rapidly in direct sunlight—with methane it is explosively violent. In some cases it is desirable to hasten the reaction by raising the temperature or by the use of a "halogen carrier." The derivatives of the paraffins react similarly (see Exp. 23).

Collect some chlorine in an inverted gas jar over a concentrated solution of brine. Pass into it an equal volume of methane and place the jar in diffused light—not in sun-light. The colour of the gas disappears and the solution becomes acidic, but the volume of the product equals that of the hydrocarbon.

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

If another equal volume of chlorine is added a second equivalent of hydrogen is displaced, but in this case the volume decreases, since dichlor-methane is a liquid. The substitution becomes slower as the exchange proceeds.

77. Properties of the Halides.—The names of the products, and their boiling points, are given below.

		B.P.
Methyl chloride, or chlor-methane	CH_3Cl	−23·7 C.
Methylene chloride, or di-chlor-methane	CH_2Cl_2	42° C.
Methanyl chloride or tri-chlor-methane	$CHCl_3$	61° C. (Chloroform)
Carbon tetrachloride	CCl_4	76° C.

Under suitable conditions the reverse action will take place; hence methane may be obtained from carbon tetrachloride, and since the latter is obtained indirectly from the elements, it provides another means to the synthesis of methane.

All the chlorides are pleasant smelling substances. The corresponding bromides and iodides are also well known.

78. Chloroform, Bromoform, and Iodoform are sufficiently important to claim special attention. They may be prepared from ethyl alcohol. Commercially they are also prepared from acetone.

We will take **Iodoform** first. It is a solid substance of a characteristic smell. It is very insoluble in water, and, as it is readily formed from alcohol, its formation is used as a test for the presence of ethyl-alcohol (or acetone).

Exp. 29.—*Preparation of Iodoform, as a Test for Alcohol.* Add a small quantity of iodine to the solution of alcohol; warm, then add caustic soda or sodium carbonate solution drop by drop until the colour of the iodine just disappears. Keep at about 70° C.

The equations cannot be given now.

Chloroform is prepared by an analogous method, but instead of the halogen and caustic soda bleaching powder is used.

Exp. 29a.—*Preparation of Chloroform.* In a three-litre flask, fitted with a long condenser, place 250 grams of bleaching powder, ground into a milk with water. Add 30 c.c. of alcohol (or, better, acetone). Heat *gently* on a sand bath till action begins. Remove the flame, finally boil the mixture till no more chloroform will come over. Shake the distillate with dilute caustic soda solution, and separate the heavy chloroform in a funnel. Stand this over fused calcium chloride for some time and redistil. Or, the chloroform may be distilled off in steam immediately the acetone is added to the bleaching powder. Fig. 19 shows how this is done. Collect distillate in brine. The theory of the process is discussed in Walker's *Physical Chemistry*.

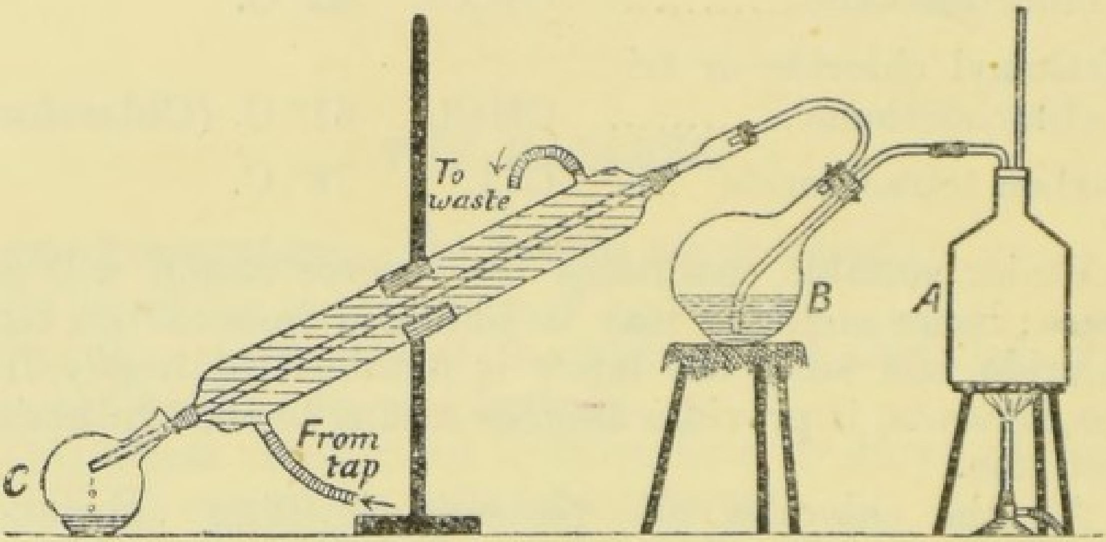


Fig. 19.

B contains the reaction mixture; A contains boiling water.

Chloroform undergoes a curious change when exposed to air and sunlight, thus

$$4CHCl_3 + 3O_2 = 2H_2O + 4COCl_2 + 2Cl_2.$$

79. Propyl Chlorides.—There are two mono-chlor propanes. The one which boils at 46·5°C. is called *normal* propyl chloride; it has the formula $CH_3CH_2CH_2Cl$. *Iso*-propyl chloride boils at 36·5° C. It has the formula $CH_3CHCl.CH_3$. There can be no doubt of this formula, since the chloride is related to, and is obtained from, acetone. $CH_3CO.CH_3$.

80. The reactions of the mono-chlor and di-chlor derivatives of the hydrocarbons we are familiar with. The reactions of the trichlor derivatives are analogous. This can be illustrated by iodoform.

Exp. 30.—*Hydrolysis of Iodoform.* Heat a little iodoform with some alcoholic caustic potash. Potassium formate and potassium iodide are formed. Neutralise and test for iodide, and afterwards for formate.

$$\mathrm{HCI_3 + 4KOH = 3KI + H.CO.OK + 2H_2O.}$$

The following table shows the relations between the halides and the products of their hydrolysis. R′ stands for any alkyl radicle.

$$\begin{tikzcd}
{} \arrow[dd, "\text{Chlorination}"'] & \mathrm{R'CH_2Cl} \arrow[r] \arrow[d, shift left] & \mathrm{R'CH_2OH} \arrow[d, shift left] & {} \arrow[dd, "\text{Oxidation}"] \\
 & \mathrm{R'CHCl_2} \arrow[u, shift left] \arrow[r] \arrow[d, shift left] & \mathrm{R'C.H.O} \arrow[u, shift left] \arrow[d, shift left] & \\
{} & \mathrm{R'CCl_3} \arrow[u, shift left] \arrow[r] & \mathrm{R'CO.OH} \arrow[u, shift left] & {} \\
 & {} \arrow[r, "\text{Hydrolysis.}"] & {} &
\end{tikzcd}$$

QUESTIONS.—CHAPTER XIII.

1. By what processes can methane be converted into ethyl alcohol? How can methane be obtained from ethyl alcohol as starting point?

2. How would you attempt to prepare bromoform?

3. Can you suggest the probable course of the reactions when chloroform is prepared from acetone?

4. Give a diagram of the apparatus you would use to convert chloroform into potassium formate.

5. Arrange an experiment for the "retrogressive" substitution (that is replacement of halogen by hydrogen) of carbon tetrachloride, using zinc and glacial acetic acid or sodium amalgam as reagents.

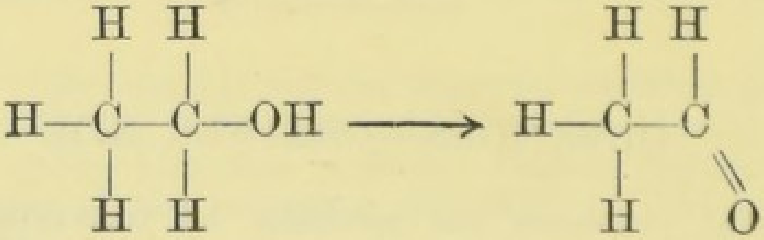
6. What would you expect to obtain by hydrolysing dichlor-acetic acid?

CHAPTER XIV.

ALCOHOLS, ALDEHYDES, AND KETONES.

ALCOHOLS.

We have discussed somewhat fully the properties of the monacid ethyl and methyl alcohols, and of the diacid glycol. In these alcohols the hydroxyl group forms a part of the "**Carbinol**" group, $-CH_2OH$. Upon oxidation the carbinol group is converted into the aldehyde group, $-CH.O$.



$$\mathrm{H{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}OH \longrightarrow H{-}\underset{H}{\overset{H}{C}}{-}\overset{H}{C}{=}O}$$

81. Isomerism of the Alcohols.—When we look to the higher homologues, we find that while there is but one propane there are two propyl alcohols, and that four butyl alcohols are derived from the two butanes.

Their boiling points are given below.

	Normal.
CH_3OH	66° C.
C_2H_5OH	78° C.
C_3H_7OH	97° C. ... 82°
C_4H_9OH	117° C. ... 100° ... 107° ... 83°

They do not all yield aldehydes upon oxidation.

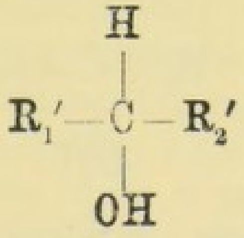
82. Propyl Alcohols.—Ordinary propyl alcohol is obtained from fusel oil, from which it is isolated by fractional distillation. It boils at 97° C. It is oxidised to propionaldehyde and propionic acid, and since the sodium salt of this acid yields ethane when it is heated with caustic soda the formula of the alcohol should be $CH_3.CH_2.CH_2OH$. Its behaviour is like that of the four alcohols previously studied. Their formulae may be written generally **$R'CH_2OH$**. Such alcohols are called **PRIMARY ALCOHOLS**.

The other propyl alcohol, which boils at 82° C., is prepared by the reduction of acetone by sodium amalgam and water. It does not yield an aldehyde on oxidation, but is reconverted into acetone. Hence it must contain two methyl groups; and its formula must be written $CH_3.CHOH.CH_3$.

This conclusion is borne out by the fact that when phosphorus trichloride acts upon the alcohol iso-propyl chloride is formed.

It is called Secondary Propyl Alcohol. It is the simplest of the **SECONDARY ALCOHOLS**; these are characterised by the group $=CH.OH$, and are distinguished from primary alcohols by yielding, without decomposition, ketones (the simplest is acetone) on oxidation.

Their general formula is—



$$\begin{array}{c} H \\ | \\ R_1'-C-R_2' \\ | \\ OH \end{array}$$

where R_1', R_2' may be the same or different alkyl radicles.

By a third method secondary propyl alcohol may be prepared from propylene. This combines with sulphuric acid or hydriodic acid to form **secondary** propyl iodide or the corresponding sulphate. This is hydrolysed to the alcohol.

Another method of preparing secondary propyl alcohol is indicated in Section 85.

83. The Butyl Alcohols.—As we might expect, there are one primary and one secondary alcohol derived from normal butane. They boil at 117° and 100° C. respectively.

$CH_3.CH_2.CH_2.CH_2(OH)$ (primary normal) $CH_3.CH_2.CH(OH).CH_3.$ (secondary normal)

There is also a primary iso-butyl alcohol of the formula $(CH_3)_2CH.CH_2OH$. It is found in the fusel oil of potato spirit.

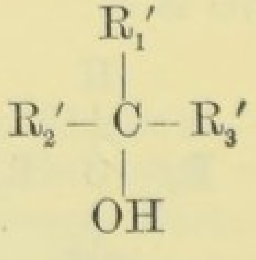
In addition there is another iso-butyl alcohol, which, however, does not, like a primary alcohol, yield an aldehyde, nor, like a secondary alcohol, does it yield a ketone without decomposition. Upon oxidation it yields chiefly acetone, water, and carbon dioxide; that is, the molecule is partially decomposed by oxidation.

This alcohol is called Tertiary (iso-)butyl alcohol. It is the simplest of the **TERTIARY ALCOHOLS**. Its formula may be deduced from its method of preparation.

It is formed when magnesium methyl iodide is properly treated with acetyl chloride, and the product is treated with water.

$$CH_3COCl + CH_3MgI. \longrightarrow (CH_3)_3COH.$$

The tertiary alcohols possess the group $\equiv C(OH)$, and the general formula



$$\begin{array}{c} R_1' \\ | \\ R_2' - C - R_3' \\ | \\ OH \end{array}$$

When oxidised their molecule suffers decomposition, ketones, more usually acids, of a lower order being produced.

Kolbe predicted secondary and tertiary alcohols in 1859; Friedel isolated secondary propyl alcohol in 1862; Butlerow prepared tertiary butyl alcohol in 1863, by the action of zinc methyl on acetyl chloride.

There are 8 alcohols of pentyl—the **Amyl** alcohols, 4 primary, 3 secondary, 1 tertiary.

84. Glycerin.—Glycerin or glycerol is obtained when fats are treated with superheated steam and in the manufacture of soap. It is obtained from solution by distillation with steam and subsequent careful evaporation. The equation will be given in Section 91. It is a sweet viscous liquid. When pure it boils at 290° C.; usually, however, it decomposes with evolution of unpleasant fumes. It is very hygroscopic.

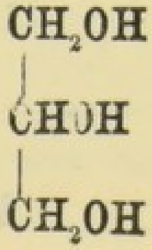
Chemical Nature.—By its formation we should judge that it is an alcohol, and that the fats are its esters. This view is confirmed by the formation of other esters from glycerin and acetic, hydrochloric, and nitric acids. Hence it is called glycerol, the ending -ol being generally applied to the names of alcohols.

85. Formula and Reactions.—Its empirical formula is found to be $C_3H_8O_3$. That it is a *tri-acid alcohol* is shown by the following reactions.

With hydrochloric acid it yields water and a dichloride, $C_3H_6OCl_2$. This is called **dichlor-hydrin.** This chloride reacts with phosphorus chloride to form **tri-chlor hydrin** $C_3H_5Cl_3$. Hence we obtain for glycerol the formula $C_3H_5(OH)_3$. Its constitutional formula may be deduced from the following reactions:—

(i) On oxidation with dilute nitric acid it yields two acids (glyceric and tartronic acids); with caustic soda and bromine, as mild oxidising reagents, it yields an aldehyde (glyceraldehyde) and a ketone (dioxyacetone). Hence it is both a primary and a secondary alcohol.

(ii) Hydriodic acid acts upon it partly as reducer, partly as an acid; two of the hydroxyl groups are reduced and one is replaced by iodine. The iodide so formed is isopropyl iodide, $CH_3.CHI.CH_3$. Hence the structural formula of glycerol must be



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

It is a di-primary monosecondary alcohol. It is evident that the derivatives of glycerol are very numerous.

(iii) Hydriodic acid in the presence of phosphorus will reduce it to propane.

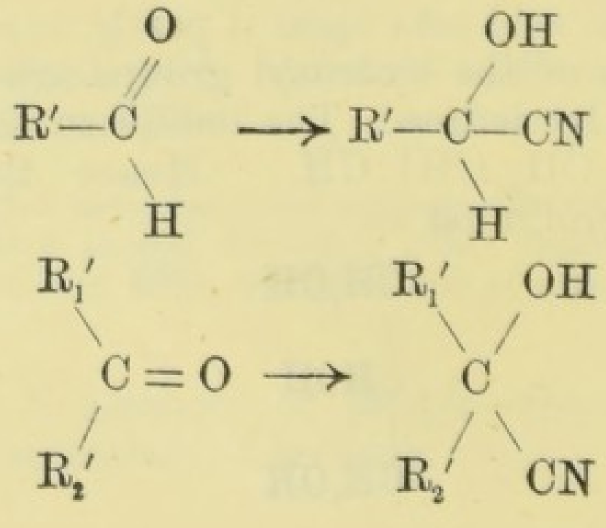
86. Glycerol Tri-nitrate.—When glycerin is added in the proper proportion to a mixture of nitric and sulphuric acids (why the latter?) a colourless oil, insoluble in water, is formed. This is the explosive *Nitro-glycerin*. The name is incorrect, but is too well established to be abandoned. The student must understand that the compound is a salt, a nitrate, $C_3H_5(NO_3)_3$. It has a sweet taste, but is poisonous. Heated quickly it explodes. The oxygen which it contains is more than sufficient for its conversion into carbon dioxide, water, and nitrogen. Diluted with diatom earth it is the essential constituent of dynamite. It is also an ingredient of smokeless powder. Watery potash "saponifies" it to sodium nitrate and glycerin.

ALDEHYDES AND KETONES.

87. The aldehydes and ketones may be considered together. Their formation from alcohols and fatty acids has already been given (Sections 20, 50, 51, and 52).

The reactions of acetaldehyde and of acetone are typical of their respective classes.

Their tendency to form addition products is attributed to the possession of a doubly linked oxygen atom. The formation of the respective hydrogen cyanide products is written thus:



88. Chloral.—One important aldehyde must be mentioned here, namely Chloral, $CCl_3.CHO$. This body is formed when chlorine is passed into alcohol.

The reaction proceeds in three stages.

Oxidation—

$$\text{(i)}\quad CH_3CH_2OH + Cl_2 = CH_3C.H.O + 2HCl.$$

Chlorination—

$$\text{(ii)}\quad CH_3C.H.O + 3Cl_2 = CCl_3C.H.O + 3HCl.$$

$$\text{(iii)}\quad CCl_3CHO + C_2H_5OH = \underset{\text{(solid chloral alcoholate)}}{CCl_3CH.O.HOC_2H_5}.$$

The chloral alcoholate is removed and distilled with concentrated sulphuric acid, when the chloral comes over.

Chloral is an oily liquid, of characteristic smell; B.P. $= 98°$. When it is mixed with water it combines with it to form a crystallisable body, **Chloral hydrate**. This is held to have the formula $CCl_3CH(OH)_2$. It is soluble in water, and is used as a soporific.

Chloral, being an aldehyde, may be oxidised to an acid. By this reaction **Trichloracetic acid** is manufactured.

$$CCl_3CHO \longrightarrow CCl_3CO.OH.$$

Concentrated nitric acid is used as the oxidiser.

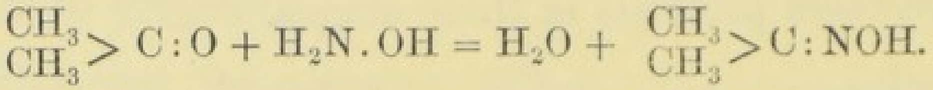
Dichloracetic acid also is prepared from chloral hydrate; the reaction is complex.

The effect of caustic alkalis on chloral is important—**chloroform** and the alkali formate are formed.

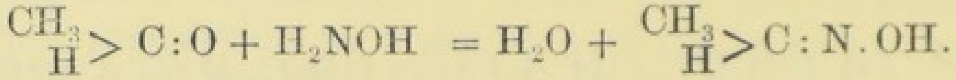
$$\begin{array}{r} CCl_3C.H.O \\ HONa \end{array} = HCCl_3 + HC.O.ONa.$$

It is evident that we have here the key to the preparation of chloroform from alcohol and bleaching powder: alcohol is first oxidised to aldehyde, and the aldehyde is then chlorinated. The chloral so formed reacts with slaked lime, when chloroform and calcium formate are produced.

Besides the condensation products mentioned in Chapter IV aldehydes and ketones condense with hydroxylamine to form **oximes**—aldoximes and ketoximes respectively.

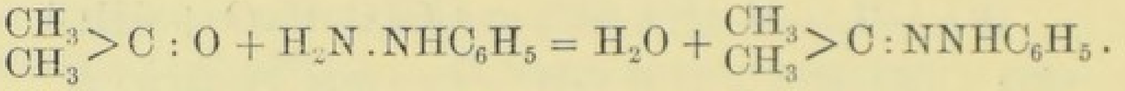


$$\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}\!>\mathrm{C:O} + \mathrm{H_2N.OH} = \mathrm{H_2O} + \begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}\!>\mathrm{C:NOH}.$$



$$\begin{matrix}\mathrm{CH_3}\\ \mathrm{H}\end{matrix}\!>\mathrm{C:O} + \mathrm{H_2NOH} = \mathrm{H_2O} + \begin{matrix}\mathrm{CH_3}\\ \mathrm{H}\end{matrix}\!>\mathrm{C:N.OH}.$$

Aldehydes and ketones also condense with phenyl-hydrazine to form **hydrazones**.



$$\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}\!>\mathrm{C:O} + \mathrm{H_2N.NHC_6H_5} = \mathrm{H_2O} + \begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}\!>\mathrm{C:NNHC_6H_5}.$$

These compounds are of especial importance in the study of the sugars (Chapter XVIII).

SUMMARY.

Alcohols may be monacid or polyacid. Examples are ethyl alcohol $C_2H_5(OH)$, glycol $C_2H_4(OH)_2$, and glycerol $C_3H_5(OH)_3$, mannitol $C_6H_8(OH)_6$. The number of hydroxyl groups is ascertained by reaction with acetyl chloride. Primary alcohols possess the group $-CH_2OH$. They are oxidised to aldehydes. These have the group $-C.H.O$. They are oxidised to acids, which have the carboxyl group $-COOH$. Secondary alcohols have the group $=CH.OH$. They are oxidised to ketones. These have the group $=CO$. When ketones are oxidised they yield acids with a *smaller* number of carbon atoms, that is, by the unlinking of carbon atoms. Tertiary alcohols have the group $\equiv C.OH$. When they are oxidised, as a rule the molecule suffers decomposition, a ketone or an acid with fewer carbon atoms being formed.

QUESTIONS.—CHAPTER XIV.

1. How is acetaldehyde made? What are its chief reactions? How is its structural formula determined?

2. Describe exactly what is meant by, and give examples of primary, secondary, and tertiary paraffins; also of primary, secondary, and tertiary alcohols. Distinguish carefully between a tertiary and a tri-hydric alcohol.

3. Describe three general methods for the preparation of alcohols. How are esters, ethers, and acids produced from alcohols?

4. How are ketones distinguished from aldehydes?

5. Why is aldehyde represented by a formula containing a carbonyl group, and how do chemists account for the behaviour of aldehydes as unsaturated compounds? How do you reconcile your suggestion with the behaviour of the carboxyl compounds?

6. A ketoxime, on analysis, was found to possess the following composition:—*Carbon* 55·2, *hydrogen* 10·3, *nitrogen* 16·1 per cent. What is the formula of this compound, and from what ketone is it derived?

7. Define the term "alcohol." Give three general methods of preparing alcohols.

8. Mention the steps by which alcohol can be synthesised from its elements.

9. Only one hydrocarbon, C_3H_8, is known, but there are two alcoholic substances of the formula C_3H_7OH, two of the formula $C_3H_6(OH)_2$, and one of the formula $C_3H_5(OH)_3$. Explain fully how the accepted theory of the structure of carbon compounds accounts for this.

10. How many substances of the formula C_3H_6O do you know? How could you distinguish them?

11. Construct the formula of all the amyl alcohols and of the oxidation products of the primary and secondary amyl alcohols.

12. Investigate the conditions for preparing ethyl palmitate.

13. How would you prepare very pure methyl alcohol?

14. Give formulae to the oxidation products of glycerol, indicate the properties and some derivatives of the products.

15. How would you obtain secondary propyl alcohol from glycerol?

16. Give structural formulae for the addition products of acetaldehyde with sodium hydrogen sulphite and ammonia.

17. Suggest a method of obtaining butyric acid, given ethyl alcohol as the carbon compound.

18. When glycol is treated with sulphur dichloride a compound of the formula C_2H_5OCl is formed—called ethylene chlorhydrin. Justify the name and give the compound a structural formula. How else is it formed? When it is treated with alcoholic potash a compound of the formula C_2H_4O is formed, which is not acetaldehyde. Give it a structural formula and a name. What properties would you expect it to exhibit? Can you compare it with any inorganic body?

19. Two substances have the formula C_2H_4O. How would you obtain them, and attempt to show the differences in their constitution?

20. Parallel with ethyl alcohol is ethyl mercaptan, C_2H_5SH. Suggest a method of preparing it. How would you attempt to prepare the corresponding thio-ether?

21. Discuss the properties of glycerol with a view to illustrating the advantages of its structural formula.

22. Suggest a method (see page 91) of obtaining *secondary* propyl from *primary* propyl alcohol. Similarly from *primary* isobutyl alcohol obtain *tertiary* butyl alcohol.

CHAPTER XV.

ACIDS AND ESTERS.

89. The acids with which we shall deal in this chapter are characterised by the carboxyl group,

$$-\mathrm{C}\begin{array}{l}=\mathrm{O}\\ -\mathrm{OH}\end{array}$$

The fatty acids have the general formula

$$C_nH_{2n+1}C.O.OH.$$

This group is formed

(i) By the oxidation of the aldehyde group,

$$-\mathrm{C}\begin{array}{l}=\mathrm{O}\\ -\mathrm{H}.\end{array}$$

(ii) By the hydrolysis of a nitrile

$$-\mathrm{C}\equiv\mathrm{N} \qquad -\mathrm{C}\begin{array}{l}=\mathrm{O}\\ -\mathrm{H}.\end{array}$$

(iii) By the hydrolysis of the $-CCl_3$ group.

In addition acids are formed by some special methods, for instance the decomposing oxidation of ketones.

The reactions of acids are typified by those of Acetic acid in Chapter IX.

90. Preparation and Properties of Esters.—Esters are the salts of organic acids and alcohols. They may be prepared

(i) By the inter-action of the alcohol and the acid.

(ii) By the inter-action of the alcohol and the acid chloride or anhydride.

(iii) By the action of an alkyl halide on a sodium or silver salt.

Reactions.—They are all hydrolysed by water, or, better, steam, and they are "saponified" by caustic alkalis.

Some yield acid amides with ammonia (Exp. 25).

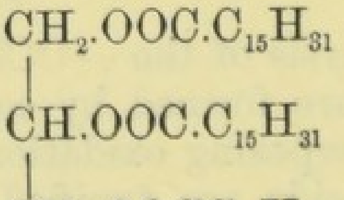
The esters are insoluble or but slightly soluble in water. Most have a pleasant fruity smell and some are used as "essences." Iso-amyl acetate is used as pear-drop essence, ethyl butyrate for pineapple essence.

91. Soap.

Exp. 31.—*Preparation of Soap and the Acids of Fat.* Make a solution of caustic soda in alcohol, in a porcelain dish over a water bath. Add a little olive oil, and warm till all is dissolved. Increase the temperature, and finally expel the alcohol. Dissolve the residue in water. Throw one part into concentrated brine. The soap floats on the surface. Treat another part with dilute hydrochloric acid and heat. The acids float. Cool, remove, and dissolve the acids in hot alcohol and let them separate out again. Test them, dissolved in alcohol, for acidity with phenol phthalein.

As we have mentioned in the previous chapter, many fats are mixtures of the esters of glycerol and certain acids. These acids are *Palmitic*, $C_{15}H_{31}CO.OH$, and *Stearic*, $C_{17}H_{35}CO.OH$, of the acetic acid series, and *Oleic*, $C_{17}H_{33}CO.OH$, an unsaturated acid.

The formula of glyceryl palmitate is—



$$\begin{array}{l} CH_2.OOC.C_{15}H_{31} \\ | \\ CH.OOC.C_{15}H_{31} \\ | \\ CH_2.OOCC_{15}H_{31}. \end{array}$$

Olive oil consists chiefly of glyceryl oleate.

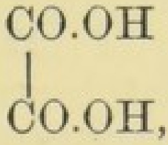
When the fats are treated with superheated steam, free glycerol and the free acids are obtained. The former is used for the manufacture of nitroglycerin, and the latter are made into candles. When the fats are treated with caustic soda, the sodium salts of the acids are formed. These are separated off as soap. (Alcoholic solution was used in Exp. 31 because the reaction is accelerated thereby.) The ordinary hard soaps are the sodium salts; if potash is used soft soaps are formed. Many soaps are manufactured from other than animal fats; thus Castile soap is formed from olive oil; while cocoanut, palm oil, and others are used for some "vegetable" soaps.

The cleansing action of soap appears to be due to the formation, by hydrolysis, of a very small amount of free alkali which dissolves a little of the fat clinging to the surface (and emulsifies the rest). The dirt is loosened from the fibres and is removed in the lather.

92. Fats.—Fats are an important article of diet (see *Second Stage Hygiene*, Chap. III.). *Milk* contains 4 per cent. of emulsified fats. On standing it separates into the *cream*, which contains most of the fat, and the *skim milk* on which the cream floats. When a centrifugal separator is used the *separated milk* is almost devoid of fats. From the cream is prepared *butter*,* which owes its flavour to some butyric and caproic acids. When rennet is added to milk (pure or skimmed) this separates into *whey* and *curds* which contain the fats. From the curd *cheese* * is made.

Oxalic Acid.

93. Oxalic Acid is a crystalline solid. Obtained by crystallisation, it contains water of hydration, which it loses when heated to 100°. (Try it in a test tube immersed in boiling water.) By combustion its simplest formula is found to be CHO_2, but since the acid is dibasic this formula must be doubled, $C_2H_2O_4$. The hydrated crystals contain two molecules of water for each acid molecule, $C_2O_4H_2.2H_2O$. It is a fairly strong acid. We should naturally represent its constitutional formula as



$$\begin{array}{l} CO.OH \\ | \\ CO.OH, \end{array}$$

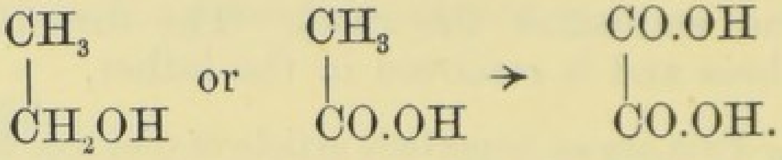
which agrees well with its properties.

Formation.—(1) By the careful oxidation of glycol (Section 60). By this reaction its relation to the diacid alcohol is established.

$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} \rightarrow \begin{array}{l} CO.OH \\ | \\ CO.OH. \end{array}$$

* See Buchanan and Gregory's *Lessons on Country Life* (Macmillan).

(2) Under certain conditions by the oxidation of ethyl alcohol and of acetic acid by alkaline permanganate. This oxidation is interesting from the fact that the methyl group is oxidised to the carboxyl group directly—no intermediate halide being necessary—a reaction common among the aromatic compounds, but rare in the aliphatic series.

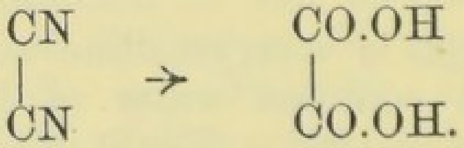


$$\begin{array}{c} CH_3 \\ | \\ CH_2OH \end{array} \text{ or } \begin{array}{c} CH_3 \\ | \\ CO.OH \end{array} \rightarrow \begin{array}{c} CO.OH \\ | \\ CO.OH. \end{array}$$

(3) An interesting synthesis is the following: Carbon dioxide, when heated to 360° C. with sodium metal, gives sodium oxalate. The temperature must not be so great as to allow the metal to give carbon and carbonate.

$$2CO_2 + 2Na = C_2O_4Na_2.$$

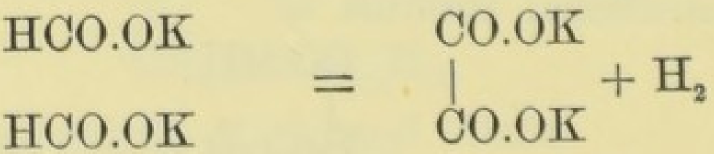
(4) It is interesting to learn that a solution of cyanogen is gradually converted into ammonium oxalate.



$$\begin{array}{c} CN \\ | \\ CN \end{array} \rightarrow \begin{array}{c} CO.OH \\ | \\ CO.OH. \end{array}$$

Since cyanogen (an endothermic compound) is formed by direct combination at high temperatures, this reaction is a true synthesis.

(5) On rapidly heating potassium formate, the oxalate and hydrogen are formed.



$$\begin{array}{c} HCO.OK \\ \\ HCO.OK \end{array} = \begin{array}{c} CO.OK \\ | \\ CO.OK \end{array} + H_2$$

94. Preparation.—Oxalic acid occurs in many plants as the calcium salt, as the potassium hydrogen salt, $KH.C_2O_4$, and as the curious quadrantoxalate (KHC_2O_4, $H_2C_2O_4$, $2H_2O$) in "salts of sorrel" obtained from Wood Sorrel.

It is prepared on the large scale by heating together in air below charring point (200°-240°) pine sawdust and a mixture of caustic soda and potash. The alkali salts, chiefly sodium oxalate, are dissolved out; the calcium salt is precipitated by adding milk of lime, filtered off and treated with the proper quantity of sulphuric acid to yield calcium sulphate and oxalic acid.

It may be prepared in the laboratory (with other products) by the method by which Scheele first prepared it in 1776, namely by the oxidation of cane sugar.

> **Exp. 32.**—*Preparation of Oxalic Acid.* In a large flask put 175 c.c. of nitric acid and add to it carefully (draught cupboard) 40 grams of cane sugar dissolved in a little water. Warm until reaction begins. Finally concentrate the solution to about one-third of its volume and allow it to stand. Separate the large crystals of oxalic acid by pouring the solution through a funnel plugged with glass wool. Redissolve in a little boiling water and filter at the pump.

95. Properties.—Oxalic acid is a poisonous substance. When heated carefully it partly sublimes, partly decomposes, according to the equations.

$$C_2O_4H_2 \begin{array}{l} \nearrow CO_2 + HCOOH \\ \searrow CO_2 + CO + H_2O \end{array}$$

When warmed with sulphuric acid it dissolves, separating again on cooling in anhydrous crystals. When heated with sulphuric acid it is decomposed into water, which is retained by the vitriol, and oxides of carbon, which are evolved.

$$H_2C_2O_4 = H_2O + CO + CO_2.$$

This method is used in the preparation of carbon monoxide (see *Tutorial Chemistry*, Vol. I., p. 397).

When oxalic acid is warmed with acidified permanganate it is oxidised completely to carbon dioxide and water. This reaction is an important operation in volumetric analysis (*Inorganic Chemistry*, p. 356, or *Chemical Analysis*, p. 172).

$$\begin{aligned} &5C_2O_4H_2 + 2KMnO_4 + 3H_2SO_4 \\ &\qquad = 10CO_2 + K_2SO_4 + 2MnSO_4 + 8H_2O. \end{aligned}$$

Oxalic acid, when treated with nascent hydrogen (from hydrochloric acid and zinc), is reduced to the substances intermediate between itself and glycol.

96. Salts.—The potassium oxalates are found in plants. Calcium oxalate also is common as crystals in plants. It is insoluble in water, and is undecomposed by acetic acid. Hence its formation is used for the detection both of oxalates and of calcium salts. It is also used in quantitative analysis. Ammonium oxalate is easily obtained. It has several applications which will be met later.

Esters.—Since oxalic acid is a fairly strong acid, it will form esters from the anhydrous acid and alcohol, without the aid of a dehydrating agent.

The methyl and ethyl esters are easily prepared: the former is a solid, M.P. = 54°, B.P. 162°, the latter a liquid, B.P. = 186°. Dimethyl oxalate is used for the preparation of pure methyl alcohol. Both esters are readily hydrolysed.

