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John Morris Weiss
Chemistry 1905.
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WORKS OF PROF. A. F. HOLLEMAN

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A Text-book of Inorganic Chemistry.

By Dr. A. F. HOLLEMAN, Professor Ordinarius in the University of Groningen, Netherlands. Rendered into English by HERMON C. COOPER, Ph.D., Instructor in Syracuse University, with the co-operation of the author. 8vo, viii + 458 pp., 84 figures. Cloth, $2.50.

A Text-book of Organic Chemistry.

Rendered into English from the Second Dutch Edition by A. JAMIESON WALKER, Ph.D. (Heidelberg), B.A., Head of Department of Chemistry, Municipal Technical College, Derby, Eng., assisted by OWEN E. MOTT, Ph.D. (Heidelberg), Demonstrator of Chemistry, Municipal Technical College, Derby, Eng., with the co-operation of the author. 8vo. xvii + 555 pages, 73 figures. Cloth, $2.50.

A companion volume to the preceding, and forming with it a comprehensive treatise on pure Chemistry.

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OF

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TRANSLATED FROM THE SECOND DUTCH EDITION BY

A. JAMIESON WALKER, Ph.D. (Heidelberg), B.A.,

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AUTHOR'S PREFACE.

MOST of the short text-books of Organic Chemistry contain a great number of isolated facts; the number of compounds described in them is so considerable as to confuse the beginner. Moreover, the theoretical grounds on which this division of the science is based are often kept in the background; for example, the proofs given of the constitutional formulæ frequently leave much to be desired. However useful these books may be for reference, they are often ill-suited for text-books, as many students have learned from their own experience.

In this book I have endeavoured to keep the number of unconnected facts within as narrow limits as possible, and to give prominence to the theory underlying the subject. For this reason, a proof of the structure of most of the compounds is given. This was not possible for the higher substitution-products of the aromatic series, so that the methods of orientation employed in it are described in a special chapter.

Physico-chemical theories, such as the laws of equilibrium, ionization, and others, are becoming more and more prominent in organic chemistry. I have attempted in many instances to show how useful they are in this branch of the science. Such important technical processes as the manufacture of alcohol, cane-sugar, etc., are also included. The book is essentially a text-book, and makes no claim to be a "Beilstein" in a very compressed form.

I am deeply indebted to Dr. A. JAMIESON WALKER for the excellent way in which he has carried out the difficult task of translating this book from the original second Dutch edition into English. Lastly, it may be mentioned that it has also been translated into German, the second edition having just appeared, and that an Italian edition is in preparation.

A. F. HOLLEMAN.

GRONINGEN, NETHERLANDS, November, 1902.

TRANSLATOR'S PREFACE.

THE cordial reception met with by Professor HOLLEMAN'S "Leerboek der Organische Chemie" in Holland, as well as by Dr. HOF'S translation in Germany, makes it desirable that English-speaking students of chemistry should share in the advantages derived from its publication by their fellow-students on the Continent of Europe.

This translation is from the second Dutch edition, published last year, and has been revised and added to by Professor HOLLEMAN and myself so as to make it as up-to-date as possible. An Italian translation of this English edition is now in preparation. The "Inorganic Chemistry" referred to in the text is Dr. COOPER'S translation of Professor HOLLEMAN'S "Leerboek der Anorganische Chemie," published last April by Messrs. JOHN WILEY & SONS.

I have to express my thanks to Professor HOLLEMAN for the great care bestowed by him on the work of revision; to Dr. OWEN E. MOTT, for his valuable assistance; to Professor SENIER of Queen's College, Galway, for reading the proof and making many important suggestions; to Dr. JOHN E. MACKENZIE of the Birkbeck Institution, London, for reading part of the proof; to Dr. HERMON C. COOPER of Syracuse University for the note regarding the law regulating the sale of alcohol in the United States; and to Messrs. JOHN WILEY & SONS for the excellent way in which they have prepared the book for publication.

A. JAMIESON WALKER.

DERBY, ENGLAND, December, 1902.

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ORGANIC CHEMISTRY.

INTRODUCTION.

1. Organic Chemistry is the Chemistry of the Carbon Compounds. The word "organic" has now only a historic meaning, being derived from a time—the beginning of last century—when it was thought that the substances which occur in *organized* nature, in the animal and vegetable kingdoms, could only be formed under the influence of a special, obscure force, called the *vital force*. Several unsuccessful attempts to prepare artificially such "organic" substances promoted this belief. Until about the year 1840, it was so general that **Berzelius** still thought that there was but little hope of ever discovering the cause of the difference between the behaviour of the elements in the mineral kingdom and in living bodies. Organic chemistry included the study of those compounds which occur in plants and animals, as well as of the more or less complicated decomposition-products which could be prepared from these compounds by various means. Among the latter many were known which did not occur in nature, but it was thought impossible to build up a compound body from its decomposition-products, or to obtain an organic compound from its elements.

In the year 1828, **Wöhler** had indeed obtained from inorganic sources the organic compound *urea*, a product of the animal economy. This discovery was at first regarded as of small importance, for it was thought that this substance occupied a position midway between organic and inorganic compounds. For a number of years the synthesis of urea was in fact the only well-known example of the kind, such observations becoming more numerous about the middle of the nineteenth century. The synthesis of many substances, including that of acetic acid by KOLBE, and of the fats by BERTHELOT, strengthened the conviction which had gradually arisen, that organic compounds are formed under the influence of the same forces as are inorganic, and that to this end no *special* force is necessary.

The natural division between organic and inorganic chemistry was thus destroyed, its place being taken by an artificial one. As it had been already noticed that all organic compounds contain carbon, the name "Organic Chemistry" was applied to the *Chemistry of the Carbon Compounds.*

Through the numerous discoveries which were made in this department of the science, especially in Germany by LIEBIG, WÖHLER, and their pupils, and in France by DUMAS, LAURENT, and GERHARDT, organic chemistry gradually acquired a totally different aspect, and the old division into groups of substances which had either the same origin, as in the case of vegetable chemistry or animal chemistry, or had single properties in common, as for example the vegetable acids, the vegetable bases, and neutral vegetable bodies, vanished. Its place was taken by a more rational classification, which gradually developed into its present form, and is based on the mutual relationships which are found to exist between organic compounds.

2. Since no essential distinction between organic and inorganic chemistry now exists, and numerous syntheses have set at rest all doubt as to the theoretical possibility of building up from their elements even the most complicated carbon compounds, such as the albumins, the question may arise as to the reason why the chemistry of the carbon compounds is still treated as a special part of the science. The answer to this question is based upon two reasons.

First, the enormous number of carbon compounds which are known. This amounts to many thousands,* and is greater than that of the compounds of all the other elements. Second, the properties of the carbon compounds. These are either not found at all in the compounds of other elements, or at least in a much less marked degree; for example, many inorganic compounds

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* Seventy-five thousand compounds are mentioned in the dictionary recently published by M. M RICHTER.

can be exposed to high temperatures without undergoing any chemical change, whereas the carbon compounds, almost without exception, are decomposed at a red heat. As a result of this, the latter are generally much less stable than the former towards chemical and physical reagents, and thus different methods are employed in the investigation of the carbon compounds and of the inorganic compounds.

A further peculiarity is that numerous organic compounds have exactly the same composition, but differ very much from one another in properties. For example, up to the year 1900, eighty-two compounds of the formula $C_9H_{10}O_3$ had been discovered. This phenomenon is called *isomerism*, and is almost unknown in inorganic chemistry, a fact which necessitates an investigation of the cause to which it is due.

All these reasons make it desirable to treat the carbon compounds in a special part of chemistry.

QUALITATIVE AND QUANTITATIVE ANALYSIS.

3. Investigation has shown that in the majority of the compounds of carbon, there only occurs a very small number of elements. The chief of these are *carbon, hydrogen, oxygen*, and *nitrogen*. *Halogen* derivatives are less numerous, and substances containing *sulphur* or *phosphorous* occur still less frequently. Carbon compounds are also known in which other elements are found, but they are exceedingly few in comparison with those which contain only the elements named above. Some elements do not occur in carbon compounds.

In order to be able to determine the nature of a compound, it is first of all necessary to ascertain what elements it contains by submitting it to *qualitative analysis*. In the case of the carbon compounds, this is very simple in theory, the process being one of oxidation. This converts hydrogen into water, nitrogen is liberated in the free state, and the other elements are brought into the form of simple compounds (carbon dioxide, sulphuric acid, phosphoric acid, etc.), which can then be detected by the ordinary reactions of inorganic analysis. If an organic compound contains a halogen, it must be oxidized before the latter can be detected, since the halogens are not usually split off in the form of ions by mere solution of their organic compounds, and cannot therefore be recognized by the simple addition of silver nitrate. When such a compound is oxidized in presence of silver nitrate, the corresponding silver halide is formed. Other elements which may be present are found, after oxidation, in the form of compounds which are easily identified.

For analytical purposes, oxidation is carried out in different ways, according to the nature of the element whose presence is suspected. Copper oxide is generally used in testing for carbon, hydrogen, and nitrogen. The substance is mixed with it, and the mixture is heated in a glass tube sealed at one end, the carbon and hydrogen being oxidized by the action of the oxygen of the copper oxide. Nitrogen is evolved in the free state, and can be recognized in exactly the same way as in the quantitative analysis of nitrogen (**7**). In the case of the halogens, sulphur, phosphorus, etc., it is easier to oxidize the substance under examination with concentrated nitric acid.

The method of oxidation is a general one for qualitative analysis; it can always be applied, and yields perfectly reliable results. There are in addition other methods which in many cases attain the desired end more quickly and easily, but as most of these methods are not of universal application, the failure of one of them to detect an element affords no certain indication of its absence. In doubtful cases the question must be decided by the oxidation process.

For example, the presence of carbon can frequently be detected by submitting the substance to dry distillation. Charring often takes place, or vapours are evolved which can be recognized as carbon compounds by their smell or other properties, such as burning with a smoky flame on ignition.

4. The nitrogen in many organic compounds can be converted into ammonia by heating with soda-lime, or with concentrated sulphuric acid. Another method very largely used in testing for this element was suggested by LASSAIGNE. It consists in heating the substance under examination with a small piece of sodium (or potassium) in a narrow tube sealed at one end. Should the compound contain nitrogen, sodium (or potassium) cyanide is formed, its presence being easily recognized by converting it into Prussian blue.

This test is carried out as follows. The tube with its contents, after having been heated to redness, is immersed in a little water, whereupon it cracks, and the alkaline cyanide which has been formed dissolves. To this is added a drop of a solution containing a ferrous and ferric salt, and then a little dilute hydrochloric acid. Should an alkaline cyanide be present, it is converted into Prussian blue, forming a blue precipitate in the liquid.

5. The halogens may be recognized by heating the substance with quicklime, the corresponding calcium halide being formed. A very delicate method of detecting them is to introduce a little of the compound on a piece of copper oxide into a colourless flame. The corresponding copper halide is formed, and volatilizes, imparting a magnificent green colour to the flame. These two methods are always applicable.

Sulphur can often be detected by heating the compound with a small piece of sodium in a narrow ignition tube. Sodium sulphide is produced, and can be detected by treating the reaction-mixture, placed on a clean silver coin, with water, when a black stain of silver sulphide is formed. Or, the reaction-mixture may be extracted with water, and sodium nitroprusside added to the solution, which then acquires a deep-violet colour.

No mention has here been made of oxygen, because no qualitative reaction is known by which it may be tested for in an organic compound. Its presence can only be detected by quantitative analysis.

6. Following on qualitative, must come *quantitative analysis;* that is, the determination of the quantity of each element present in the compound. The methods used for qualitative analysis in inorganic chemistry are often very different from those employed in quantitative determinations; in organic chemistry the methods of qualitative and quantitative analysis are alike in principle, oxidation being made use of in both.

Carbon and hydrogen are always estimated together. The principle of the method of organic analysis which is chiefly used was worked out by LIEBIG (1803–1873). It is usually carried out as follows. In the combustion furnace, *k* (Fig. 1), is a hard glass tube, *ab*, open at both ends. A complete drawing of it is shown in the figure above the furnace. It is partly filled with granulated copper oxide, *ff*, and with a spiral of copper gauze, *c*, which has been oxidized by heating to redness in the air or in a stream of oxygen. About one-third of the length of the tube is left empty, and into this, after removal of the copper spiral, a platinum or porcelain boat, *d*, containing a weighed quantity of the substance to be analyzed, is introduced. The end of the tube next the boat is connected with a drying-apparatus, *g*, *h*, *j*, in which the air or oxygen is freed from water-vapour and carbon dioxide; *g* contains concentrated caustic potash, *h* soda-lime, and *j* calcium chloride. To the end of the tube furthest from the boat is attached a weighed calcium chloride tube, *l*, for the purpose of collecting the water produced by the combustion of the substance. The weighed potash bulbs, *m* (shown enlarged in Fig. 2), are connected to this, and in them the carbon dioxide formed is absorbed by concentrated caustic potash. The gases enter the apparatus by the tube *b* on the right, pass through the three bulbs containing potash, and escape through the tube *a*, which is filled with soda-lime. As soon as it is certain that all the joints of the apparatus are gas-tight, the burners are lighted, except beneath the place where the boat is. When the tube is hot, the substance is burned by carefully heating this part of the tube, while at first a slow stream of air, and later a slow stream of oxygen, are led through the drying-apparatus into the tube. The oxygen has the effect of burning more easily and quickly the particles of carbon which have

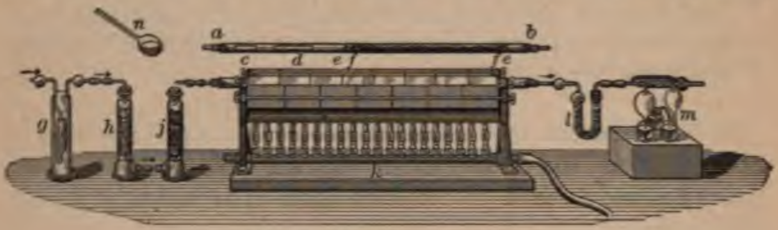


FIG. 1.—ORGANIC ANALYSIS.

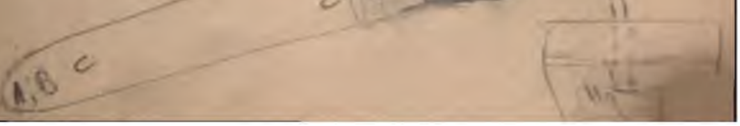
FIG. 2.

deposited, and the red-hot copper oxide serves to fully oxidize the gaseous decomposition-products to carbon dioxide and water. The increase in weight of the calcium chloride tube and of the potash bulbs gives the quantity of water and carbon dioxide formed, from which the amount of hydrogen and carbon in the compound may be calculated.

Should the compound contain nitrogen or halogens, a freshly-reduced spiral of copper is placed at the end of the tube next the absorption-apparatus *l* and *m*. The hot copper decomposes any nitrogen oxides which may be formed, and which would otherwise be absorbed in the potash bulbs, and at the same time combines with and retains the halogens.

Sometimes the analysis is carried out in a different manner, the substance to be analyzed being mixed with finely-powdered copper oxide and heated in a tube drawn out at one end to a fine point in the shape of a bayonet, and connected at the other with the absorption-apparatus. In order to drive over into the absorption-apparatus the water-vapour and carbon dioxide which remain in the tube after the combustion, the point of the tube is broken, and a stream of air drawn gradually through the whole apparatus. Substances which burn with great difficulty are mixed with lead chromate instead of copper oxide, the former being the more energetic oxidizing-agent. This substance is also used when the compound contains sulphur, the sulphur being converted, by heating in contact with the chromate, into lead sulphate, which is stable at red heat. If copper oxide is used, sulphur dioxide is formed and is absorbed in the potash bulbs, thereby introducing an error into the carbon estimation. Another method of retaining sulphur dioxide consists in having a layer of lead dioxide, PbO_2, at the end of the tube next to the absorption-apparatus. This layer is gently heated, and takes up all the sulphur dioxide, with formation of lead sulphate.

7. Nitrogen is usually estimated by DUMAS' method. A weighed quantity of the substance B is mixed with finely-powdered copper oxide and placed in a tube closed at one end. A substance which on heating easily evolves carbon dioxide is previously placed at the end of the tube, magnesium carbonate A being often used for this purpose. The remaining space is filled with granulated copper oxide, C and a roll of clean, freshly-reduced copper gauze D is placed at the end. The open end of the tube is closed with a rubber stopper fitted with a delivery tube, the end of which dips under mercury. As soon as the air has been driven out of the



apparatus by heating the magnesium carbonate, the front part of the tube, containing the copper spiral and the granulated copper oxide, is heated. The combustion is then begun, and the evolved gases are collected in a graduated tube open at the bottom (measuring tube), the end of which dips into the mercury bath, and which is filled partly with mercury, and partly with concentrated caustic potash to absorb the carbon dioxide. The reduced copper spiral has the effect of decomposing any nitrogen oxides which may be formed. The magnesium carbonate is again heated as soon as the combustion is over, the carbon dioxide evolved driving all the nitrogen remaining in the apparatus into the graduated tube. The latter, along with the mercury, potash, and gas which it contains, is then placed in a wide cylinder filled with water. The mercury and potash are displaced by the water, and after the level of the liquid inside and outside the tube has been made to coincide, the number of cubic centimetres of nitrogen is read off. From this the amount of nitrogen in the compound is calculated.

In many cases nitrogen may be estimated by a method which was discovered by KJELDAHL and improved by WILFARTH. It depends upon the fact that the nitrogen of many organic substances is wholly converted into ammonia when the compound is heated for some time with concentrated sulphuric acid in presence of phosphoric anhydride and a drop of mercury, the latter going into solution. Usually the mixture first turns black, owing to charring; after heating for one or two hours, a point is reached at which the liquid again becomes perfectly colourless. The carbon has then been fully oxidized by the oxygen of the sulphuric acid, which is reduced to sulphurous acid. The process is facilitated by the mercury salt, which probably plays the part of an "oxygen carrier" between the sulphuric acid and the organic substance, being continually converted from the mercuric to the mercurous state, and then back again by the boiling acid into the mercuric state. As soon as the liquid has become colourless, it is allowed to cool, diluted with water, excess of alkali added, and the ammonia distilled into a measured quantity of acid of known strength. By titrating, the quantity of ammonia is found, and hence the amount of nitrogen. This neat and easy method is usually not applicable to compounds which contain oxygen linked to nitrogen. In this case the latter element is only partially converted into ammonia.

8. The halogens can be estimated by the method either of LIEBIG or of CARIUS. In the former, the substance is heated with quicklime, and in the latter, at a high temperature with a little concentrated nitric acid and a crystal of silver nitrate in a sealed glass tube. This is carried out without risk in the tube furnace (Fig. 3), in which the glass tubes are placed in wrought-iron cylinders with thick walls.

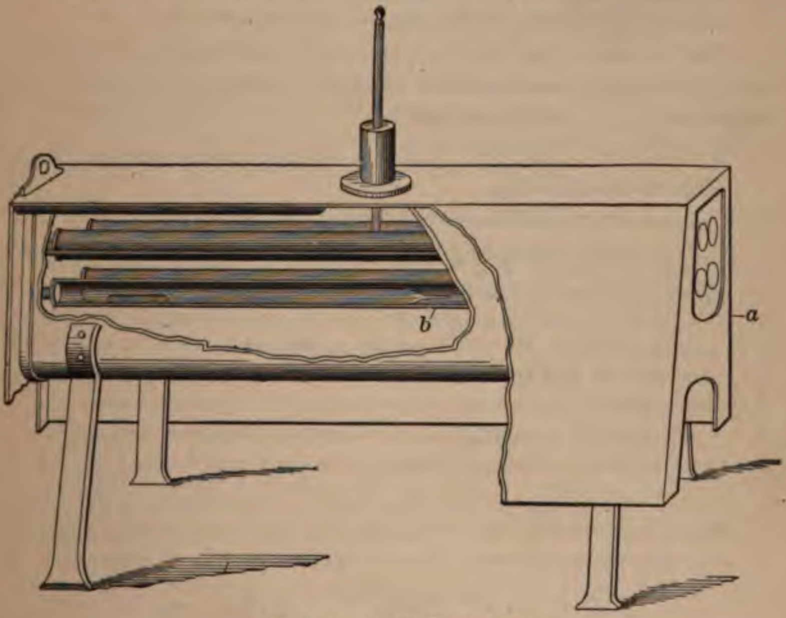


FIG. 3.—TUBE FURNACE.

CARIUS' method can also be applied to the estimation of sulphur, phosphorus, etc. Non-volatile substances containing sulphur or phosphorus can also be oxidized by fusion with nitre.

9. The results of a quantitative analysis are expressed in percentage-numbers. If the total of these percentage-numbers is very nearly 100, then no other elements are present in the compound; but if appreciably less than 100, there is another element present which has not been taken account of in the analysis, because there is no suitable method known for its estimation.

This element is *oxygen*. The percentage-amount of oxygen is therefore found by subtracting the total of the percentages of the other elements from 100. This has the disadvantage that the errors of experiment are all included in the percentage-number of the oxygen.

Carbon estimations are usually too low, owing to the loss of a little carbon dioxide through the various connections of the apparatus. The hydrogen estimations are generally too high, because copper oxide is hygroscopic, and can only be freed from traces of moisture with great difficulty. These errors balance one another more or less, so that the want of accuracy in the oxygen percentage is diminished.

The method by which the percentage-composition and formula of a substance are calculated from the results of analysis is best explained by one or two examples.

First Example. The following numbers were obtained in the analysis of a substance:

(*a*) 0·2581 g. substance gave 0·7654 g. CO_2 and 0·1623 g. H_2O.

(*b*) 0·2170 g. substance gave 0·6414 g. CO_2 and 0·1360 g. H_2O.

Since there are 12 parts by weight of C in 44 parts by weight of CO_2, and 2 parts by weight of H in 18 parts by weight of H_2O, the number obtained for CO_2 must be multiplied by $\frac{12}{44} = \frac{3}{11}$ to find the amount of C, and the number found for H_2O by $\frac{2}{18} = \frac{1}{9}$ to obtain the amount of H.

(*a*) 0·2581 g. substance contain 0·2087 g. C and 0·0181 g. H.

(*b*) 0·2170 g. substance contain 0·1749 g. C and 0·0151 g. H.

In order to calculate from this the percentage-numbers, the figures found for C and H must be divided by the weight of substance used in the analysis, and the quotient multiplied by 100. This gives

(*a*) 80·8% C and 7·0% H.
(*b*) 80·6% C and 6·9% H.

Since the sum of C and H is 87·8 in (*a*), and 87·5 in (*b*), the compound analyzed must contain oxygen. According to (*a*) the percentage of this element is 12·2; according to (*b*) it is 12·5.