Exp. 33.—*Preparation of Methyl Oxalate.* Dehydrate 40 grams of powdered crystallised oxalic acid by heating to 100° C. in a boiling tube until it loses its water of hydration ($11\frac{1}{2}$ grams). Place the powder in a flask, add 30 c.c. of methyl alcohol, and heat on water bath for two hours (upright condenser). Then distil; collect separately that which comes over up to 100° C. Then through an air condenser distil over the methyl oxalate. It will solidify. Filter by suction, and recrystallise from rectified spirit. Keep the mother liquor for Exp. 35.

MALONIC ACID.

97. Malonic Acid owes its name to its preparation by the oxidation of Malic acid. Its calcium salt is found in beet-root. It is a colourless crystalline substance, M.P. = 132°, readily soluble in water. When heated to 140° C. it loses carbon dioxide and is converted into acetic acid: it is to this property, shared by its derivatives, that its great importance is due. Its formula is established by the common method of formation (see Section 45) from chloracetic acid.

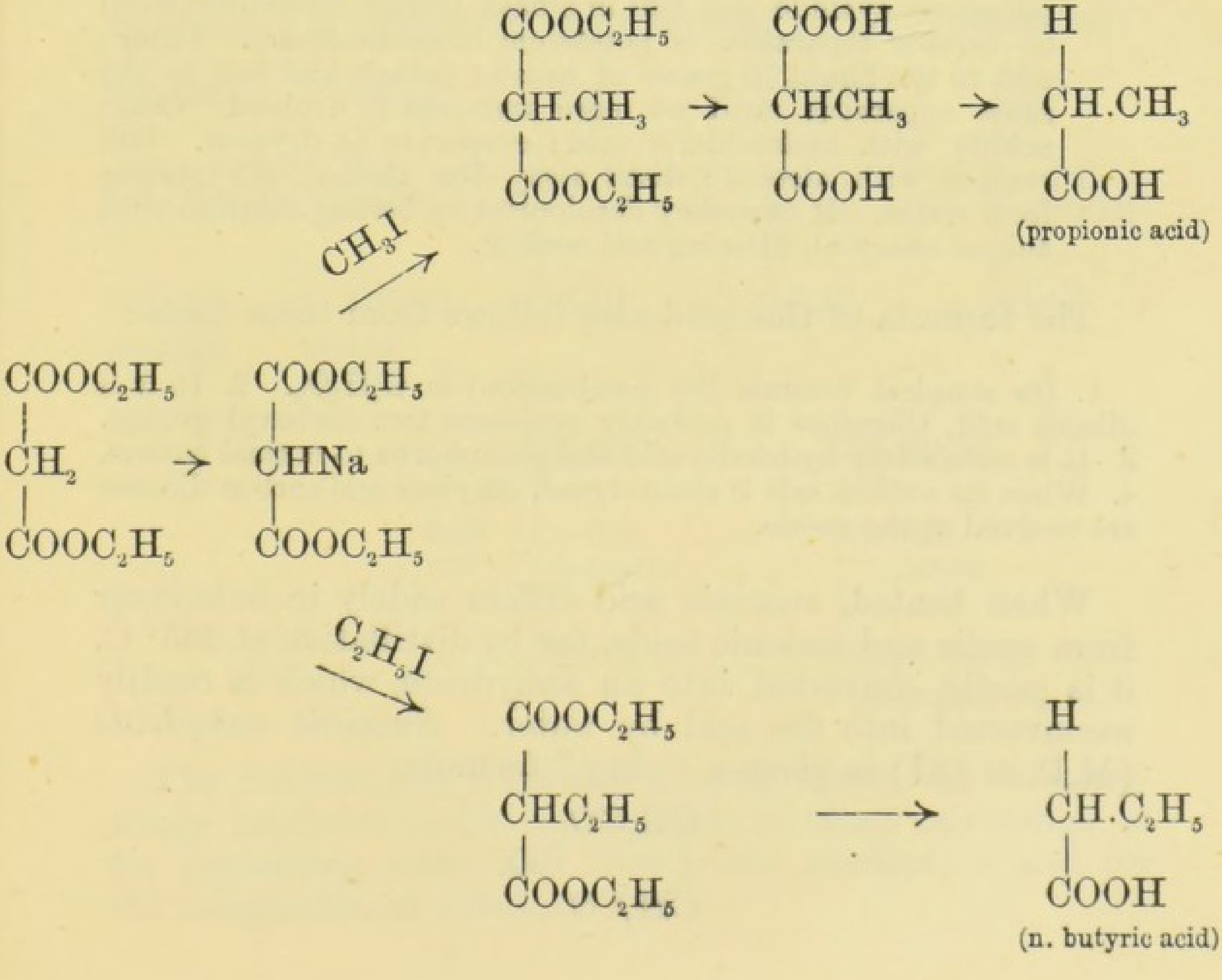
$$CH_3COOH \xrightarrow{Cl_2} CH_2ClCOOH \xrightarrow{KCN} CH_2CNCOOH$$

$$\xrightarrow{H_2O} CH_2(COOH)_2.$$

The ethyl ester is used in large quantities (see Cohen's *Practical Organic Chemistry*, pp. 84, 86; Gattermann, p. 161). It has the property of reacting in such a manner that one or both of the hydrogen atoms of the methylene group ($CH_2 =$) are displaced by sodium. This sodium reacts with alkyl halides, so that the alkyl group replaces the sodium; hence a large number of homologues of malonic ester are formed. These all, when heated, lose carbon dioxide, and are converted into fatty acids.

The following is the method adopted. The malonic ester is mixed with the required quantity of sodium ethoxide dissolved in absolute alcohol. The required quantity of the alkyl halide is also added, and the mixture is heated on the water bath. The alcohol is distilled off, the sodium halide dissolved out, and the required ester extracted with ether.

Take two illustrations:—



$$\begin{array}{c}COOC_2H_5\\ |\\ CH_2\\ |\\ COOC_2H_5\end{array} \rightarrow \begin{array}{c}COOC_2H_5\\ |\\ CHNa\\ |\\ COOC_2H_5\end{array}$$

$$\xrightarrow{CH_3I} \begin{array}{c}COOC_2H_5\\ |\\ CH.CH_3\\ |\\ COOC_2H_5\end{array} \rightarrow \begin{array}{c}COOH\\ |\\ CHCH_3\\ |\\ COOH\end{array} \rightarrow \begin{array}{c}H\\ |\\ CH.CH_3\\ |\\ COOH\end{array}$$

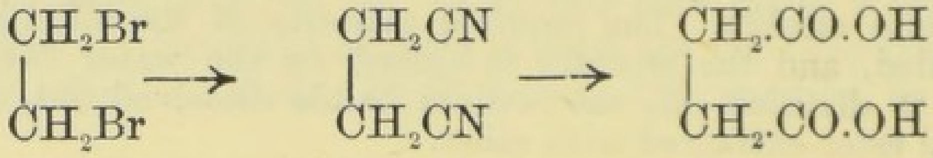
(propionic acid)

$$\xrightarrow{C_2H_5I} \begin{array}{c}COOC_2H_5\\ |\\ CHC_2H_5\\ |\\ COOC_2H_5\end{array} \longrightarrow \begin{array}{c}H\\ |\\ CH.C_2H_5\\ |\\ COOH\end{array}$$

(n. butyric acid)

Succinic Acid.

98. Succinic Acid owes its name to its formation by the distillation of amber (*L.-succinum*). Some is still produced by this method. It is formed, with fusel oil, during the fermentation of glucose. It is actually prepared by the fermentation of malic and tartaric acids. The reaction —which can be imitated by the reduction of these acids by means of concentrated hydriodic acid—is important in that it helps towards establishing the structural formulae of malic and tartaric acids. The formula of succinic acid follows from its preparation from ethylene dicyanide.



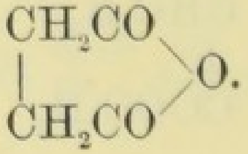
$$\begin{array}{l}CH_2Br\\ |\\ CH_2Br\end{array} \longrightarrow \begin{array}{l}CH_2CN\\ |\\ CH_2CN\end{array} \longrightarrow \begin{array}{l}CH_2.CO.OH\\ |\\ CH_2.CO.OH\end{array}$$

Exp. 34.—*Preparation of Succinic Acid.* Mix 100 grams of ethylene dibromide with 150 c.c. of alcohol, add 75 grams of powdered potassium cyanide and boil in a flask (reflux condenser) until no further separation of potassium bromide occurs. Filter; add to the liquid 70 grams of caustic potash and boil in the same apparatus until no more ammonia is evolved. Cool; acidify with hydrochloric acid; evaporate to dryness. Boil residue with alcohol; distil away the alcohol. Crystallise from water. If necessary decolourise by boiling solution with animal charcoal, filtering and cooling.

The formula of this acid also follows from these facts:

1. Its simplest formula (by combustion) is $C_2H_3O_2$. 2. It is a dibasic acid, therefore it probably possesses two carboxyl groups. 3. It is reduced by hydriodic acid and phosphorus to normal butane. 4. When its sodium salt is electrolysed, ethylene and carbon dioxide are evolved at the anode.

When heated, succinic acid differs widely in behaviour from oxalic and malonic acids, for by distillation at 235° C. it is partly converted into an anhydride, which is readily reconverted into the acid by water. *Succinic anhydride* (M.P. = 121) is given a "ring" formula.



99. Citric Acid.—We shall conclude this chapter with a few remarks concerning

CITRIC ACID.

This acid occurs free in the juice of unripe lemons to the extent of about 7 per cent. From this source much of it is obtained. As a calcium salt it occurs in many other plants. It is also prepared by the fermentative action of some fungi (*citromyces pfefferianus*) upon glucose.

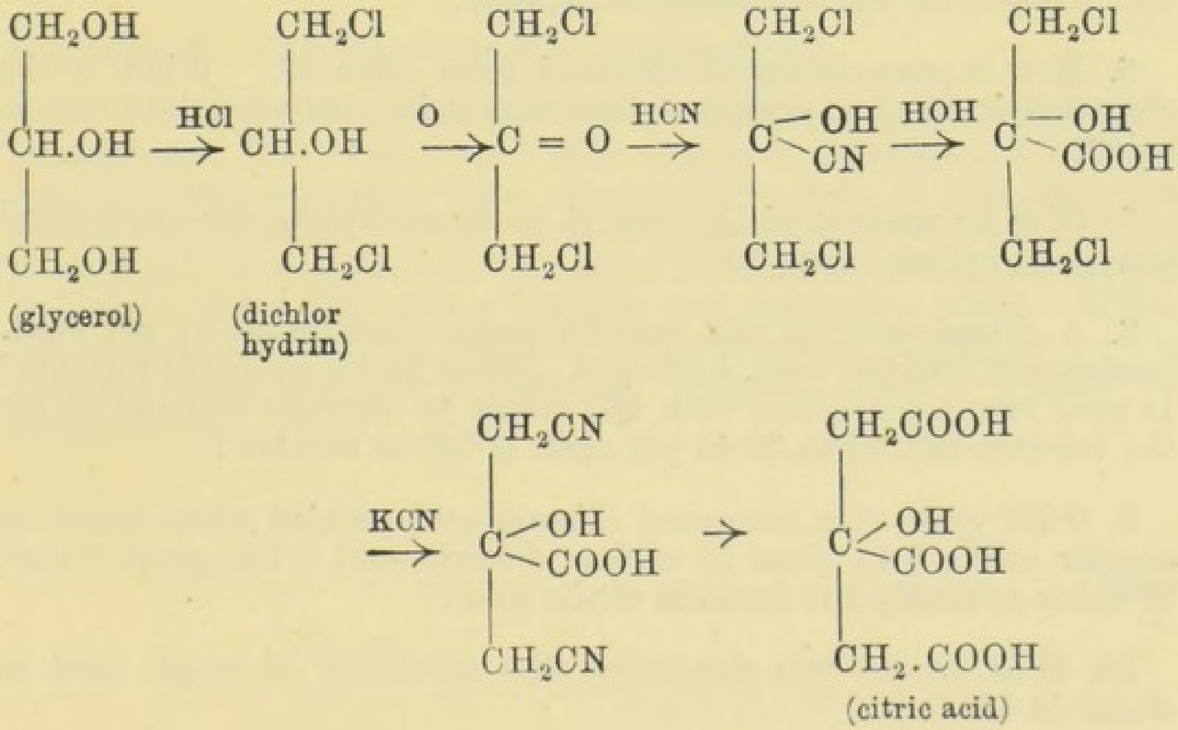
Formula.—Its simplest formula is $C_6H_8O_7$.

It is a tribasic acid.

It is oxidised to acetone and carbon dioxide.

Other reactions point to its possession of three carboxyl and one secondary alcohol groups.

Its structural formula is obtained from, and its relation to glycerol is proved by, the following series of reactions:



$$\begin{array}{c}CH_2OH\\ |\\ CH.OH\\ |\\ CH_2OH\\ \text{(glycerol)}\end{array}\xrightarrow{HCl}\begin{array}{c}CH_2Cl\\ |\\ CH.OH\\ |\\ CH_2Cl\\ \text{(dichlor hydrin)}\end{array}\xrightarrow{O}\begin{array}{c}CH_2Cl\\ |\\ C=O\\ |\\ CH_2Cl\end{array}\xrightarrow{HCN}\begin{array}{l}CH_2Cl\\ |\\ C\begin{smallmatrix}-OH\\ -CN\end{smallmatrix}\\ |\\ CH_2Cl\end{array}\xrightarrow{HOH}\begin{array}{l}CH_2Cl\\ |\\ C\begin{smallmatrix}-OH\\ -COOH\end{smallmatrix}\\ |\\ CH_2Cl\end{array}$$

$$\xrightarrow{KCN}\begin{array}{l}CH_2CN\\ |\\ C\begin{smallmatrix}-OH\\ -COOH\end{smallmatrix}\\ |\\ CH_2CN\end{array}\rightarrow\begin{array}{l}CH_2COOH\\ |\\ C\begin{smallmatrix}-OH\\ -COOH\end{smallmatrix}\\ |\\ CH_2.COOH\\ \text{(citric acid)}\end{array}$$

The calcium salt is soluble in cold water, but comparatively insoluble in hot water; this is taken advantage of for separating citric acid from other substances, and for the recognition of citrates.

QUESTIONS.—CHAPTER XV.

1. "Formic acid differs more from the rest of the fatty acids than they differ from each other." What facts can you cite in support of this statement? What explanation of it can be given?

2. How are the organic acids prepared, and how are they converted into their chief derivations?

3. State what you consider to be the characteristic properties of the groups of organic substances represented by ethyl alcohol, acetic acid, and acetone respectively. Given an aqueous solution containing all three of these substances, explain how you would prepare from it a pure specimen of each.

4. How many acids are there of the composition $C_4H_8O_2$? Write their graphic formulae and give one method of preparation of each.

5. Give the constitutional formula of formic acid, and the evidence on which it is based. Compare the action, if any, of concentrated sulphuric acid and of oxidising agents on formic and acetic acids, and account for the differences observed.

6. How is pure oleic acid obtained from olive oil? What is the constitution of oleic acid, and how may it be converted into stearic acid?

7. Give an account of the use of sodium ethylate for synthetical purposes, giving examples.

8. A dibasic acid of the paraffin series contains 34·61 per cent. *carbon* and 3·85 per cent. *hydrogen*. What is its probable formula? Is your result consistent with the result of strongly heating in air the calcium salt when 39·44 per cent. is left as residue?

9. 0·295 gram of a saturated dibasic acid yielded when burnt in copper oxide 0·44 gram of carbon dioxide, and 0·135 gram water. What is probably the formula of the acid?

10. How would you determine the solubility of oxalic acid in water at 15° C.?

11. Several substances are represented by the formula $C_3H_6O_2$. Describe the experiments you would make in order to (*a*) identify them, (*b*) determine the constitutional formula of one of them.

12. Describe fully the experiments you would make to determine the basicity of an acid whose formula is $C_4H_6O_6$.

13. Very many of the organic compounds which are acids are said "to contain the group CO.OH." Give a definite meaning to this expression, and indicate the chief hypotheses which are assumed in the expression.

14. Does the formation of ethylene in the electrolysis of sodium succinate throw light on the theory of "saturation"?

15. When sodium propionate is electrolysed between carbon electrodes, the products at the *anode* differ according to conditions:

(*a*) at 100° C. (a low current density and dilute solution are also favourable) oxygen is liberated and propionic acid formed;

(*b*) at low temperature, with large current density and concentrated solution, ethylene is liberated and propionic acid left.

Can you suggest what takes place to lead to these products? From the example of acetic acid, what hydrocarbon would you have expected under (*b*) conditions?

16. Formic acid is prepared by heating a mixture of oxalic acid and glycerol. At the same time some "monoformin,"

$$C_3H_7O_2.HCO_2,$$

is formed. At a higher temperature allyl alcohol,

$$CH_2{:}CH.CH_2OH,$$

is produced. Can you suggest an explanation?

17. When glycerol is heated with potassium hydrogen sulphate it is converted into water and allyl aldehyde (*acroleïn*—it has the odour of burning fat). Give an equation, and, if you can, use structural formulae. When acroleïn is treated with silver oxide it is oxidised to an acid with the same number of carbon atoms per molecule. Give the acid a formula and suggest a name. When the acid is reduced, by addition of hydrogen a saturated acid is formed. Give this also a formula. Suggest another method of obtaining it.

CHAPTER XVI.

STEREO - ISOMERISM.

LACTIC, MALIC, AND TARTARIC ACIDS.

Lactic Acid.

100. Lactic Fermentation.—When milk goes sour, lactic acid is formed. This acid is more conveniently prepared by the fermentation of sugar. To a solution of sugar some tartaric acid is added, and, after a day, some putrid cheese and sour milk to supply the "ferment"—*bacillus lacti*. The solution is kept at 35° to 40° for several days. The presence of free acid inhibits the action of the bacteria, and zinc carbonate is therefore added to keep the solution neutral. The zinc lactate separates out. Since another "ferment" is present which will cause the lactic acid to be decomposed into butyric acid, carbon dioxide and free hydrogen, the process is stopped in time to prevent considerable decomposition of the yield. The lactic acid is obtained from its zinc salt by decomposing this with hydrogen sulphide. It is a syrupy liquid. Lactic acid is also formed when glucose is heated with caustic soda.

101. Formula of Lactic Acid.—The simplest formula of lactic acid is CH_2O. It is a monobasic acid. Its ethyl ester reacts with acetyl chloride with the introduction of the acetyl group, hence lactic acid contains an alcoholic hydroxyl group. If we assume that as an acid it contains the carboxyl group, it must possess at least three oxygen atoms per molecule, $C_3H_6O_3$. In further support of this formula we have the fact that when lactic acid is treated with hydriodic acid under suitable conditions it is *reduced* to propionic acid. The following two formulae suggest themselves :—

$$CH_3CH(OH)COOH \quad \text{or} \quad CH_2(OH)CH_2COOH.$$

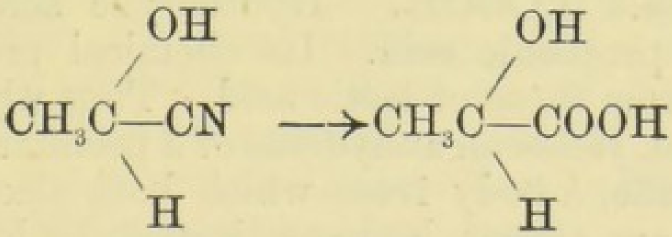
In the first the hydroxyl group is attached to the same carbon atom as the carboxyl. This is called the α-position. In the second the hydroxyl is attached to the carbon atom next to that to which the carboxyl is attached. This is called the β-position.

That fermentation lactic acid is α-hydroxy-propionic acid (therefore called ethylidene lactic acid also) is proved by the following:

1. It is converted into a-chlor propionyl chloride by phosphorus chloride; and by boiling α-chlor propionic acid with water, lactic acid is reformed.

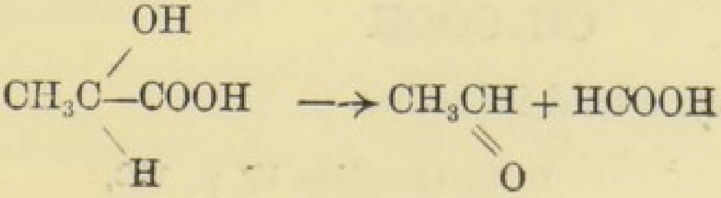
$$\left\{\begin{array}{l} CH_3CHOH.COOH \longrightarrow CH_3CHCl.COOH \\ CH_3CHCl.COOH \longrightarrow CH_3CH(OH)COOH. \end{array}\right.$$

2. It is formed when acet-aldehyde cyanhydrin is hydrolysed.



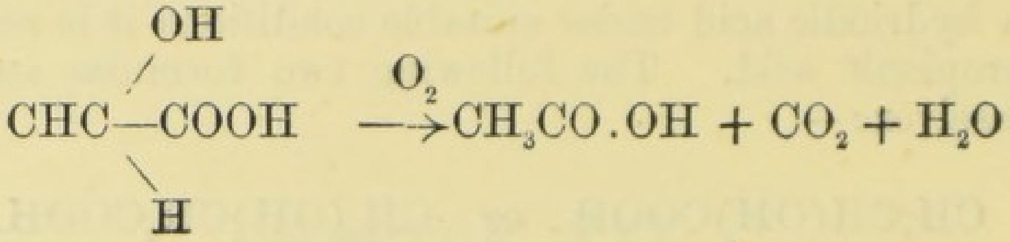
$$CH_3\overset{OH}{\underset{H}{C}}{-}CN \longrightarrow CH_3\overset{OH}{\underset{H}{C}}{-}COOH$$

What may be regarded as corresponding to the reverse process takes place when lactic acid is heated with dilute sulphuric acid to 120°-130°.



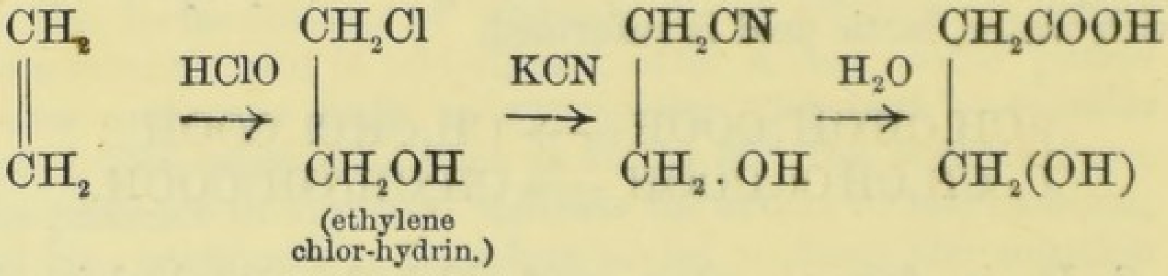
$$CH_3\overset{OH}{\underset{H}{C}}{-}COOH \longrightarrow CH_3\underset{O}{\underset{\|}{C}H} + HCOOH$$

3. When carefully oxidised it yields acetic and carbonic acids.



$$\begin{array}{c}OH\\ /\\ CHC\text{—}COOH\\ \backslash\\ H\end{array}\xrightarrow{O_2}CH_3CO.OH+CO_2+H_2O$$

102. Hydracrylic Acid.—If $CH_3CHOH.COOH$ is the correct formula for fermentation lactic acid, it should be possible to synthesize an acid corresponding to the formula $CH_2OH.CH_2COOH$, and to show that it differs from fermentation lactic acid. Such a compound is known and is called **Hydracrylic acid**. It is formed by the following series of reactions (wherefore it is also called ethylene lactic acid).



$$\begin{array}{c}CH_2\\ \|\\ CH_2\end{array}\xrightarrow{HClO}\begin{array}{c}CH_2Cl\\ |\\ CH_2OH\\ \text{(ethylene}\\ \text{chlor-hydrin.)}\end{array}\xrightarrow{KCN}\begin{array}{c}CH_2CN\\ |\\ CH_2.OH\end{array}\xrightarrow{H_2O}\begin{array}{c}CH_2COOH\\ |\\ CH_2(OH)\end{array}$$

Phosphorus chloride converts it into β-chlor propionic acid, $CH_2Cl.CH_2COOH$. Hydracrylic acid is therefore β-hydroxy propionic acid. Its chemical properties differ markedly from those of lactic acid. Thus while lactic acid, when heated, yields an anhydride of a peculiar kind, $C_6H_8O_4$, called **Lactide**, a body from which both alcoholic and acid properties are absent, hydracrylic acid, by loss of water, is converted into another *acid*, an unsaturated acid, called ACRYLIC* ACID, $\begin{array}{l}CH_2\\ \|\\ CH.COOH\end{array}$. This latter reaction has given to hydracrylic acid its name.

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* See Question 17, p. 109.

103. Sarcolactic Acid.—The above paragraphs provide a simple explanation of the isomerism of lactic and hydracrylic acids. But there occurs in meat-juices an acid which differs chemically not at all from ordinary lactic acid, yet it has a different solubility, while its zinc salt is more soluble and its calcium salt less soluble than the corresponding ordinary lactates; moreover, corresponding salts of the respective acids possess different proportions of water of hydration. This new acid, whose constitutional formula is identical with that of fermentation lactic acid, is called **Sarcolactic acid.** Its most important difference from ordinary lactic acid is that, while the latter has no effect upon polarised light, sarcolactic acid rotates the plane of polarisation to the right (its salts to the left). Hence sarcolactic is also called *dextro*-lactic acid (written d-lactic) and fermentation lactic is called *inactive*-lactic acid (written i-lactic). It is clear that the theory of isomerism offered in earlier chapters requires further development to enable it to explain these two acids. Structural formulae do not account for their separate existence. It may be mentioned that the sarcolactate of ammonium is left in solution when the mould *Penicilium glaucum* feeds upon a solution of ammonium i-lactate.

It must further be recorded that a lactic acid is formed when *bacillus laevo-lacti* acts on cane sugar. The acid has the chemical and physical properties of d-lactic acid, the same solubility, the same melting point; even its salts have the same solubilities as those of the d-acid. In one thing only it differs: it rotates the plane of polarisation as much to the left as sarcolactic acid does to the right. It is called **Laevo-lactic acid** (written l-lactic).

One more important reaction: when equal weights of zinc l-lactate and zinc d-lactate, which are very soluble, are mixed in concentrated solution, the sparingly soluble zinc i-lactate separates out.*

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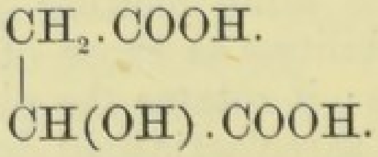
* For historical accounts of the subject of this chapter see Freund, *Study of Chemical Composition*, Chap. XVII. (Camb. Univ. Press); Muir, *Chemical Theories and Laws* (Wiley); Cohen, *Organic Chemistry* (Arnold).

Malic Acid.

104. Malic Acid, together with Tartaric, Citric and Oxalic acids, is responsible for the tartness of most unripe fruits: it owes its name to its presence in unripe apples (*L.-malum*). It is best prepared from the nearly ripe fruit of another Rosaceous plant—the Mountain Ash. The berries are crushed, and the juice is boiled with milk of lime. The calcium malate is converted into calcium hydrogen malate by solution in hot dilute nitric acid. This salt separates out on cooling. The free acid may be obtained from it by the action of sulphuric acid. Like Lactic and Tartaric acids, the free acid was first isolated by Scheele.

Malic acid is a crystalline solid (M.P. = 100°), deliquescent in air.

105. Formula.—Its simplest formula is $C_4H_6O_5$. It forms two series of salts, therefore it should have two carboxyl groups, $C_2H_4O(CO.OH)_2$. Its di-ethyl ester reacts with acetyl chloride, hence the acid contains the alcoholic hydroxyl group also, $C_2H_3(OH)(COOH)_2$. When treated with hydriodic acid it is reduced to succinic acid, $C_2H_4(CO.OH)_2$. [See Section 98.] When treated with hydrobromic acid it is converted into monobrom succinic acid, $C_2H_3.Br(CO.OH)_2$. Therefore it must be hydroxy-succinic acid.



$$\begin{array}{l}CH_2.COOH.\\ |\\ CH(OH).COOH.\end{array}$$

When heated it yields two isomeric acids by loss of water, maleïc and fumaric acids, $C_2H_2(COOH)_2$. Malic acid rotates the plane of polarisation of light, either to the left or the right according to the concentration.

We have said that the acid is converted by hydrobromic acid into monobrom succinic acid. This product is likewise laevo-rotatory. So also is Aspartic acid, the natural amino-succinic acid, which is converted into malic acid by nitrous acid (Section 39).

If, however, monobrom-succinic acid is formed by the action of bromine and phosphorus on succinic acid, it is inactive towards light; and when this inactive variety is treated with silver (hydr)oxide the malic acid produced is also inactive. This i-*Malic acid* is also formed by heating fumaric acid with water. Otherwise the i-malic and l-malic acids differ only in physical properties. We have therefore another case of "physical" isomerism. To complete the series a d-*Malic acid*, which is identical with the l-acid in all other respects, is formed by the *partial* reduction of tartaric acid by means of hydriodic acid. When equal weights of the d- and l- acids are mixed, the i-acid is formed.

TARTARIC ACIDS.

106. Tartaric acid occurs in plants, sometimes free, more often as the hydrogen potassium salt. This salt, not very soluble in water, is much less soluble in alcohol, hence, during the fermentation of grape juice, in which it occurs, it is deposited with impurities as "*argol*." From argol the pure salt "cream of tartar" is obtained. In order to prepare the acid, the potassium salt is converted into the insoluble calcium salt, and this is treated with the required quantity of dilute sulphuric acid. The calcium sulphate is filtered off, and from the saturated solution tartaric acid separates out, anhydrous, in large hard monoclinic crystals. The acid was isolated by Scheele in 1769. It melts at 168° to 170° C.; a little above this temperature it chars, emitting vapours resembling those of burnt sugar, at the same time yielding also pyrotartaric and pyruvic acids.

107. Formula.—The simplest formula of tartaric acid as obtained by combustion methods is $C_2H_3O_3$. It forms two series of salts; therefore it is dibasic, and probably contains two carboxyl groups. The di-ethyl ester reacts with acetyl chloride with the introduction of *two* acetyl groups successively; therefore the acid should possess *two* alcoholic hydroxyl groups. It is reduced by hydriodic acid to d-malic acid and succinic acid in succession.

Hydrobromic acid converts it into di-brom succinic acid. We must therefore regard tartaric acid as di-hydroxy-succinic acid.

$$\begin{array}{l}\mathrm{CH(OH)COOH.}\\ |\\ \mathrm{CH(OH)COOH.}\end{array}$$

108. Tartaric acid may also be prepared by careful oxidation of sugar of milk with nitric acid.

It is readily oxidised, and is used as a reducing agent. Its ability to reduce ammoniacal silver nitrate is used as a test.

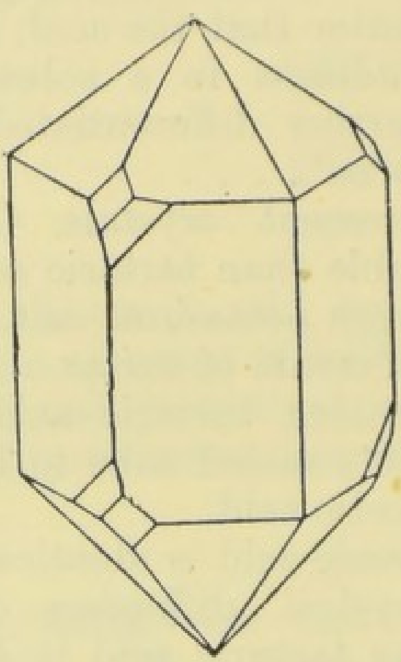
109. Salts.—Its salts are important. The normal potassium salt is more soluble than the hydrogen salt. The latter is called "cream of tartar"; it must not be confused with "tartar emetic," which is formed by heating a solution of cream of tartar with antimony oxide and has the formula $[C_4H_4O_6(SbO)K]_2, H_2O$. This compound is soluble in water; it is used as an emetic and as a mordant. Calcium tartrate ($C_4H_4O_6Ca$, $4H_2O$) is only moderately soluble in water, but is readily dissolved by acetic acid. Tartaric acid also forms soluble salts of the heavy metals, which are not decomposed by caustic alkalis; the cupric salt is valuable in analysis as Fehling's solution (Section 146). Rochelle salt, $C_4H_4O_6K.Na$, $4H_2O$, discovered by Seignette at Rochelle in 1672, is very soluble and forms fine large crystals.

110. Racemic Acid.—In 1829 Berzelius discovered, in fermented grape juice from which argol had been removed, a hydrogen potassium salt of an acid which he isolated and called Racemic acid. He found that Racemic acid . . . "has the same neutralising power and the same composition as tartaric acid. It differs from tartaric acid by its lesser solubility in water, and that in the crystalline state it contains . . . water [of hydration] . . . and by not giving with potash and soda a double salt crystallising like Rochelle salt. . . . But the greatest difference of all between these acids is presented by the . . . lime salt, which is so slightly soluble in water that the acid, after a time, produces considerable cloudiness in a solution of gypsum. . . . These salts are further differentiated from each other by their crystalline form. . . ."

Racemic acid, *rhombic* efflorescent crystals, $C_4H_6O_6$, H_2O (M.P. = 206°), is less soluble than tartaric acid; it may be obtained from its hydrogen potassium salt, which we have said is more soluble than cream of tartar. It may be more easily prepared by heating tartaric acid with water in molecular proportions in a sealed tube to 175° C. Its calcium salt is insoluble in acetic acid.

The chemical behaviour of racemic acid is identical with that of tartaric acid; the physical difference of the greatest interest is that whereas tartaric acid is dextro-rotatory to polarised light, racemic acid is inactive. Hence the one is called d-tartaric acid and the other i-tartaric acid. Tartaric acid, when partially reduced with hydriodic acid, yields d-malic acid; in the same circumstances racemic acid yields i-malic acid.