The mean of the two analyses gives the following percentage-composition for the substance:

C 80·7
H 6·9
O 12·4

The atomic weight of carbon is 12, of hydrogen 1, and of oxygen 16; in order to find the ratio of the number of the atoms of these elements in the compound, their atomic weights must be divided into the percentage-numbers. From this we obtain

C	H	O
6·7	6·9	0·8

Since there cannot be less than one atom of each element in a compound, and since the figure representing the number of atoms must always be a whole number, we must divide the above ratio by 0·8, which makes O = 1, and the other numbers as follows:

C	H	O
8·7	9·0	1

It is evident that the ratio of the numbers of the atoms is very nearly 9 : 9 : 1, which corresponds with the formula C_9H_9O. Inversely, if the percentages of carbon, hydrogen, and oxygen be calculated for a substance of this constitution, there is obtained

C 81·2 H 6·8 O 12·0

which approximates to the mean of the results of the analyses given above. The simplest or *empirical* formula of the substance is therefore

$$C_9H_9O.$$

Second Example. The analysis of a substance containing nitrogen gave the following numbers:

0·2169 g. substance gave 0·5170 g. CO_2 and 0·0685 g. H_2O.
0·2218 g. substance gave 17·4 c.c. N, measured over water at 6° C. and 762 mm. barometric pressure.

The weight of the nitrogen is calculated in the following way. Since it is saturated with water-vapour, the tension of this expressed in mm. of mercury must be subtracted from the barometric pressure in order to obtain the true pressure of the nitrogen. At 6° C. the tension of aqueous vapour is 7·0 mm. The actual pressure of the nitrogen is therefore 762 — 7 = 755 mm. Since 1 c.c. of nitrogen at 0° and 760 mm. weighs 1·2562 mg., at 755 mm. and 6° C. the weight of this volume expressed in milligrammes is

$$\frac{1{\cdot}2562}{1 + 6 \times 0{\cdot}00367} \times \frac{755}{760} = 1{\cdot}2211.$$

Therefore the 17·4 c.c. of nitrogen obtained weigh 1·2211 × 17·4 = 21·247 mg., from which the percentage of nitrogen is found to be 9·6.

By applying the method described in the first example, the percentage of carbon and hydrogen is found to be C = 65·0 and H = 3·5.

The sum of these percentage-numbers is 78·1, so that the percentage of oxygen in the substance analyzed is 21·9. The percentage-composition given by the analysis is therefore

C 65·0
H 3·5
N 9·6
O 21·9

On dividing these values by the numbers representing the atomic weights of the corresponding elements, we have

C	H	N	O
5·4	3·5	0·7	1·4

These numbers divided by 0·7 give:

C	H	N	O
7·9	5·1	1	2·0

These numbers approximate very closely to those required by the formula $C_8H_5NO_2$. The percentage-composition corresponding to this formula is

C 65·3 H 3·4 N 9·5

which agrees well with the analysis.

DETERMINATION OF MOLECULAR WEIGHT.

10. An analysis only gives the empirical formula of a compound, and not its molecular formula, because $C_aH_bO_c$ has the same percentage-composition as $(C_aH_bO_c)_n$. When the empirical formula has been ascertained by analysis, the *molecular weight* has still to be determined.

This cannot be decided by chemical means, although it is possible to thus obtain a minimum value for the molecular weight. For example, the empirical formula of benzene is CH. There is easily obtained from benzene a compound, C_6H_5Br, which can be reduced again to benzene. It follows from this that the molecule of this substance must be represented at least by C_6H_6. The molecular formula, however, could also be $C_{12}H_{12}$, or, in general, $(C_6H_6)_n$; the bromine compound would then have the formula $(C_6H_5Br)_n$. Assuming the formula to be $C_{12}H_{12}$, that of the bromine compound would be $C_{12}H_{10}Br_2$. It is evident that in this case two hydrogen atoms would have been directly replaced by bromine, and experiments would be made for the purpose of obtaining $C_{12}H_{11}Br$. Should these not attain the desired result, the probability that the simpler formula C_6H_5Br is correct would be increased, although it would not be perfectly established, because it might happen that the conditions necessary to the formation of the compound $C_{12}H_{11}Br$ had not been found. The chemical method only furnishes us with a proof that the molecule of benzene cannot be *smaller* than that expressed by the formula C_6H_6. It is, however, impossible to decide in this way whether it is a multiple of this or not.

In order to ascertain the real molecular weight, physical methods must be made use of. These consist in the determination either of the specific gravity of the compound in the gaseous state, or of certain values which depend on the osmotic pressure of the substance in dilute solution. It will be seen later that there is a close connection between these apparently totally different methods.

Determination of the Molecular Weight from the Vapour Density.

11. According to AVOGADRO's law ("Inorganic Chemistry," **31, 32,** and **35**), equal volumes of different gases measured at the same temperature and pressure contain the same number of molecules. From this it follows that the weights of the molecules of these gases must stand in the same relation to one another as the weights of these equal volumes. Since the atomic weight of hydrogen is taken as unity, and a molecule of hydrogen contains two atoms, the molecular weight of hydrogen is 2. If an equal volume of another gas under the same conditions as to temperature and pressure weigh a times as much as hydrogen,* then its molecules also will weigh a times as much, and the molecular weight of the gas will be $2a$.

In order to be able to calculate the *vapour density* (the specific gravity of the substance in the gaseous state), four quantities—the weight of substance converted into the gaseous state, the volume of the resulting vapour, the temperature at which the volume is measured, and the barometric pressure—must be known.

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* a is therefore the specific gravity of the gas referred to hydrogen.

12. Vapour density is usually determined by a method suggested by VICTOR MEYER. The apparatus necessary for this (Fig. 4) consists of a glass tube *b* with an internal diameter of about 4 mm. This tube is closed at the top with a stopper, and has underneath a wider cylindrical portion of about 200 c.c. capacity, closed at the lower end. Near the top of the tube is sealed on a delivery tube *f* for the gas, which is collected over water in a graduated tube *g*. The apparatus is partly surrounded by a wide glass (or metal) jacket *a*. This contains a liquid of higher boiling-point than that of the substance whose vapour density is being determined. This liquid is heated to boiling, some of the air in *b* being in consequence expelled. A point is soon reached when no more air escapes from the delivery tube, that in the wider part of the tube having a constant temperature, very nearly equal to that of the vapour of the boiling liquid. The graduated tube is now filled with water and placed over the open end of the delivery tube *f*. The stopper is then withdrawn, and a weighed quantity of the substance under examination, usually enclosed in a little glass tube, is dropped into the apparatus, and the stopper replaced, care being taken to make it air-tight. The substance vaporizes quickly in the heated wide portion of the tube. Its vapour expels air from the apparatus, which is collected in the graduated tube, and is equal in volume to that of the vapour itself. While, however, the

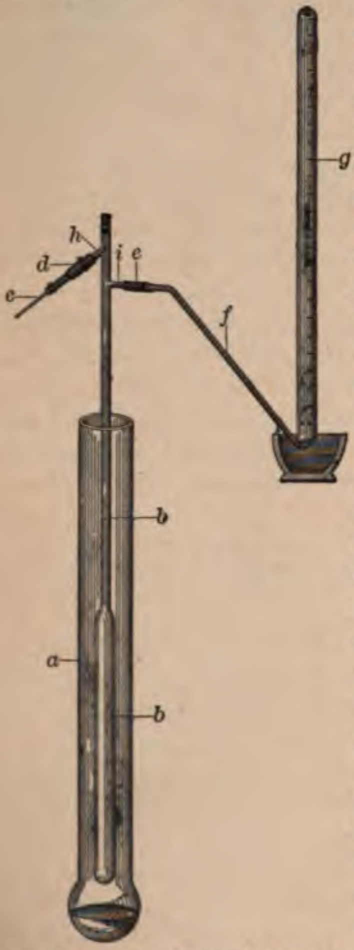


FIG. 4.—VICTOR MEYER'S VAPOUR DENSITY APPARATUS.

air in the hot part of the apparatus has the local temperature, in the graduated tube it acquires the temperature of the latter, so that this must be taken into account in making the calculation. The experiment gives a volume which is equal to that which the weighed portion of the substance in the form of vapour would occupy, if it were possible to convert it into a gas at the ordinary temperature and under the barometric pressure.

For ease of manipulation this method leaves nothing to be desired. It possesses, moreover, the great advantage over the other methods, that it is not necessary to know the temperature to which the apparatus has been heated, since no use is made of this in the calculation. It is only necessary that the temperature should remain constant during the short time occupied by the experiment.

The result is calculated in the following way. Suppose that g mg. of the substance were weighed out, and yielded V c.c. of air, measured over water, with the level the same inside and outside the tube; suppose further that the barometric pressure were H, the temperature t, and the tension of aqueous vapour b, then, under a pressure of $H - b$ mm. and at $t°$, g mg. of the substance would occupy a volume of V c.c., so that under these conditions the unit of volume (1 c.c.) would contain $\frac{g}{V}$ mg. of the substance.

One c.c. of hydrogen under $H - b$ mm. of pressure, and at $t°$, weighs

$$\frac{0{\cdot}0895}{1 + 0{\cdot}00367t} \times \frac{H - b}{760},$$

from which it follows that the vapour density D compared to hydrogen is

$$D = \frac{g}{V} \times \frac{1 + 0{\cdot}00367t}{0{\cdot}0895} \times \frac{760}{H - b}.$$

The molecular weight M being twice the density,

$$M = 2D.$$

Victor Meyer's method cannot as a rule be applied to substances which decompose when boiled under a pressure of one atmosphere. Substances of this kind can often be converted into vapour without decomposition under diminished pressure. To determine the vapour density of such substances **Hofmann**'s method may be employed. This was in general use up to the time of **Victor Meyer**'s discovery, but it is now seldom employed, as it is much more complicated than the latter. In HOFMANN's method a weighed quantity of the substance, contained in a very small bottle with a ground glass stopper, is introduced into the vacuum of a barometric tube, divided into tenths of a cubic centimetre. This tube is surrounded with a glass jacket through which is passed the vapour of a boiling liquid, the boiling-point of which is higher than that of the substance in the vacuum. The necessary data for calculating the vapour density are obtained by reading the volume which the substance occupies in the gaseous state, the height of the mercury in the tube, the atmospheric pressure, and the temperature of the apparatus.

Determination of the Molecular Weight from the Lowering of the Freezing-point or the Raising of the Boiling-point.

13. In "Inorganic Chemistry" (**40–43**) reference is made to the fact that solutions contained in a vessel made of a semi-permeable material, which separates them from the solvent, exercise an *osmotic pressure;* these solutions obey the laws of BOYLE and GAY-LUSSAC. It is also stated that the numerical value of the osmotic pressure is equal to that of the vapour pressure. In other words, whenever a certain quantity of a substance in the gaseous state occupies a given volume, it exercises a vapour pressure which is exactly equal to the osmotic pressure which would be obtained by dissolving the same weight of the substance in a liquid and diluting to the same volume.

Accordingly the law of AVOGADRO holds good for dilute solutions, for supposing we have an equal number of molecules dissolved in equal volumes at the same temperature, then we know from the equality of the vapour and osmotic pressures that each will exert an exactly identical osmotic pressure; and, inversely, there will be the same number of molecules of the dissolved substance contained in equal volumes of the solvent, under like conditions of temperature and osmotic pressure.

We have here a very important extension of this law. For it is possible not only to compare the weights of equal volumes of gases at the same temperature and pressure with one another, and hence to calculate the molecular weight; but we know further, that in the case of solutions at the same temperature and with the same osmotic pressure, the weights of the substances present in equal volumes of the solution are proportional to their molecular weights.

Just as the molecular weight of gaseous substances is arrived at by determining their temperature, pressure, weight, and volume, so for dilute solutions this is obtained by determining the volume and temperature of the solution, together with the quantity of substance dissolved, and the *osmotic* pressure. The molecular weights of all substances which are soluble in any liquid can be determined in this way, and since many more substances are soluble than are obtainable in the form of vapour, it is now possible to determine the molecular weight of a much greater number of compounds than was previously the case.

There is, however, a difficulty of a practical nature; a direct determination of the osmotic pressure is by no means easy. This would indeed make the method almost useless, if it were not for the fact that in order to determine the molecular weight it is sufficient to observe whether two solutions have the *same* osmotic pressure, without knowing its absolute value; because AVOGADRO'S law only requires that the volume, temperature, and pressure (osmotic or gaseous) shall be equal, apart from the question of what the absolute values of these quantities are, so long as they do not exceed certain limits. It is easy to measure quantities which are proportional to the osmotic pressure, and to infer from these whether there is equality of osmotic pressure or not. These quantities are the *lowering of the freezing-point*, and the *raising of the boiling-point*, or the differences between the freezing-points and the boiling-points respectively, before and after the substance has been dissolved, the effect of which is to lower the freezing-point, and to raise the boiling-point, of the solvent ("Inorganic Chemistry," **42** aud **43**).

14. The lowering of the freezing-point, and the raising of the boiling-point, furnish a means of determining whether solutions are *isotonic*, i.e. whether they have the same osmotic pressure. The freezing-point of a substance, phenol for example, is ascertained, and a gramme-molecule of a substance of known molecular weight is dissolved in a known weight, and hence in a known volume, of the solvent. This lowers the freezing-point by a certain amount, which is always the same for the same solvent, no matter what the substance may be, provided that the volume of solution, containing one gramme-molecule, is the same. This is due to the fact that such solutions are isotonic. The lowering of the freezing-point caused by a gramme-molecule is therefore a constant for this solvent. If a 1% solution of a substance of unknown molecular weight M be made in phenol, and the lowering of the freezing-point of this determined, which we will call A, then

$$AM = \text{Constant};$$

because the lowering of the freezing-point is, between certain limits, proportional to the concentration.

It is easily seen that this formula is equally applicable to the raising of the boiling-point. M is here the only unknown quantity, and may be calculated from this equation.

Example. If phenol is used as the solvent, it has been shown by numerous determinations that the product of the lowering of the freezing-point of a 1% solution of the substance by its molecular weight is equal to 75. We have then for phenol

$$AM = 75.$$

In the case of a substance whose empirical formula is $C_7H_7N_2O$, the lowering of the freezing-point of a 2·75% solution of the substance in phenol amounted to 0·712°. In the case of a 1% solution the lowering would have been $\frac{0 \cdot 712}{2 \cdot 75} = 0 \cdot 258$; therefore $A = 0 \cdot 258$ from which it follows that the molecular weight is $\frac{75}{0 \cdot 258} = 291$.

Since $C_7H_7N_2O$ corresponds to the molecular weight 135, and that of $C_{14}H_{14}N_4O_2$ to 270, the latter comes nearest to the molecular weight found, so that double the empirical formula must be assigned to the compound.

The constants for the lowering of the freezing-point (*molecular lowering of the freezing-point*) for a number of solvents are given in the following table:

Solvent.	Molecular Lowering of the Freezing-point.	Melting-point.
Water	19	0°
Acetic acid	39	16·5°
Benzene	53	6°
Nitrobenzene	70	5°
Phenol	75	39·6°
Urethane	51·4	48·7°
Stearic acid	45	53°
p-Toluidine	52·4	42·5°

The last four solvents are very useful, and are better than glacial acetic acid, which is still often employed, because they are not hygroscopic, and, having melting-points higher than the ordinary temperature, obviate the necessity for a cooling-agent. In addition, their constants are high.

The constants for the raising of the boiling-point (*molecular raising of the boiling-point*) are 21 for *ether*, 11·5 for *ethyl alcohol*, 26·7 for *benzene*, 36·6 for *chloroform*, etc. These numbers are on the whole much smaller than those for the molecular lowering of the freezing-point. The extent to which the boiling-point is raised is therefore less than that to which the freezing-point is depressed, from which it follows that the latter determination gives greater accuracy.

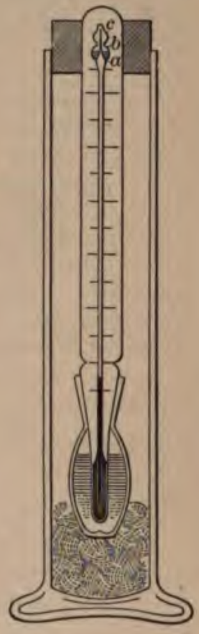


FIG. 5.—EYKMAN'S DEPRESSIMETER.

15. EYKMAN has constructed an apparatus by which the depression of the freezing-point may be easily determined (Fig. 5). This consists of a small thermometer divided into twentieths of a degree, to which is attached a little flask, as shown in the figure. The whole is contained in a glass cylinder, is held at the top with a stopper, and supported underneath on cotton wool. The latter has the effect of making the cooling take place more slowly, since it is a bad conductor of heat. A weighed quantity of the solvent is placed in the flask, and its freezing-point determined. Then a known weight of the substance is introduced, and the freezing-point again observed. In this way a depression of the freezing-point is obtained, from which A may be calculated as in the example given on p. 18.

The laws of osmotic pressure only hold good when the solutions are very dilute, and the same is true of the equation $AM =$ Const., since it is derived from these laws.

It is not strictly correct to determine A by means of a solution of finite concentration, as was done in the example on p. 18. In order to determine M accurately, the value of A should be derived from a solution of infinite dilution; but as this is not possible, **Eykman** has described the following *graphic method* of determining A for such a solution. A is determined for three or four concentrations, and the values obtained are represented graphically as in Fig. 6, in which the values of A are the ordinates, and those of the percentage-strength of the solutions are the abscissæ. **Eykman** states that in a very great many cases the line which can be drawn through the tops of the ordinates is very nearly a straight one. If it is produced till it cuts the ordinate OA, OP_0 gives the value of A for infinite dilution.

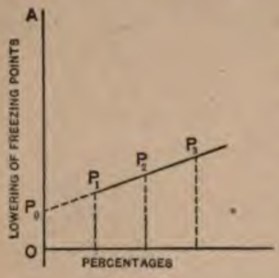


Fig. 6.

For determining the raising of the boiling-point, McCoy has constructed a very convenient apparatus. It consists of two vessels, A and B, fitted tightly together. The inner tube A is graduated near the lower end, and is joined to a narrow tube ab, opening to the exterior at a. A side tube c leads from the mouth of A to a condenser. The jacket B is enlarged at the bottom, and has a side tube d, closed by a rubber tube and pinch clamp. About 50 c.c. of the pure solvent and a small piece of clay tile (to promote regular boiling) are placed in the jacket, and 12–16 c.c. of the solvent in the inner tube. The liquid in the jacket is heated to boiling, and its vapour warms the other liquid. As soon as the latter becomes hot, the vapour in the jacket forces its way through ab and raises the temperature of the liquid in the graduated tube to boiling, whereupon a slow distillation into the condenser takes place. Superheating is thus avoided. The reading may be taken within five to ten minutes from the beginning of the operation.

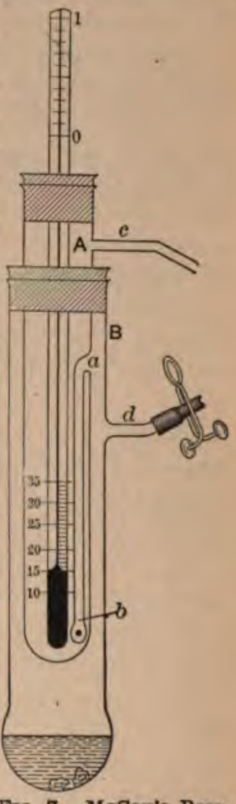


Fig. 7.—McCoy's Boiling-point Apparatus.

On cooling, *d* is opened to prevent the liquid from being sucked out of the graduated tube. The boiling-point of the pure liquid having been found, a carefully weighed portion of the substance whose molecular weight is to be determined is introduced into *A*, the thermometer and cork being temporarily removed for this purpose. As soon as the boiling-point of the solution has been determined, the boiling is stopped, the thermometer removed, and the volume of the solution observed. The formula is the same as that given above, volume being substituted for weight, and the constant calculated on that basis. EYKMAN's graphic method (p. 20) of finding *A* for infinite dilution may be applied in this case also.

THE ELEMENT CARBON.

16. Carbon occurs in three allotropic forms: *diamond*, *graphite*, and *amorphous carbon*. For a description of these the reader is referred to "Inorganic Chemistry," **176–179**, which deals also with the compounds of carbon with metalloids and metals, as well as with the determination of its atomic weight. It will therefore be here sufficient to refer to certain facts regarding the *molecule of carbon*. There is no doubt that this consists of a great number of atoms; how great, has not yet been ascertained. It is supposed that there are more atoms in the molecule of graphite than in that of amorphous carbon, and more in the molecule of the diamond than in that of graphite, because graphite and diamond are more difficult to decompose by chemical means, and because their specific gravities are greater than that of amorphous carbon.

The determination of the vapour density of carbon is impossible, owing to the high temperature necessary to convert it into the state of gas. The depression of the point of solidification which carbon causes when dissolved in molten iron cannot be determined with sufficient accuracy, because no method is known of measuring differences of temperature of one-fiftieth to one-hundredth of a degree at the melting-point of iron. Moreover, the phenomenon would be complicated by the fact that iron enters into combination with carbon.

It can be shown, however, in the following ways that the number of atoms in the molecule of carbon is a large one. When amorphous carbon is oxidized with potassium permanganate, *mellitic acid* is formed, containing twelve atoms of carbon in the molecule. This makes it to a certain extent probable that the molecule of carbon contains at least twelve atoms, because when organic compounds are oxidized, substances are formed which nearly always contain either a smaller or the same number of carbon atoms in the molecule as the substance which has been submitted to oxidation. For the following reasons, however, it is believed that the number of atoms in the molecule of carbon is greater than this. Among the products obtained by leading *marsh gas*, CH_4, through a heated tube, is found *ethylene gas*, C_2H_4. When this is treated in the same way, *acetylene*, C_2H_2, is formed, which in its turn yields *benzene*, C_6H_6. When benzene-vapour is led through a white-hot tube it forms *naphthalene*, $C_{10}H_8$, and *pyrene*, $C_{16}H_{10}$, etc. On heating naphthalene or pyrene to a still higher temperature in absence of air, carbon is produced. From this it is seen that, as the temperature rises, compounds are formed containing more carbon atoms in the molecule. This makes it probable that the final product of these reactions, carbon itself, contains a considerably greater number of atoms in its molecule than the number of carbon atoms in the molecule of pyrene.

A third proof of the great number of atoms in the molecule of carbon is found by examining the boiling-points of its hydrogen compounds. If these be denoted by the general formula C_nH_{2n-p}, then, even when n and p are both large numbers, the boiling-points of these substances are relatively low, and rise with the increase of both n and p. For carbon itself, $2n = p$, and, on account of the extraordinary non-volatility of this substance, the value of n must be very great.

VALENCY.