111. Pasteur's work on the Tartaric Acids.—In 1848 Pasteur discovered that crystals of tartrates have "hemihedral" facets. Acting upon a hint of Herschel's that the hemihedral facets of quartz crystals—right and left—have some relation to the opposite effects upon polarised light of these different quartz crystals, he sought to show that similar salts of racemic acid—being inactive—are devoid of such hemihedral faces. With this object he prepared a saturated solution of sodium ammonium racemate (by mixing saturated solutions of equivalent weights of sodium racemate and ammonium racemate), and allowed it to evaporate spontaneously at ordinary temperatures. He obtained fine large crystals, which however *did* possess hemihedral facets; but the crystals were, like those of quartz, of two kinds, in about equal bulk: some had their hemihedral faces to the right, others to the left (Figs. 20 and 21). He separated the two kinds of crystals, dissolved



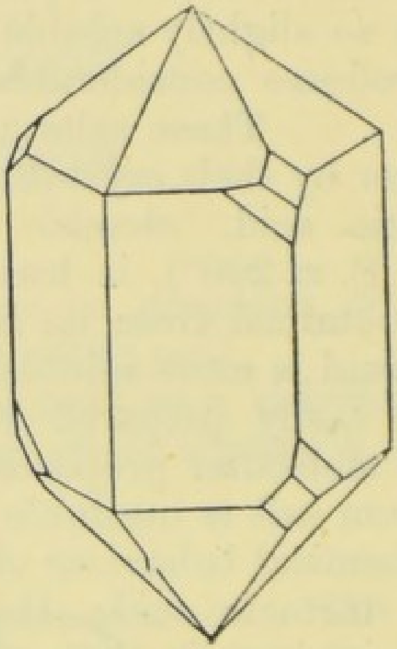


Fig. 20.—*l*- AND *r*-QUARTZ CRYSTALS.

them, and examined the effects of their solution upon polarised light: he found that those crystals which have the right-handed hemihedral facets are dextro-rotatory, those with left-handed hemihedral facets are laevo-rotatory. And that

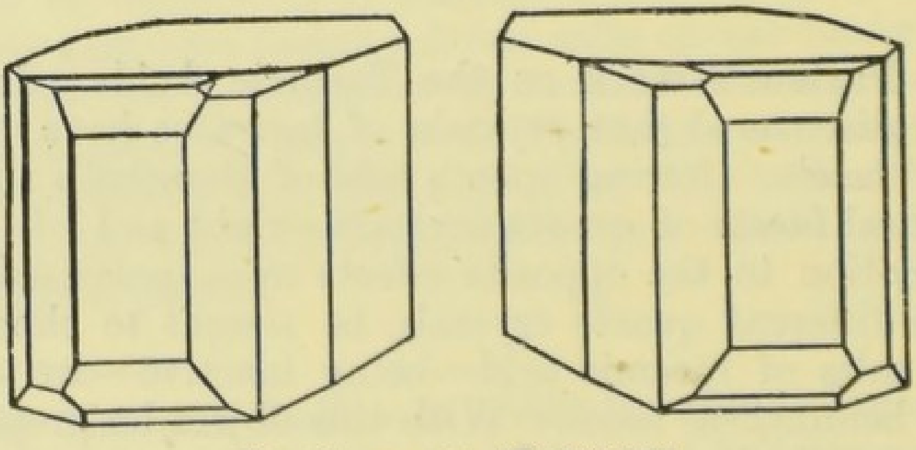


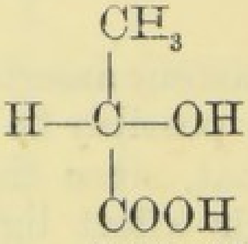
Fig. 21.—*r*- AND *l*-TARTRATES.

is the only difference between the two kinds of crystals: they are *equally* soluble. From the two kinds of crystal he isolated two acids which also differ only in this one property; their solubility, their melting point (170° C.), every chemical and every other physical property being identical. They are called d- and l-tartaric acids. The dextro acid is *ordinary* tartaric acid. When the l-acid is partially reduced with hydriodic acid it yields ordinary l-malic acid. When equal quantities of the d- and l-acids are brought together in concentrated solution, a rise of temperature takes place and racemic acid is formed.

112. Stereo- or Space-isomerism.—Pasteur asserted that the difference in the quartz crystals may possibly be due to difference in molecular structure, but that, since the solutions as well as the solid tartaric acids affect light, the differences between the acids must lie in the molecules themselves. He attributed this "physical" isomerism to an asymmetry of the molecules, such that a molecule of one of the active acids cannot be superposed on a molecule of the other. The racemic forms he regarded as compounds of equal quantities of the l- and d-acids, which consequently are inactive by *external* compensation.

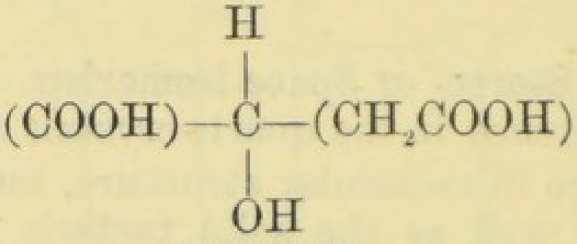
In 1873 Wislicenus was at work upon the much debated lactic acids. As a result of his work he concluded "that it is not possible to explain the differences except by the assumption that they are caused merely by a different arrangement *in space* of the atoms which are united with one another in the same order . . . that, in the case of molecules identical in structure, differences in geometrical sequence, which in the first instance could produce variations in the magnitude and shape of the molecules, would make themselves noted by variations in . . . these properties lying on the boundary line of the physical and chemical relationships, such as solubility, crystalline form, water of crystallisation, etc. Thus we should be led to . . . the strict conception of 'physical isomerism' in contradistinction to the different kinds of 'chemical isomerism.'"

Wislicenus' work on the one hand and Pasteur's suggestion on the other inspired Van t'Hoff and Le Bel, respectively, to bring forward simultaneously, in 1874, an hypothesis to account for this physical isomerism, or, as it is now called, **stereo- or space-isomerism** (στερεός = solid). Van t'Hoff based his hypothesis upon the doctrine of the tetravalency of carbon. He regarded the valencies as "directed" towards the four corners of a tetrahedron with the carbon centrally placed. He asserted that all optically active substances possess an "asymmetric" carbon atom, that is, one which is connected with four unlike groups, thus



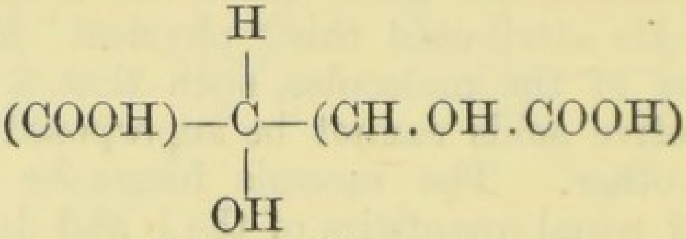
$$\begin{array}{ccc} & \mathrm{CH_3} & \\ & | & \\ \mathrm{H}- & \mathrm{C} & -\mathrm{OH} \\ & | & \\ & \mathrm{COOH} & \end{array}$$

(lactic acid)



$$\begin{array}{ccc} & \mathrm{H} & \\ & | & \\ \mathrm{(COOH)}- & \mathrm{C} & -\mathrm{(CH_2COOH)} \\ & | & \\ & \mathrm{OH} & \end{array}$$

(malic acid)



$$\begin{array}{ccc} & \mathrm{H} & \\ & | & \\ \mathrm{(COOH)}- & \mathrm{C} & -\mathrm{(CH.OH.COOH)} \\ & | & \\ & \mathrm{OH} & \end{array}$$

(tartaric acid)

and he soon showed that what were then held to be exceptions (styrene, C_8H_8, etc.) were misunderstood, because the experimental specimens had been contaminated with impure

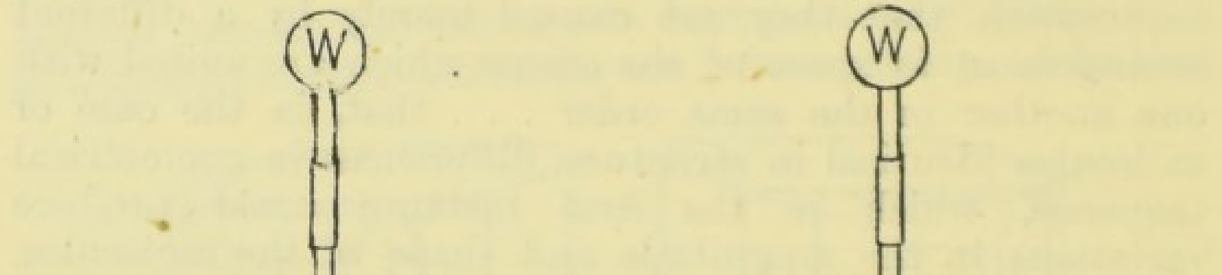


Fig. 22.

active substances. In order most easily to follow the theory as it explains stereo-isomerism the student is urged to obtain the model of Fig. 22.

It consists of a central ball to represent the carbon atom, bearing four short pegs, so that, if the carbon atom is supposed to be centrally placed in a tetrahedron, they point towards its corners. To these pegs four balls, differently coloured to represent different groups and provided with one peg each, are joined by rubber connections.

If two such models, with the balls arranged as in Fig. 22, are placed side by side, it will be seen that one is the mirror image of the other, like the right and left hands, and that, like the hands, one of them cannot be superposed on the other. Apart from this property one model is not different from the other.

If we consider either of these models as representing a d-substance, then the other model will represent the corresponding l-substance.

The racemic (inactive) form can only be represented by both together.

113. Meso-tartaric Acid.—During his researches* (1851) Pasteur prepared an inactive tartaric acid which differs in several respects from racemic acid. Its formula, $C_4H_6O_6$, H_2O, is the same, but although the crystals are efflorescent, they are rectangular plates. In addition it has a much lower melting point, namely 143° C.; the potassium hydrogen salt is readily soluble in cold water; the calcium salt is insoluble in water and in acetic acid.

Unlike sodium-ammonium racemate its sodium-ammonium salt cannot be resolved into the d- and l-tartrates by crystallisation. Pasteur named it **Meso-tartaric acid.** It may be formed by heating d-tartaric acid with the molecular proportion of water in a sealed tube to 165° C. When heated under the same conditions to 175° C. racemic acid is formed. The meso-acid (or rather its salt) is also formed when the dextro acid is boiled in a flask (reflux condenser) for several hours with a large excess of caustic soda. Van t'Hoff's hypothesis is able to account for this new acid.

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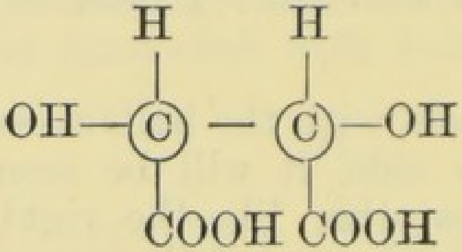
* Pasteur's account of his work is presented in No. 14 of the Alembic Club reprints, *Researches on Molecular Asymmetry.*

114. If we consider the formula for tartaric acid we recognise therein *two* asymmetric carbon atoms, both of which are attached to similar groups.



$$\begin{array}{ccccc} & H & & H & \\ & | & & | & \\ OH- & C & - & C & -OH \\ & | & & | & \\ & COOH & & COOH & \end{array}$$

Let us have recourse to the models.

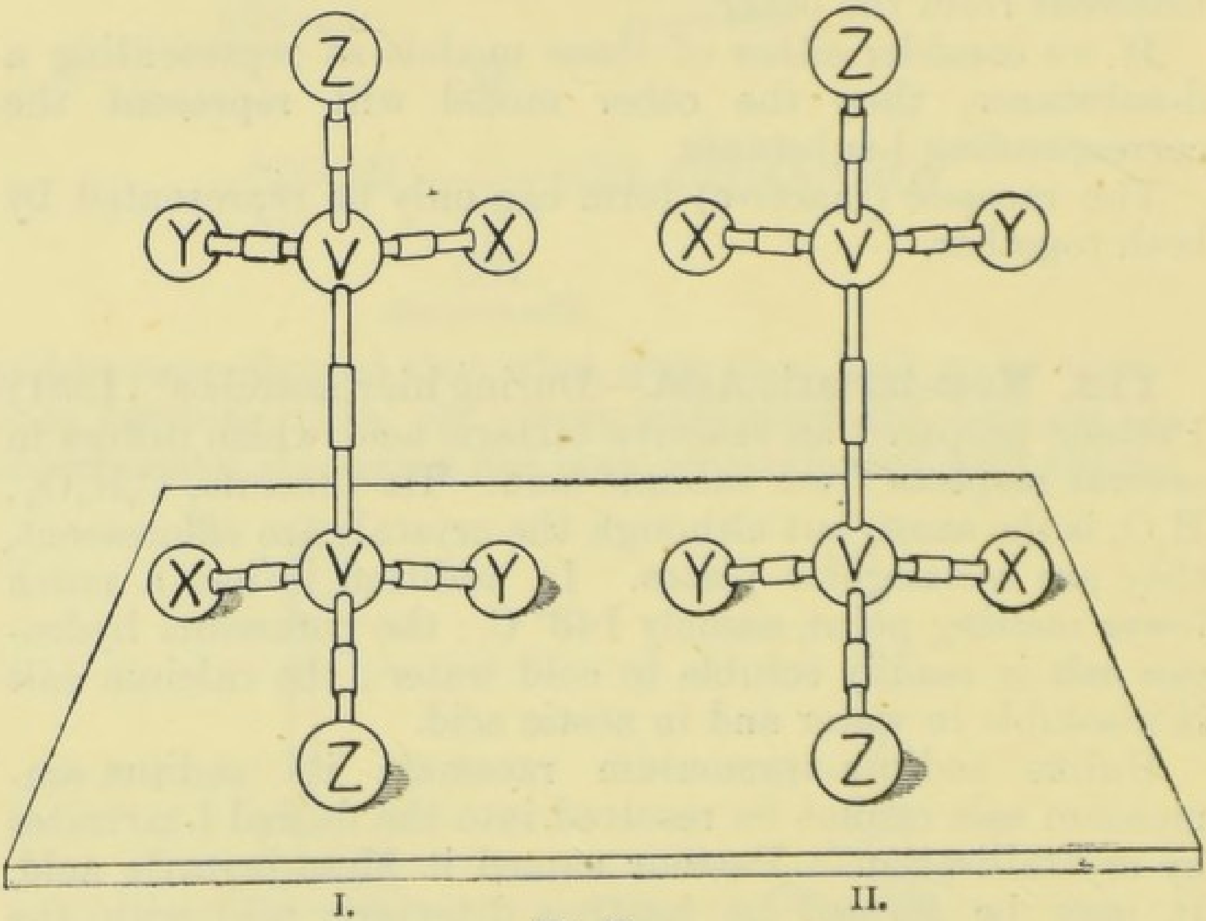


Fig. 23.

Choose the arrangement I. of Fig. 22, to represent the d-acid. In place of the top ball we can put another model similarly arranged (less the corresponding ball). Then both parts have the same effect towards light. Similar treatment with the arrangement II. gives us a representation of the l-tartaric acid. These two are mirror images of each other. Both together represent the externally compensated racemic acid.

If, however, we take away the top balls from one each of arrangements I. and II. of Fig. 22 and join the residues

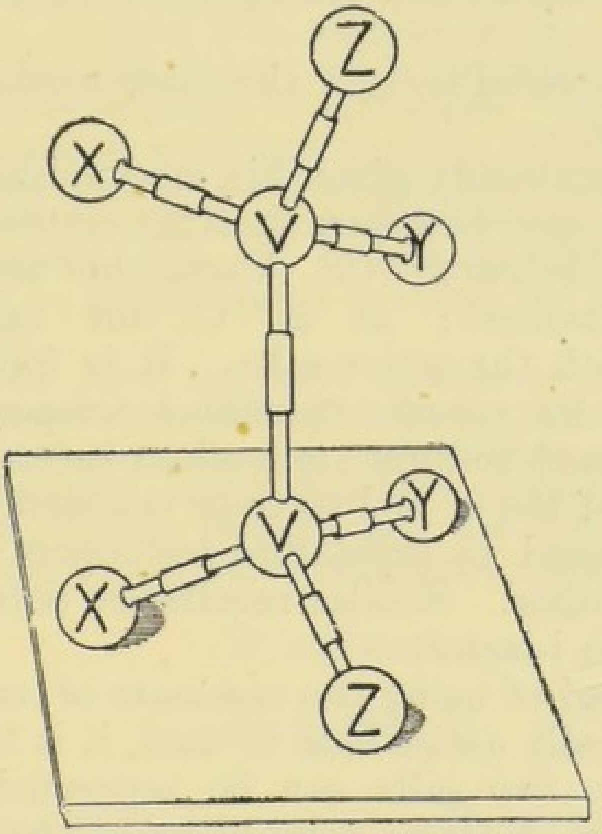
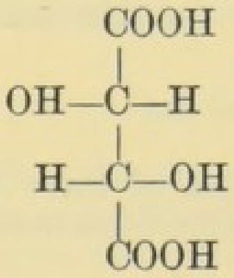


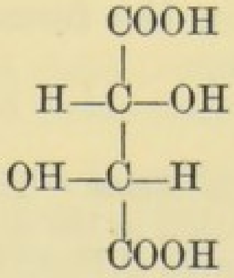
Fig. 24.—Internally Compensated Tartaric Acid.

we have Fig. 24 in which the top and bottom parts of the model represent equal parts of the molecule with equal but opposite effects upon light, that is to say an acid inactive by *internal* compensation, one which should not be resolvable. This is held to represent Meso-tartaric acid.

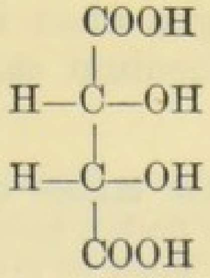
In order to avoid the clumsy "solid" formulae their "projection" formulae are used, thus



$$\begin{array}{c} \mathrm{COOH} \\ | \\ \mathrm{OH{-}C{-}H} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{COOH} \end{array}$$



$$\begin{array}{c} \mathrm{COOH} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{OH{-}C{-}H} \\ | \\ \mathrm{COOH} \end{array}$$



$$\begin{array}{c} \mathrm{COOH} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{COOH} \end{array}$$

115. Methods of resolving "Racemic" Compounds.—As we have already remarked, the salts of d- and l-acids are equally soluble and are formed in equal quantities, consequently they cannot be separated by fractional crystallisation.

Pasteur discovered each of the three methods of separation still in use.

(i) We have already given his mechanical method. It is necessary to say, however, that the crystallisation must be carried out below 27° C. Above this temperature the racemate crystallises; at 27° C. the racemate is in equilibrium with the active salts. It is found that every substance has its specific transition temperature. If to the *cold* saturated sodium-ammonium racemate solution a crystal either of the d- or l-tartrate is added, the respective salt will be found to crystallise out upon it, uncontaminated by the other. Similar results are obtained with the zinc ammonium i-lactate.

(ii) If instead of using the racemate of an inactive base one of an optically *active* base is used, it is found that the crystals of the two salts can be separated fractionally, since they have *different* solubilities. The alkaloids are such optically active bases. Pasteur prepared l-cinchonine racemate and found the l-tartrate the less soluble. Similar use was made of the cinchonine malate, while Wislicenus employed the strychnine i-lactate.

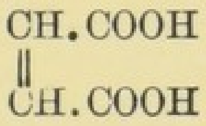
(iii) When moulds and bacteria feed upon racemic compounds it is usual for them to attack either the d- or the l- compound more readily, so that, if their attack is arrested in time, one or the other optically active body is left. Pasteur found that the green mould, *Penicillium glaucum* (commonly seen on decaying oranges), when sown in ammonium racemate destroyed the d-tartrate the more rapidly. And, as we have mentioned above, the same fungus when it is fed on the fermentation lactate leaves ammonium sarco-lactate.

116. Maleïc and Fumaric Acids.—The isomerism of these two acids finds a simple explanation in the doctrine of stereo-isomerism. Both must be given the formula $C_2H_2(COOH)_2$.

Maleïc acid owes its name to its formation. Fumaric acid is found in Fumitory. Both are formed when malic acid is heated ; if the temperature is kept at 145° C. mainly fumaric acid is formed, but if the malic acid is heated rapidly, maleïc anhydride is chiefly produced. The fumaric acid remains in the flask.

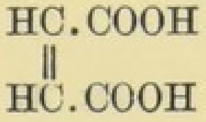
Maleïc acid is obtained from solution in large prisms and is readily soluble in cold water ; while fumaric acid forms small prisms and is nearly insoluble in cold water. Maleïc acid has an unpleasant acid taste, it is fairly strong ($K = 1{\cdot}7$) ; fumaric acid has a purely acid taste and is much weaker ($K = {\cdot}093$). Maleïc acid distils unchanged, except for partial transformation into maleïc anhydride (converted into the acid again with water) ; while fumaric acid has no anhydride : it sublimes and is converted into maleïc anhydride.

That they must have the same formula is evident from the following reactions : both acids when reduced are converted into succinic acid ; both combine with hydrobromic acid to yield the same brom-succinic acid ; and both combine with water to yield the same malic acid. Since fumaric acid has been prepared from acetylene di-iodide, $C_2H_2I_2$, as starting point, their formula is



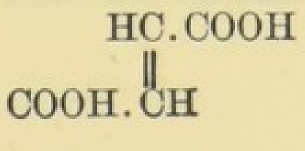
$$\begin{array}{l} \mathrm{CH.COOH} \\ \| \\ \mathrm{CH.COOH} \end{array}$$

To express their differences, maleïc acid, which forms an anhydride, is written as



$$\begin{array}{c} \mathrm{HC.COOH} \\ \| \\ \mathrm{HC.COOH} \end{array}$$

and fumaric acid, which forms no anhydride, as



$$\begin{array}{rl} & \mathrm{HC.COOH} \\ & \;\| \\ \mathrm{COOH.} & \!\!\mathrm{CH} \end{array}$$

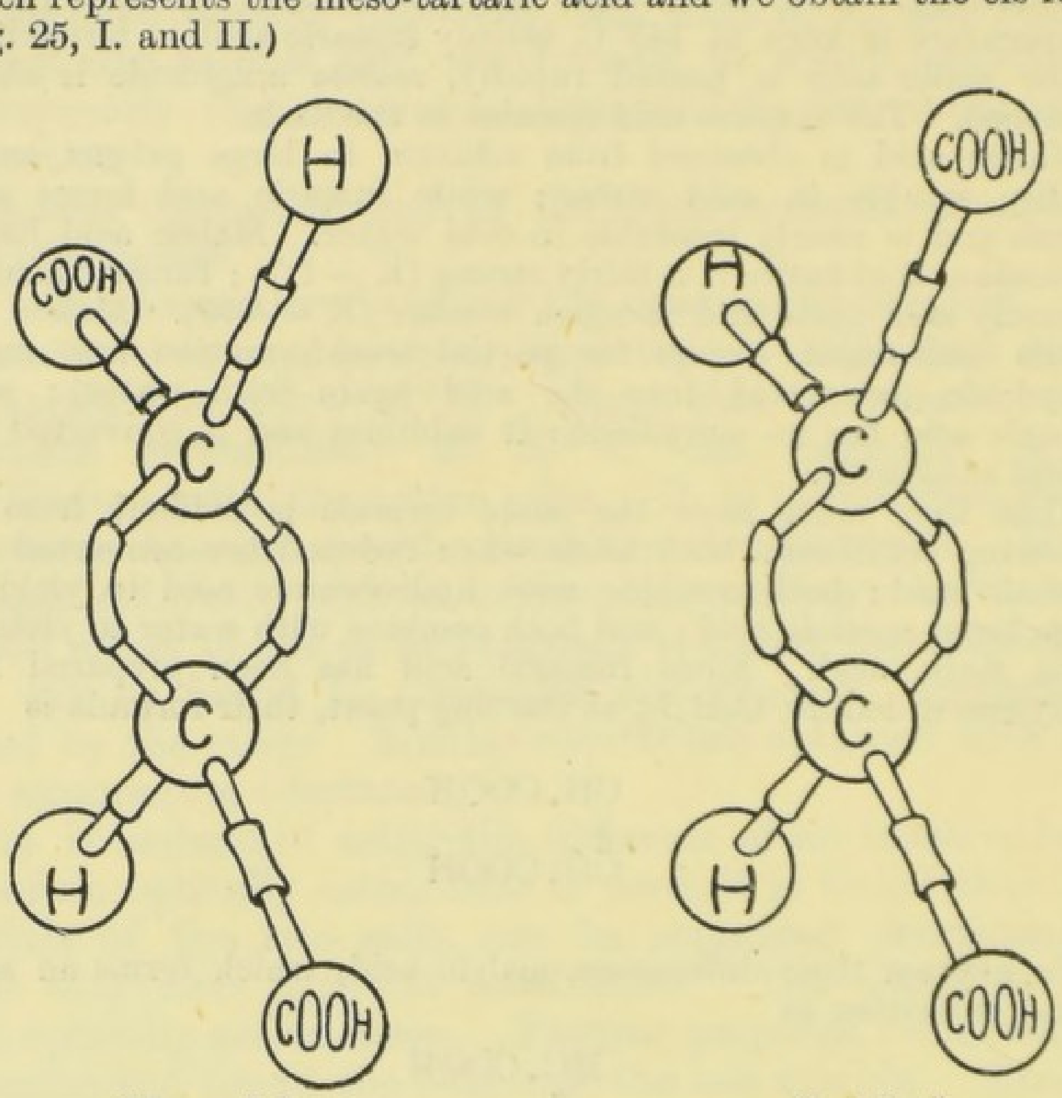
The former is called the "cis" form, the latter the "trans" form.

These formulae find their justification in the following facts, and their expression in solid formulae.

By careful oxidation

maleïc acid yields meso-tartaric acid
but fumaric acid yields racemic acid.

To make the solid formulae in conformity with these reactions, take a model which represents either of the active tartaric acids, remove the balls which represent hydroxyl and connect the free linkages. We get the trans-form. Similarly deal with the model which represents the meso-tartaric acid and we obtain the cis-form. (Fig. 25, I. and II.)



"Trans." I. II. "Cis."

Fig. 25.

The double linkage is represented as preventing rotation of the two parts ; in the tartaric acid models there is free movement about the joined single linkage.

QUESTIONS.—CHAPTER XVI.

1. How are fumaric and maleïc acids prepared, what are their principal properties, and how may they be converted into one another?

2. What is the relationship between succinic and tartaric acids, and how can each be obtained from the other? By what means has the presence of "alcoholic hydroxyl" in tartaric acid been established?

3. Explain the following expressions:—α-bromopropionic acid; γ-bromobutyric acid; d-tartaric acid; r-tartaric; *cis*-crotonic acid ($CH_3CH:CH.COOH$).

4. What is meant by "optical activity"?

5. Compare the use of hydriodic acid with that of hydrobromic acid as a reagent in organic chemistry.

6. How can calcium chloride as a reagent be used to indicate oxalic, tartaric, and citric acids when these are mixed together in solution?

7. With the models described in this chapter, make the space formulae of ethane, ethylene, and acetylene.

CHAPTER XVII.

SOME NITROGEN COMPOUNDS.

I. ALKYL NITRITES AND NITRO-PARAFFINS.

117. Ethyl Nitrite.—When an alcohol is treated with nitrous acid (sodium nitrite and sulphuric acid), the corresponding *nitrite* is formed.

$$C_2H_5OH + HNO_2 = C_2H_5NO_2 + H_2O.$$

Ethyl nitrite is a pleasant smelling liquid boiling at 16° C. In the impure condition it is used in medicine as "sweet spirits of nitre." Caustic soda reacts with it, as we should expect, saponifying it into sodium nitrite and ethyl alcohol.

$$C_2H_5NO_2 + NaOH = NaNO_2 + C_2H_5OH.$$

Ethyl nitrite can be converted into alcohol by the reducing action of nascent hydrogen [tin + hydrochloric acid]; at the same time, hydroxylamine and some ammonia are formed.

$$C_2H_5NO_2 + 2H_2 = C_2H_5OH + NH_2OH.$$

This reminds us of the reduction of nitrous acid and nitric oxide to hydroxylamine and ammonia by the same reagent.

118. Nitro-ethane.—When an attempt is made to prepare ethyl nitrite by double decomposition of dry silver nitrite and dry ethyl iodide [flask and reflux condenser] only about half the expected quantity of the nitrite is formed, the remainder is a liquid which boils at 114° C.

and has a smell different from that of ethyl nitrite. Yet it has exactly the same composition. Caustic soda does not hydrolyse it, and nascent hydrogen reduces it to ethylamine and water.

$$C_2H_5NO_2 + 3H_2 = C_2H_5NH_2 + 2H_2O.$$

The substance cannot be a nitrite; it is an isomeride of the latter, and is called **Nitro-ethane.**

That it is reduced to ethylamine suggests that the nitrogen is directly combined with carbon, whereas the ease with which the nitrite is hydrolysed is accepted as evidence that, in this compound, the nitrogen and carbon are *not* directly united. Hence the formulae

$C_2H_5.O.NO$ and

$$C_2H_5N\begin{smallmatrix}=O\\=O\end{smallmatrix}$$

(ethyl nitrite) (nitro-ethane)

119. When a mixture of methyl iodide and silver nitrite is distilled only the nitro compound is formed. With ethyl iodide, as we have seen, the nitrite and nitro compound are produced in equal proportions, but with the halides of the higher hydrocarbons the proportion of nitro-paraffin becomes less and less. The higher nitro-paraffins are therefore prepared by another method, namely, by the action of concentrated nitric acid on the hydrocarbon itself. The normal paraffins resist the action more than the iso-paraffins. The lower paraffins are oxidised to carbon dioxide and water if they are acted upon at all by nitric acid.

The formation of the nitro compound by this method is more serviceable in another series of hydrocarbons, and the preparation of an important nitro compound will be described in Chapter XX. Since water is formed by the loss of oxygen as well as hydrogen from the acid, it is obvious that a nitro compound is not a salt of nitric acid.

$$C_8H_{18} + HONO_2 = C_8H_{17}NO_2 + H_2O.$$

The student will remember that nitro-glycerin is not a nitro compound, but glycerin trinitrate.

II. NITRILES AND CARBYLAMINES.

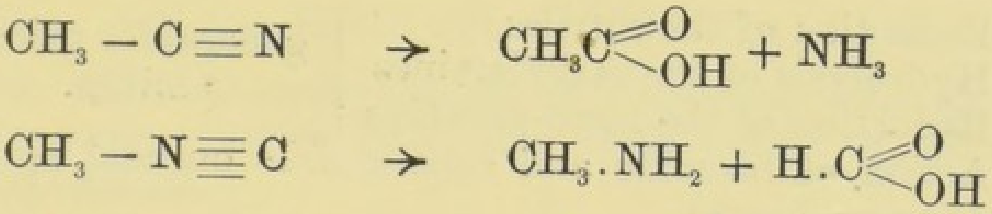
120. The Cyanides or Nitriles—Hydrocyanic Acid.—The preparation of acetonitrile by two methods has been given in Sections 40 and 49. In this section we shall consider these compounds more generally. In Section 93 the hydrolysis of cyanogen to oxalic acid was noticed. The simplest cyanide is hydrocyanic acid, HCN. This acid is contained in the aqueous liquors of coal tar. It is usually produced by the action of hydrochloric acid on potassium cyanide. This salt, which can be produced by passing nitrogen over a heated mixture of potash and carbon, is excessively poisonous, and very soluble. In solution it is hydrolysed to yield the free acid. The acid is one of the weakest known, yet $\frac{1}{10}$ grain is fatal to human life. Its solution is slowly hydrolysed on standing into ammonium formate and some other products. This reaction, which is quite analogous to that of the alkyl cyanides under the same conditions, gives the name **formonitrile** to hydrogen cyanide.

$$HCN + 2H_2O = H.CO.ONH_4.$$

121. The Isocyanides or Carbylamines.—If we take into consideration that chloroform can also be hydrolysed to formic acid (Section 80), we can regard the following interesting reaction as corresponding to the reverse of the foregoing.

$$CHCl_3 + NH_3 = 3HCl + HCN.$$

Not only ammonia, but also substituted ammonias (amines) will react with chloroform. When chloroform and methylamine are brought together in alcoholic solution which also contains an excess of potash, a reaction proceeds, but, instead of the pleasant smelling methyl cyanide which boils at 82° C., a liquid is formed boiling at 60° C. of a most intolerable odour. Nevertheless, this substance has the same composition as methyl cyanide. It is called methyl **isocyanide**. Unlike acetonitrile, it is not hydrolysed by caustic potash. On the other hand, while acetonitrile must be heated with hydrochloric acid for hydrolysis to take place at a reasonable rate, the isocyanide is hydrolysed almost explosively even at the ordinary temperature [reflux condenser] when dilute hydrochloric acid is added to it. In this case, however, methyl-amine is formed and formic acid. For this reason the new compound is called methyl **carbylamine.** The different results of hydrolysis are accepted as indicating the structures of these isomeric substances. Since from the nitrile the nitrogen atom is lost (to form hydrogen amine, HNH_2) and the carbon remains to form the alkyl carboxyl, while in the case of the carbylamine the nitrogen is retained to form the alkyl amine but the carbon is lost (to form hydrogen carboxyl, $H.COOH$), the formulae are written



$$CH_3-C\equiv N \rightarrow CH_3C\begin{smallmatrix}=O\\ -OH\end{smallmatrix}+NH_3$$

$$CH_3-N\equiv C \rightarrow CH_3.NH_2+H.C\begin{smallmatrix}=O\\ -OH\end{smallmatrix}$$

The formation of carbylamine may now be written

$$CH_3NH_2+CHCl_3+3KOH=CH_3NC+3KCl+3H_2O.$$

122. Properties and Preparation of the Carbylamines.—Methyl isocyanide is the simplest member of the carbylamines. These substances are all extremely poisonous; have insufferable odours; are insoluble in water, but soluble in alcohol; are hydrolysed to the corresponding amine and formic acid; have lower boiling points than the isomeric cyanides.

They can be prepared by another method, for instance:

(1) When potassium ethyl sulphate is distilled with anhydrous potassium ferrocyanide, or ethyl iodide with potassium cyanide, chiefly propionitrile is formed, but that there is also a small quantity of the ethyl carbylamine is advertised by the unendurable odour.

(2) But if silver cyanide is used, the chief product is ethyl iso-cyanide, with a smaller proportion of the nitrile This is a general method for preparing carbylamines.

The iso-cyanides are obtained pure by the chloroform method; the cyanides by dehydrating the acid amides (Section 49). The carbylamines do not undergo reduction in the same manner as the nitriles (Section 40). When moist and heated to 200° C., they are converted into the nitriles.

III. The Alkyl Amines and Amino-acids.

123. Preparation of the Amines.—The amines or substituted ammonias may be prepared by several methods, not one of which is convenient in all cases. Amongst these methods are the following.

1. Reduction of the nitriles
2. Hydrolysis of the carbylamines
3. Reduction of the nitro-paraffins

} general for primary amines.

4. Action of bromine and caustic soda on acid amides (for lower members).
5. Action of ammonia on alkyl halides (yields mixtures of bases).

124. Properties of the Amines.—The first to be isolated was Ethylamine, which was obtained accidentally by Wurtz in 1848, by treatment of ethyl isocyanate, C_2H_5NCO, with caustic soda. This method is related to 4 above. The amines had been predicted by Hofmann a year before. The alkyl amines behave in almost all respects like ammonia itself; the lower members are soluble gases with ammoniacal and fishy odour; the higher are insoluble odourless solids. They all form soluble salts by addition with acids. The hydrochlorides are the most important. With chloroplatinic acid the bases form chloroplatinates insoluble in alcohol, salts which, on ignition, are decomposed and leave platinum behind. Hence they are used to determine the molecular weights of some amines.

$$C_2H_5NH_2 \rightarrow (C_2H_5NH_2H)_2PtCl_6 \rightarrow Pt.$$

Some of the amines will replace ammonia in alums, for instance $(CH_3NH_3)_2SO_4,Al_2(SO_4)_3,24H_2O$ is well known.

125. Hofmann's Method.—When an alcoholic solution of ammonia and an alkyl halide are heated together in a sealed tube, four products are obtained. It will be simplest to consider the methyl products in the order in which they are probably formed.