17. The atoms of some elements have the property of being unable to combine with more than one atom of any other element. The halogens on the one hand, and hydrogen on the other, yield only compounds of the type HX, in which X stands for the halogen atom. This property is called *monovalency.*

Of other elements, for example those of the oxygen group (O, S, Se, Te), one atom is able to combine with two *monovalent* atoms. Such elements are therefore called *divalent.*

The number of atoms of a monovalent element which can unite with one atom of another element therefore serve as a measure of the latter's valency. Thus nitrogen combines with three atoms of hydrogen, and is therefore *trivalent.* But the compound NH_3 can still unite with HCl to form NH_4Cl, in which there are five monovalent atoms attached to one nitrogen atom, so that nitrogen can also be *pentavalent.* Many elements besides nitrogen have more than one degree of valency.

Carbon forms with monovalent elements compounds of the type CX_4. *It is therefore tetravalent, and it is on this foundation that the whole superstructure of organic chemistry rests.*

FIG. 8. — HEATING SUBSTANCES IN AN OPEN FLASK.

FIG. 9. — FLASK WITH REFLUX-CONDENSER.

The compound CO_2 is also an instance of the tetravalency of carbon. In carbon monoxide, CO, on the other hand, the carbon atom must be looked upon as divalent, at least if the divalency of oxygen is retained. Other compounds are well known in which carbon may be looked upon as divalent, but their number is very small in comparison with those, numbering many thousands, in which carbon must be regarded as tetravalent.

LABORATORY METHODS.

18. Before we proceed with the description of the organic compounds, it is desirable, to prevent repetition, to give a short account of the most important processes used in their preparation and investigation.

Heating Substances Together.—This process is very often used with the object of inducing reaction between bodies, since the velocity of reactions increases largely with rise of temperature ("Inorganic Chemistry," **13** and **104**). The process varies according to the temperature to which they must be heated. If this is considerably below the boiling-point of the most volatile compound, they are simply mixed together in a flask fitted with a thermometer, as in Fig. 8. The flask is immersed in a bath of liquid, water, oil, or molten lead, Rose's alloy or other metal, etc., being used for this purpose. Should, however, the boiling-point of one of the substances be reached or overstepped, then the flask must be connected with a condenser, as in Fig. 9. The invention of this form of condensing-apparatus is usually attributed to Liebig, although it was first constructed by Weigel in 1771. It consists of a glass tube *aa*, enclosed in a jacket of glass or metal *b*, through which a stream of cold water can pass. If the substance has a high boiling-point, it is sufficient to connect a long glass tube to the flask; the air keeps this sufficiently cool, so that a tube of this kind is called an *air-condenser*. The effect of this condenser is easily understood, the boiling liquid being condensed in it and dropping back again into the flask. When it is necessary to

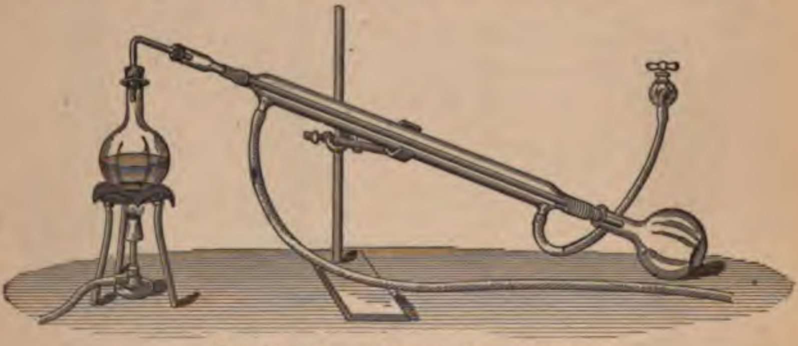


Fig. 10.—Distillation Apparatus.

heat substances above their boiling-points, they are placed in a thick-walled glass tube sealed at one end, which is then sealed at the other, and heated in a tube furnace (Fig. 3, page 9).

19. *Distillation.*—For this purpose the apparatus shown in Fig. 10 is used. If, however, the liquid to be distilled is of such a nature that it would become contaminated by the action of its vapour on the cork or rubber stopper shown in the figure, a distilling-flask (Fig. 11) is substituted for the ordinary one, and, if its neck be sufficiently long, allows the substance to be distilled without coming in contact with the stopper.

FIG. 11.—FRACTIONATING-FLASK.

20. Many substances decompose when heated at the ordinary pressure to their boiling-points, but distil unchanged under diminished pressure, because the boiling-point is then much lower.

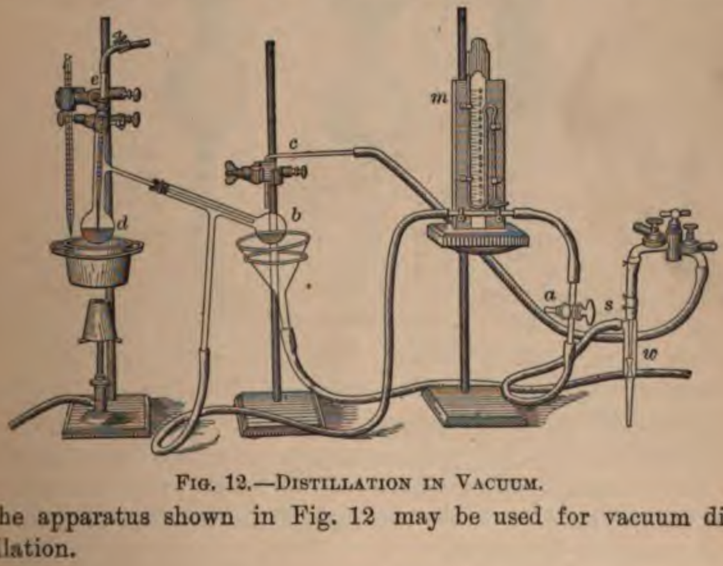
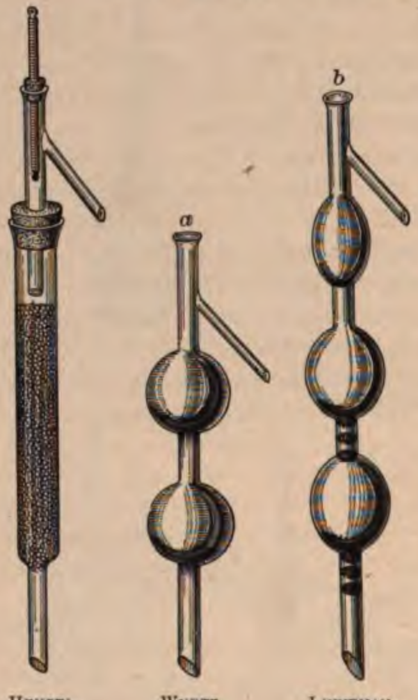


FIG. 12.—DISTILLATION IN VACUUM.

The apparatus shown in Fig. 12 may be used for vacuum distillation.

The liquid which is to be distilled is placed in *d*. A glass tube *e*, drawn out to a very fine point, dips into the liquid, and a thermometer is placed inside this tube. As soon as the apparatus has been made vacuous by the water-pump *w*, a stream of small bubbles of air escapes from the very fine point of the tube *e*. This is to prevent the violent "bumping" which occurs when liquids are boiled under diminished pressure, caused by the sudden and intermittent formation of vapour, whereby boiling-over sometimes occurs, or the flask is broken. The receiver *b* is kept cool by a stream of water from *c*; *m* is a mercury manometer; *a* a two-way stop-cock which permits access of air to the apparatus after the distillation, and at the same time serves to cut off the connection between the air-pump and the rest of the apparatus when the pump "strikes back"; that is, when the water rises through the tube *s* into the apparatus.



HEMPEL. WURTZ. LINNEMAN.

FIG. 13.—FRACTIONATING-COLUMNS.

21. The separation of a mixture of volatile substances is effected by *fractional distillation*. If a mixture of two liquids, boiling say at 100° and at 130°, is distilled, the one that boils at 100° will distil over principally at the beginning, and the one which boils at 130° at the end of the operation. If what passes over before the thermometer reaches 110° is collected separately in one fraction, and similarly what passes over between 120° and 130°, a rough separation has already been effected, while the middle fraction still consists of a mixture. To måke the separation as complete as possible, the fraction 100°–110° is put back into the fractionating-flask and distilled over till the thermometer reaches 110°, the fraction 110°–120° being now mixed with the residue in the fractionating-flask. The distillation is then continued till the thermometer again stands at 110°. Another receiver is now employed, and the distillation continued till the thermometer reaches 120°. When this is the case, the fraction 120°–130° is added, but the receiver is only changed when the thermometer again indicates 120°. The portion which distils after this is collected separately. By repeating this process several times, during which it is usually desirable to collect the fractions between narrower limits of temperature, and thus to increase their number, it is possible in many cases to effect an almost complete separation.

This separation is greatly facilitated by using a fractionating-column (Fig. 13), which is connected to the neck of the boiling-flask, and has the effect of condensing the least volatile part of the vapour. This is attained by increasing the cooling-surface by means of bulbs, or by putting obstructions, such as platinum gauze or glass beads, in the way of the vapour.

22. A mixture of liquids cannot always be separated by fractional distillation. Whether this is possible or not, depends on the following considerations. If two liquids with different vapour tensions are mixed in such a way that a small quantity of the one is continually added to the other, it is often found that the vapour tension of this mixture, the temperature remaining the same, rises or falls continually, till finally, when a great excess of the second liquid has been added, the vapour tension of the latter is very nearly reached. This is graphically represented by the line AB in Fig. 14. The vapour tensions of the mixtures all lie between those of the two pure substances, which constitute the maximum B and minimum A for the whole series. In some cases, however, it has been shown that in this way a *mixture* is obtained whose vapour tension is a maximum (Fig. 15) or a minimum (Fig. 16). It is then impossible to effect separation by fractionating, as may be seen in the following way. The most volatile portion of a liquid always distils first, and in the case of a mixture with a maximum vapour tension, this is the most volatile portion of an arbitrary mixture of the two liquids. On this account there will be finally obtained a fraction having the composition of the mixture with maximum vapour tension ; which of the two substances will be obtained in the pure state will depend upon which of them was present in greater proportion in the original, not in the final, mixture.

If there exists a mixture of two liquids with minimum vapour tension, this is the least volatile part of the liquid, and it will be obtained as the final residue after the distillation. Which of the two substances can be obtained pure from the mixture will again depend, as before, on the ratio of the quantities of the two liquids which were originally present.

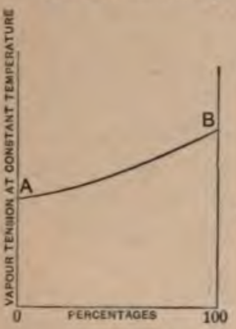


FIG. 14.

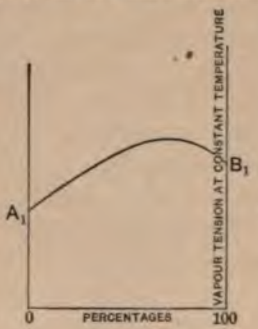


FIG. 15.

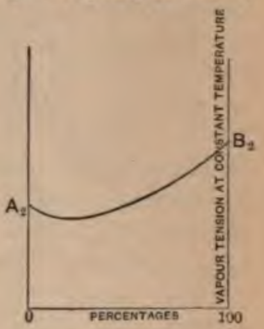


FIG. 16.

The separation of a mixture of liquids by fractionation is also impossible when the boiling-points of its constituents are close together, because the essential characteristic of the whole method consists in the unequal volatility of the portions of which the mixture is made up, in consequence of which one substance distils over before the other. If, however, the substances have about the same boiling-point, then they both attain to a vapour tension of one atmosphere at almost the same temperature, being, in other words, almost equally volatile. It is therefore impossible under these conditions to apply the method successfully.

23. *Steam Distillation.*—In the preparation of many organic substances a crude reaction-product is often obtained containing tarry or pitch-like matter along with the required compound. In order to free the substance from this, use is often very advantageously made of the property possessed by many substances of distilling in a current of steam, the tarry matters remaining behind. Fig. 17 shows the method by which such a distillation is carried out.

Water is boiled in the can *a*, which is fitted with a delivery tube *c* and a safety tube *b*, the evolved steam being passed into the bottom of the distilling-flask *d*. If the distillation is interrupted, cooling causes diminished pressure in *a*, air being then able to enter the tube *b*. If *b* were not used, the liquid in *d* would flow back into *a*, owing to the fall in the steam pressure.

FIG. 17.—STEAM DISTILLATION.

Steam distillation is also of service in separating compounds, some of which are volatile with steam and others not. In the case of substances which are insoluble in water, the distillate is a milky liquid, because the water which has distilled over is mixed with fine, oily drops, there being at the same time an oily layer above or beneath the water.

When distilling with steam, the pressure of the mixture of vapours must be equal to that of the barometer, since the liquid is boiling. The boiling-point must be lower than that of the lower-boiling of the two substances under ordinary pressure, because the partial pressure is necessarily smaller than the total one, which is equal to the atmospheric pressure. The same result is therefore obtained as when distilling under diminished pressure, viz., the volatilization of the substance at a temperature lower than its boiling-point under ordinary pressure.

Whether a substance distils quickly or slowly with steam, depends on its partial pressure and on its vapour density, together with the values of these physical constants for water. If the pressures are p_1 and p_2, and the vapour densities d_1 and d_2, the quantities which distil over simultaneously are p_1d_1 (substance), and p_2d_2 (water). If the ratio $p_1d_1 : p_2d_2$ is large, the substance distils over with a small quantity of water, the distillation being quickly carried out; the reverse takes place when the ratio $p_1d_1 : p_2d_2$ is small.

24. *Separation of Two Immiscible Liquids.*—A *separating-funnel* is used for this purpose (Fig. 18); the method of using it may be inferred from the drawing without further explanation. It is also employed for the *extraction* of aqueous solutions. The aqueous solution of a substance soluble in a volatile liquid not miscible with water, such as *ether, petroleum-ether, chloroform, carbon bisulphide,* is transferred to a separating-funnel; ether, if that is the solvent selected, is added, and after the mouth of the funnel has been closed by a glass stopper, the two liquids are mixed together by vigorous shaking, when the substance which is dissolved in water passes partly into the ether. The ethereal solution is allowed to rise to the top, and separated from the water by opening the stop-cock after removal of the stopper. The water which has dissolved in the ether during the shaking, is removed by chloride of calcium, or some other drying-agent, and finally the ether is distilled off. The extraction is completed quickly when the dissolved substance is only slightly soluble in water, and easily soluble in ether; it is then possible to almost wholly exhaust the aqueous solution by repeating the operation a few times with fresh ether. Otherwise, the shaking must be repeatedly carried out, and even then the extraction is imperfect.

FIG. 18.—SEPARATING-FUNNEL.

When two immiscible solvents are simultaneously in contact with a substance which is soluble in both, the latter distributes itself in such a way that the ratio of the concentrations reached in both solvents is constant (law of BERTHELOT). If a quantity X_0 of the substance is dissolved in a quantity l of the first solvent (water), and this solution is shaken up with a quantity m of the second solvent (ether), there will then remain a quantity X_1 in the first solution, so that $X_0 - X_1$ has passed into the second solvent.

The value of the quantity X_1 is, in accordance with the above law, given by the equation

$$\frac{X_1}{l} = K\frac{X_0 - X_1}{m} \quad \text{or} \quad X_1 = X_0\frac{Kl}{m + Kl},$$

for $\frac{X_1}{l}$ and $\frac{X_0 - X_1}{m}$ are the two concentrations after the solvents have been shaken up, and K is the number expressing the constant ratio, or the *coefficient of distribution* (German, *Teilungskoeffizient*).

A second extraction with the same quantity m of the second solvent gives

$$\frac{X_2}{l} = K\frac{X_1 - X_2}{m},$$

or, substituting the value of X_1 from the first equation,

$$X_2 = X_0\left(\frac{Kl}{m + Kl}\right)^2,$$

and for the nth extraction,

$$X_n = X_0\left(\frac{Kl}{m + Kl}\right)^n.$$

Thus X_n, the quantity remaining in the first solvent (water), diminishes as n increases, and as m and K are respectively greater and less. Complete extraction is impossible, because although $\left(\frac{Kl}{m + Kl}\right)^n$ can approach zero very closely, it can never become equal to it.

It can be further shown from this equation by the use of the differential calculus that with a given quantity of the second solvent (ether) a more complete separation is effected by extracting frequently with small quantities than by using larger quantities a correspondingly fewer number of times.

FIG. 19.—FILTERING-FLASK.

Separation of Solids and Liquids.—This is effected by filtration, which can be materially accelerated by fitting the funnel, by means of a rubber stopper, in a flask a (Fig. 19), which is connected through b to a water air-pump. To prevent rupture of the point of the filter-paper, it must then be supported by a hollow platinum cone c.

25. *Separation of Solids from one Another.*—This usually depends on difference in solubility. If there are two substances, one soluble and the other insoluble, the operation is very simple. If both substances are soluble, the method of *fractional crystallization* must be used. The mixture is dissolved in the least possible quantity of a boiling liquid, and allowed to cool. The more insoluble substance crystallizes out first. The mother-liquor is poured off before crystals of the second body begin to separate, and the second compound is crystallized either by further cooling or by concentrating the liquid by evaporation. On repeating these operations several times, the substances are obtained separated from one another. The separation of substances in this way is sometimes very difficult, even if there is a very great difference of solubility between the pure compounds, because the solubility of one substance may be very considerably modified by the presence of another. Water, alcohol, ether, glacial acetic acid, benzene, and other substances are used as solvents.

26. It is seen from the foregoing how substances may be obtained in the pure state: solid substances are usually purified by crystallization, and liquids by distillation. An *indication of purity* is that the physical constants remain unchanged after the substance has been purified anew. Although every physical constant could serve this purpose, the *melting-point* and the *boiling-point* are those most used, because they are easily determined, and slight impurities exercise a very material influence upon them. They are also often a means of identifying substances. Should a compound, supposed to be one already known, have been obtained by some process, it is strong evidence in favour of the supposition if the melting-point and boiling-point of the substance coincide with those of the compound with which it is supposed to be identical. Determinations of melting-points and boiling-points are for this reason very often carried out.

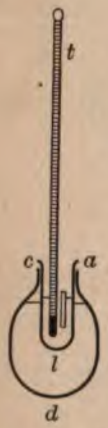


FIG. 20.—DETERMINATION OF THE MELTING-POINT.

To determine the *melting-point*, the substance is placed in a narrow thin-walled small tube sealed at one end (Fig. 20); this tube is attached to a thermometer *t*, the bulb of which dips into a liquid of high boiling-point, such as concentrated sulphuric acid or liquid paraffin **(33)**, the viscosity of which causes the small tube to adhere to the thermometer. The tube *alc*, in which the bulb of the thermometer and the little tube are placed, is loosely fixed in a small round glass flask *adc*, containing the same liquid as the tube *alc*. When *adc* is heated, the contents of the tube *alc* are warmed uniformly, and the moment of fusion of the substance, at which the thermometer is read, can be very accurately observed.

The *boiling-point* is determined by heating the liquid to boiling in a fractionating-flask with a high side tube. Short thermometers are used, so that the whole of the mercury column is surrounded by the vapour of the boiling liquid. In order to avoid inconveniently small graduations, these thermometers are constructed so that they can only be employed for a comparatively small range of temperature, six or seven different instruments being used for temperatures between 0° and 360°.

27. Sometimes other physical constants besides the melting-points and boiling-points are determined in the investigation of organic compounds. 1. The *specific gravity* can be determined with the *pyknometer*, the most useful form of which is shown in Fig. 21. It consists of two thick-walled capillaries *ab* and *cd*, which terminate in a wider tube *bc*. The parts *aa* and *dd* are furnished with a millimetre scale. The capacity of the apparatus is first determined, as well as of the space between two divisions, by filling it several times up to different divisions with water of known temperature, and then weighing. The liquid whose specific gravity is to be determined is then placed in the apparatus, which is weighed after the positions of the menisci in the capillaries have been observed; from this the required number may be calculated.

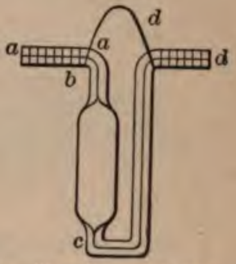


FIG. 21.—PYKNOMETER.

2. The rotation of the *plane of polarization* is another constant of importance.

Some substances, such as turpentine, a solution of sugar, etc., have the property of *rotating* the plane of a ray of polarized light which is passing through them out of its original position. This phenomenon is called the *rotation of the plane of polarization*, and substances which possess this property are said to be *optically active*. *Polarimeters* have been constructed for measuring the angle through which the plane of polarization has been rotated by an optically active substance; of these LAURENT'S (Fig. 22) is one of the best known. The yellow sodium light of the burner TT is polarized in the part of the apparatus marked BD, and then passes through a tube placed in the channel L, the length of which is accurately known (200–500 mm.), containing the liquid or solution whose optical activity is to be determined; the part OC of the apparatus serves to measure the rotation of the plane of polarization.

The extent to which the plane of polarization is rotated is proportional to the length of the tube, and is expressed in different ways. The rotation of a substance is expressed, for example, in terms of the effect produced by a given length of the tube above referred to; this is the angle which is read off directly from the instrument. It is usually denoted by α. By convention, the *specific rotatory power* is defined as the quotient obtained by dividing α by the product of the length of the tube into the specific gravity of the liquid. This value is denoted by $[\alpha]$, so that

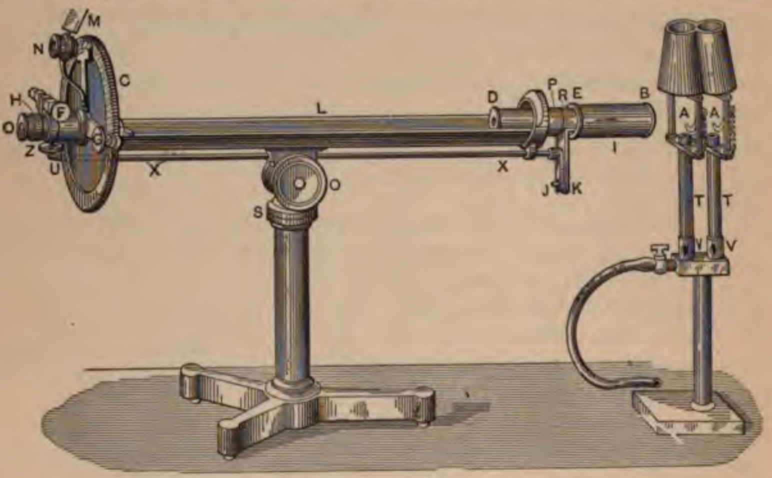


FIG. 22.—LAURENT'S POLARIMETER.

$$[\alpha] = \frac{\alpha}{ld},$$

where l is the length of the tube, and d is the specific gravity of the liquid. Under these conditions $[\alpha]$ expresses the rotatory power of a substance per unit length of the tube (1 decimetre), and for unit weight of the substance divided into the unit of volume.

The extent of the rotation is dependent on the colour of the light. In many cases the measurement is carried out with sodium light, which gives a yellow line in the spectroscope, denoted by *D*. This is expressed by the symbol $[\alpha]_D$.