The first reaction produces **Methyl-amine** and hydriodic acid.

$$\text{(i)} \qquad CH_3I + HNH_2 = CH_3NH_2 + HI\,;$$

the hydriodic acid combines partly with methylamine to form methyl ammonium iodide, CH_3NH_2HI, and partly with ammonia; some methylamine remains free; this reacts with more methyl iodide, like ammonia itself, but more readily, to form **di-methyl-amine**.

$$\text{(ii)} \qquad CH_3I + HNH.CH_3 = NH(CH_3)_2 + HI\,;$$

again, some di-methyl-amine is converted into its salt, while some remains free; this again reacts to form **tri-methyl-amine**.

$$\text{(iii)} \qquad CH_3I + HN(CH_3)_2 = N(CH_3)_3 + HI.$$

The new product contains none of the ammonia hydrogen. It will combine with hydriodic acid to form its salt, $N(CH_3)_3HI$. In addition, it will combine with methyl iodide to form **tetra-methyl ammonium iodide**.

$$CH_3I + N(CH_3)_3 = N(CH_3)_4I.$$

Thus, whenever ammonia and an alkyl iodide are heated together, four salts are formed. As a rule the first and the last products predominate, but in some cases it is possible to arrange the conditions so that one product can be formed almost to the exclusion of the rest.

126. Quaternary Bases.—When the mixture is heated with caustic potash, all except the tetra-methyl compound behave like ammonium iodide, the substituted ammonias being expelled; they are collected by solution in water. Tetra-methyl ammonium iodide is unacted upon by caustic alkalis, but silver (hydr)oxide reacts with it,

$$N(CH_3)_4I + AgOH = AgI + N(CH_3)_4OH,$$

to produce *Tetra-methyl-ammonium hydroxide.* This substance in solution is almost as strong a base as caustic potash itself. It is a colourless hygroscopic solid which rapidly absorbs carbon dioxide with formation of a stable carbonate. It is called a QUATERNARY AMMONIUM BASE.

127. Primary, Secondary, and Tertiary Bases.—Methyl amine, di-methyl amine, and tri-methylamine are the simplest examples of the PRIMARY, SECONDARY, AND TERTIARY ammonia BASES respectively. The primary amines are characterised by the *amino* group, $NH_2—$. They alone form isocyanides with chloroform, which distinguishes them from the other two classes. The secondary amines contain the *imino* group, $NH=$. The tertiary amines differ from the other two classes in many properties and are therefore easily separated. The separation of the primary and secondary bases is tedious.

128. Separation of the Bases.—Hofmann separated the three amines by shaking their solutions with ethyl oxalate. The tertiary amine is not affected and can be distilled off. The primary amine forms a solid substituted oxamide, whereas the secondary amine forms a liquid substituted oxamate. These are separated by filtration, and the amines are recovered. The student will easily understand this separation when he arrives at Exp. 35 and Section 134.

Another method depends upon the action of nitrous acid.

The primary amine is converted into an alcohol, from which it cannot be recovered. The secondary amine forms an insoluble liquid called a *nitroso* compound, $(CH_3)_2N.NO$, from which it can be obtained again by heating with concentrated hydrochloric acid. The tertiary amine remains unaffected as the dissolved salt.

129. The amines and amino-acids are common products of decomposition and putrefaction. *Methyl amine*, B.P. $-6°$, is contained in herring brine and is formed in the distillation of wood. It occurs also in the common weed Dogs-mercury. It is most easily prepared from formalin or acetamide (by process 4) (see Cohen, *Practical Organic Chemistry*, p. 72, or Gattermann, p. 151).

In the first case formaldehyde reacts with a large excess of saturated ammonium chloride solution at 60° to 100°.

$$2H.CHO + HNH_2HCl = CH_3NH_2HCl + HCOOH.$$

In the second the bromine at ordinary temperature substitutes hydrogen to form acetobromamide.

$$CH_3CONH_2 + Br_2 = CH_3CONHBr + HBr.$$

With this compound *cold* potash reacts to replace the second amine hydrogen,

$$CH_3CONHBr + KOH = CH_3CONKBr + H_2O,$$

and this, treated with hot concentrated potash, is converted via isocyanate to methylamine.

$$CH_3CONKBr \longrightarrow CH_3NCO \longrightarrow CH_3NH_2.$$

Di-methyl amine (B.P. 7°) also occurs in herring brine.

Tri-methylamine (B.P. 9°) is obtained from the betaine in "vinasse" from beet-root sugar. It exists in many plants and in herring brine. It is used instead of ammonia in the "Solvay" process for the preparation of potassium carbonate.

130. The Amino-acids also are prepared by Hofmann's method: from chloracetic acid and ammonia,

$$CH_2ClCOOH + 2NH_3 = CH_2NH_2COOH + NH_4Cl.$$

In this case also secondary and tertiary products are formed. The amino-acids may also be prepared by the action of ammonia on the cyanhydrins of aldehydes, when the hydroxyl is replaced by the amino group.

$$CH_3CH(OH)CN \longrightarrow CH_3CH(NH_2)COOH.$$

They are of very great importance, since many of the proteins when "hydrolysed" give almost quantitative yields of a mixture of these acids, some of which also contain sulphur. The most important of them is

Glycine (Glycocoll, amino-acetic acid), which we have partly considered in Section 43. Emil Fischer has declared how important a part this compound must play in the hoped-for syntheses of the proteins, which compounds appear to have extraordinarily complex molecules made up of various amino-acids.

Glycine is obtained from the decomposition of gelatine and glue. It may also be prepared from hippuric acid (a constituent of the urine of herbivora), in which it occurs condensed with benzoic acid. It is both an amino base and an acid. It is very nearly neutral in solution; if, however, the hydrochloride is formed,

$$CH_2(NH_2HCl)COOH,$$

its esters can readily be prepared. Ethyl glycine,

$$CH_2NH_2COOC_2H_5,$$

is then found to be *strongly* basic. Glycine is readily converted into glycollic acid by nitrous acid.

$$CH_2NH_2COOH \longrightarrow CH_2(OH)COOH.$$

131. Ethyl Diazo-acetate.—Curtius has obtained an intermediate product from the ethyl ester. This is ethyl *diazo*-acetate.

$$CHN_2.COOC_2H_5.$$

With water it yields nitrogen and glycollic acid. This reaction is especially interesting in view of similar products from aromatic amines (Chapter XX.).

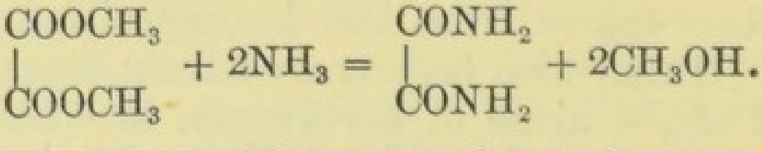
132. Other important amino-acids are :—

Sarcosine, the methyl derivative of glycine, found in flesh. *Betaine*, tri-methyl glycocoll. *Alanin*, α-amino propionic ; a decomposition product of proteins. *Tyrosin*, a substituted alanin. *Leucin*, α-amino isocaproic acid. *Aspartic* acid, amino-succinic acid and its amide *asparagin*, and *Glutamic* acid and *Glutamin*, the next higher homologues of the former.

IV. The Acid Amides.

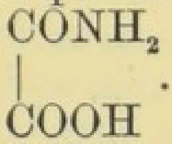
133. Preparation and Properties.—The acid amides may be prepared by the dehydration of the ammonium salts of carboxylic acids (Section 53). They may also be prepared by the action of ammonia on acid chlorides ; in this case, however, the secondary and tertiary products are formed at the same time. They may further be prepared by the action of ammonia upon esters.

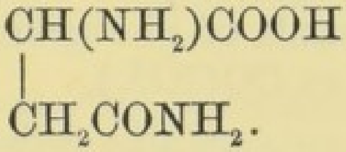
Exp. 35.—*Preparation of Oxamide.* Add ammonia to the first distillate of Exp. 33 and shake. Oxamide separates out as a crystalline powder. Filter, wash, and dry it.



$$\begin{array}{l}COOCH_3\\ |\\ COOCH_3\end{array} + 2NH_3 = \begin{array}{l}CONH_2\\ |\\ CONH_2\end{array} + 2CH_3OH.$$

The lower acid amides are soluble in water, and are neutral. All, when heated with caustic alkalis or hydrochloric acid, are converted into the corresponding acid (or salt), and ammonia.

134. Amic Acids.—Dibasic acids may be converted into intermediate compounds, in which one hydroxyl is replaced by the amide group. These are called **amic acids**: such as oxamic acid,  $\begin{array}{l}CONH_2\\ |\\ COOH\end{array}$. Asparagin is amino succinamic acid,



$$\begin{array}{l}CH(NH_2)COOH\\ |\\ CH_2CONH_2.\end{array}$$

135. The most important acid amide is *Carbamide* or UREA.

Urea was discovered in urine by Ruelle in 1773. It may be obtained from urine, by evaporation to a thin syrup. To this is added an equal bulk of nitric acid, when the nitrate is precipitated. This is removed, dissolved in hot water, and treated with barium carbonate. Carbon dioxide escapes. The solution is evaporated to dryness, and the urea dissolved out from the barium nitrate and excess of carbonate by absolute alcohol. It is obtained from solution in crystals.

136. Preparation from Inorganic Materials.—In 1828, Wöhler, in attempting to prepare ammonium cyanate from potassium cyanate, obtained from the solution urea, instead of the former salt with which it is isomeric. This discovery provoked great interest at the time, since urea was the first organic substance obtained from inorganic materials. Urea is most conveniently prepared in the laboratory by this method.

Exp. 36.—*Preparation of Urea.*

(*a*) *Preparation of Potassium Cyanate.*—Melt 50 grams of 98 per cent. potassium cyanide in an iron dish (blowpipe). Add, in small portions, 140 grams of red lead, cool and powder the product, separating it from the metallic lead; add 200 c.c. of cold water, leave for 1 hour; filter.

(*b*) *Preparation of Urea.*—To the solution add 50 grams of ammonium sulphate in concentrated solution and evaporate to dryness on the water bath. Extract with methylated spirit and evaporate till the cooled solution deposits crystals.

137. Formula.—The structural formula of urea follows from the syntheses considered below, which show it to be the diamide of carbonic acid. Hence the term **Carbamide.**

(i) Carbonyl chloride (formed from carbon monoxide and chlorine), when heated with ammonia, under great pressure and at a high temperature, yields urea and hydrochloric acid. Since the formula of phosgene gas must be $COCl_2$, that of urea follows as $CO(NH_2)_2$.

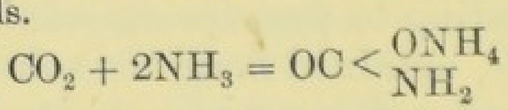
The following reactions show that carbonyl chloride is the acid chloride of carbonic acid.

(1) With water it is hydrolysed to carbon dioxide and hydrochloric acid.

(2) When treated with sodium ethoxide for some time it yields a compound of the formula $CO(OC_2H_5)_2$. This same compound is formed when silver carbonate is heated with ethyl iodide. Hence it is *di-ethyl carbonate*. When di-ethyl carbonate is heated in a sealed tube with ammonia to 180° C., urea and alcohol are formed.

(ii) When ammonium carbonate is heated in a sealed tube at a high temperature and under great pressure some urea is formed.

An intermediate product is **ammonium carbamate**, this is the ammonium salt of the unknown carbamic acid. The ammonium salt is readily prepared by passing carbon dioxide through a saturated solution of ammonia in absolute alcohol. The ammonium carbamate separates in crystals.



$$CO_2 + 2NH_3 = OC < \begin{matrix} ONH_4 \\ NH_2 \end{matrix}$$

When this salt is heated, urea is formed.

$$OC > \begin{matrix} ONH_4 \\ NH_2 \end{matrix} \longrightarrow OC < \begin{matrix} NH_2 \\ NH_2 \end{matrix}$$

[The esters of carbamic acid are important bodies and are called **urethanes**; they are formed by the action of ammonia on ethyl carbonate. See p. 360, *I.C.*]

(iii) From Cyanamide. When a mixture of acetylene and nitrogen is sparked, some hydrocyanic acid is formed. This reacts with chlorine with formation of hydrochloric acid and cyanogen chloride (CNCl). The latter reacts with ammonia to yield cyanamide, $CN.NH_2$, whose solution, when heated with bases, gives urea.

$$C_2H_2 \xrightarrow{N_2} HCN \xrightarrow{Cl_2} CNCl \xrightarrow{NH_3} CN.NH_2 \xrightarrow{H_2O} CO(NH_2)_2.$$

138. Reactions.—The formula of urea illustrates well its reactions.

When heated with water to 180° C. in a sealed tube it is converted into ammonium carbonate. The reaction takes place more readily when a caustic base is used; and the method is employed for estimating urea—by finding the carbon dioxide formed.

This process goes on naturally by the aid of bacteria—*micrococcus ureae.* In this way urea, the final product of the decomposition of albumins in the body, though useless to plants as such, is converted into carbon dioxide and the ammonia from which nitrates are built up.

When urea is treated with nitrous acid carbon dioxide and nitrogen are formed.

$$CO(NH_2)_2 + 2HNO_2 = CO_2 + N_2 + 3H_2O.$$

When alkaline sodium hypobromite (made by dissolving bromine in excess of cold caustic soda) is added to urea, about 93 per cent. of it is oxidised according to the following equation :—

$$CO(NH_2)_2 + 3NaOBr + 2NaOH = Na_2CO_3 + N_2 + 3H_2O + 3NaBr.$$

By collecting the nitrogen and applying the correction, the quantity of urea may be approximately estimated.

139. Properties.—Urea is a crystalline substance, resembling potassium nitrate in appearance, very soluble in water and alcohol. It is a weak *monacid* base. Of its salts the oxalate and nitrate, $CO(NH_2)_2HNO_3$, are well known; they are sparingly soluble in the free acids. All urea salts are hydrolysed considerably in solution. Urea also forms addition compounds with some oxides, and with certain salts such as sodium chloride. When it is heated, urea melts at 132° C., but it soon begins to decompose with evolution of much ammonia and some carbon dioxide. **Biuret** is left. This substance has the formula

$$H_2N-CO-NH-CO-NH_2.$$

$$NH_2CO.NHH + H_2N.CO.NH_2 \longrightarrow NH_2CO.NH.CONH_2$$

(when its solution, made alkaline with caustic potash, is treated with a little dilute blue vitriol, a characteristic red colour is produced). It melts at 190° C.: when heated more strongly it is converted, by loss of ammonia, into **Cyanuric acid.** This acid is a polymer of cyanic acid. The latter is usually produced by passing carbon dioxide over cyanuric acid heated to redness.

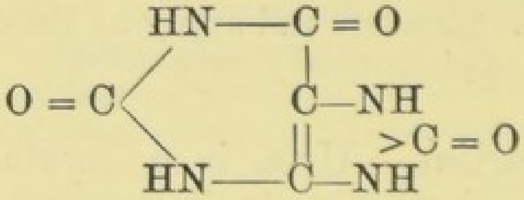
$$C_3H_3N_3O_3 = 3HCNO.$$

Cyanic acid, as we know, can be used for the synthesis of urea.

Cyanic acid can be condensed to a liquid, but when its temperature is allowed to rise above 0° C. it polymerises to cyamelide $(CNOH)_x$.

140. Uric Acid.—Uric acid is an excretion product of birds and reptiles ; the excrement of serpents is mainly ammonium urate. It also occurs to a slight extent in urine. It is very insoluble and may separate out in bladder stones, or in the joints, as in gouty patients, either as the free acid or as the acid sodium and ammonium salts. One fortieth of a gram dissolves in one litre of water. Two of its hydrogen atoms are replaceable by metals, but they are the hydrogen of imido groups, for uric acid is not a carboxylic acid.

It has been shown to have four imido (= NH) groups ; its relation to urea is represented in its accepted formula,



When it is dissolved in nitric acid, effervescence takes place. If the solution is evaporated to dryness a red powder is left. To this a drop of ammonia is added—purple colour—and then a drop of caustic soda—violet blue colour. This is the "murexide" test for uric acid.

QUESTIONS.—CHAPTER XVII.

1. Describe briefly the preparation and properties of the chief types of organic compounds containing nitrogen.

2. How may urea be prepared synthetically? Give a careful account of the chemical properties of urea, and mention the tests by which it can be identified.

3. Compare ammonia and ammonium iodide with the compounds which contain the methyl group in the place of all the hydrogen in these compounds. How are these methyl compounds obtained?

4. How is glycine obtained, and how is the existence of an amido group in this compound demonstrated?

5. Given chloroform describe the preparation from it of as many compounds as you can which contain only one atom of carbon per molecule.

6. Distinguish between amines and amides. Describe the chief properties of each class and show how they are related to other classes of organic compounds.

7. Attempt to define the terms "allotropy" and "isomerism" so that there shall be no confusion between them. Give illustrations, and amongst them include ammonium cynate and urea, and also oxygen and ozone.

8. There are two compounds of methyl of the formula C_2H_3NO called cyanate and isocyanate respectively. The latter on hydrolysis yields methylamine and carbon dioxide (compare carbylamine). Suggest distinctive structural formulae for these isomerides.

9. What reactions do primary amines undergo which the secondary and tertiary compounds do not?

10. Parallel with urea is thio-carbamide $CS(NH_2)_2$. Suggest a method of preparing it.

11. What methods of synthesis can you suggest for a substance of the formula $CH_2(NH_2).CH_2COOH$? What properties would you expect a body with such a constitution to possess?

CHAPTER XVIII.

THE CARBOHYDRATES.

141. The name Carbohydrate was given to certain compounds—such as cellulose, starch, and sugar—which are undoubtedly related, and whose formulae are generally expressed by $C_xH_{2y}O_y$. The name is still retained, but the group now includes some sugars which cannot be so represented; on the other hand there are compounds—such as Acetic acid and Lactic acid—whose formulae can be written $C_xH_{2y}O_y$ which are not included in the group. In this chapter we shall consider only the commonest carbohydrates.

142. Cellulose occurs very widely in the cell walls of plants. To its mechanical properties the rigidity and elasticity of plants are chiefly due. To these properties of cellulose also, together with its resistance to weathering agents, the usefulness of *wood* is due. *Linen*—from the fibres of the stem of flax—and *Cotton*—the hair of the seed—are used for clothing, etc.; both are nearly pure cellulose. From wood, linen, and cotton *paper* is made. In some plants—for instance the stone of the Date—cellulose is an important reserve food: when required for assimilation it is hydrolysed by the enzyme *Cytase*. Herbivorous animals digest cellulose. Concentrated sulphuric acid will char it, withdrawing the elements of water. This acid will also form sulphates with cellulose. These when brought into solution and boiled are completely converted into sugar, in most cases into glucose. The simplest formula for cellulose is $C_6H_{10}O_5$, but, since the molecular weight is unknown and is believed to be great, the formula is written $(C_6H_{10}O_5)_x$. Cellulose dissolves in an ammoniacal solution of copper sulphate; it is precipitated, unchanged, from the solution by acids.

Like glycerol, cellulose forms explosive nitrates. One, the so-called hexanitrate, to which the formula $C_{12}H_{14}O_4(NO_3)_6$ is arbitrarily given, is *gun cotton*; it is used for making smokeless powder, for instance in *cordite*. A lower nitrate is used as *collodion* for photographic plates, and, mixed with camphor, is called *celluloid*, a substance of which many articles are made; when brought near a flame it is often found to explode violently.

143. Starch, Inulin, and Glycogen are very nearly related. They all have the same formula as cellulose—$(C_6H_{10}O_5)_x$. **Glycogen** occurs in the muscles and livers of animals, probably as a reserve food; it is rapidly hydrolysed to Glucose. **Inulin** is found in the tubers of some Compositae, as well as in some Monocotyledons. It may be seen slowly crystallising in the cells of the Dahlia tuber when a slice of this is kept in alcohol under a microscope. It is hydrolysed completely by dilute acids to fructose, a sugar sweeter than glucose.

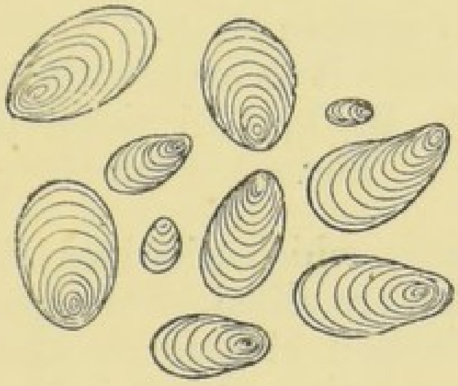


Fig. 26.

Starch from Potato × 200.

Fig. 27.

Starch from Wheat × 200.

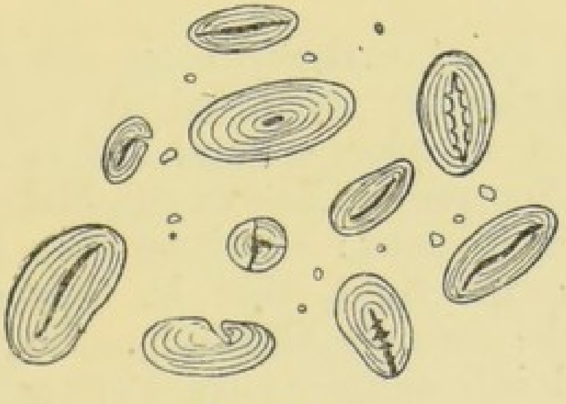


Fig. 28.

Starch from Pea × 200.

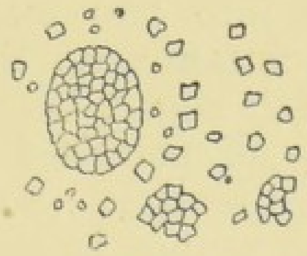


Fig. 29.

Starch from Oat × 200.

Starch occurs very widely in plants in small granules, which vary in size and shape according to the plant in which they are formed.* It is quite insoluble in cold water, but with boiling water it forms a colloidal solution, from which it is thrown down by alcohol. It forms, with iodine, a compound of a characteristic deep blue colour. This coloration is used as a test both for starch and for iodine; it is discharged by heating, but reappears on cooling.

When starch paste is treated with dilute acids for some time it is entirely converted into glucose (Exp. 1); under the influence of the enzyme diastase it is eventually converted into the sugar maltose, $C_{12}H_{22}O_{11}$. In either case intermediate products are formed. These are called

144. Dextrins, $C_6H_{10}O_5$, a name which signifies their influence on polarised light They are allied to the gums. Dextrin, prepared by the brief action of acid on starch, is used as an adhesive. It is formed when starch is heated to 200° C.: hence it occurs in bread crust; and as the gloss produced on starched linen by the action of the hot iron.

145. The Sugars.—The sweet carbohydrates are the sugars. Some, whose molecules are converted by hydrolysis into two molecules of simpler sugars, are called DISACCHAROSES. Such are Sucrose or Cane sugar, Maltose or Malt sugar, Lactose or Milk sugar: all three turn the plane of polarised light to the right, that is, they are dextro-rotatory: all have the formula $C_{12}H_{22}O_{11}$. Sugars which cannot be hydrolysed into simpler sugars are called MONO-SACCHAROSES. The most important are Glucose (dextro-gyrate) and Fructose (laevo-gyrate). To these may be added Mannose and Galactose. All four have the empirical formula $C_6H_{12}O_6$. Many of the sugars form *additive* compounds with certain mineral salts and oxides; compounds which in some cases serve to isolate and purify them. *Cane Sugar* is found in many plants, particularly

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* For a short account of starch as used for foods see *Second Stage Hygiene*, pp. 74 and 87.

in the sugar cane, sugar maple, and sugar beet. Its appearance and uses are too well known to need description. It can be made to crystallise from solution in fine large crystals. It is not attacked by *zymase*, but dilute acids and the enzyme *invertase* cause a rapid hydrolysis into equal parts of glucose and fructose (see Experiments 2 and 4).

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6.$$

Since fructose is more laevo-rotatory than glucose is dextro-rotatory the solution becomes progressively more laevo-rotatory as hydrolysis proceeds. Hence the process is called *inversion* ; a term which has now become general for analogous conversions.

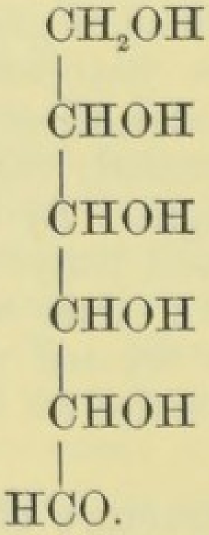
The change is of great service in many reactions. **Malt Sugar** is hydrolysed completely by *maltase* to Glucose. From solution it crystallises with one molecule of water of hydration; this is lost at 100° C. It differs from cane sugar in that it reduces alkaline copper solutions. **Milk Sugar** or Lactose is a hard, rather insoluble and not very sweet sugar, obtained by evaporating whey. Like Maltose it reduces alkaline copper solutions. By the lactic ferment it yields lactic acid. By dilute acids it is hydrolysed into glucose and the very similar galactose. **Glucose** occurs in many plants either free, dissolved in the cell sap (thus the name Grape Sugar), or in combination in the Glucosides—such as the Amygdalin of bitter almonds. It occurs in Honey, from which it gradually separates out in crystals. In the disease diabetes, when the tissues no longer oxidise carbohydrates, these appear in the urine as glucose. Glucose was formerly called Dextrose because of its action on polarised light. By the various ferments it is converted into Lactic and Butyric acids, or into Alcohol.

De Bruyn has shown that when either Mannose, Fructose, or Glucose is treated with very dilute alkali, a solution is obtained in which *all three* sugars occur.

146. Reactions and Structure of Glucose and Fructose.—Glucose is a reducing agent. It will reduce an alkaline solution of cupric oxide to cuprous oxide.

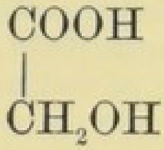
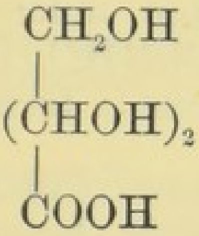
The concentration of a glucose solution can be determined quantitatively, either by using an excess of the reagent and weighing the dried cuprous oxide, or by adding the glucose drop by drop to a known quantity of the boiling Fehling's solution until this is just rendered colourless. Fehling's solution can be prepared in the following manner. Dissolve 160 grams of Rochelle salt in water, add a little carbolic acid (to prevent the growth of moulds), dilute to 500 c.c. and filter. Dissolve 75 grams of caustic soda and dilute to 500 c.c. Dissolve 51·96 grams of copper sulphate and make up to 500 c.c. When the titration is to be made (not before) mix exactly equal volumes of the three solutions thoroughly. 1 c.c. of the Fehling's solution is reduced by ·05 gram of glucose.

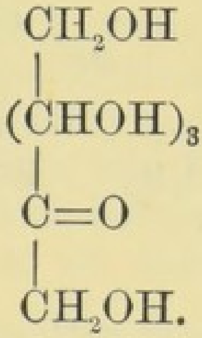
The glucose is oxidised in the process to gluconic acid, $C_6H_{12}O_7$, a monobasic acid *with the same number of carbon atoms* as the glucose. This, together with the fact that glucose forms a cyanide *by addition*, and that it reacts with hydroxylamine to yield an oxime, points to the possession by glucose of the aldehyde group. Upon reduction it yields the alcohol sorbitol, $C_6H_{14}O_6$, which is reduced to hexane, C_6H_{14}, by hydriodic acid. Sorbitol reacts with acetyl chloride to form a hexacetate, while glucose, in like circumstances, forms a pentacetate. Hence glucose must be a derivative of hexane with five alcoholic hydroxyl groups as well as the aldehyde group. In addition, with nitric acid as oxidiser glucose yields another acid—saccharic acid—$C_6H_{10}O_8$, so that it should contain the carbinol group $-CH_2OH$. These and other reactions of glucose have led to the structural formula



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ HCO. \end{array}$$

To Mannose the same formula is given, the two sugars being stereo-isomers.

Isomeric with glucose is *fructose*. This sugar also combines with hydrocyanic acid and reduces Fehling's solution, but by its oxidation not one but two acids are formed, both of which contain fewer than six carbon atoms. Therefore fructose should possess the ketone group, $=CO$. When mercuric oxide is the oxidiser glycollic  $\begin{array}{l}COOH\\ \vert\\ CH_2OH\end{array}$ and tri-hydroxy butyric  $\begin{array}{l}CH_2OH\\ \vert\\ (CHOH)_2\\ \vert\\ COOH\end{array}$ are the acids formed. Hence the formula



$$\begin{array}{l}CH_2OH\\ \vert\\ (CHOH)_3\\ \vert\\ C{=}O\\ \vert\\ CH_2OH.\end{array}$$

147. Aldoses and Ketoses.—All the mono-saccharoses are found to contain either the $-CHOH.CHO$ group, like glucose, or the $-CHOH.CO.CH_2OH$ group, like fructose. The former are called **ALDOSES** and the latter **KETOSES**. Sugars with six carbon atoms are called hexoses (aldhexoses or kethexoses) and so on.

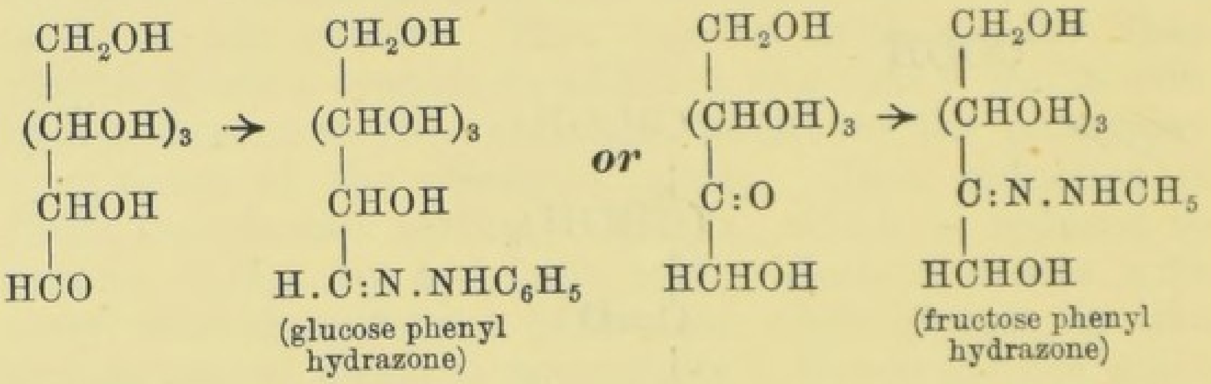
It may be noted that alternative formulae have also recently been suggested for these sugars.

148. Hydrazones and Osazones.—One of the most important reactions for the aldoses and ketoses was discovered by Emil Fischer, namely, the formation of HYDRAZONES and OSAZONES. The latter are usually yellow insoluble substances, with well defined melting points. They serve to identify sugars.

Exp. 37.—*Preparation of Phenyl-Glucosazone.* Dissolve about 1 gram of glucose in 10 c.c. of water. Dissolve rather more phenyl hydrazine in the necessary quantity of dilute acetic acid. Filter each solution and mix them thoroughly in a tube. Place the tube in a beaker of boiling water for about half an hour. Allow to cool. Wash and dry the precipitate and find its melting point.

[Instead of the acetate, phenyl hydrazine hydrochloride with twice its weight of sodium acetate may be used.]

When a sugar is treated with not too much phenyl hydrazine (the acetate in practice), $H_2N.NHC_6H_5$, a reaction occurs whereby the phenyl hydrazone is formed.

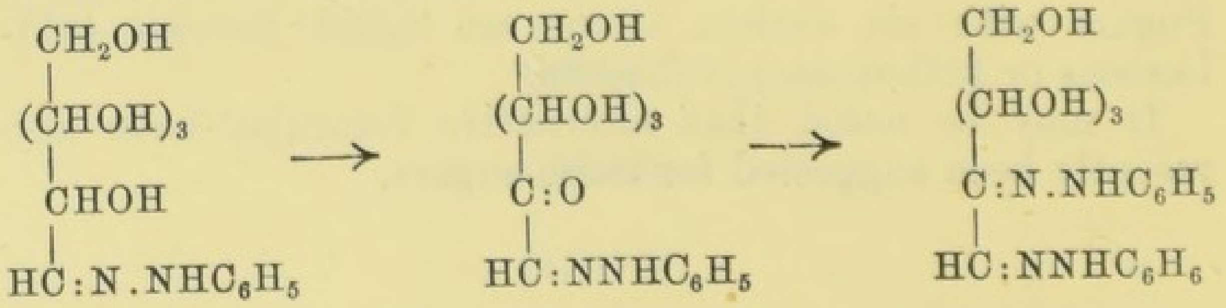


$$\begin{array}{c}CH_2OH\\|\\(CHOH)_3\\|\\CHOH\\|\\HCO\end{array}\rightarrow\begin{array}{c}CH_2OH\\|\\(CHOH)_3\\|\\CHOH\\|\\H.C:N.NHC_6H_5\end{array}\quad\text{or}\quad\begin{array}{c}CH_2OH\\|\\(CHOH)_3\\|\\C:O\\|\\HCHOH\end{array}\rightarrow\begin{array}{c}CH_2OH\\|\\(CHOH)_3\\|\\C:N.NHCH_5\\|\\HCHOH\end{array}$$

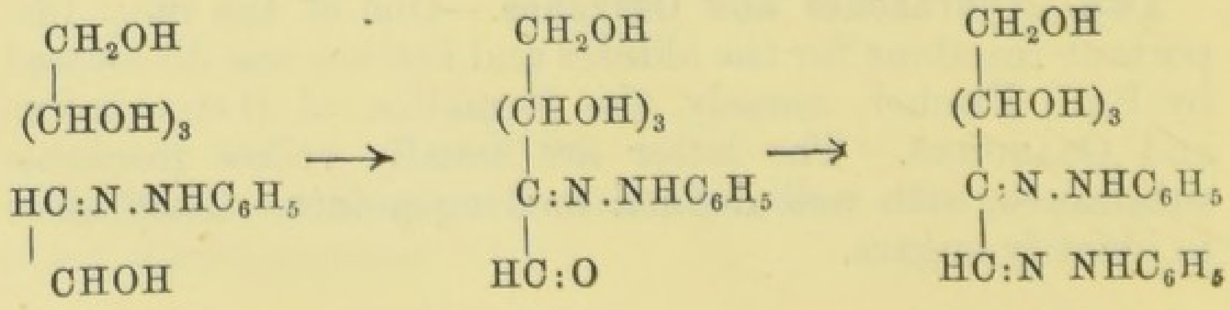
(glucose phenyl hydrazone)

(fructose phenyl hydrazone)

The hydrazones will react with excess of phenyl hydrazine to form the osazones. The formation is preceded by the oxidation of the hydrazone with production of a carbonyl group (the phenyl hydrazine being reduced to aniline and ammonia). This group reacts with a new quantity of the reagent.



$$\begin{array}{c}CH_2OH\\|\\(CHOH)_3\\|\\CHOH\\|\\HC:N.NHC_6H_5\end{array}\longrightarrow\begin{array}{c}CH_2OH\\|\\(CHOH)_3\\|\\C:O\\|\\HC:NNHC_6H_5\end{array}\longrightarrow\begin{array}{c}CH_2OH\\|\\(CHOH)_3\\|\\C:N.NHC_6H_5\\|\\HC:NNHC_6H_6\end{array}$$



$$\begin{array}{c}CH_2OH\\|\\(CHOH)_3\\HC:N.NHC_6H_5\\|\\CHOH\end{array}\longrightarrow\begin{array}{c}CH_2OH\\|\\(CHOH)_3\\|\\C:N.NHC_6H_5\\|\\HC:O\end{array}\longrightarrow\begin{array}{c}CH_2OH\\|\\(CHOH)_3\\|\\C:N.NHC_6H_5\\|\\HC:N\ NHC_6H_5\end{array}$$

Fructosazone and glucosazone are found to be identical (M.P. = 204° to 205° C.): therefore chemists conclude that the parts of their several molecules which are not affected by the reaction are identical in their space arrangement.

When an osazone is cautiously warmed with hydrochloric acid, two molecular proportions of phenyl hydrazine are disengaged and an OSONE is formed.

$$\mathrm{CH_2OH(CHOH)_3CO.CHO.}$$

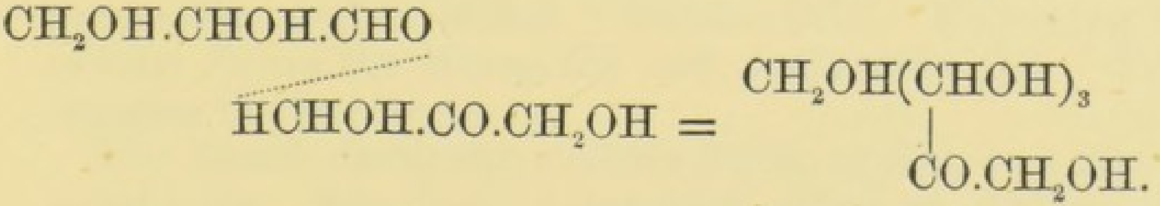
This on reduction yields fructose. Thus glucose can be converted into fructose.

149. Syntheses of Hexoses.—(i) By the careful oxidation of mannitol, which is found in many plants, mannose is formed; similarly sorbitol, from the same source, yields glucose. Fenton's reagent (hydrogen peroxide with a little ferrous iron salt) is commonly used.

(ii) *a. Glycollic aldehyde,* which has the essential structure of an aldose and which behaves like one, when treated with alkalis condenses to an inactive variety of fructose (also called i-acrose).

b. When glycerol is oxidised by Fenton's reagent, a sugar-like substance called *Glycerose* is obtained. This is a mixture of Glycerine aldehyde—an aldose—and dihydroxy acetone—a ketose. Suitably treated this suffers the "aldol" condensation to i-fructose.

The "aldol condensation" takes place, as indicated in the following equation, by the aldehyde combining with a compound so as to convert the aldehyde group into a secondary alcohol group.



$$\begin{array}{l}\mathrm{CH_2OH.CHOH.CHO} \\ \qquad\qquad \mathrm{HCHOH.CO.CH_2OH} = \begin{array}{l}\mathrm{CH_2OH(CHOH)_3} \\ \qquad | \\ \qquad \mathrm{CO.CH_2OH.}\end{array}\end{array}$$

c. When formic aldehyde is treated with Baryta or Limewater it is condensed to *Formose,* a mixture of sugars, one of which is i-fructose.

$$6\ \mathrm{H_2C{:}O} \longrightarrow \mathrm{CH_2OH(CHOH)_3C{:}O.CH_2OH.}$$

QUESTIONS.—CHAPTER XVIII.

1. Explain the meaning, in its widest sense, of hydrolysis. Illustrate your answer by giving as many types of hydrolysis as you can.

2. Write a short account of the different substances which may be obtained by the action of the more common ferments on sugar.

3. Illustrate the use of processes of oxidation and reduction in determining the constitution of organic substances.

PART III.

SOME AROMATIC COMPOUNDS.

CHAPTER XIX.

BENZENE AND THE PHENYL HALIDES.

150. Coal Tar.—When coal is heated in closed retorts, for instance in the manufacture of coal gas, in addition to the coke which remains in the retorts, and the illuminating gas which is stored in the gas holders, some volatile solids and liquids are formed, which collect in the condensers.

The product so obtained is called Coal Tar. It is a liquid of a pleasant odour, rendered black by fine particles of carbon, and is found to be a mixture of a large number of substances, some of which are of great importance in other industries. When coal tar is redistilled, about one and a half per cent. comes over at 150°-170° C. This fraction floats upon the water in which it is condensed and has received the name "*Light Oil.*" The next portion of the distillate sinks; the earlier part of this is collected separately, and is called "*Middle Oil.*" Following the middle oil are the *Heavy Oil* and *Anthracene Oil.* Pitch remains in the retorts.

The liquid distillates contain basic, acidic, and neutral substances. The basic substances—such as Aniline and Pyridine—(and any Olefines) are removed by shaking with cold concentrated sulphuric acid. The acid substances—of which the most important is Carbolic acid (carbo = coal, oleum = oil)—are removed by treatment with caustic soda. The residue, which contains the neutral bodies, is dried and submitted to fractional distillation. The complete separation of the mixture is accomplished in various ways.

From the Light Oil the hydrocarbons **Benzene**, C_6H_6, **Toluene**, C_7H_8, **Xylene**, C_8H_{10}, are obtained. The most important compounds in the middle oil are **Naphthalene**, $C_{10}H_8$ (4 per cent.), and Carbolic acid, or as chemists prefer to term it, **Phenol**, C_6H_6O. From the last of the distillate **Anthracene** (ἄνθραξ = coal), $C_{14}H_{10}$, is obtained.

151. Benzene.—From the light oil, Benzene is finally separated by the freezing method (compare Section 24). It is a colourless mobile liquid of a slight pleasant odour. It is the simplest of a series of hydrocarbons the lower members of which have likewise a pleasant smell: a property which has earned for them the title of the AROMATIC HYDROCARBONS. Benzene melts at 5·4° C., and boils at 80·5° C. It readily takes fire, burning with a luminous but very smoky flame. It will not mix with water, but is an excellent solvent for many other substances, especially organic compounds.

It owes its name to one of its earlier sources, namely Benzoic acid, which was originally obtained by distilling gum benzoin. From the point of view of a perfectly satisfactory nomenclature, this method of naming benzene was unfortunate.

Faraday discovered benzene in 1825 in cylinders of compressed coal gas. In 1870 Berthelot synthesised it by the polymerisation of Acetylene, C_2H_2. Its vapour density and its chemical properties require the formula C_6H_6.

152. Chemical Properties of Benzene.—Considering its method of synthesis and its formula C_6H_6, we should naturally suppose that benzene, in common with its isomeride dipropargyl (Section 74), would be an unsaturated hydrocarbon, one of the simpler members of a series perhaps. Its chemical behaviour, however, does not support this view.

It will not combine with cold concentrated sulphuric acid, and moreover, when, at higher temperatures, it does react with this reagent, it is by substitution, not by addition. Nor will it combine with the haloid acids; hydrochloric and hydrobromic acids are without action upon benzene, and although hydriodic acid will attack it when the two compounds are heated together for a long time, it is only to convert benzene into Hexa-hydrobenzene, C_6H_{12}, a compound which is not related to Hexane (C_6H_{14}). Even the halogens combine with benzene only under special conditions, and the products formed are not more stable than benzene, but less so. Thus when a mixture of benzene vapour and chlorine in excess is exposed to strong sunlight a crystalline compound of the formula $C_6H_6Cl_6$ is deposited, but when it is heated this compound readily undergoes a peculiar decomposition whereby a *substitution* product of benzene—trichlor-benzene—is formed.

$$C_6H_6Cl_6 = C_6H_3Cl_3 + 3HCl.$$

Bromine behaves similarly. In the most favourable circumstances the benzene molecule has never been induced to combine with more than six atoms of a halogen, whereas the dipropargyl molecule readily adds on eight to form a stable hexane derivative.

On the other hand, when chlorine or bromine is passed into heated benzene, reaction takes place readily enough, but the hydrocarbon behaves like a saturated paraffin, for the six hydrogen atoms in the molecule are successively *substituted* by the halogen.

Benzene is not readily oxidised—another difference from the unsaturated hydrocarbons.

153. The Phenyl Halides.—The halides of benzene formed by addition are practically unimportant. Those formed by substitution, however—the chlor-benzenes and brom-benzenes—have some uses.

The latter compounds may be prepared by the direct action of chlorine or bromine upon boiling benzene. The speed of halination is accelerated by the influence of a "carrier" such as the corresponding Ferric halide, or Iodine, or Iron, or Aluminium amalgam.

The student will remember that the halides of the paraffins are commonly employed in the preparation of a large number of other derivatives; amongst other substances they react with caustic alkalis, ammonia, potassium cyanide, and sodium. But, with the exception of sodium, these reagents are without effect upon the benzene derivatives, which are comparatively inactive. With sodium, however, they react readily and in a manner which recalls Wurtz' method for the synthesis of the paraffins. The parallel method applied to the aromatic compounds is called Fittig's synthesis.

When mono-brom-benzene, C_6H_5Br, or, to give it its other name, phenyl bromide, is heated with sodium, **Diphenyl**, $C_{12}H_{10}$, is formed.

$$2C_6H_5Br + 2Na = C_6H_5 . C_6H_5 + 2NaBr;$$

compare $$2C_2H_5Br + 2Na = C_2H_5 . C_2H_5 + 2NaBr.$$

When a mixture of phenyl bromide and an alkyl bromide is treated with sodium, the reaction takes place more readily, with the production of the alkyl-benzene. By this method it has been shown that synthetic methyl benzene, $C_6H_5 . CH_3$, is identical with the Toluene, C_7H_8, found in light oil and obtained from Tolu balsam by destructive distillation. In illustration of Fittig's reaction we will here describe the preparation of Ethyl benzene, $C_6H_5 . C_2H_5$, starting, however, with benzene itself.

Exp. 38.—*Preparation of Ethyl-Benzene.*

(i) Preparation of Phenyl Bromide (Cohen's method).

[In this process the carrier employed must be prepared immediately before use. A saturated solution of corrosive sublimate ($HgCl_2$) is poured upon narrow strips of thin clean aluminium foil. Leave one minute and then pour off the solution. *Rapidly* wash the foil well, first with water, then with alcohol, and lastly with a little benzene. Drop it at once into the reaction flask containing the benzene.]

For the next part of the experiment a dropping funnel should also be fitted at the top of condenser (Fig. 30); a double surface condenser is most convenient.

Fifty grams of benzene have been placed in the flask of Fig. 30. As soon as the carrier has been admitted and the apparatus joined up, 60 grams of bromine are added slowly, drop by drop, from the funnel. Hydrobromic acid is evolved and absorbed by the water in the trap. When all the bromine has been added, dilute caustic soda is poured in and shaken up with the reaction product. The alkali must be in excess. The lower layer is removed and dried over calcium chloride, and, when the mixture is clear, it is filtered. It is then distilled: the unattacked benzene comes over first; the phenyl bromide comes over at 140°-170° C. This is collected separately and redistilled, the portion which comes over at 150°-160° C. is preserved.

(ii) Fittig's reaction.

[In order that the reaction may be successful, dry ether, free from alcohol, must be used. To prepare it the commercial ether is shaken with about half its volume of water and separated in a funnel: this operation is repeated. The ether is then dried by a fairly large quantity of calcium chloride and filtered.]

To about 50 c.c. of this ether, contained in a ½-litre flask fitted with a reflux condenser, add 13 grams of sodium cut into thinnest slices, and leave it until no further action occurs between the sodium and the remaining water. Pour through the condenser a mixture of 30 grams of dry mono-brom-benzene and 30 grams of dry ethyl bromide. If the liquid begins to boil, cool it. Leave the flask in cold water over night (empty condenser). Decant from the solid and wash out with a little ether. [Put the flask in a convenient place out of doors so that the excess of sodium may be rendered harmless by throwing water on it from a safe distance.] Distil off the ether on a water bath. Fractionate the remainder with a pear-still-head. Ethyl benzene boils at 134° C.

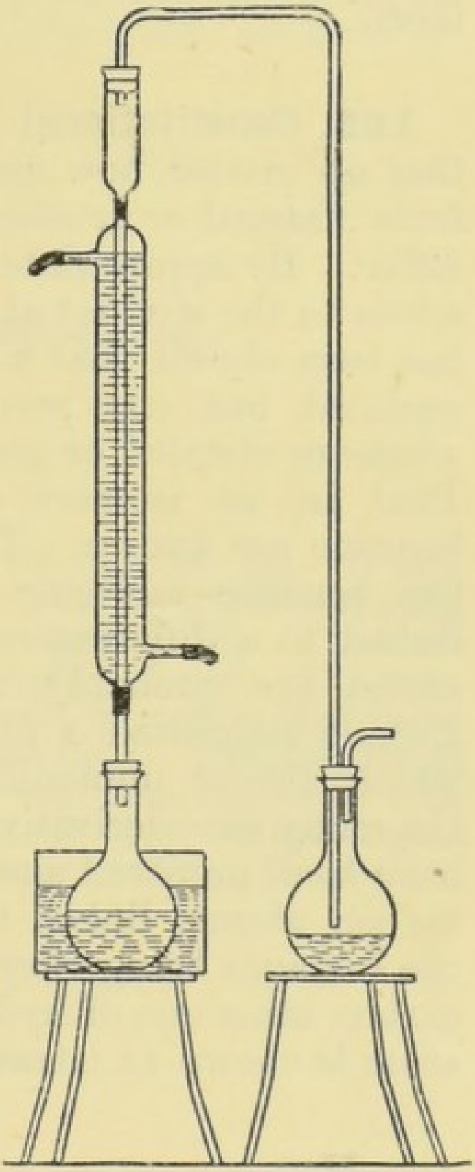
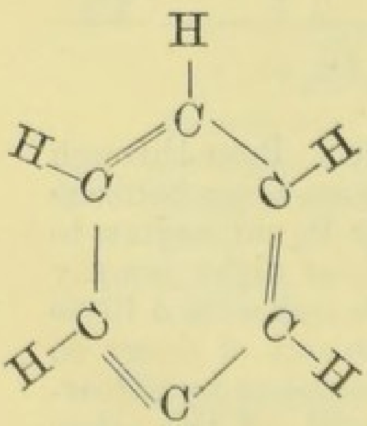
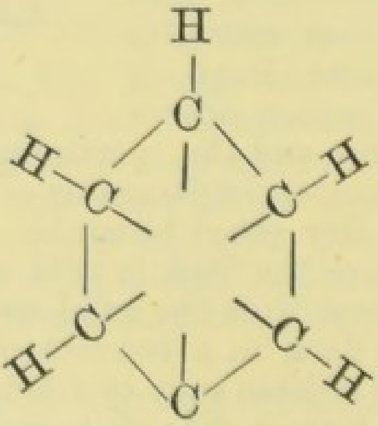


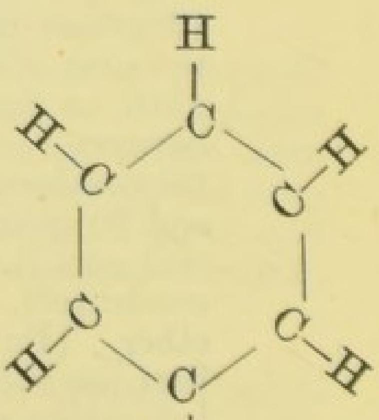
Fig. 30.

154. Methyl and ethyl benzenes are homologues of benzene. In them the phenyl portion (C_6H_5) is called the "**nucleus,**" the alkyl portion is called the "**side chain.**" These terms have reference to the accepted structural formulae of the homologues of benzene and their derivatives.

155. Constitutional Formula of Benzene.—It is found that no matter how methyl benzene is prepared, whether from natural or artificial compounds, the products do not differ. By appropriate methods, which may suggest themselves to the student at a later stage (Chapter XXIII.), it has been shown that whichever of the hydrogen atoms is replaced but one product is formed. And this is true whatever element or group substitutes the hydrogen atom. That is, no isomers of mono-substitution products of benzene are known. Therefore chemists conclude that in the benzene molecule each hydrogen atom is directly linked to a different carbon atom, and that the carbon atoms are probably not arranged in an open chain. Kekulé suggested a formula, which bears his name, and which, almost unmodified, has been found to illustrate all the many new derivatives, some of great complexity, which have been prepared since it was devised. He arranged the carbon atoms, linked together in a closed chain or ring, the linkages being alternately single and double. To each carbon atom one of hydrogen is linked. Thus each carbon atom is shown as tetravalent. This method of writing the

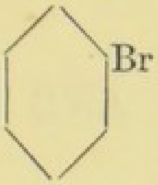




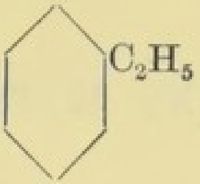


linkages is not free from objection,* and it is now more usual either to write the fourth valency directed to the centre of the ring (Armstrong's modification), or, neglecting it altogether, to leave the question of valency open.

When the formula is written, the carbon and hydrogen atoms are "understood," and only side chain or halogen, etc., are filled in: thus



and



represent in writing brom-benzene and ethyl-benzene.

SUMMARY.

Benzene is obtained from the Light Oil of Coal Tar. It is a hydrocarbon of the formula C_6H_6 which, while it can form addition products, forms substitution derivatives more readily. These are characteristic of it. The radicle C_6H_5 is called Phenyl. This term is derived from Phenol, the Carbolic acid formed in the manufacture of illuminating gas (φαινειν = to give light). The substituted halides of benzene are inactive. They will, however, react with sodium and the alkyl halides (Fittig's reaction) to form homologues of benzene. Such is Toluene or methyl benzene, C_7H_8. Benzene has been given Kekulé's cyclic formula.

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* The chief objection seems to have been removed. See *Annual Reports on the Progress of Chemistry for* 1907 issued by the Chemical Society.

CHAPTER XX.

REACTIONS WITH SULPHURIC AND NITRIC ACIDS.

PHENOL.

156. Action of Sulphuric Acid.—As we have said above, concentrated sulphuric acid and benzene will not react in the cold, but at higher temperature reaction readily takes place. The benzene gradually disappears as such, and a strongly acid body is formed which is very soluble in alcohol and water. It forms stable salts, whose composition shows that we are dealing with a monobasic acid. It reacts with phosphorus chloride with the substitution of chlorine for hydroxyl. It is given the formula

$$C_6H_5.SO_2(OH),$$

and is called **Benzene Sulphonic acid.** In its formation, hydrogen from benzene and hydroxyl from sulphuric acid yield water, and the residues unite. The process is called ***"sulphonation."***

$$C_6H_5.H + (HO)_2SO_2 = C_6H_5(HO)SO_2 + HOH.$$

The properties of this body are such that it is not regarded as a sulphite, but the formula is commonly written $C_6H_5.HSO_3$. It is stable in solution, but, when mixed with concentrated sulphuric acid and treated with steam, the reverse process takes place.

$$C_6H_5.SO_2OH + HOH = C_6H_5H + H_2SO_4.$$

157. The alkali benzene sulphonates and the corresponding calcium salts are soluble in water. They are stable in solution. When they are fused with the caustic alkalis they are converted into *Phenol*, C_6H_6O.

Exp. 39.—*Preparation of Phenol from Benzene.*

(i) Preparation of Sodium Benzene-sulphonate.

Pour a mixture of 30 c.c. of benzene and 60 c.c. of concentrated sulphuric acid into a round-bottomed 300 c.c. flask, fitted with an upright condenser. Keep the mixture just boiling until the benzene has disappeared as such. This will take several hours: if fuming sulphuric acid were used at 0° C. the reaction would be complete in a few minutes. When reaction is complete add the liquid drop by drop to four times its volume of saturated brine. The brine is kept at 0° C. by surrounding the beaker with ice and stirring it throughout the reaction. If crystals do not soon separate, induce them to do so by adding to the solution some which have been formed by more strongly cooling a little of the liquor contained in a test tube. Filter at the pump and recrystallise from alcohol.

$$C_6H_5SO_2(OH) + NaCl = C_6H_5SO_2(ONa) + HCl.$$

(ii) Preparation of the Phenol.

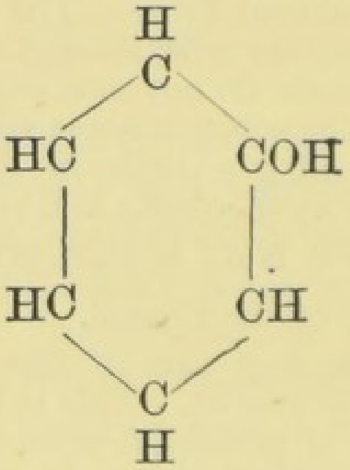
[Throughout the first part of this experiment the mixture must be constantly stirred. This is best done with a thermometer whose bulb is protected from the potash by a glass or steel tube closed at the lower end.]

In a nickel dish or large crucible dissolve 40 grams of caustic *potash* in the least quantity—about 6 c.c.—of water, heating it to 250° C. Still maintaining this temperature, add gradually 20 grams of the powdered sodium benzene sulphonate—dried at 110° C. After an hour, cool; dissolve the product in a little water and acidify with concentrated hydrochloric acid. Some of the phenol separates out as a yellow oil. Extract this with its own volume of ether in three equal lots. Dry the extracted solution with potassium carbonate and distil off the ether over a water bath. Collect the distillate (air condenser) coming over at 175°-185° C.

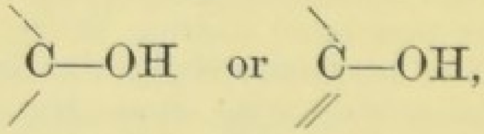
$$C_6H_5SO_2ONa + NaOH = C_6H_6O + Na_2SO_3.$$

158. Phenol is a colourless, crystalline body, which melts at 43° C. and boils at 181° C. It is very corrosive to some materials and very poisonous. It is used largely as an antiseptic and deodoriser. It is not very soluble in water. It is called Carbolic acid on account of its slightly acidic property. This is very slight, however, for although it will react with caustic alkalis to produce the corresponding "phenates," these are decomposed even by carbon dioxide. We need not be surprised, therefore, that phenol will not react with alkali carbonates nor, when pure, will change the colour of blue litmus.

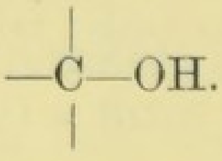
Constitution of Phenol.—When treated with phosphorus pentachloride, phenol yields phenyl chloride: it is clear, therefore, that phenol has the phenyl nucleus and that one hydrogen atom of benzene is replaced by hydroxyl; that is to say, phenol is phenyl hydroxide.



In this formula we have the group



which to some extent recalls the tertiary alcohol group



$$—\overset{|}{\underset{|}{C}}—OH.$$

Phenol gives some feeble evidence of alcoholic character. It will not react with haloid acids, but with acetic anhydride it yields the *ester* phenyl-acetate, $CH_3COOC_6H_5$; with the alkyl halides sodium phenate yields *ethers*, $C_6H_5.O.C_6H_5$ and $C_6H_5O.CH_3$. The methyl-phenyl ether is known as anisol.

159. Note on Nomenclature.—The radicle of phenol, C_6H_5', as we have mentioned above, is called phenyl. It bears to benzene the same relation that methyl bears to methane. The student's attention is called to this peculiar nomenclature, which is not uncommonly confusing to beginners. The name Benzene is derived from Benzoic acid, as we have mentioned above. There are also radicles known as Benzyl, Benzal, and Benzoyl, quite different from Phenyl. Benzene itself is known as Benzol in commerce (the German name for Benzene is spelt in the same way), a term which might easily be mistaken for a synonym for Phenol. In addition there are aromatic substances known as Benzil and Benzoïn. And we may add that Benz*i*ne (or Benzoline) is a trade name given to certain mixtures of paraffins of low boiling point, which contain little or no benz*e*ne. The French word for benzene is written Benz*i*ne.

160. Action of Nitric Acid.—Benzene is readily attacked by concentrated nitric acid. The reaction is quite analogous to that with sulphuric acid, just described. But since nitric acid possesses but one hydroxyl group per molecule, it is not surprising that the product of the reaction is a neutral substance. It is called Nitro-benzene, and the process is called ***"nitration."***

$$C_6H_5H + (HO)NO_2 = C_6H_5.NO_2 + H_2O.$$

161. Nitro-benzene is parallel with the nitro-paraffins, and this direct method of formation recalls that mentioned in Section 119. It is a heavy yellow substance, which melts at 5° C. and boils at 209° C. It has an odour resembling that of bitter almond oil. Its vapour is poisonous. It is not soluble in water. It is manufactured in large quantities for the preparation of aniline dyes.

Since nitric acid will replace one or more than one hydrogen equivalent by the nitro group, according to the conditions of its concentration and the temperature of the reaction mixture, the student must pay careful attention to these details. The preparation of di-nitrobenzene will be described in Chapter XXIV.

Exp. 40.—*Preparation of Nitro-benzene.*

[In this preparation the reaction mixture must be shaken continually until the heating is begun, and then occasionally.]

Add gradually 48 c.c. of concentrated nitric acid to 60 c.c. of concentrated sulphuric acid. Add slowly to the mixed acids 38 c.c. of benzene, keeping the temperature below 50° C. by immersing the flask in water from time to time. Now fit the flask with a vertical air condenser, and heat on the water bath for half an hour. Allow to cool; the nitro-benzene which floats *on* the excess of acids is separated in a funnel. Shake it with water; it will now sink. Wash it once or twice with water in the same way, then place it in a dry flask with solid calcium chloride and leave till clear. Pour from the solid into a dry fractionating flask and distil (dry air condenser). The nitro-benzene comes over about 200°-207°C.

QUESTIONS.—CHAPTERS XIX. AND XX.

1. What do you think of the statement that the distinction between organic chemistry and inorganic chemistry is only of historical importance?

2. Write the structural formulae for (*a*) diphenyl, (*b*) propyl benzene.

3. Is phenol an alcohol? Compare, in a table, its properties with those of ethyl alcohol.

4. Can you construct a "space" formula for benzene?

CHAPTER XXI.

ANILINE AND PRODUCTS OF DIAZOTISATION.

162. Reduction of Nitro-benzene.—Just as the nitro-paraffins when treated with "nascent" hydrogen are converted into alkylamines, so nitro-benzene is converted into amino-benzene (phenylamine).

$$C_6H_5NO_2 + 6H = C_6H_5NH_2 + 2H_2O.$$

Phenylamine is called Aniline, because it was first obtained from the natural dye Indigo (*Portuguese* Anil). It occurs free in coal tar, from which it may be isolated, but the chief source is nitro-benzene, and therefore eventually benzene itself. Commercially the nitro-benzene is reduced by ferrous salts in the presence of excess of iron, but the change can also be effected by the hydrogen liberated in electrolysis (see Perkin's *Practical Methods of Electro-Chemistry*). In the laboratory it is found more convenient to employ granulated tin and hydrochloric acid. The operations should readily be understood if the student bears in mind that he is preparing an amine.

Exp. 41.—*Preparation of Aniline.* Place 50 grams of nitro-benzene and 90 grams of granulated tin in a large flask provided with a long upright air condenser. Warm the flask and then add 200 c.c. of concentrated hydrochloric acid, beginning with about 5 c.c. and gradually increasing the amounts, waiting each time for the action to moderate. Then heat the mixture on the water bath for about one hour—until the odour of nitro-benzene is no longer evident. To the warm mixture (it solidifies when cold) add 100 c.c. of water and follow this with a solution of 150 grams of caustic soda in 200 c.c. of water. [This is to decompose a compound of the formula* $(C_6H_5NH_2HCl)_2SnCl_4, 2H_2O$, which is the product of the earlier

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* Compare the compound $(NH_4)_2SnCl_6$.

reaction.] If boiling threatens at this stage, prevent it by immersing the flask in cold water.

Now distil with steam * (see Exp. 29a) and collect the distillate as long as this is milky, and perhaps a little of the clear distillate. Salt out the aniline by adding finely-powdered salt, shaking till a saturated solution is obtained. Extract with ether; dry the ethereal solution with solid caustic potash; † distil off the ether on the water bath; and then, with empty condenser, drive over the aniline.

163. Aniline, when pure, is a colourless oily liquid, having an odour which is easily recognised. It boils at 183° C. and melts at − 8° C. It darkens when exposed to air and light.

It is very interesting to compare the properties of aniline with those of the primary alkylamines discussed in Parts I. and II. In the first place, it is but slightly soluble in water, and its solution barely affects litmus. It readily forms salts by addition with the stronger acids. But these are acidic in solution; that is, unlike ammonium salts, they are hydrolysed in solution, for aniline is a *weaker* base than ammonia. Ammonia is displaced from ammonium salts by aniline: this is due to the greater volatility ‡ of the former compound. The hydrochloride of aniline, $C_6H_5NH_3Cl$, has been used in Exp. 41. It is soluble in water: it readily forms the chloroplatinate $(C_6H_5NH_3)_2PtCl_6$. The sulphate $(C_6H_5NH_3)_2SO_4$ is formed when aniline is poured into the somewhat diluted acid.

164. Acetanilide.—Like other primary amines, aniline reacts with acetyl chloride to form an acetyl compound. This is called **Acetanilide.** It is used under the name of Antifebrine for lowering the temperature in cases of fever. A derivative of it, Phenacetin, is even more commonly used for this purpose. Acetanilide forms fine white crystals, M.P. = 112°. These are but slightly soluble in

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* Notice that since the vapour pressures of steam and aniline together equal that of the barometer, the aniline is being distilled at lower temperature and pressure than if it were distilled under ordinary conditions.

† Calcium chloride cannot be used since it combines with aniline compare ammonia).

‡ *Inorganic Chemistry*, page 256.

water. It is prepared on the large scale by a method very easily managed in the laboratory. Equal volumes of glacial acetic acid and aniline are boiled in a flask (inverted air condenser) for several hours. The product is distilled, the acetanilide passing over above 280° C. It is dissolved in hot water, filtered, and the filtrate allowed to cool.

$$C_6H_5NH_2 + CH_3COCl = C_6H_5NHCOCH_3 + HCl.$$

165. Secondary and Tertiary Amines.—Since ammonia does not react with brom-benzene, this method cannot be employed for the preparation of secondary and tertiary bases. These are well known, however. **Diphenyl-amine,** $(C_6H_5)_2NH$, is formed when aniline is treated with its own hydrochloride. This compound, like aniline, is largely used in the dye industry. Another typical secondary amine is methyl aniline, $C_6H_5NH.CH_3$.

166. Azoxy-benzene, etc.—Aniline is readily oxidised. Unless it is quite pure, the addition of bleaching powder produces a violet colouration: this is used as a very delicate test for aniline. Persulphates oxidise it to nitro-benzene again. Several intermediate compounds are known. They are very easily prepared by the successive use of gentle reducing agents upon nitro-benzene; thus alcoholic sodium methoxide reduces nitro-benzene to **Azoxy-benzene** $(C_6H_5N)_2O$; this is converted by "reduced" iron into **Azo-benzene** $(C_6H_5N)_2$; caustic soda with zinc dust reduce azo-benzene to **Hydrazo-benzene** $(C_6H_5NH)_2$. Other intermediate products are known also.

167. Replacement of the Amine Group by Hydroxyl.—One of the most important reactions of primary alkyl-amines is that which they undergo with nitrous acid. The same change takes place very readily with aniline, which is converted in this way into phenol.

$$C_6H_5NH_2 + HO.NO = C_6H_5OH + N_2 + H_2O.$$

To an ice-cold solution of aniline hydrochloride in excess of acid, a solution of sodium nitrite is added until the liberated nitrous acid is seen to be in excess. This point is indicated by starch iodide paper.* No *apparent* action takes place, since no nitrogen is evolved, but when the solution is heated to 40°-50° C. nitrogen appears and phenol is formed. The latter is distilled over with steam, and extracted with chloroform.

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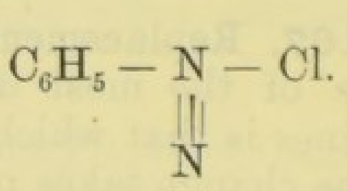
* *Non-Metals*, p. 273; *Inorganic Chemistry*, p. 293.

168. Diazo-benzene Compounds.—In 1860 P. Greiss showed that when aniline salts are treated with nitrous acid at low temperatures substances are formed which react with hot water to form phenol, nitrogen, and the free acid. These substances may be isolated quite easily, by treating the ice-cold solution of the aniline salt, either with the anhydride of nitrous acid (N_2O_3) or with amyl nitrite ($C_5H_{11}NO_2$) in an excess of acid solution. When alcohol is added these bodies are precipitated in the crystalline state. Generally they are explosive when dry, but quite harmless in solution. The chloride has the formula, $C_6H_5N_2Cl$, and the sulphate, $C_6H_5N_2HSO_4$. These bodies are called Diazo-benzene Chloride and Diazo-benzene Sulphate respectively. With chloroplatinic acid they yield a chloroplatinate of the formula $(C_6H_5N_2)_2PtCl_6$. When the chloride in solution is treated with silver (hydr)oxide, silver chloride is precipitated and a strongly alkaline solution remains which contains an hydroxide of the formula $C_6H_5N_2OH$.

The reactions of this base resemble those of ammonium hydroxide, for which reason it is called **Benzene diazonium hydroxide**.

Opinions differ as to the suitability of certain structural formulae for these compounds. Thus for diazo-benzene chloride some chemists incline to

$C_6H_5 - N = N - Cl$, and others to  $C_6H_5 - \underset{\underset{N}{|||}}{N} - Cl$.

We cannot discuss here the arguments urged in their favour.

169. Reactions of Diazo Compounds.—The salts are of immense importance in practice because of the variety of their reactions. And since these reactions take place readily in solution, and because, in addition, there is no necessity to isolate the diazo compounds, the preparation of comparatively complex substances is in practice simple. For example, the reaction is of supreme importance in the azo-dye industry.

We shall give here a selection of examples.

(i) When the solution of a diazo salt is warmed—in some cases when this is left standing—the hydroxyl group is introduced into the nucleus (Section 167)

$$C_6H_5N_2HSO_4 + HOH = C_6H_5OH + H_2SO_4 + N_2.$$

(ii) When the solution of a diazo salt in alcohol is warmed, either the alcohol acts as a substituted water to yield an ether,

$$C_6H_5N_2.HSO_4 + HOC_2H_5 = C_6H_5.O.C_2H_5 + H_2SO_4 + N_2,$$

or, under certain conditions, it acts as a reducing agent, hydrogen entering the nucleus.

$$C_6H_5N_2HSO_4 + HOC_2H_5 = C_6H_5H + H_2SO_4 + N_2 + CH_3CHO.$$

(iii *a*) When the solution of the diazo salt is warmed with potassium iodide solution, phenyl iodide separates out.

$$C_6H_5N_2Cl + KI = C_6H_5N_2I + KCl$$
$$C_6H_5N_2I = C_6H_5I + N_2.$$

This reaction is of special importance, for iodine will not by itself attack benzene.

As this preparation admirably illustrates the process of "***diazotisation***," we will describe it here. The student should not fail to carry out the reaction.