When the rotatory power of a substance is small, or when, on account of its slight solubility, it can only be obtained in dilute solution, the rotation can be increased in many cases by adding a solution of boracic acid, molybdic acid, uranium salts, etc. The cause of this phenomenon is not fully understood.

It is often important to determine other constants, such as the *index of refraction*, the *molecular electric conductivity*, and the *heat of combustion*.

CLASSIFICATION OF ORGANIC CHEMISTRY.

28. It is usual to arrange the extraordinarily great number of organic compounds in two main divisions. One of these includes the *fatty* or *aliphatic compounds*, and the other the *aromatic compounds*. The first of these owes its name to the fact that the animal and vegetable fats belong to it; the second, to its containing many compounds, among the first to be discovered in this division, characterized by an agreeable smell or aroma.

The fatty compounds and the aromatic compounds are regarded as being derived from methane, CH_4, and benzene, C_6H_6, or compounds related to it, respectively.

It will be shown later that there are important differences between the general properties of these two classes of compounds.

FIRST PART.

THE FATTY COMPOUNDS.

SATURATED HYDROCARBONS.

29. The fatty compounds are defined in **28** as those which may be regarded as derived from *methane*, CH_4. It is therefore advisable to begin the study of these compounds with this hydrocarbon.

Methane occurs in nature in the gases evolved from volcanoes; it escapes in coal-mines during the working of the coal-seams, and is called *fire-damp* by the miners. It is also called *marsh gas*, because it is present in the gases, due to decay of vegetable matter, which rise out of marshes. It is an important constituent of coal-gas, in which it is present to the extent of 30–40%.

It can be prepared in different ways.

1. (*a*) By BERTHELOT'S synthesis. A mixture of H_2S and CS_2 is led over red-hot copper contained in a tube, when the following reaction occurs:

$$2H_2S + CS_2 + 4Cu = 4CuS + CH_4.$$

(*b*) By SABATIER and SENDERENS' synthesis. When a mixture of hydrogen and carbon monoxide is passed over reduced nickel at 200°–250°, methane is formed:

$$CO + 3H_2 = CH_4 + H_2O.$$

The nickel undergoes no apparent change, and can be used repeatedly. At a temperature of 230°–300°, carbon dioxide reacts similarly with hydrogen in presence of finely-divided nickel:

$$CO_2 + 4H_2 = CH_4 + 2H_2O.$$

Reduced cobalt has a similar action, but requires a somewhat higher temperature. Since CS_2, H_2S, CO, and CO_2 can be obtained by direct synthesis from their elements, these reactions furnish methods of preparing methane synthetically.

2. By acting on the compound CH_3I, *methyl iodide*, with nascent hydrogen:

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

Nascent hydrogen can be obtained in different ways: from sodium amalgam and water, from zinc and hydrochloric acid, or by bringing zinc which has been immersed in a dilute solution of copper sulphate, to coat it with a layer of copper, into contact with water. By the last method, which was discovered by **Gladstone** and **Tribe**, hydrogen is evolved at the ordinary temperature in a form in which it is able to convert methyl iodide into methane.

Methyl iodide can also be reduced to methane by hydriodic acid:

$$CH_3I + HI = CH_4 + I_2.$$

To effect this a concentrated aqueous solution of hydriodic acid is heated with methyl iodide.

The iodide formed is converted back again into HI by the addition of amorphous phosphorus. The hydriodic acid is regenerated :

$$P + I_3 + 3H_2O = H_3PO_3 + 3HI:$$

and is available to effect further reduction.

3. By decomposing zinc-methyl, ZnC_2H_6 (82), with water:

$$Zn\overset{(CH_3)_2}{C_2H_6} + 2H_2O = Zn(OH)_2 + 2CH_4.$$

4. By heating sodium acetate with barium hydrate:

$$CH_3COONa + ba^*OH = baNaCO_3 + CH_4.$$

30. *Physical and Chemical Properties.*—Methane is an odourless and colourless gas of sp. gr. 0·559 (air = 1), liquefying at 11° and 180 atmospheres. It boils at − 162°, and solidifies at − 186°. It is only slightly soluble in water, but more so in alcohol. It is decomposed into carbon and hydrogen by the sparks of an induction coil, or in the electric arc. Oxidizing-substances, such as nitric and chromic acids, do not attack it, or only very slightly, while concentrated sulphuric acid and strong alkalis have no action upon it. It burns with an almost non-luminous flame. When mixed with air or oxygen it forms a violently explosive mixture, the reaction being in accordance with the equation

crit. Temp

$$CH_4 + 2O_2 = CO_2 + 2H_2O.$$

This so-called "fire-damp" is the cause of the explosions which

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* ba = ½Ba.

sometimes occur in coal mines. Chlorine and bromine react with methane, the hydrogen atoms of the latter being replaced by halogen atoms, and a haloid acid formed:

$$CH_4 + \underset{Cl_2}{2Cl} = CH_3Cl + HCl.$$

The replacement of one atom by another is called Replacement *substitution.* If chlorine or bromine is present in excess, the final product is CCl_4 or CBr_4.

31. There exists a series of hydrocarbons, the general chemical properties of which are identical with those of methane. Examples of these compounds are *ethane* C_2H_6, *propane* C_3H_8, *butane* C_4H_{10}, *pentane* C_5H_{12}, *hexane* C_6H_{14}, etc., *pentatriacontane* $C_{35}H_{72}$, and *hexacontane* $C_{60}H_{122}$. These formulæ can be summed up in the general expression C_nH_{2n+2}; for methane, $n = 1$. These hydrocarbons can be prepared by the methods described in 2, 3, and 4. It should be observed, however, that by means of the zinc compounds only the lower members, those containing a small number of carbon atoms, are obtained, because the higher zinc derivatives are not known. The hydrocarbons C_nH_{2n+2} resemble methane in their power of resisting oxidation, and are unacted on by concentrated sulphuric acid, while halogens react with them with substitution of hydrogen and formation of compounds $C_nH_{2n+1}Cl$, $C_nH_{2n}Cl_2$, etc.

In addition to the methods mentioned above, the higher hydrocarbons may be obtained by building up from the lower ones. For example, ethane can be obtained from methane by replacing a hydrogen atom in the latter by halogen, and then treating the halogen compound thus obtained with sodium:

$$2CH_3I + 2Na_{\cancel{2}} = C_2H_6 + 2NaI.$$

Propane can be prepared in accordance with the following equation:

$$CH_3I + C_2H_5I + Na_2 = C_3H_8 + 2NaI;$$

and, in general, C_nH_{2n+2} is obtained by the action of sodium upon $C_mH_{2m+1}I + C_pH_{2p+1}I$, when $m + p = n$.

In this reaction C_4H_{10} is formed from $2C_2H_5I$, and C_2H_6 from $2CH_3I$, the result being that three hydrocarbons are formed. This is always the case in syntheses of this kind.

Since methane can be prepared synthetically, it is evidently possible to synthesize each hydrocarbon of the formula C_nH_{2n+2}.

32. *Nomenclature.* — The hydrocarbons C_nH_{2n+2} are always denoted by the termination "ane." The first four members, methane, ethane, propane, and butane, have special names; the others are denoted by the Greek or Latin numeral corresponding to the number of carbon atoms. Thus C_8H_{18} is called *octane*, $C_{12}H_{26}$ *dodecane*, $C_{31}H_{64}$ *hentriacontane*, etc.

It will often be necessary to consider groups of atoms which cannot be obtained in the free state, but which are derived from the hydrocarbons C_nH_{2n+2} by removal of a hydrogen atom. These groups have the general formula C_nH_{2n+1}, and are usually called *alkyl-groups;* they are denoted individually by changing the termination "ane" of the corresponding hydrocarbon into "yl." In this way, CH_3 is called *methyl*, C_2H_5 *ethyl*, C_3H_7 *propyl*, C_4H_9 *butyl*, $C_{12}H_{25}$ *dodecyl*, etc.

The hydrocarbons C_nH_{2n+2} have the general name of *saturated hydrocarbons*, because they are saturated with hydrogen: that is, are unable to take up any more hydrogen atoms into the molecule. They are also called *paraffins*, because paraffin-wax consists of a mixture of the higher members; the word paraffin is derived from *parum affinis*, indicating that this substance is but slightly acted upon by chemical reagents.

33. *Occurrence in Nature.*—The hydrocarbons C_nH_{2n+2} occur in nature in enormous quantities. Crude American petroleum consists of a mixture of a great number of these compounds, from the lowest to the highest members of the series. Three principal products are obtained from this petroleum by fractional distillation, after treatment with acids and alkalis to free it from substances which are not hydrocarbons of the formula C_nH_{2n+2}. The most volatile portion is called *petroleum-ether*, *benzine*, *naphtha*, or *ligroïn;* it distils between 40° and 150°, and contains lower members, chiefly C_6H_{14}, C_7H_{16}, and C_8H_{18}. It is extensively employed as a solvent for fats, oils, and resins, and is also applied to the removal of stains from clothing ("Dry-cleaning process").

The portion which distils at 150°–300° is ordinary *petroleum*, and is used on a large scale for lighting and cooking.

The danger involved in its use is by no means small, 40–50% of accidents by fire being attributable to this source. The fact that fires are often caused by the overturning of petroleum lamps is traceable to the presence in the petroleum of a part of the more volatile products, whose vapour produces an inflammable mixture with air. If a lamp is filled with petroleum from which the more volatile portions have been removed by careful fractionation, upsetting extinguishes it. Petroleum of this kind is found in commerce under the name of *kerosene* or *refined petroleum.*

For the purpose of ascertaining whether a sample of petroleum contains these more volatile products, its *flash-point* is determined by heating it slowly in a specially constructed apparatus, devised by Sir FREDERICK ABEL, and observing the temperature at which the mixture of vapour and air over the petroleum can just be ignited. Experience has shown that there is no danger with a flash-point of 40° C. Large quantities of petroleum come into the market with a flash-point of 22°–24° C.; these are the cheaper kinds, which are used by the largest proportion of the population, and constitute a great source of danger from fire. It would be very advantageous if the law insisted upon a flash-point of about 40° C., which has already been adopted in some countries.

The portion of the crude petroleum which does not distil below 300°, but remains in the still, is named *vaseline.* It is a semi-solid substance at ordinary temperatures, white when pure, and is used in pharmacy in the preparation of ointments. It is further made use of for covering the surface of metallic articles to protect them from oxidation, for which purpose it is better than fat, because the latter turns sour and then attacks the surface of the metal, whereas vaseline has a neutral reaction, and remains unchanged in the air.

Paraffin-wax, as already mentioned, is a mixture of the highest members of the series C_nH_{2n+2}. Some kinds of crude petroleum, notably that obtained from Java, contain considerable quantities of these highest members, which occur to only a small extent in American petroleum.

Liquid paraffin is a product of high boiling-point, obtained in the dry distillation of brown coal.

Earth-wax, or *ozokerite*, is found in Galicia, and consists chiefly of paraffin. This substance is also obtained in the dry distillation of the brown coal found in Saxony.

34. Petroleum has probably been formed from fats under the influence of high temperature combined with great pressure. In fact, ENGLER has obtained a liquid very similar to American petroleum, by distilling these substances under increased pressure. Opinion is divided concerning the origin of these fats. According to some, they are due to fish; but it is difficult to understand how the enormous quantities of petroleum found in some places could have been formed in this way. Another explanation attributes its formation to very small organisms, called *diatoms;* these were present in enormous numbers in the earlier geological periods. They produced a sort of wax, which yields petroleum when distilled under pressure.