Exp. 42.—*Diazotisation of Aniline.* Dissolve 10 grams of aniline in 200 c.c. of dilute hydrochloric acid (1 in 4), and cool the solution with ice. To the cold solution add, little by little, a solution of sodium nitrite (1 part in 5 parts of water) containing about 8 grams of this salt, until the required quantity has been added.

[During the addition of the nitrite the temperature is kept low by adding occasionally to the reaction mixture a piece of ice.]

After each small addition of nitrite solution, wait a short time, and then take one drop of the reaction mixture, dilute it, and bring a drop on to starch iodide paper. Provided sufficient acid is present, the reaction is complete when a blue colour is produced on the test paper by a drop of the solution when this has stood for five minutes.]

Now add to the cold solution in a 500 c.c. flask, a solution of 25 grams of potassium iodide in 50 c.c. of water. Keep the mixture cool and allow to stand for some hours. Now heat gently on a water bath until no more nitrogen is evolved.

Neutralise the excess of acid and make the solution alkaline with caustic soda; distil the phenyl iodide with steam. Separate in a funnel; dry with calcium chloride; and redistil. Iodo-benzene boils at 189° C.

(iii *b*) In a similar way the chloride and bromide may be made to replace the amino group, but the reaction is not nearly so readily accomplished. In practice **Sandmeyer's method** is employed. When the chloride is to be formed, the diazotised solution is poured into a hydrochloric acid solution of cuprous chloride; for the bromide a hydrobromic acid solution of cuprous bromide.

Not only is this method suitable for the introduction of halogens into the nucleus, it is also very convenient for the preparation of cyanides. For this purpose cuprous cyanide dissolved in potassium cyanide is used. [See Gattermann, p. 221, and Cohen's *Practical Organic Chemistry*, p. 146.]

(iv) When diazobenzene chloride is treated with the required quantity of stannous chloride in acid solution, the hydrochloride of **Phenyl hydrazine** is formed.

$$2SnCl_2 + 4HCl = 2SnCl_4 + 4H.$$

$$C_6H_5N.NCl + 4H = C_6H_5NH.NH_2.HCl.$$

Exp. 43.—*Preparation of Phenyl Hydrazine.*

[To diazotise, follow the directions of Exp. 42. Use 10 grams of aniline distilled afresh; shake it with 25 c.c. concentrated hydrochloric acid diluted to 100 c.c. with water. Use 10 grams of sodium nitrite in 50 c.c. of water.]

Saturate the diazo-benzene chloride solution with 30 grams of well powdered common salt; pour from the residue. Treat the ice-cold liquid with an ice-cold solution of 60 grams of crystallised stannous chloride in 20 c.c. of concentrated hydrochloric acid. The white crystalline phenyl hydrazine hydrochloride separates out. Allow it to stand for several hours (cold); filter by suction; wash with a little saturated brine; press out on a porous plate; remove it to a flask and add an excess of caustic soda. The oily base separates out: extract it with ether; dry the ethereal solution with solid potassium carbonate; distil off the ether on a water bath.

[The product can only be purified further by distillation at a low temperature; this is done under reduced pressure; we shall not describe this method here.]

170. Phenyl hydrazine is a colourless oil which turns brown in air. Its solid melts at 17·5° C. and the oil boils at 241° C. It dissolves sparingly in water. Its value in the study of the sugars, with which it forms hydrazones and osazones, has already been considered (Section 148). As a base it forms well defined salts.

SUMMARY.

Nitro-benzene is easily reduced to amino-benzene or aniline. This amine reacts with nitrous acid to yield "diazo" compounds, from which a large number of derivatives of benzene are readily obtained.

QUESTIONS.—CHAPTER XXI.

1. Aniline is easily purified by distillation in a current of steam, though its boiling point is 184° C. Explain clearly what occurs in the process. Would it be possible or convenient to substitute a current of hydrogen for the steam?

2. How may a hydrogen equivalent in (*a*) methane, (*b*) benzene, be replaced by the OH, CH_3, NH_2, NO_2, COOH groups? Point out any differences in the chemical behaviour of the compounds when the groups are associated with the methyl and phenyl residue respectively.

3. Describe exactly how you would set to work to prepare a solution of diazo-benzene chloride. By what experiments would you demonstrate the chief properties of this solution?

4. How is phenyl-hydrazine prepared? Describe its principal properties and its action on aldehydes and ketones. Of what is it the derivative?

5. Compare the properties of ammonia, phosphine, and aniline in order to illustrate (*a*) the effect of *substitution*, (*b*) the term *compound radicle*, (*c*) the term amine.

6. What reaction would you expect to take place when you treat aniline with chloroform and excess of potash? If you attempt it, do so out of doors and with very small quantities.

7. Give the structural formulae for Azobenzene, Azoxybenzene, and Hydrazobenzene, and for diphenylamine.

CHAPTER XXII.

SOME OXIDATION PRODUCTS OF TOLUENE.

171. **Toluene** is now obtained from coal tar; it was once prepared by distilling the balsam of Tolu, from which it obtained its name. It is a colourless liquid of a pleasant odour. It boils at 110° C.; it is not easily solidified.

Its formula, $C_6H_5.CH_3$, follows from Fittig's synthesis (Section 153). Another synthetic method is that due to Friedel and Crafts. This reaction is remarkable for the fact that the hydrocarbon itself is caused to react with the alkyl halide, under the catalytic influence of anhydrous aluminium chloride.

$$C_6H_5H + BrCH_3 = C_6H_5.CH_3 + HBr.$$

The reaction does not cease with the production of mono-methyl-benzene, for some di and tri derivatives are also formed. The method is more usefully employed for preparing other bodies such as aromatic ketones, where the acid halide is used instead of the alkyl halide.

172. **Substitution Derivatives of Toluene.**—Like Benzene, Toluene reacts with Nitric and Sulphuric acids, with substitution of hydrogen in the nucleus by the sulphonic and nitro groups. Like Benzene too, it forms substitution products with Chlorine and Bromine, but in this case *two* classes of halides are formed—those in which the Halogen enters the nucleus and those in which it enters the side chain.

The former are called chlor- or brom-toluenes: like the chlor-benzenes they are comparatively inactive; they have a faint but pleasant odour. They are formed by passing chlorine into, or adding bromine to, Toluene

(1) at a low temperature,

(2) in the presence of a carrier,

(3) in poor light, better still in dark.

But the halogen enters the side chain when it reacts with Toluene

(1) at a high temperature (boiling point)

(2) in the absence of a carrier, and

(3) most important of all, in good light, best in sunlight.

The substitution of the hydrogen atoms is successive, although no one pure product is formed. When bromine is used, the proper amounts of bromine and toluene are weighed out and mixed (compare Experiment 38 (i), p. 156); but when chlorine is used the desired product is obtained when the toluene has increased to the weight demanded by the equation. The operation is described in Experiment 44.

$$C_6H_5CH_3 + Cl_2 = C_6H_5CH_2Cl + HCl.$$

Unlike the chlor-toluenes these products have a strong irritant effect; when preparing them great care must be taken to avoid contact with the hands and to prevent the fumes reaching the eyes.

They are named

Benz*yl* chloride, $C_6H_5CH_2Cl$, B.P. 179° C.,

Benz*al* chloride, $C_6H_5CHCl_2$, B.P. 206° C.,

and Benzotrichloride, $C_6H_5CCl_3$, B.P. 213° C. respectively.

Exp. 44.—*Preparation of Benzyl Chloride.* Pour 100 grams of Toluene into a weighed retort fitted with a condenser sloping upward (Fig. 31). Arrange for escaping chlorine to be absorbed, and expose the apparatus to sunlight if possible.

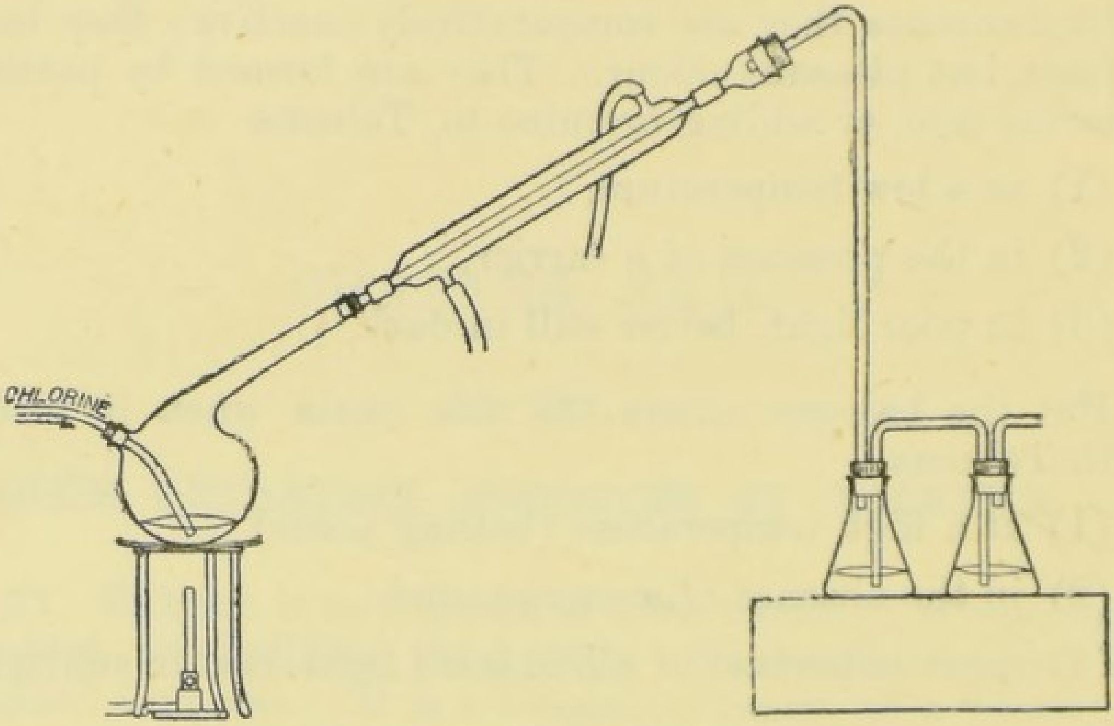


Fig. 31.—PREPARATION OF BENZYL CHLORIDE.

Pass *dry* chlorine through the tubulure into the gently boiling toluene until this gains 37 grams in weight. Transfer the product to a distilling flask, and collect the fraction at 166° to 190° C. Redistil with a still-head and collect fraction at 176° to 180° C.

173. Benzyl Alcohol, $C_6H_5.CH_2OH$, can be obtained by treating benzyl chloride at the boiling point for several hours with a solution of potassium carbonate.

$$2C_6H_5.CH_2Cl + K_2CO_3 + H_2O$$
$$= 2C_6H_5.CH_2OH + 2KCl + CO_2.$$

The product is extracted with ether, and dried with solid potassium carbonate. It is a colourless liquid, boiling at 204° C., moderately soluble in water. As we might predict from its formula, it behaves like a primary alcohol. Its differences from phenol are strongly marked. It reacts readily with hydrochloric acid, even without the assistance of a dehydrating agent, to reform benzyl chloride. It is very readily oxidised by dilute nitric acid, etc., to

174. Benzaldehyde, $C_6H_5.CHO$.—This important compound is prepared on a large scale by the action of limewater on Benzal chloride (compare Section 22)

$$C_6H_5CHCl_2 + Ca(OH)_2 = C_6H_5CHO + CaCl_2 + H_2O.$$

But it is convenient, in the laboratory, to prepare it from the alcohol, which, however, is not isolated. Benzyl chloride is treated with a solution of copper nitrate at the boiling point (reflux condenser), the oxides of nitrogen being expelled by a constant current of carbon dioxide before they can exert a further oxidising action. The alcohol is first produced by hydrolysis and then oxidised. The product is extracted from the mixture by ether, and separated from impurities by causing it to form the sodium hydrogen sulphite compound.

Benzaldehyde occurs naturally in the glucoside Amygdalin, from which it may be obtained by the hydrolysing action of dilute sulphuric acid, or by that of the ferment *Emulsin*, which also occurs in the cells of the bitter almond.

$$\underset{\text{(amygdalin)}}{C_{20}H_{27}O_{11}N} + 2H_2O = C_6H_5.CHO + \underset{\text{(glucose)}}{2C_6H_{12}O_6} + HCN.$$

Benzaldehyde resembles in its behaviour the aliphatic aldehydes. It readily combines with sodium hydrogen sulphite and with hydrocyanic acid; but with ammonia it behaves quite differently: water and a condensation product being formed.

Benzaldehyde forms many "condensation" products, the majority of which are important. We can mention here the compound obtained by what is known as "Perkins' synthesis": Sodium acetate in the presence of acetic anhydride condenses with benzaldehyde to form the sodium salt of Cinnamic acid.

$$C_6H_5CHO + H_2CH.COONa$$
$$= C_6H_5CH:CH.COONa + H_2O.$$

With some amines benzaldehyde condenses to form important dyes.

Benzaldehyde is a colourless liquid, with the characteristic smell of almond oil. It boils at 179° C. It is readily reduced to benzyl alcohol, and as readily oxidised to

175. Benzoic Acid, $C_6H_5.COOH$.—The oxidation occurs even when the aldehyde is exposed to air; indeed much of the benzoic acid on the market is a bye-product of the manufacture of benzaldehyde. The latter is almost as easily prepared from the acid by reduction, and is sometimes obtained by heating a mixture of calcium benzoate and calcium formate (see Section 52).

$$(C_6H_5COO)_2Ca + (HCOO)_2Ca = 2C_6H_5CHO + 2CaCO_3.$$

When benzaldehyde is treated with alkalis it is converted into both alcohol and acid—a peculiar case of hydrolysis which is accompanied by oxidation and reduction.

$$2C_6H_5CHO + KOH = C_6H_5CH_2OH + C_6H_5COOK.$$

Benzoic acid may be prepared in the laboratory from benzyl chloride by the hydrolytic action of potassium carbonate, followed by the oxidising action of alkaline permanganate.

$$3C_6H_5CH_2OH + 4KMnO_4 = 3C_6H_5COOK + 4MnO_2 + KOH + 4H_2O.$$

By passing into the cold product a stream of sulphur dioxide, the manganese dioxide is dissolved as sulphate and dithionate, the potash is neutralised, and the acid is displaced from its salt (see Cohen's *Practical Organic Chemistry*).

In commerce the acid is also prepared by the hydrolysis of benzo-trichloride (compare Section 80).

$$C_6H_5CCl_3 + 2HOH = C_6H_5.COOH + 3HCl.$$

It may also be prepared by the hydrolysis of benzonitrile (see Section 40).

$$C_6H_5CN + 2HOH = C_6H_5COONH_4.$$

And lastly we may mention that it is obtained by the oxidation of Toluene by dilute nitric acid. It is likewise obtained from ethyl benzene and every other aromatic hydrocarbon with only one side chain; the oxidising agent being suitably chosen. This reaction is of the greatest importance theoretically (compare Section 179).

$$C_6H_5.CH_3 \longrightarrow C_6H_5COOH.$$
$$C_6H_5.C_2H_5 \longrightarrow C_6H_5COOH.$$

176. Properties of Benzoic Acid.—Benzoic acid is a colourless crystalline solid, practically insoluble in water. It is readily volatilised and is volatile with steam. Upon heating it sublimes without decomposition. It melts at 121° C. and boils at 250° C.

It occurs in nature in resins. At one time it was obtained from *Hippuric acid*, a normal constituent of the urine of horses. This is hydrolysed by hydrochloric acid into glycine hydrochloride and benzoic acid. Hippuric acid is most easily understood as glycine in which one atom of hydrogen in the amino group is replaced by the radicle benzoyl.

$$\begin{matrix}C_6H_5.CO.NHCH_2COOH\\ +\\ HOH\end{matrix} = C_6H_5CO.OH + NH_2CH_2COOH$$

Benzoic acid forms well defined salts and esters. The latter are prepared in the same manner as the acetates; they have pleasant odours, are almost insoluble in water, and are used for the detection and estimation of certain alcohols.

When pure sodium benzoate is heated with pure soda lime *pure* benzene is formed (compare and contrast with Section 54).

$$C_6H_5COONa + NaOH = C_6H_6 + Na_2CO_3.$$

177. Aromatic Ketones.—When calcium benzoate is distilled the corresponding diphenyl ketone is formed.

$$(C_6H_5COO)_2Ca = CaCO_3 + C_6H_5CO.C_6H_5.$$

This is called **Benzophenone**. Ketones which contain the phenyl group (C_6H_5) are called PHENONES to distinguish them from another class of aromatic compounds of a ketonic character called Quinones. The Phenones are best prepared by Friedel and Craft's method from the hydrocarbon and an acid chloride.

$$C_6H_6 + CH_3COCl = \underset{\text{(aceto phenone.)}}{CH_3CO.C_6H_5} + HCl.$$

178. Benzoyl Compounds.—By treating benzoic acid with phosphorus pentachloride **Benzoyl chloride** is formed.

$$2C_6H_5CO.OH + PCl_5 = 2C_6H_5CO.Cl + POCl_3 + H_2O.$$

This body is much less reactive than acetyl chloride, and for that reason is preferred in some cases for testing. It is hydrolysed by cold water but slowly. It is a colourless liquid, boiling at 198° C.

By the usual method **Benzoic anhydride** $(C_6H_5CO)_2O$ is obtained from the chloride (see Section 47). This also is relatively stable towards water, in which it is insoluble. It is a colourless crystalline solid, melting at 39° C.

By the action of ammonia the chloride yields **Benzamide,** $C_6H_5CONH_2$. This is a crystalline solid soluble in hot water. Derived from this is *Benzanilide,* $C_6H_5NH.COC_6H_5$, which is readily prepared by adding drops of benzoyl chloride and small pieces of caustic potash to aniline, and shaking the cooled mixture. Caustic potash is then added until the smell of benzoyl chloride disappears. The benzanilide is filtered off pure.

SUMMARY.

The derivatives of Toluene, which are formed by changes taking place in the side chain only, react exactly as we might expect of those of a substituted Methane, for such Toluene is. The isomeric bodies, in which the substitution occurs in the nucleus, act like Toluene itself and like the substituted benzenes.

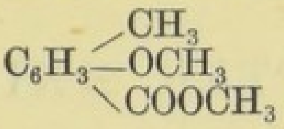
QUESTIONS.—CHAPTER XXII.

1. What is the constitutional formula of toluene? On what evidence is this based? What is the action of (*a*) chlorine, (*b*) nitric acid, (*c*) oxidising agents, on this substance?

2. Describe the various steps in the synthesis of cinnamic acid from toluene.

3. How does toluene resemble marsh gas on the one hand and benzene on the other? How, starting with the two latter substances, could you obtain the former?

4. How can benzoic acid be built up from its elements ?

5. How may the presence of the three methyl groups in the compound of the formula  $C_6H_3{<}\begin{matrix}CH_3\\ OCH_3\\ COOCH_3\end{matrix}$ be shown ?

6. In what respects do the hydroxyl groups of the compound whose formula is  $C_6H_4{<}\begin{matrix}CH_2OH\\ OH\end{matrix}$ differ in their chemical behaviour ?

7. The products of the interaction of two or more substances often vary when

(i) changes are made in the relative masses of the substances,
(ii) the temperature is altered,
(iii) the substances are exposed to sunlight or kept in the dark.

Describe carefully as many reactions as you can, both from inorganic * and from organic chemistry, which illustrate these statements.

8. When cinnamic acid (Section 174) is heated with lime Styrene, C_8H_8, is formed. Can you give this hydrocarbon a structural formula ?

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* See *Inorganic Chemistry*, pp. 255 and 266.

CHAPTER XXIII.

HIGHER HOMOLOGUES OF BENZENE.

179. Xylenes.—The formulae of **Toluene** (B.P. 110° C.) and of **Ethyl benzene** (B.P. 136° C.) have already been given: they follow from Fittig's syntheses. Both are oxidised to Benzoic acid.

Isomeric with Ethyl benzene is **Xylene**, C_8H_{10} (B.P. 138°-142° C.). This hydrocarbon, when oxidised, yields benzene dicarboxylic acid, known as Phthalic acid, $C_6H_4(COOH)_2$. Moreover it is synthesised from benzene and *methyl* chloride by Friedel and Craft's method. Xylene must therefore be dimethyl benzene, $C_6H_4(CH_3)_2$. But there are no less than *three* hydrocarbons of this formula, that is to say, there are three xylenes. They boil at 142°, 139°, and 138° C. respectively: all three are found in coal tar, but they cannot be separated by fractional distillation. Each xylene, upon oxidation, yields a methyl benzoic acid, $C_6H_4(CH_3)COOH$, but the three acids produced differ considerably in many points. They are called **Toluic acids.** Each toluic acid when oxidised yields a **Phthalic acid,** and each phthalic acid is distinct from the others.

The xylene which boils at 142° C. yields ordinary phthalic acid, a compound of considerable practical importance, which is obtained from *Naphthalene*; that which boils at 139° C. yields iso-phthalic acid; and the third xylene yields terephthalic acid, which is also obtained by the oxidation of turpentine (*Terebinthus*).

When the sodium salts of the three toluic acids are heated severally with soda lime, they yield Toluene, which has no isomers.

$$C_6H_4CH_3(COONa) + NaOH = C_6H_5CH_3 + Na_2CO_3.$$

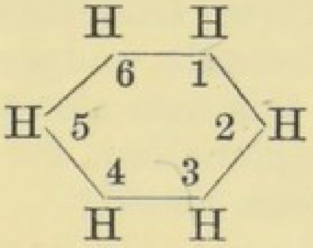
Similarly all three phthalic acids yield successively Benzoic acid and Benzene.

It is evident that neither the xylenes, nor the toluic acids, nor the phthalic acids are stereo-isomers, for they differ considerably in their chemical properties. The occurrence of three disubstitution products is found to be quite general whether the groups be alike or unlike. Thus there are three di-chlor-benzenes, three di-nitro-benzenes, three mono-chlor-toluenes (making with benzyl chloride *four* isomers of the molecular formula C_7H_7Cl), and so on.

Can we ascribe to these isomers structural formulae that shall account for their separate existence?

180. Orientation.—If we consider the ring formula of benzene we shall have no difficulty in admitting that while each *single* hydrogen is similarly placed with regard to the nucleus, this is not true of *pairs* of hydrogen atoms.

If we number the six atoms, in order, 1.2.3.4.5.6,

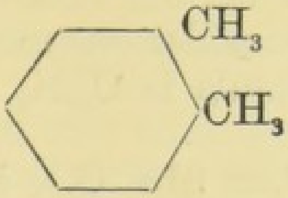


we recognise three possible arrangements of pairs,

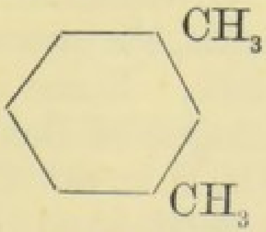
$$1.2\ (=1.6),\ \ 1.3(=1.5),\ \ \text{and}\ \ 1.4,$$

and no more are possible. Hence we have no need even to modify the ring formula to express our new idea.

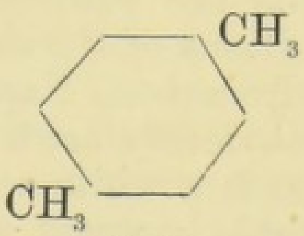
The xylene formulae can be written



(1.2)



(1.3)



(1.4).

The first is called the "**ortho**"; the second, the "**meta**" and the last, the "**para**" position. The theory so far is clear. It remains to find adequate reasons for selecting one of these formulae for each individual xylene. We shall return to this point, after we have shortly considered a few more homologues of benzene.

181. Aromatic Hydrocarbons of the Formula C_9H_{12}.—Eight hydrocarbons of the molecular formula C_9H_{12} are known; of these the most important are:

(i) **Cumene.**—This is a liquid boiling at 153° C. Its synthesis from benzal chloride shows it to be iso-propyl benzene, $C_6H_5.CH(CH_3)_2$. It is oxidised to benzoic acid.

Its next higher homologue, *Cymene*, is methyl iso-propyl benzene. On oxidation it yields terephthalic acid, like the Terpenes, $C_{10}H_{16}$, to which it is related.

(ii) **Mesitylene,** a liquid boiling at 165° C. This important hydrocarbon is found with its isomers Pseudo-cumene (B.P. = 169·5) and Hemimellithene (B.P. = 175° C.) in coal tar. These three compounds when oxidised yield eventually three separate *tri*-carboxylic acids. They are all tri-methyl benzenes.

The existence of three tri-substituted compounds of benzene of the same formula, and not more than three, is the general rule. In this case also the ring formula provides an adequate explanation, for there are but three different sets of positions, namely

$$\underset{\text{(consecutive)}}{1.2.3\ (=1.5.6)},\ \underset{\text{(irregular)}}{1.2.4\ (=1.2.5,\ 1.3.4,\ 1.4.5)},\ \text{and}\ 1.3.5.$$

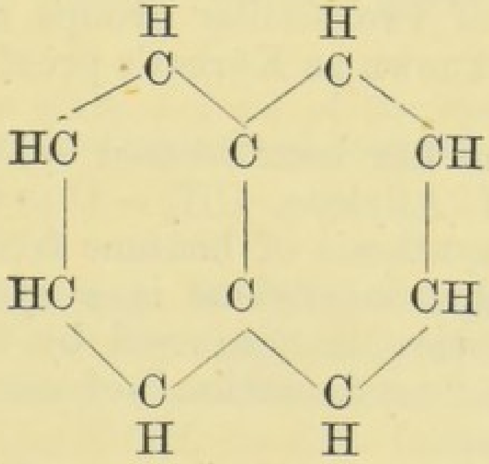
The last is called the "*symmetrical*" position.

182. The Oxidation of Naphthalene.—Before we continue the subject of "Orientation," that is, the relative positions of the side chains, etc., we must consider one more hydrocarbon, Naphthalene. Since its formula is $C_{10}H_8$, it is obviously *not* a homologue of Benzene.

It is a white solid (M.P. = 80° C., B.P. = 218° C.), insoluble in water, very volatile, and having a very characteristic odour. It has antiseptic and insecticide properties, and is well known as "moth balls." It burns with a very luminous but smoky flame, and is a valuable constituent of illuminating gas. A large number of dyes are amongst its derivatives.

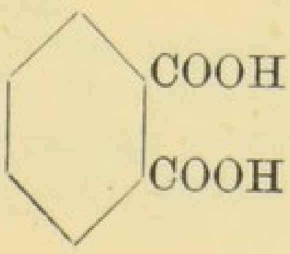
Although it is not a homologue of benzene, its chemical properties recall those of benzene more decidedly even than do those of many of the homologues of benzene. With nitric and sulphuric acids it yields nitro-naphthalenes and naphthalene-sulphonic acids respectively. The nitro compounds are reduced to the amines in the ordinary way.

When it is oxidised it yields ordinary phthalic acid. It must therefore possess a benzene nucleus, and, if we had no further evidence, we might judge it to have two side chains. When mono-nitro-naphthalene is oxidised a *nitro*-phthalic acid, $C_6H_3(NO_2)(COOH)_2$, is formed, as we should expect seeing that nitric acid nitrates in the nucleus. But, when nitro-naphthalene is reduced to amino-naphthalene and this is oxidised, ordinary phthalic acid and not the amino-phthalic acid is formed. In this case therefore the nucleus containing the amino group is oxidised away, and still a nucleus is left intact. For this and other reasons chemists conclude that naphthalene contains *two* benzene nuclei. The only possible formula to indicate this is



We may contrast this formula with that of di-phenyl.

In this book we do not intend to study the chemistry of naphthalene; the importance of the above argument to us is that ordinary phthalic acid must be an "ortho" compound, that is its carboxyl groups are in the 1·2 position.



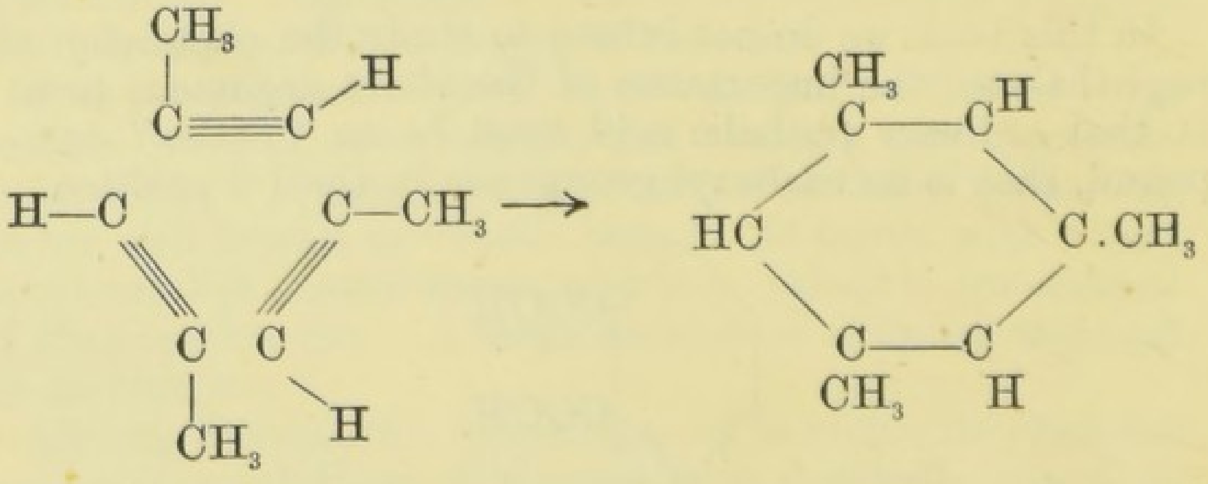
As some support to this conclusion we find that ordinary phthalic acid, when heated, loses water to form an anhydride, $C_6H_4(CO)_2O$, whereas iso- and tere-phthalic acids do not.

183. Identification of Ortho-Compounds.—We can now recognise one of the xylenes. For it is evident that whatever di-substituted product can be shown to be related to ortho-phthalic acid must also be an "*ortho*" compound. The xylene which on oxidation yields ortho-phthalic acid melts at − 28° C. and boils at 142° C.

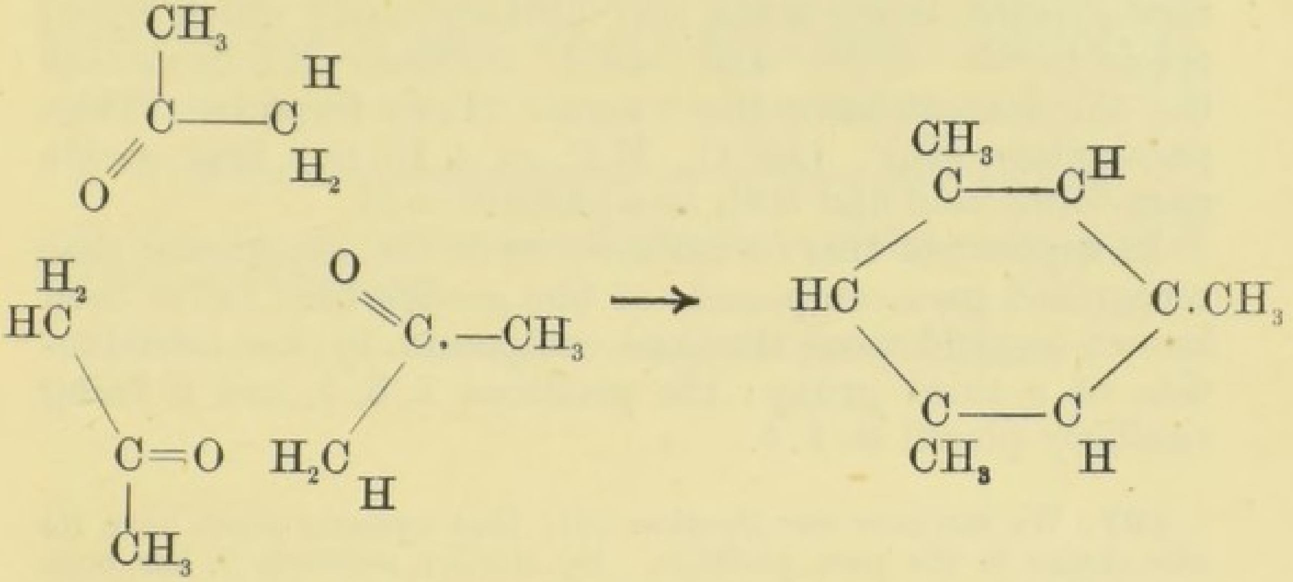
An independent proof of this conclusion is afforded by the experience that recognised ortho-compounds yield only two isomeric tri-derivatives by the introduction of any given group into the nucleus. By the ring formula these two positions for the new group are 3 (= 6) and 4 (= 5). The argument contemplates ortho-compounds formed by the introduction of two similar groups into the benzene nucleus. This is known as Körner's proof.

184. Mesitylene has been formed synthetically by the polymerisation of Allylene, $CH_3 - C \equiv CH$, a reaction which recalls the synthesis of benzene from acetylene and which suggests that mesitylene is a symmetrical 1.3.5 compound. This view is reinforced by the formation of mesitylene by the "condensation" of acetone in presence of sulphuric acid.

We can most easily represent these syntheses by assuming the symmetrical structure for mesitylene.



and



This formula is supported by the experience that only one product has ever been obtained by the introduction of any single new group—whether methyl or not—into the nucleus.

Ladenburg has given a proof of the symmetrical structure of mesitylene. It is not convenient, however, for us to discuss it in this book.

185. Identification of Meta-Compounds.—Now when mesitylene is carefully oxidised by nitric acid, the methyl groups are successively oxidised to carboxyl. Mesitylenic acid, $C_6H_3(CH_3)_2COOH$, is first formed. This also is a 1.3.5 compound. When this is heated it loses carbon dioxide and yields the xylene which boils at 139° C. This must therefore be the **meta-xylene** (1.3). Meta-xylene on further oxidation yields a toluic acid, and finally *iso*-phthalic acid.

These compounds, therefore, and all others which can be converted into them by simple methods, must likewise be meta-compounds.

We may add that *three*, but not more than three, isomers have been obtained by the introduction of a new group into meta-compounds having like groups. The positions of the new group are 2, 4 (= 6), and 5.

186. Identification of Para-Compounds.—Since we have now xylenes, toluic acids, and phthalic acids which correspond to the "ortho" and "meta" formulae, it follows that the third must have the "para" (1.4) formula. Thus para-xylene (B.P. 138° C., M.P. = + 13° C.) first yields para-toluic acid and then *tere*-phthalic acid.

In support of this formula we have the experience that recognised para-compounds of like groups have never been known to yield more than one compound by the introduction of a third group: the positions 2, 3, 5, and 6 being similarly placed to 1.4.

187. We can now see (Section 181) that cymene must have its side chains in the para position. By similar methods it has been shown that the (tri-methyl) isomers of mesitylene, hemimellithene and pseudo-cumene are 1.2.3 and 1.2.4 compounds respectively.

SUMMARY.

When two groups enter the benzene nucleus, three isomeric compounds can be formed, whether the groups be alike or different. Similarly there are three isomerides of tri-substituted benzene, provided the groups are alike. There are three possible isomers of tetra-substituted benzene having like groups, but no isomers of penta-substituted benzene with like groups. These and many facts of a like nature are explained with Kekulé's benzene ring formula; that this is possible justifies the acceptance of this formula.

Amongst the methods adopted to discover the proper formula of any given compound, the simplest in principle is Korner's: in which the number of isomeric derivatives which can be obtained from the substance is determined. From amongst the reactions cited in this chapter, the student can select such as illustrate the equality of the six hydrogen atoms of the benzene molecule.

QUESTIONS.—CHAPTER XXIII.

1. Give the names and constitutional formulae of the aromatic hydrocarbons which have the formula C_8H_{10}. How can they be prepared and by what reactions distinguished from one another?

2. What constitution is assigned to naphthalene? From *a priori* considerations, how many naphthols (monohydroxy naphthalenes) would you expect to exist? What formulae would you give them.

3. Write a short essay on the phenomenon of isomerism.

4. Write the structural formulae for the tetra-chlor-benzenes.

5. Write the structural formulae for the monochlor derivatives of the tri-methyl benzenes.

6. How would you attempt to obtain Tri-phenyl methane?

CHAPTER XXIV.

FURTHER ACTION OF REAGENTS ON BENZENE. SOME COMPLEX PHENOLS.

188. The Position of the Entering Group.—We can now discuss with advantage the effect of the continued action of reagents upon benzene, its homologues and derivatives, a subject which we have hitherto purposely avoided.

It might be thought that when nitric acid acts upon nitro-benzene, all three di-nitro-benzenes would be produced in approximately equal quantity. This is far from being the case in practice, for nearly 90 per cent. of the nitro-benzene is converted into meta-di-nitro-benzene, and only about 1½ per cent. into the para-compound. And if the experiment is performed at higher temperatures the yield of the meta-compound increases and that of the isomeric compounds decreases, that of the para-compound sinks to 1 per cent.

Similarly when nitro-benzene is chlorinated, the 1.3 chlor-nitro-compound is almost exclusively formed ; but, curiously enough, when chlor-benzene is nitrated, the 1.4 chlor-nitro-benzene is chiefly formed, with a low proportion of the ortho-compound.

Again, the continued action of bromine on benzene yields the para-di-brombenzene with but little of the ortho-compound.

It has been found that the position at which new groups tend to enter the nucleus depends mainly upon

(1) the particular group already present,

and, to a less extent,

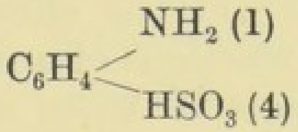
(2) the group to be introduced,

(3) the temperature of the reaction.

Thus aniline by direct action tends to form *para*-compounds almost entirely, so that when meta- or even ortho-derivatives of aniline are desired, these must be prepared from other meta- or ortho-compounds.* Toluene also tends to form para-compounds with a less proportion of the respective ortho-compound, while Benzoic acid tends to form meta-derivatives, and so on.

Exp. 45.—*Preparation of m di-nitro-benzene.* Add 10 grams of nitro-benzene slowly to a mixture of 25 grams of concentrated sulphuric acid, and 15 grams of fuming nitric acid. Heat for half an hour on the water bath. Cool somewhat, and then add the product, with constant stirring, to much cold water. Filter, wash the solid with cold water, and recrystallise the crude product once or twice from dilute alcohol—the small quantities of the ortho- and para- products will be left in the solution.

Exp. 46.—*Preparation of Sulphanilic Acid*—aniline sulphonic acid,



$$C_6H_4\langle\begin{array}{l}NH_2\ (1)\\ HSO_3\ (4)\end{array}$$

To 60 c.c. of concentrated sulphuric acid contained in a dry flask add slowly 30 grams of aniline (recently distilled); during the addition shake thoroughly. Now heat the reaction mixture in the oil bath to about 190°-200° C., until a little of the product treated with dilute caustic soda displaces no aniline. This condition will be reached only after several hours; it marks the time when all the aniline sulphate has been transformed into sulphanilic acid.

$$(C_6H_5NH_3)HSO_4 = C_6H_4(NH_2)HSO_3 + H_2O.$$

Now transfer the product to cold water. Filter at the pump; wash the solid with water; recrystallise it from hot water, and, if necessary, decolourise with animal charcoal.

Sulphanilic acid and its meta-isomer—metanilic acid, which is obtained by the reduction of meta-benzene nitro-sulphonic acid—are largely used in the dye industry.

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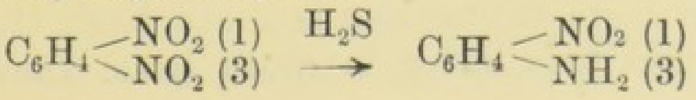
* The preparation of meta nitraniline is described in Norman, *Systematic Practical Organic Chemistry*, p. 56; m di-nitro-benzene is reduced with hydrogen sulphide.



$$C_6H_4\langle\begin{array}{l}NO_2\ (1)\\ NO_2\ (3)\end{array} \xrightarrow{H_2S} C_6H_4\langle\begin{array}{l}NO_2\ (1)\\ NH_2\ (3)\end{array}$$

189. Influence of Substituting Groups upon Reactiveness.—Not only does the presence of a group in the nucleus determine the position at which a new group will enter, it will also affect the ease of the reaction considerably. Thus the monacid phenols are very easily nitrated, even by dilute nitric acid (see Norman's *Practical Organic Chemistry*). With phenol itself, for instance, both the ortho (M.P. = 45° C.) and the para- (M.P. = 114° C.) nitro-phenols are formed: the ortho-compound in greater quantity at low temperatures, but the para-compound in greater quantity at higher temperatures. The readiness with which certain reactions take place is of help in testing for some substances. Thus when an aqueous solution of phenol is treated with bromine water, tri-brom-phenol, $C_6H_2Br_3OH$, is thrown down as a white solid (insoluble in caustic soda); while aniline in similar circumstances is converted into tri-brom-aniline.

As a further instance of the effect of the substituted group we can mention reactions of aniline with substituting agents, to which aniline is far more sensitive than benzene itself: but since the amino group is readily oxidised this is usually "protected" by converting the aniline into acetanilide.

So also methyl benzene (toluene) is much more easily sulphonated than benzene itself, and so on.

190. Influence of Substituting Groups upon Chemical Character.—The characteristic properties of the original compound are intensified or weakened, according to

(1) the nature of the new group, and
(2) its position.

Thus nitro-phenols are more acidic than phenol itself: they will form "phenates" even with the alkali carbonates.

The nitr-anilines are less basic than aniline, and the sulphonic group has the same influence.

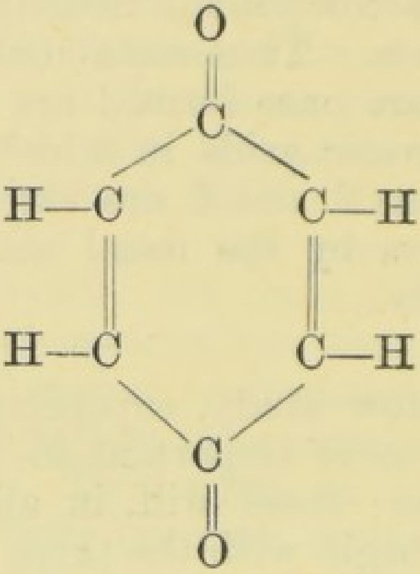
The nitranilines afford good instances of the effect of position, for meta-nitraniline is more basic than the para-compound, and this latter is more basic than the ortho-compound, that is in the ortho-position the greatest influence is exerted, and in the meta-position the least. On the other hand the meta-compounds usually offer the greatest resistance to reagents. Thus meta-acids form esters least readily, but the esters once formed are more stable. But the substituted benzoic acids in which a group occupies each of the positions 2 and 6 are exceptional, since they will not form esters by the usual method, whereas the isomers do so readily.

191. We shall now study, superficially for the most part, a few of the more important di- and tri-substituted products of benzene; these will, in all but one case, be phenols. We will begin with the three

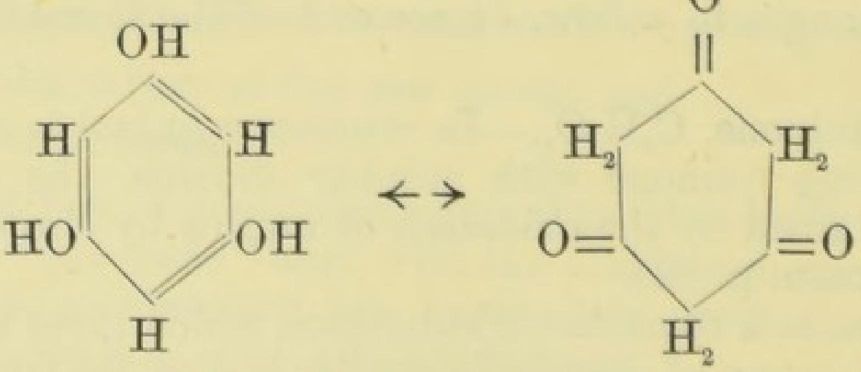
192. Di-hydroxy Benzenes.—**Catechol** (or Pyrocatechol), M.P. = 104° C., the ortho-; **Resorcinol**, M.P. = 118° C., the meta-; and **Quinol** (or Hydro-quinone), M.P. = 169° C., the para-compound. In common with the other phenols they are readily oxidised in air, becoming darkened in tint. They are useful reducing agents; they reduce silver compounds and are used as developers in photography. Resorcinol is also used, with phthalic anhydride, for the preparation of Fluorescein and Eosin (see Gattermann, p. 323). All three isomers yield colourations with ferric chloride, a common reaction of phenols: catechol, a green, which changes to violet when ammonia is added; resorcinol, a dark violet; and quinol, a green; this, however, by oxidation changes to yellow, on account of the formation of

193. Quinone, $C_6H_4O_2$.—In commerce quinol is obtained by reducing quinone with sulphur dioxide, the quinone being obtained by the oxidation of aniline by chromic acid (see Norman, p. 82).

Quinone is a remarkable substance, which gives the class name to a group of chemically similar bodies, the QUINONES. Its relation to "hydroquinone" shows it to be a para-compound. In many ways it acts like a di-ketone; for instance, it forms a di-oxime. It will also *combine with* bromine to form a tetra-bromide. Its formula is usually written

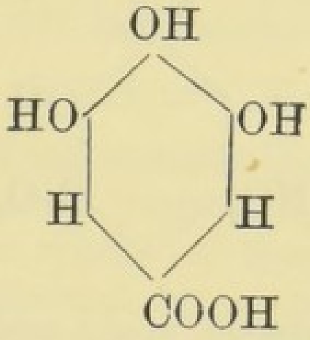


194. Of the **Tri-hydroxy Benzenes** we shall consider but two; phloroglucinol the 1.3.5, the symmetrical, compound, and pyrogallol, the 1.2.3 compound. **Phloroglucinol** gives a violet colouration with ferric chloride, and is a good reducing agent. It is particularly interesting from the theoretical point of view, because it exhibits the properties of a tri-acid phenol in some circumstances, but in others those of a tri-ketone. To this not uncommon phenomenon the term "*tautomerism*" is given. In this case it is attributed to the mobility of the three hydroxyl hydrogen atoms, whose supposed conduct is represented in the following scheme:—



Pyrogallol, M.P. 132° C., is a powerful reducing agent, and is used as a photographic developer. Its alkaline solution absorbs oxygen rapidly, whereby it undergoes oxidation chiefly to carbon dioxide. It is useful in gas analysis. It yields a red colouration with ferric chloride. Unlike phloroglucinol, it does not act like a ketone. It is used as an antiseptic. It has well-developed acidic properties, and is generally known as pyrogallic acid. It is obtained by heating

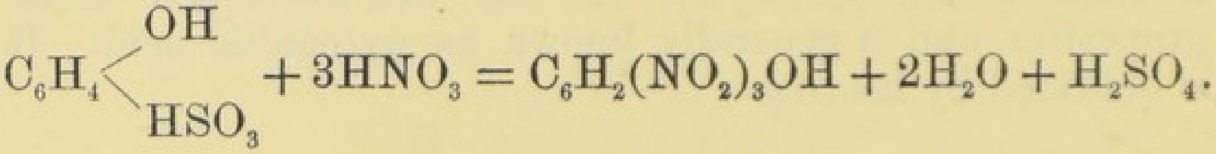
195. Gallic Acid.—This compound is a tri-hydroxy benzoic acid of the formula



It is obtained by the hydrolysis of a di-gallic acid,

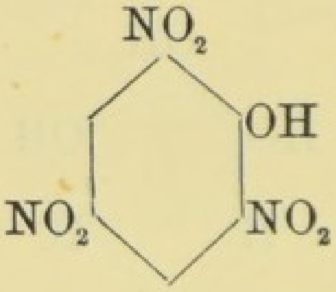
196. Tannic Acid, and from other Tannins, some of which are obtained by the hydrolysis of glucosides. Tannin is obtained from oak- and various other galls; as much as 50 per cent. of these structures may consist of tannin. Many properties of tannin are put to important practical uses. With some alkaloids it forms insoluble compounds which are therefore precipitated from solution. It acts upon albumins and gelatin in the same way, thus the astringent taste of tea produced by the dissolved tannin is removed by the addition of milk—a regrettable disguise is thus furnished for the unwholesome tannin, which would have afforded an indication of tea that has been "brewed." To the same property, together with its antiseptic properties, is due the value of this compound to tanners, for when animal skins are exposed to its solution for considerable periods, these are gradually converted into leather, a substance which neither swells up in water, nor putrifies, nor is affected by the weather in any way. Tannin forms an insoluble blue-black compound with ferric chloride; this is used for making writing inks.

197. Picric Acid, or tri-nitro-phenol, is prepared by the action of concentrated nitric acid on phenol-sulphonic acid (see Norman, p. 60).



$$C_6H_4\begin{cases}OH\\HSO_3\end{cases} + 3HNO_3 = C_6H_2(NO_2)_3OH + 2H_2O + H_2SO_4.$$

The nitro groups are symmetrical.



It is strong monobasic acid, and readily decomposes alkaline carbonates. Many of its salts with organic bases and alcohols are insoluble, wherefore it is used to remove the latter from solution. Some of its metallic salts, including ammonium picrate, are explosive. The acid itself explodes with shock: in the melted condition it is the explosive "lyddite." It also finds use as a yellow dye, and as an antiseptic. It has a bitter (πικρος) taste.

198. Salicylic Acid is obtained from the glucoside salicin, $C_{13}H_{18}O_7$, which occurs in Willow (*Salix*) bark, The glucoside is hydrolysed to glucose and saligenin (ortho-hydroxy benzyl alcohol). The latter is oxidised to salicylic acid or ortho-hydroxy benzoic acid, $C_6H_4(OH)COOH$. It occurs free in some species of Spiræa. From the Canadian Wintergreen (*Gaulteria procumbens*) is obtained "Oil of Wintergreen," which contains methyl salicylate. This is easily hydrolysed, and is the chief source of the salicylic acid used in medicine.

It is a valuable medicine in cases of rheumatism, though its prolonged use may cause unpleasant after-effects, *e.g.* temporary deafness and nervous irritability. It is also used for outward application, and as a preservative for foods.

It is a colourless crystalline substance, sparingly soluble in cold water, but readily in hot. It melts at 155° C., and can be sublimed, but when heated rapidly it decomposes into carbon dioxide and phenol (Section 54). The reaction takes place more readily when caustic soda is added in excess. As we shall see later, the sodium compound can be formed by the reverse process. As a substituted benzoic acid (it is fairly strong) it forms salts and esters; as a substituted phenol (it gives a violet colour with ferric chloride) its sodium salt still reacts with caustic soda.

$$C_6H_4(OH)COONa + NaOH = C_6H_4(ONa)COONa + H_2O.$$

It can be obtained from anthranilic acid (o-amino benzoic acid); some is obtained commercially by this method, naphthalene being the source of the amino acid. But the largest quantity is obtained by a modification of Kolbe's method. Kolbe's method is convenient in the laboratory, and since it is a general method of preparing certain aromatic oxy-acids we will now describe it.

Exp. 47.—*Preparation of Salicylic Acid.*

(i) Preparation of perfectly anhydrous sodium phenate.

The success of the preparation depends almost entirely upon making and keeping the sodium phenate absolutely dry, and no pains should be spared to accomplish this part of the experiment.

Fix a nickel dish over a burner very securely; place in it 12½ grams of *pure* caustic soda and 20 c.c. of water. Add slowly, stirring the whole, 30 grams of *pure* phenol. Heat the dish cautiously, stirring the contents constantly and endeavouring all the while to reduce it to a fine powder as water is expelled. When it is dry, and still hot, transfer it to a clean dry mortar and powder it thoroughly and rapidly before it is cold. Then heat it once more. If there is not time to finish the experiment in one day leave the phenate in a vitriol desiccator.

(ii) Preparation of sodium salicylate.

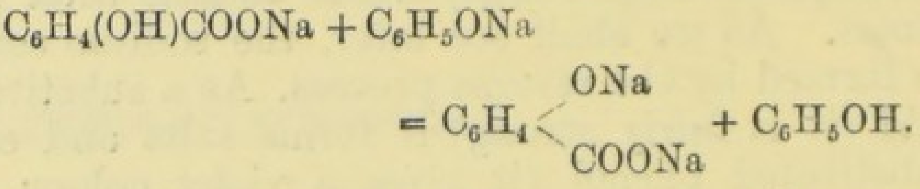
Place the powder in a small retort heated in an oil bath at 120° C. Pass a current of well dried carbon dioxide over the phenate by a tube which nearly reaches it. After some time raise the temperature *very gradually* to 190° C., occasionally scraping over the powder with a dry rod, thrust through the tubulure while the gas delivery tube is raised a little. This part of the process should last at least four hours.

The following reactions have taken place :—

(1) $$C_6H_5O.Na + CO_2 = C_6H_5O.COONa.$$

(Sodium phenyl-carbonate)

(2) $$C_6H_5.OCOONa = C_6H_4(OH)COONa.$$

(3) 

$$C_6H_4(OH)COONa + C_6H_5ONa = C_6H_4\left\langle\begin{matrix}ONa\\COONa\end{matrix}\right. + C_6H_5OH.$$

[It will be seen that the last stage entails loss of phenol: this is avoided in the commercial method by effecting the reaction under pressure, at 140° C.]

To complete the process, the heating and the passage of the gas is continued for one hour at 200° C.

(iii) Setting free the acid.

The *solid* is then removed through the tubulure, without moving the phenol, which should have condensed in the neck. The residue is washed out with water. The ice-cold solution of the salt is treated with a large excess of hydrochloric acid.* The crude acid is filtered at the pump and washed with a little cold water.

The best way to purify the crude substance is to distil it with *superheated* steam, but it will be sufficient to recrystallise it from the least quantity of boiling water.(do not boil too long as the acid is volatile with steam).

199. An interesting difference occurs when potassium phenate is employed. Up till 150° C. salicylic acid is chiefly formed, but above this temperature the proportion of para-hydroxy benzoic acid begins to predominate until at 220° C. this is the sole product.

SUMMARY.

The position taken up by a new group is influenced by the groups already present in the nucleus. These also have an effect upon the ease with which the body reacts. In its turn the new group modifies the properties of the original body.

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* The weaker and less soluble acid is displaced and precipitated.

QUESTIONS.—CHAPTER XXIV.

1. A white crystalline acid containing nitrogen was found to give the following reactions :—

(*a*) On distillation with lime it yielded aniline.

(*b*) When warmed with nitrous acid, nitrogen was evolved and a white crystalline acid formed. This acid was free from nitrogen, gave in aqueous solution a violet colouration with ferric chloride, and on distillation with lime yielded phenol.

Discuss these changes and draw your conclusions as to the constitution of the original acid.

2. Write the formulae for resorcinol and quinol. How can these substances be formed from benzene, and distinguished from one another?

3. How would you determine experimentally the relative position of the nitro groups in ordinary di-nitro-benzene, and in picric acid?

4. By what methods can *o*-, *m*-, and *p*-nitranilines be prepared?

5. Give examples of three general reactions by which the number of carbon atoms per molecule can be increased. Do you know of any general reactions by which the number of carbon atoms per molecule can be diminished?

6. Organic acids are sometimes defined as containing the group COOH. Discuss, with examples, the meaning and correctness of this statement.

7. What do you understand by the ortho position in the case of di derivatives of benzene? How would you prepare and identify ortho-di-methyl benzene?

8. The influence of a present group upon the position taken by an entering group is summarised in Professor Crum Brown's rule, "If the compound formed by adding a hydrogen atom to the radicle already present is *readily oxidised*, the new group enters the META position mainly, while if this compound is *not* readily oxidised the PARA (and ORTHO) position is taken up."

From this rule state what compounds will be formed by chlorinating (1) chlor benzene, (2) nitro benzene, (3) toluene, (4) benzoic acid, (5) phenol, (6) aniline, (7) benzene sulphonic acid, and by nitrating (8) m di-nitro benzene, (9) o di-nitro benzene.

How would you attempt to prepare m aniline sulphonic acid?

9. Can you suggest a method for preparing phloroglucinol?

10. How would you attempt to prove the constitution of picric acid?

CHAPTER XXV.

OTHER NOTEWORTHY COMPOUNDS.

200. The aim of the preceding chapters has been to illustrate the principles and typical methods of organic chemistry with the help of a sufficient but necessarily small number of examples.

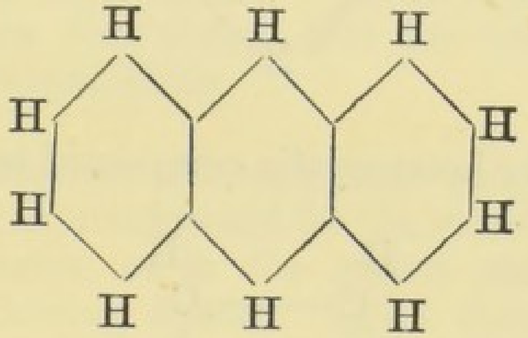
201. Compounds of Sulphur.—It has been necessary to leave for later study many series of compounds, some of which are of great interest and importance. Thus no account has been given of the *Mercaptans*, sulphur compounds analogous to the alcohols; the *Thio-cyanates*; the *Thio-carbamines*, among which are the mustard oils; or the *Thio-ureas*. We have not considered metallic compounds such as cacodyl, a very poisonous compound of arsenic.

202. Hydrocarbons.—In passing we have alluded to the *Naphthenes*, hydrocarbons found in Russian petroleum; and to the *Terpenes*, another series of hydrocarbons included among the "essential oils," obtained from many plants such as the conifers, the orange, thyme, and eucalyptus. Of these turpentine is the best known. Many are antiseptic and insecticide, and have medicinal value. Amongst their derivatives are the camphors: artificial camphor is now on the market, it is said that it cannot be recognised as distinct from the natural products.

From the theoretical point of view the cyclic hydrocarbons intermediate between the aliphatic and the aromatic are very important; but they are outside the scope of this book.

Naphthalene has been considered only for the purposes of Chapter XXIII. Its use in the manufacture of artificial indigo and other dyes is full of interest.

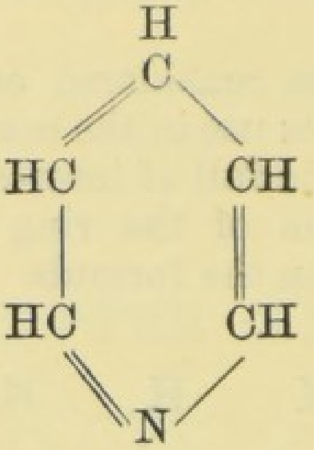
Another hydrocarbon of the ring type is *Anthracene*, $C_{14}H_{10}$, to which is given the formula



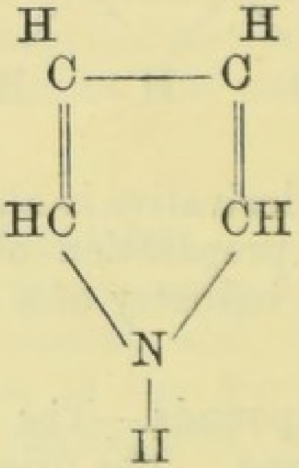
Its most important derivative is alizarin, the dye known as Turkey red. The preparation of this dye artificially has changed the staple industry of a large tract of country.

203. Nitrogen Compounds.—The nitrogen compounds are of the highest interest. The uric acid compounds constitute the *Purine* group. Its most important members, besides, are the two alkaloids theobromine and theine (or caffeine), the active principles of cocoa, tea, and coffee. Both have been synthesised from uric acid.

204. Many other alkaloids are more or less complex derivatives of *Pyridine*, C_5H_5N. This remarkable substance, which occurs in coal tar, was first isolated from bone oil. Although it acts as a strong base and forms a chloroplatinate, this compound behaves chemically very much like benzene. It resists oxidising agents, reacts to form substitution rather than addition products, and forms sulphonic acids which may be converted into phenols. To express its many reactions it is given a cyclic formula in which a $\equiv CH$ group of benzene is replaced by an atom of nitrogen. Such a formula is called "heterocyclic."



Another simple heterocyclic compound is *Pyrrol.*



205. The majority of the *alkaloids* are derivatives of one or both of these compounds. Many are highly poisonous, but in proper doses are valuable drugs. Very delicate tests have been elaborated for some of the most important. They exhibit stereo-isomerism.

The best known are: *Nicotine,* which occurs as malate and tartrate in tobacco leaves. This alkaloid, even as vapour, is very poisonous. In smoking, however, much of it is destroyed by burning. From the deadly nightshade, the thorn apple, and the henbane, *Atropine* and *Hyoscyamine* are prepared. The former is of service in ophthalmic surgery and for other purposes. From coca *Cocaine* is obtained: this alkaloid produces local anaesthesia by injection and otherwise. From cinchona bark are prepared *Cinchonine* and *Quinine*. It is almost impossible to overestimate the value of the latter drug, both as a remedy and a prophylactic.

The dried latex of the poppy is used as a drug under the name of opium. Its alcoholic solution is called laudanum. The chief alkaloid of opium is *Morphine*. The beneficence of this alkaloid in all its forms is only equalled by its lethal character when misapplied.

Lastly we may mention *Strychnine* and *Brucine*, obtained from Strychnos nux-vomica. These in overdoses produce tetanic muscular convulsion, but the former has a tonic value in minute quantities.

206. The *proteins* are extremely complex nitrogenous compounds which are formed by the constructive processes of living organisms, or in the earlier stages of their disintegration, following death. Upon their further decomposition they yield very largely amino-acids and their derivatives. Their molecular weight is extremely high, being placed at a minimum of 14,000. They consist of carbon (51-55 per cent.), hydrogen (7 per cent.), oxygen (20-30 per cent.), nitrogen (15-17 per cent.), sulphur (·4-2·5 per cent.).

They are divided into somewhat ill-defined groups in terms of their solubility (colloidal) in water, and in certain solutions of definite concentration.

207. How they are synthesised in the green plant from inorganic materials is a very interesting problem which has not so far found a solution. Interesting suggestions have been made, some of which are plausible, and one not without a measure of support. The historic theory for the beginning of the process is that formaldehyde is produced from water and carbon dioxide. The change in question has been accomplished in the laboratory. The aldehyde is then supposed to polymerise to form a sugar (see Section 149). It has been further suggested that the sugar may either be converted into starch for the time being, or be at once elaborated with nitrates to amino-acids, such as asparagin, by the protoplasm already in existence. Further elaboration of these bodies which are already complex, through stages which have not been traced, may be supposed to lead to proteid in various forms.

On the death of the animal or plant, the protoplasm is ultimately reconverted, by the aid of bacteria, into hydrogen sulphide, ammonia, water, and carbon dioxide.

QUESTION.—CHAPTER XXV.

Comment on the statement made by Liebig in 1837 that organic chemistry is the chemistry of the compound radicles.

PART IV.

ANALYSES AND MOLECULAR WEIGHTS.

CHAPTER XXVI.

PURIFICATION OF ORGANIC COMPOUNDS.

208. In this chapter we propose to consider the methods of finding the composition and molecular formula of an organic compound.

Before it is analysed the substance must be obtained pure. Most of the methods of purification have been applied in the experiments described in the body of the book. Differences in solubility, volatility, and melting point are taken advantage of, just as they are in the purification and separation of inorganic compounds, and these methods are often aided, or even superseded, by purely chemical methods. We have mentioned such cases when describing the separation of the products of the distillation of wood (Sections 24 and 28). The preparation of aldehyde (Section 20) is an additional example.

209. Methods Based on Differences in Solubility.—The separation of a soluble from an insoluble portion needs no description. Many solvents are available. The commonest are water, methyl and ethyl alcohols, ether, benzene, benzine, acetic acid, and carbon disulphide. Brine also is of service in "salting out" processes. When every constituent of a mixture is soluble, the method of "fractional crystallisation" is resorted to, if part is solid at an ordinary or attainable temperature. Colloidal substances may be separated from crystalloids by dialysis.

210. Methods Based on Differences in Volatility.—When it is possible, mixed liquids are separated by fractional distillation (coal tar products, crude petroleum, and alcohol for instance). With some mixtures this is excessively tedious. Fractions are collected separately, and these fractions are again distilled, the fractions belonging to certain ranges of temperature being brought together and distilled again, and so on until the pure substances are gradually separated.

Some substances may be conveniently separated by distillation in steam (see Aniline and Phenol).

Many substances which decompose when heated under ordinary conditions may be isolated by distillation under reduced pressure.

211. The purification of substances by the freezing method has been mentioned in the description of the purification of benzene and acetic acid.

212. Recognition of Purity.—Every pure substance, which is stable under the conditions of the determination, has a definite melting point or boiling point, or both. By these it can be identified. The presence of an impurity usually causes depression of the freezing point, and, as a rule, the melting point is not sharp. A non-volatile impurity in a liquid causes elevation of the boiling point of the latter, and the boiling point rises as the concentration of the solution increases. When the impurity is volatile the mixture may have either a lesser or greater vapour pressure, and therefore a higher or lower boiling point than either of the constituents. In all cases the boiling point changes during the distillation unless the mixture happens to be one, such as a 96 per cent. alcohol, 4 per cent. water, which boils with unchanged composition.

Exp. 48.—*Determination of the Melting Point.* The most exact method is to place a thermometer bulb in about 20 grams of the substance contained in a thin test tube, and to heat this very gradually in a suitable bath; this must be stirred well throughout the heating. The usual liquids used in baths are concentrated sulphuric acid, glycerin, and paraffin wax.

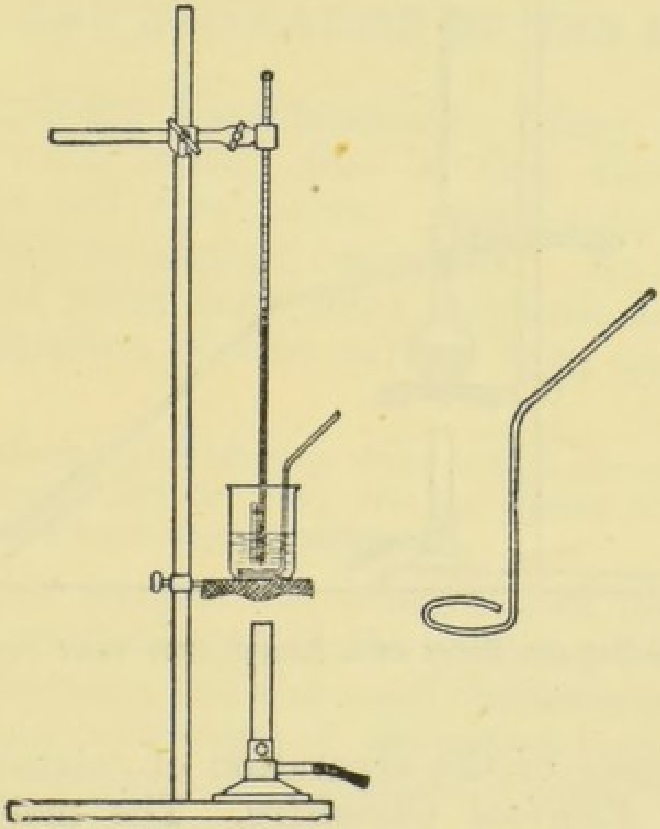


Fig. 32.—MELTING POINT.

As a rule only small quantities of the substance can be spared for the determination, and in this case it is carried out with a thin-walled tube of fine bore, sealed at one end. This is made by drawing out a piece of soft glass tubing. The dried, well-powdered solid is put into the tube and tapped to the bottom.

The tube is then fastened against the thermometer by a narrow rubber band, so that the substance comes next to the bulb of the thermometer (the rubber band is not usually employed, for the tube is kept in place by surface tension). This may be used as a stirrer, or a stirring rod, circular at the end, may be employed. Two readings should be taken (Fig. 32)

Exp. 49.—*Determination of the Boiling Point.* This is usually determined in a small distilling flask fitted with condenser to prevent loss of the liquid. The thermometer bulb is placed near the side tube, and the liquid boils rapidly.

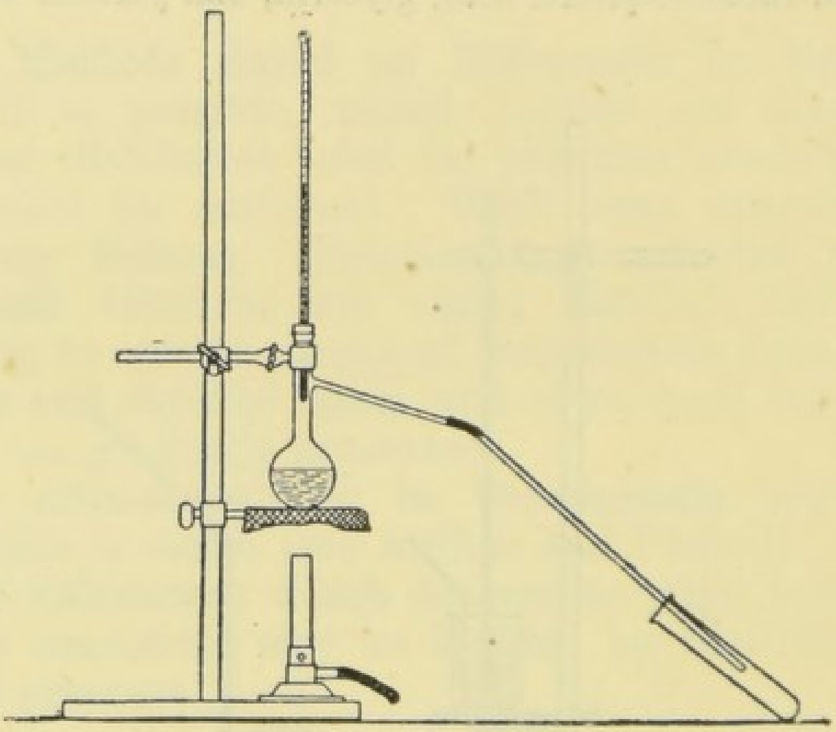


Fig. 33.—Boiling Point of a Liquid (not very volatile).

The principles of the separation of mixtures are given in Walker's *Physical Chemistry.* The methods are described in detail in Lassar-Cohn's *Laboratory Manual of Organic Chemistry,* Chapters II., IV., and VI.

CHAPTER XXVII.

DETECTION AND ESTIMATION OF THE ELEMENTS.

213. Preliminary Considerations.—Many organic substances char when heated, that is they decompose into volatile bodies and free carbon. Any substance which chars is certainly an organic compound. By withdrawing the elements of water from them sulphuric acid will also cause the separation of free carbon from many organic substances.

Not all substances which blacken when heated have charred. Two familiar instances of the contrary are the effects of heating red mercuric oxide and basic copper carbonate.

Many organic compounds, when heated, not only char, but also yield ammonia among the volatile products. The evolution of ammonia and the smell characteristic of burning hair are sure indications of the presence of nitrogen in a compound; but the non-formation of ammonia does not prove the absence of nitrogen.

But many organic substances do not char when heated: alcohol, for instance, evaporates. Some, even when burning, give a clear flame: alcohol again; others, such as petroleum, will burn in a poor draught with a smoky flame, while some, such as benzene, always disengage much free carbon when burning. A few decompose violently when they are heated. Among these latter bodies are the organic nitrates.

214. Detection of Carbon and Hydrogen.—The majority of carbon compounds contain both carbon and hydrogen. Both these elements are detected, in one experiment, by burning the compound completely to carbon dioxide and water. The oxygen is supplied by copper oxide. Of course the oxide and the substance to be tested must be perfectly dry, otherwise the appearance of water does not prove the existence of hydrogen in the body under examination.

Exp. 50.—The substance, finely powdered, is mixed with four or five times its volume of dry finely powdered copper oxide. The mixture is put in a hard glass test tube, and then covered with more dry oxide. In the upper part of the tube a small loose plug of filter paper keeps in place a little anhydrous copper sulphate above it.

The test tube is then fitted with a delivery tube which leads to a solution of slaked lime or baryta. Heat is first applied to the copper oxide above the substance, and afterwards to the mixture. Water condenses in the cool upper part of the tube, and is prevented from returning by the filter paper. Even if the substance is poor in hydrogen the anhydrous copper sulphate will turn blue, thus showing that water has been produced. The lime water becomes turbid by the formation of calcium carbonate.

215. Detection of Nitrogen.—Nitrogen can be detected in organic compounds, when these are heated, by the formation of ammonia. If the substance is strongly heated with soda lime, ammonia is in most cases formed and evolved still more readily. A more certain way of detecting nitrogen is to bring about the formation of potassium cyanide, which can be recognised by the usual tests.

Exp. 51.—Some of the substance to be examined is powdered if solid, and heated in a test tube with a piece of sodium about the size of a pea. Potassium is more reactive, but sometimes dangerous. The heating is gradual at first, but finally the tube is brought to redness: this will ensure the formation of the alkali cyanide. The hot test tube is dipped in water contained in a mortar, great care being taken to avoid the consequences of an explosion caused by any uncombined metal. The contents are ground up and the solution poured off. To the alkaline liquid a little ferrous sulphate is added; the hydroxide will be produced, and this will react with the cyanide present.

$$FeSO_4 + 2NaOH = Fe(OH)_2 + Na_2SO_4,$$

$$Fe(OH)_2 + 6NaCN = Na_4Fe(CN)_6 + 2NaOH.$$

Acidify with hydrochloric acid. Some ferric chloride, formed by oxidation (or a little ferric chloride specially added at this stage), will react to form ferric ferrocyanide, or Prussian blue, a sure indication of nitrogen in the body tested.

$$3Na_4FeCy_6 + 4FeCl_3 = Fe_4(FeCy_6)_3 + 12NaCl.$$

216. Detection of the Halogens.—The halogens may be detected in some compounds by taking advantage of the volatility of the copper halides and their property of colouring the Bunsen flame green.

Exp. 52.—A piece of copper oxide is placed in a platinum loop and heated until it no longer colours the flame, or the end of a piece of thin copper wire is oxidised in the flame. The substance to be examined is dusted on to the copper oxide and this is again heated. The green colouration indicates a halogen. This method may fail, and in any case it gives no indication of which halogen is present. Therefore a more certain method is followed. This is initially the same as that given above for nitrogen. The sodium halide will be formed.

Exp. 53.—Follow directions of Experiment 51 to the formation of the alkaline solution. Acidify this with nitric acid and then add silver nitrate solution. Proceed as in ordinary qualitative analysis, or evaporate to dryness and heat with manganese dioxide and concentrated sulphuric acid.

217. Detection of Sulphur.—Sodium sulphide is formed and recognised.

Exp. 54.—Proceed as for Experiment 51, but place a little of the solution on a silver coin; blackening is due to formation of silver sulphide. Acidify the main portion of the solution with acetic acid and add lead acetate. Lead sulphide will be precipitated if sodium sulphide is present. The alkaline solution yields a violet colouration when treated with sodium nitro-prusside, $Na_2Fe(NO)Cy_5$.

218. Estimation of the Percentage Composition of Compounds.—When the qualitative composition of a compound has been discovered, the relative proportion of the component elements can be estimated. Generally speaking but one method has been adopted, namely, to oxidise the carbon and the hydrogen of the body to carbon dioxide and water respectively, but the special methods and the oxidising agents differ with the physical condition of the body and the constituent elements.

Thus gaseous and some liquid hydrocarbons may be burnt in oxygen gas; the carbon dioxide and water produced are absorbed by potash and calcium chloride respectively:

from the weight of these products those of the carbon and hydrogen they contain are easily deduced. If the mass of the hydrocarbon is known, this will serve as a control; the sum of the weight of the carbon and hydrogen found should be in agreement.

Liquids which are not very volatile—placed in a containing tube—and solids which contain carbon and hydrogen, or carbon, hydrogen, and oxygen, are oxidised by heated copper oxide.

From the carbon dioxide and water collected the weight of carbon and hydrogen are calculated. If these together do not account for the whole of the substance, the difference represents the combined oxygen.

When the substance to be analysed is a compound of nitrogen, oxides of nitrogen might leave the tube and be collected in the absorption apparatus. To prevent this a piece of copper gauze is placed at the exit of the tube and heated to reduce such oxides. The free nitrogen is not absorbed, nor does the copper reduce carbon dioxide or water. In any case a special combustion is undertaken to estimate the nitrogen; in this case it is the nitrogen which is collected and the carbon dioxide and water which are neglected.

If the substance to be analysed contains a halogen this may escape in the free state and will be absorbed, or it may yield a copper halide which is vapourisable at the temperature of the combustion. Similar difficulties occur with sulphur compounds, for copper sulphate will be formed, which, when strongly heated, will yield sulphur dioxide. These difficulties are overcome by using pieces of fused lead chromate instead of copper oxide, when the less volatile lead halide or sulphate is formed. The combustion is also carried out at a lower temperature, the last precaution to avoid the formation of the fusible lead silicate at the expense of the tube. In stubborn cases a heated spiral of silver gauze is placed at the exit of the tube: this is an efficient stop to free halogens.

The halogens and the sulphur are estimated in a special experiment. In this case the oxidising agent used is concentrated nitric acid. The halogens are liberated in a closed tube in presence of silver nitrate, whereby the silver halide is formed. The sulphur is oxidised by the nitric acid to sulphuric acid and is estimated as barium sulphate.

In this section we have made a general discussion of the principles of the analyses; in the following three sections we shall give an account of the special details.

219. Carius' Method of Estimating the Halogens and Sulphur.—The oxidation is accomplished in a bomb tube, that is a glass tube with thick walls to withstand pressure. This is about 50 cms. in length. If a halogen is to be determined, about ·5 gram of powdered silver nitrate is introduced. By means of a long funnel 2 c.c. of pure fuming nitric acid are poured into the bottom without wetting the sides. A small glass tube containing a weighed quantity of the substance to be oxidised is then let down the side of the inclined bomb tube: it will stop partly immersed in the acid with the open end clear. When properly managed the acid and substance will not come in contact until after the tube is sealed up. This is done by drawing out the open end to a long stout walled capillary and fusing this (Fig. 34.)

Fig. 34.

"Bomb" tube ready for furnace.

The sealed tube is now placed in a sloping metal tube under a hood. This arrangement minimises the ill effects of an explosion, should one occur. Here it is heated gradually up to 300° C., which temperature is maintained for some time. Before the substance is emptied out of the tube, the pressure within is relieved by softening the end of the capillary in a flame. To avoid accidents, the cold tube is wrapped in a duster at this stage. The top of the tube is now cut off and the contents carefully washed out. The silver halide is collected on a filter, washed, dried, and weighed by the methods usual in gravimetric analysis.*

When sulphur is to be estimated no silver salt is added, and the acid solution is diluted and treated with barium nitrate in excess. The barium sulphate is collected, dried,

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* See *Inorganic Chemistry*, pp. 97, 231; *Chemical Analysis*, p. 152.

and weighed by the usual method.* From the weight of the precipitate that of the halogen or sulphur can easily be calculated.

220. Liebig's Method of Estimating Carbon and Hydrogen.

(i) When only carbon, hydrogen, and oxygen are present. A hard glass tube, a few inches longer than the Erlenmeyer gas furnace in which it is to be heated, is charged nearly $\frac{3}{4}$ full with well-dried coarse copper oxide. This is kept in position by two short lengths of oxidised copper gauze spirals; see Fig. 35. The lengths which will protrude from the furnace are kept free. The rest of the space—which will be at the end where oxygen enters the tube—will be occupied by a boat containing the substance to be oxidised. This is kept in place by a long oxidised copper gauze spiral, which can easily be taken out to admit or remove the boat.

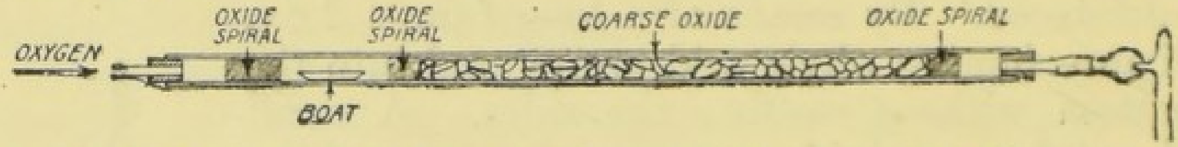

Fig. 35.—Estimation of Carbon, Hydrogen, and Oxygen by Combustion.

The copper oxide and the spirals are previously oxidised and dried by heating them in a current of dry oxygen or air. As soon as the boat end of the tube is cool, the absorption apparatus is fixed to the exit end of the tube. This consists of a weighed U-tube containing fused calcium chloride to absorb the water, and a weighed set of Geissler potash bulbs to absorb the carbon dioxide (Fig. 36). The

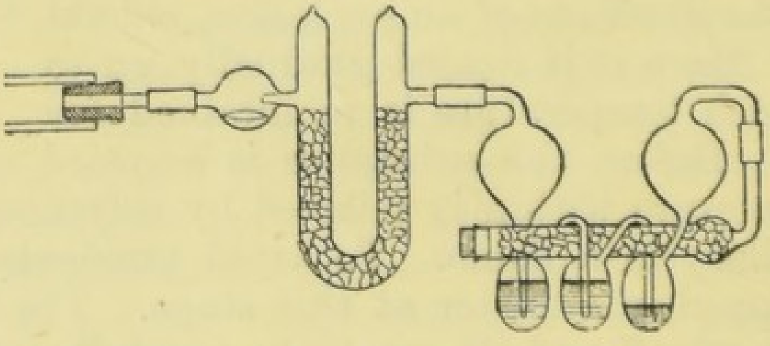

Fig. 36.—Absorption Apparatus for Estimation of Carbon and Hydrogen.

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* See *Inorganic Chemistry*, pp. 97, 231; *Chemical Analysis*, p. 152.

weighed substance, contained in a weighed boat, is introduced into the combustion tube, and oxygen is passed through so slowly that the bubbles can easily be counted as they traverse the drying apparatus. Heating is begun at the end remote from the substance, and the burners are gradually lit from before backwards. The long spiral is then ignited, and finally the substance itself. The heating is now general. By this means all the substance is oxidised and none travels backward.

When the bubbles passing through the potash do not decrease in size the combustion is finished. The tube is cooled gradually in a current of air to displace oxygen from the absorption apparatus. The U-tube, potash bulbs, and boat are reweighed, and the composition of the substance calculated.

(ii) When the substance contains nitrogen.

The arrangement in the combustion tube is modified. The end copper oxide spiral and part of the copper oxide are replaced by a dry reduced-*copper* gauze spiral. This is not placed in position until the substance itself has been introduced. The oxidation is carried out at first *without* the passage of the dry air or oxygen; in the final stage dry air is passed through and the direct heating of the copper spiral is discontinued. The nitrogen escapes unabsorbed.

(iii) The modifications necessary when the substance contains sulphur or a halogen have been sufficiently indicated above.

221. Dumas' Method of Estimating Nitrogen.—The method is essentially that of § 220 (ii), except that the

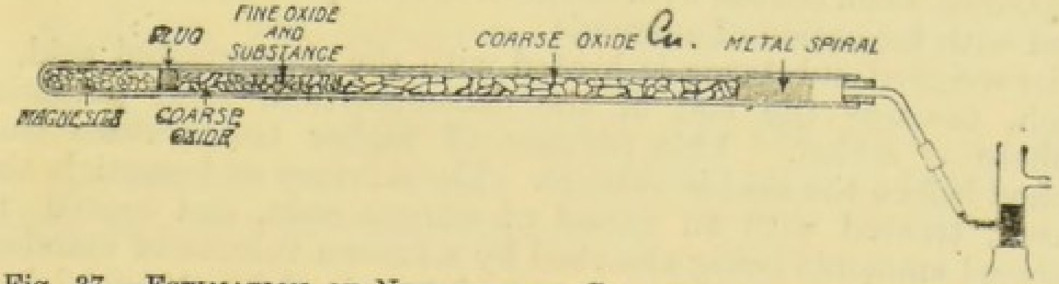

Fig. 37.—Estimation of Nitrogen by Combustion with Copper Oxide.

nitrogen is collected in a graduated tube (a Schiff's nitrometer) over concentrated potash solution in which carbon dioxide is absorbed and water condensed. The substance is generally mixed with finely divided oxide and poured into the tube, being "washed in" by more oxide.

A *closed* tube is employed, and at the closed end, which does not protrude from the furnace, a considerable quantity of lump magnesite is placed. Near to this is the substance mixed with oxide. The air is driven out by heating the magnesite, which liberates carbon dioxide; when all the escaping gas is absorbed the tube is air-free. The magnesite is now heated more gently, and the oxide and copper gauze at the other end are heated. Finally the heating of the oxide, etc., is made general. When oxidation is complete the magnesite is again raised to red heat. When all the evolved gas is again absorbed the gas-collecting tube is removed; the nitrogen is transferred to a nitrometer containing water, and the volume is read.

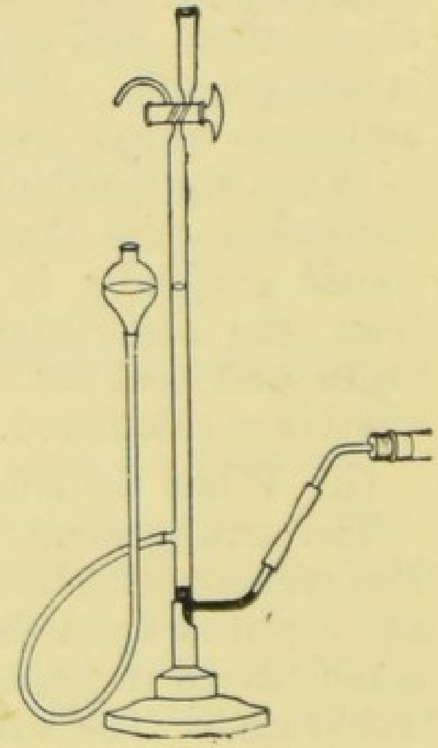

Fig. 38.
SCHIFF'S NITROMETER.

This precaution is advisable because the vapour pressures of solutions of potash are not sufficiently well known. From the volume of the nitrogen its weight can be deduced.

222. Kjeldahl's Method for Estimating Nitrogen.—This method is suitable for beginners, but is otherwise used only for rough commercial analysis. It depends upon the fact that organic nitrogen compounds when heated with concentrated sulphuric acid are decomposed with formation of ammonia.

The weighed substance is heated with the concentrated acid, to which, towards the end of the decomposition, solid potassium sulphate is added. This permits of higher temperature being reached before the acid is volatile. The mixture so formed is then diluted, treated with an excess of caustic soda, and heated, the displaced ammonia being absorbed by a known volume of standardised acid in excess. This excess is determined by standard base, and the quantity of ammonia formed is deduced.*

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* See *Inorganic Chemistry*, p. 211.

CHAPTER XXVIII.

MOLECULAR WEIGHTS AND FORMULAE.

223. Determination of Empirical Formulae.—The aim of the estimations described above is usually to provide a formula for the substance examined. For this purpose the percentage composition need not be specially calculated. The simplest way to convey the method is to give an example in illustration.

Data.

0·25 gram when oxidised gave 0·6027 gram carbon dioxide,
0·339 „ water,
·20 „ „ „ „ 33·4 c.c. nitrogen at 20° C. and 750 m m.

∴ (i) 0·25 gram contains ·1644 gram carbon (3/11)
„ ·0373 „ hydrogen (1/9)
(ii) 0·25 „ „ ·0484 „ nitrogen

·2501

Evidently the substance contains these three elements only.

Divide these numbers—which give the ratio by mass—by the atomic weights and we get the ratio of atoms. This must be given in whole numbers.

$$\left.\begin{array}{r} \frac{1644}{12} = 137 \\ \frac{373}{1} = 373 \\ \frac{484}{14} = 34{\cdot}5 \end{array}\right\} \begin{array}{c} \text{divide by} \\ 34{\cdot}5 \end{array} \rightarrow \begin{array}{c} 4 \\ 10{\cdot}8 \\ 1 \end{array}$$

This result corresponds nearly to the empirical formula $C_4H_{11}N$. The hydrogen value departs more than usual from the nearest whole number, so that it must be accepted with reserve. The molecular formula of a compound cannot usually be known until the vapour density has been determined.

224. Molecular Formula of a Gaseous Hydrocarbon.—The molecular formula of a gaseous hydrocarbon can, however, be simply determined from the volume relations alone.

Thus

3·4 c.c. of a hydrocarbon were mixed with 12·4 c.c. of oxygen.

After explosion 9·0 c.c. of gas were left, 6·8 c.c. of which were absorbed by caustic potash and the remainder by alkaline pyrogallol.

Hence

3·4 c.c. of hydrocarbon were completely oxidised by 10·2 c.c. of oxygen to yield 6·8 c.c. carbon dioxide as well as water. These numbers are in the ratio of 1 : 3 : 2.

$$C_xH_y + 3O_2 = 2CO_2 + ?H_2O,$$

wherefore

$$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O.$$

225. Vapour Density Determination.—The density of gases is determined by Regnault's method.* A modification of this method for volatile liquids is that of Dumas.† But by far the most important method in use of organic chemists is that of Victor Meyer. In this operation a weighed quantity of the substance is vapourised at such a temperature that the vapour behaves in accord with Boyle's and Charles' Laws. This temperature is considerably above the boiling point of the liquid. The volume of the vapour under these conditions is not determined directly, but an equal volume of air at *the same temperature and pressure* is expelled from the apparatus. This air is collected over water or mercury and measured at ordinary temperature. It is evident that the vapour itself, if it continued to behave according to these laws under ordinary conditions, would contract to the same volume as that of the air actually collected.

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* See *Inorganic Chemistry*, p. 19.

† This is described in *Inorganic Chemistry*, p. 140. *Metals*, p. 3.

When a substance which is readily oxidised under the conditions of the experiment is to be volatilised an atmosphere of nitrogen is used instead of air. By using metal vessels the vapour density of substances which have a high boiling point can be determined. We will now describe the experiment for an ordinary liquid of low boiling point, such as chloroform.

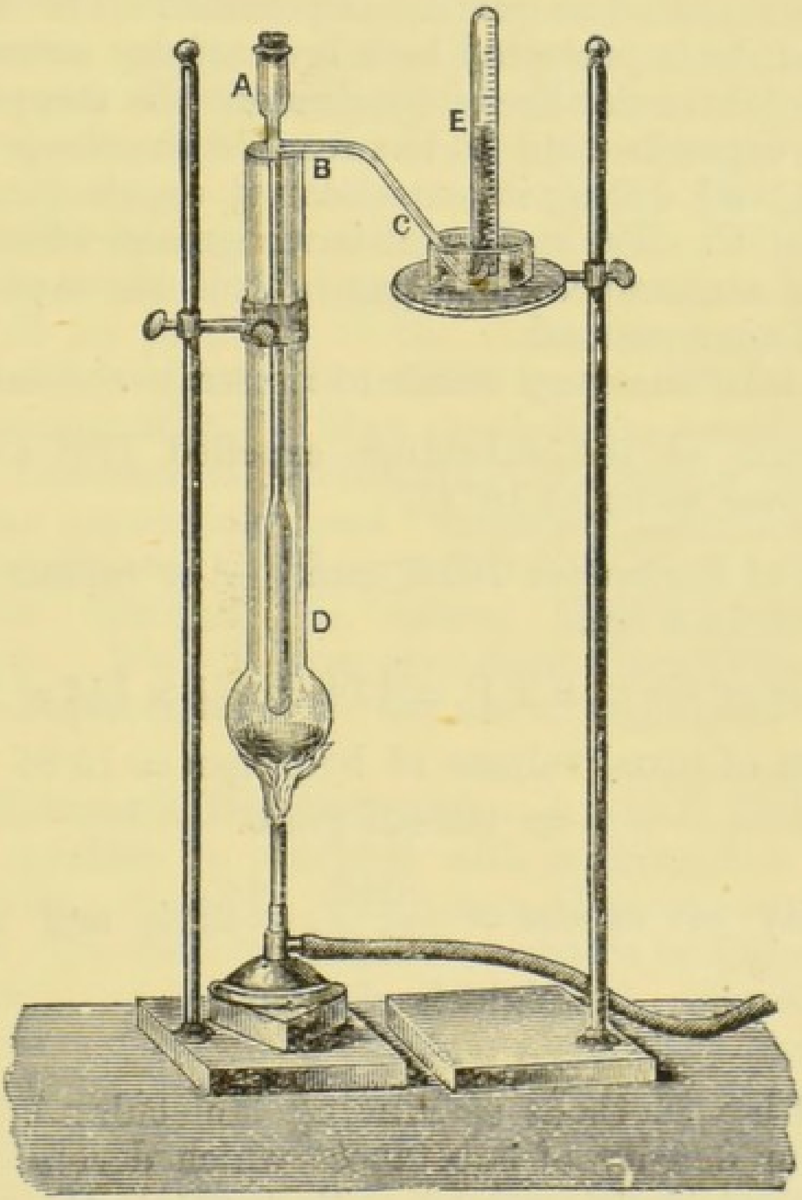

Fig. 39.

Victor Meyer's apparatus is illustrated in Fig. 39. The inner vessel has a short side tube of fine bore leading to the collecting trough; it is full of air. The air is brought to a constant temperature proper for the experiment by boiling a suitable liquid—in this case water (B.P. of chloroform 61° C.)—in the jacket tube. When all the air has gained the temperature of the jacketing vapour, no more bubbles will escape from the delivery tube. The receiver is now placed over the delivery tube; the stopper is removed for the admission of a tiny stoppered flask which contains a known mass of the chloroform. The stopper is replaced as quickly as possible. The bottom of the inner tube is protected by a layer of dry asbestos. As the chloroform volatilises it pushes out the stopper of the flask and expands until it has reached the temperature of the steam, and during its expansion it expels air, which is also at 100° C. The end point is recognised when no more bubbles of air escape. The gas tube is removed and the volume of air measured.

Let us take an actual result to illustrate the calculation.

·042 gram of the substance expelled 17·8 c.c. of air collected over water at 16° C.

Height of barometer 731·5 mm. Aq. vapour pressure at 16° C. = 13·5 mm.

$$\therefore \text{ Volume of air at S.T.P.} = 17{\cdot}8 \times \tfrac{273}{289} \times \tfrac{718}{760} = 15{\cdot}85 \text{ c.c.}$$

$$\therefore \text{ Weight of equal volume of hydrogen} = 15{\cdot}85 \times {\cdot}00009 = {\cdot}001427 \text{ gram.}$$

$$\therefore \text{ Density of vapour} = \frac{{\cdot}042}{{\cdot}001427} = 29{\cdot}4, \text{ and molecular weight is about } \mathbf{59}.$$

226. Other Methods of Finding Molecular Weights.—The vapour density of substances which decompose when heated cannot be determined. Fortunately the researches of Raoult[*] have provided two methods of finding the molecular weights of some soluble substances. He and others have shown that when a substance is dissolved in a

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[*] This subject is treated simply in *Inorganic Chemistry*, pp. 322-329 ;and from a different point of view in *Metals*, pp. 94-98. See also Wagstaff, *Properties of Matter*, §§ 241-246.

liquid and the solution is found not to conduct the electric current—

(i) For the same solute the freezing point of the solvent is depressed, and the boiling point of the solvent is raised by amounts approximately proportional to the quantity of the substance dissolved.

(ii) When different substances are dissolved in the same solvent, masses in molecular proportion dissolved in the same mass of solvent produce the same depression or elevation as the case may be. It is important to remember that these laws are actually true only for dilute solution and when the solute is not vapourised with the solvent.

But Raoult also calculated what depressions and elevations would be produced if the molecular mass of a substance could be dissolved in 100 grams of a solvent on the supposition that the laws given above would still hold true for concentrated solutions. These he called the "molecular depression" and "molecular elevation." They are usually denoted by the symbol K. Thus for water as solvent he obtained the values 18·9° C. and 5·2° C. respectively. We will now give short descriptions of two methods simple enough for the use of beginners.

227. Eijkman's Depressimeter.—A small flask to contain the solution is provided with a ground-in thermometer reading to $\frac{1}{20}$° C., which acts also as a stopper for the flask. The flask is jacketed as shown in Figure 40.

The weight of the flask is determined. Some water is placed in it sufficient to cover the bulb of the thermometer, its weight is found, and the thermometer replaced. The freezing point of the water is marked by immersing it in a freezing mixture. As soon as freezing begins the depressimeter is removed and shaken thoroughly. As the water freezes the mercury runs up the tube (the water having been overcooled), the highest point the mercury reaches before falling again is the freezing point of water. A small weighed quantity of the substance is now introduced and the new freezing point determined. A second determination can be made by adding a little more of the substance, and so on with more and more concentrated solutions.

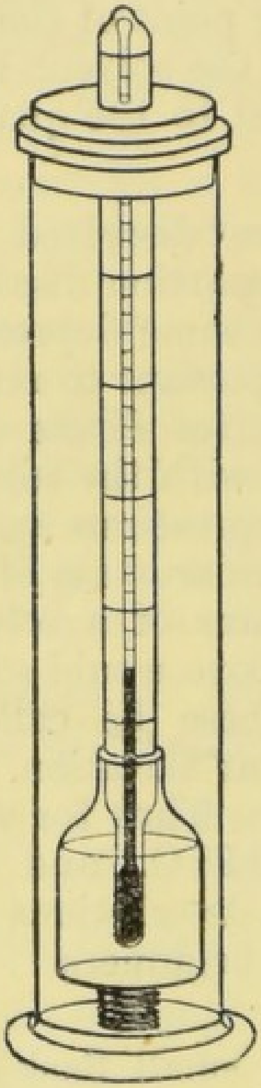

Fig. 40.
Eijkman Apparatus.

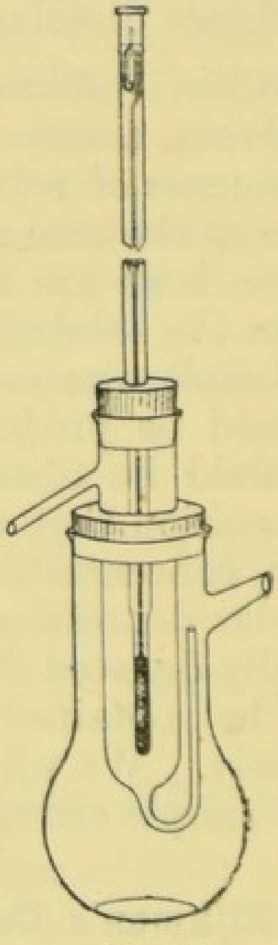

Fig. 41.
Landsberger-MacCoy Apparatus.

The following is a result with acetic acid as solvent:—

The acetic acid froze at 16·5° C. [K = 39].

Weight of acetic acid taken, 10 grams.

Weight of substance added, ·06 gram.

New freezing point, 16·2° C.

·06 gram dissolved in 10 grams solvent
= ·6 ,, ,, ,, 100 ,, ,,

This concentration produces depression of 0·3° C.

Therefore the concentration which would produce 39° C. = 78 grams = molecular weight approximately.

228. Landsberger-MacCoy Modification of Boiling Point Method.—The apparatus is shown in Fig. 41. Either a Beckmann thermometer, or one reading to $\frac{1}{20}$° C. can be used. The main part of the solvent is placed in the outer vessel. The inner vessel is of known weight. It communicates with the outer vessel by a capillary tube. Some of the solvent is also placed in the inner tube.

The experiment is begun by boiling the solvent in the jacket. When the exit tube of the jacket is closed the vapour is forced to traverse the inner tube; here it condenses and soon raises the solvent to boiling. This point is registered by the thermometer. The inner tube is removed, dried, and weighed with the contained liquid. A known mass of substance is added, the tube replaced, and the experiment begun as before. On this occasion, since the quantity of solvent is always increasing in the inner tube, immediately a reading is made, and *as rapidly as possible*, the exit of the inner tube is closed; the exit of the jacket is opened. The inner tube is then removed, dried outside, and weighed again. The new weight will give, by subtraction, the concentration of the solid. Another reading can now be taken, and this time of course a *more dilute* solution will be formed.

We will again give an example (the substance is the same as before).

Weight of water = 79·4 grams.
,, ,, substance = 5·7 grams.
Elevation of B.P. = ·52.

Concentration of solution = 7·3 grams per 100 of water. Therefore the quantity of substance which would produce an elevation of 5·2° = **73** grams = M. Wt. (approx.).

229.—*Molecular Weights of Acids and Some Bases.* The equivalent weights of some organic acids can be found by decomposing weighed quantities of their silver salts and weighing the silver (see Exp. 19, p. 36). Similar help is given for amines, etc., by the results of experiments in which weighed quantities of chloroplatinates (see Section 124) are decomposed. The salt washed with alcohol is collected in a weighed porcelain crucible, dried in an air bath, weighed, ignited, and the crucible weighed again.

(i) ·76918 gram of silver benzoate yielded ·36247 gram of silver.

∴ 108 grams of silver are combined with 121·2 grams acid radicle.

∴ (since acid is monobasic),

$$\text{Molecular weight} = \underset{\text{(acid radicle)}}{121{\cdot}2} + \underset{\text{(acid hydrogen)}}{1} = 122{\cdot}2.$$

(ii) The substance of Section 223 was taken. Its vapour density had also been found to be 37.

2·02 grams of chloroplatinate yielded 0·7091 gram platinum.

This is 35·1 per cent. yield of platinum, which very nearly corresponds to the formula $(C_4H_9NH_2.H)_2PtCl_6$.

QUESTIONS.—CHAPTER XXVIII.

1. A volatile organic liquid of vapour density 37·5 referred to hydrogen was analysed with the following results:—0·1503 gram of the substance gave 0·1765 gram carbon dioxide and 0·0902 gram water: 0·1250 gram of substance gave 0·0233 gram of nitrogen.

What is the molecular formula of the substance? What structural formulae may it possess, and how would you proceed to determine which is the true one?

2. 50 c.c. of a gas, or mixture of gases, were mixed with 150 c.c. of oxygen: after explosion the volume diminished to 100 c.c., and after absorption with potash 50 c.c. of oxygen remained. What was the composition of the original gas? What further experiments are required in order to determine its nature?

3. An organic substance gave on analysis the following results:—·2501 gram of substance gave ·5506 gram of carbon dioxide and ·2998 gram water. Its vapour density is 30. What is its formula? What structures may it possess, and how would you decide between them?

4. A certain gas, known to contain only the elements carbon and hydrogen, was mixed with excess of oxygen, and the mixture was exploded in an eudiometer. The following numbers (here corrected to S.T.P.) were obtained:—Contraction after explosion and cooling, 28 c.c.; contraction on treating residue with caustic potash 14 c.c.

What simple hydrocarbon would you suppose this gas to be? Show that the same results might be obtained from a mixture of equal volumes of hydrogen and a certain other hydrocarbon.

5. A certain solid hydro-carbon was found to have the composition—*Carbon*, 93·75 per cent.; *Hydrogen*, 6·25 per cent.

Describe as fully as you can the experimental method of arriving at these figures, and deduce from them the simplest possible (or empirical) formula for the hydrocarbon. Why would not this formula, so deduced, represent the probable molecular weight?

6. An acid containing carbon, hydrogen and oxygen only, gives on analysis 26·66 per cent. of carbon and 2·22 per cent. of hydrogen.

The acid cannot be vapourised unchanged. Explain the steps you would take to ascertain the molecular formula of the acid.

7. Do you think the silver method of finding the equivalent weight of an acid suitable for formic and tartaric acids?

8. Two liquids, one boiling at 83° C., and the other at 57° C., gave, on analysis, the same results, viz. 0·2376 gram gave on combustion 0·2112 gram carbon dioxide and 0·0684 gram water; 0·121 gave with nitric acid and silver nitrate 0·351 gram silver chloride. Calculate the simplest formula for these substances. How do you account for two substances having the same composition, and what do you regard as the true formula of each compound?

9. ·25 gram of an organic substance when burnt with copper oxide yielded ·5942 gram of carbon dioxide and ·3044 gram of water. The vapour density was 2·58 compared with air. Find the formula.

10. On combustion, ·1135 of a compound gave ·2928 gram of carbon dioxide and 0·0603 gram of water. When ·1326 gram was dissolved in 12 grams of water the freezing took place at – ·33° C. Calculate the formula.

11. Combustion—
Weight of compound burned ·200 gram
,, ,, carbon dioxide ·677 ,,
,, ,, water ·139 ,,
V.D.—
Vacuous flasks (capacity 250 c.c.) weighed 60·347 grams
+ vapour (at S.T.P.) 61·230 ,,
Calculate the formula.

12. 1·044 gram of silver salt of an acid when heated gave ·675 gram silver. What is the equivalent of the acid?

ANSWERS.

Chapter I. (2) C_2H_6O. Chapter II. (2) C_4H_7BrO.

Chapter III. (4) CH_4; C_2H_4; C_2H_2. Chapter VI. (14) C_3H_9N.

Chapter XII. (5) C_6H_{10}. Chapter XIV. (6) Methyl-ethyl-ketone.

Chapter XV. (8) Malonic acid. (9) $C_4H_6O_6$.

Chapter XXVIII. (1) $C_2H_5NO_2$; (2) 75 per cent. Carbon, 25 per cent. Hydrogen; (3) C_3H_8O; (4) CH_4, $C_2H_6+H_2$; (5) $C_{10}H_8$; (6) Oxalic, find basicity; (8) $C_2H_4Cl_2$; (9) $C_4H_{10}O$; (10) C_4H_4O [? Toluic acid]; (11) C_6H_6; (12) 60.

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