Another hypothesis has been suggested by MOISSAN. This attributes the formation of petroleum to the action of water on certain metallic carbides which have been formed by the intense heat of volcanoes. On treatment with water, most of these carbides yield gaseous hydrocarbons, especially methane or acetylene, and it has been proved that the latter yield a petroleum-like liquid when exposed to high pressure and temperature. Since petroleum varies greatly in composition, according to the place where it has been obtained, it is possible that both hypotheses are true (*cf.* **133**).

Homologous Series.

35. Each of the hydrocarbons C_nH_{2n+2} differs in composition from the rest by $n \times CH_2$, as is at once seen from the general formula. It has been already pointed out that this difference exercises but a slight influence on their chemical properties.

Whenever organic compounds show great resemblance in their chemical properties, and have at the same time a difference in composition of $n \times CH_2$, they are said to be *homologous,* the name *homologous series* being given to such a group of compounds. Many of these series are known, as will be seen later.

It is easy to understand how much this simplifies the study of organic chemistry. Instead of having to consider the chemical properties of each compound individually, it is sufficient to do so for one member of a homologous series, as this gives the principal characteristics of all the other members. In addition to the main properties common to each member of a homologous series, there are peculiarities special to each individual member. Except in a few instances, this book will not deal with these, because they only need to be considered in a more extensive survey of the subject.

36. The *physical properties,* such as the melting-points and boiling-points, specific gravities, and solubilities, of the members of a homologous series, generally change uniformly as the number of carbon atoms increases. In general it may be said that the melting-points and boiling-points rise from the lower to the higher members of a homologous series.

A table of some of the physical constants of a number of normal members (**40**) of the paraffin series is given below.

It is seen from this table that the first four members are gases at the ordinary temperature, those from C_5 to C_{16} liquids, and the higher members solids. Although methane is odourless, the liquid members have a characteristic petroleum-like smell; the solid members, on the other hand, are perfectly free from smell. They are all almost insoluble in water.

Formula.	Name.	Melting-point.	Boiling-point.	Specific Gravity.
CH_4	Methane	− 186°	−164°	0·415 (at − 164°)
C_2H_6	Ethane	− 172·1°	− 84·1°	0·446 (at 0°)
C_3H_8	Propane	——	− 37°	0·536 (at 0°)
C_4H_{10}	Butane	——	1°	0·600 (at 0°)
C_5H_{12}	Pentane	——	37°	0·627 (at 14°)
C_6H_{14}	Hexane	——	69°	0·658 (at 20°)
C_7H_{16}	Heptane	——	98°	0·683 ,, ,,
C_8H_{18}	Octane	——	125°	0·702 ,, ,,
C_9H_{20}	Nonane	− 51°	150°	0·718 ,, ,,
$C_{10}H_{22}$	Decane	− 31°	173°	0·730 ,, ,,
$C_{11}H_{24}$	Undecane	− 26°	195°	0·774 at the melting-point
$C_{12}H_{26}$	Dodecane	− 12°	214°	0·773 ,, ,, ,, ,,
$C_{14}H_{30}$	Tetradecane	4°	252°	0·775 ,, ,, ,, ,,
$C_{16}H_{34}$	Hexadecane	18°	287°	0·775 ,, ,, ,, ,,
$C_{20}H_{42}$	Eicosane	37°	205° *	0·778 ,, ,, ,, ,,
$C_{21}H_{44}$	Heneicosane	40°	215°	0·778 ,, ,, ,, ,,
$C_{23}H_{48}$	Tricosane	48°	234°	0·779 ,, ,, ,, ,,
$C_{31}H_{64}$	Hentriacontane	68°	302°	0·781 ,, ,, ,, ,,
$C_{35}H_{72}$	Pentatriacontane	75°	331°	0·782 ,, ,, ,, ,,
$C_{60}H_{122}$	Hexacontane	101°	——	——

* At 15 mm. pressure, and the same for those following.

It should be further remarked that the differences between the melting-points and boiling-points respectively of successive members of the series become smaller with increase in the number of carbon atoms. This phenomenon is usually found in homologous series.

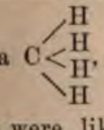
Isomerism and Structure.

37. There is only one substance known with the formula CH_4; this is methane. Similarly, there is only one compound having the formula C_2H_6, and one with the formula C_3H_8. There are, however, two compounds known with the formula C_4H_{10}, three with the formula C_5H_{12}, five with the formula C_6H_{14}, etc. The phenomenon of two or more compounds being represented by one formula is called *isomerism* (**2**), and compounds having the same formula are called *isomers*. This is explained by a consideration of the way in which the atoms are grouped in the molecule.

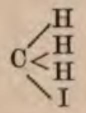
One of two hypotheses may be adopted. In the first place, the arrangement of the atoms may be regarded as continually changing, a molecule being represented as like a planetary system, the configuration of which changes from moment to moment. This hypothesis, however, cannot explain the phenomenon of isomerism; indeed, it is not apparent how, for example, the four carbon atoms and ten hydrogen atoms in butane could form two different substances if the arrangement were indeterminate, for there are trillions of molecules present in as little as one cubic millimetre, and all the possible configurations of these fourteen atoms must therefore be supposed to occur every moment.

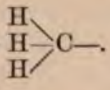
Isomerism can at once be understood by assuming that there is a definite and unchanging arrangement of the atoms in the molecule, because the difference in the properties of isomeric compounds may be then explained by a difference in the arrangement of equal numbers of the same atoms.

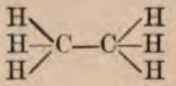
A definite and unchanging arrangement of the atoms in a molecule does not involve their being immovable in relation to one another. They may be supposed, for example, to revolve round a position of equilibrium without any alteration in their order of succession.

38. Since the phenomenon of isomerism leads to the assumption of a definite arrangement of the atoms in the molecule, it is necessary to answer the question as to what the arrangement of the atoms in the molecules of different compounds is. The starting-point for this is the tetravalency of the carbon atom. In the case of methane the arrangement of the atoms may be represented by the formula , in which the four linkings of the carbon atom act, as it were, like four points of attraction, each one holding a monovalent hydrogen atom fast. This is the only possibility, because the hydrogen atoms cannot be bound to one another, since the only point of attraction, or single linking, of each of them is already in union with one of the linkings of the carbon atom.

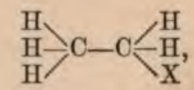
We shall now try to ascertain the arrangement of the atoms in ethane, C_2H_6. This substance can be obtained by the action of sodium upon methyl iodide, CH_3I (**31**). We have here a tetravalent carbon atom, three monovalent hydrogen atoms, and one monovalent iodine atom. It must therefore be represented thus:



Sodium reacts with methyl iodide in such a way that the iodine atoms are abstracted from two molecules, with formation of ethane. The removal of the iodine atom has the effect of setting free the carbon linking previously attached to this atom, with the production of two groups . Since the formula of ethane is C_2H_6, it is evident that the only possible arrangement of its atoms is the one in which the two free linkings of the methyl-groups are united to one another:

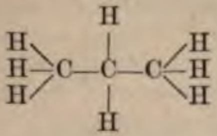


The arrangement of the atoms in propane can be determined in an exactly analogous manner. It has been mentioned (**31**) that propane is formed by the action of sodium on a mixture of methyl and ethyl halides. Since ethane can be prepared in the way mentioned above, the formula of an ethyl halide can only be



where X represents a halogen atom.

If the halogen is taken away from this and from methyl iodide at the same time, the residues unite together, showing that propane has the following structure:

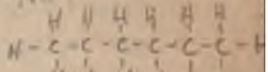


or shortly $H_3C \cdot CH_2 \cdot CH_3$.

An arrangement of symbols like this, which expresses the configuration of the atoms in a molecule, thus indicating the form or structure, is called a *structural* or *constitutional formula.*

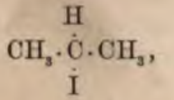
39. The following example makes it clear how cases of isomerism can be explained by differences in structure. Among the five known hexanes there is one which boils at 69° and has a specific gravity of 0·6583 at 20·9°, and another which boils at 58° and has a specific gravity of 0·6701 at 17·5°. The first is obtained by the action of sodium on *normal propyl iodide,* $CH_3 \cdot CH_2 \cdot CH_2I$. It follows from what has been said above that this hexane must have the structure $2C_3H_7I + 2Na \rightarrow C_6H_{14} + NaI$

$$CH_3 \cdot CH_2 \cdot CH_2—CH_2 \cdot CH_2 \cdot CH_3.$$



It is called *dipropyl,* on the assumption that it has been formed by the union of two propyl-groups.

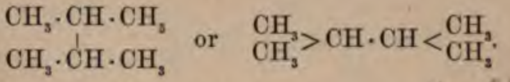
In addition to this normal propyl iodide, an isomer is known having the name *isopropyl iodide.* Both compounds can be easily converted into propane, $CH_3 \cdot CH_2 \cdot CH_3$. Assuming that the isomerism is due to a different arrangement of the atoms in the molecule, it follows that the isomerism of the two compounds C_3H_7I can only be explained by a difference in the position occupied by the iodine atom in the molecule, because the arrangement of the atoms in propane is known, and the propyl iodides only differ from propane in having one of the hydrogen atoms in the latter replaced by iodine. Isopropyl iodide must therefore have the structure



$$CH_3 \cdot \overset{H}{\underset{I}{C}} \cdot CH_3,$$

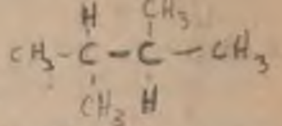
if the constitution of normal propyl iodide is $CH_3 \cdot CH_2 \cdot CH_2I$.

The hexane boiling at 58° is produced by the action of sodium on isopropyl iodide. From this method of formation it is evident that this hexane has the structure



$$\begin{array}{l} CH_3\cdot CH\cdot CH_3 \\ \qquad\ | \\ CH_3\cdot CH\cdot CH_3 \end{array} \quad \text{or} \quad \begin{matrix}CH_3\\CH_3\end{matrix}\!>CH\cdot CH<\!\begin{matrix}CH_3\\CH_3\end{matrix}.$$

For this reason it is called *di-isopropyl.*



$$CH_3-\underset{CH_3}{\overset{H}{C}}-\underset{H}{\overset{CH_3}{C}}-CH_3$$

Carbon Chains.

40. It is evident from the foregoing that the facts necessitate the assumption of a bond between carbon atoms in the molecules of organic compounds. *This bond is a very strong one,* for, as we have already seen (**31**), the saturated hydrocarbons resist the action of powerful chemical reagents. The property possessed by carbon atoms of combining together to form a series of many atoms, a *carbon chain,* like that in the hexanes above described, furnishes a marked distinction between them and the atoms of all the other elements, which either have not this power, or only in a very inferior degree. The fact that the number of carbon compounds is so enormous is due to this property, in conjunction with the tetravalency of the carbon atom.

A carbon chain like that in normal hexane (dipropyl) is said to be *normal.* On the other hand, there is the *branched* chain, an example of which is furnished by di-isopropyl. Each carbon atom in the normal chain is linked directly to not more than two others; in branched chains there are carbon atoms which are directly linked to three or four others. A normal-chain compound is usually denoted by putting *n* before its name; branched-chain compounds are often distinguished by the prefix *iso.*

A few other definitions may find a place here. A carbon atom which is only linked to one other carbon atom is called *primary.* If it is linked to two carbon atoms it is named *secondary;* if to three, *tertiary;* if to four, *quaternary.* A carbon atom situated at the end of a chain is called *terminal.* The carbon atoms of a chain are distinguished by numbers, the terminal one being denoted by 1, the one next it by 2, etc.; for example,

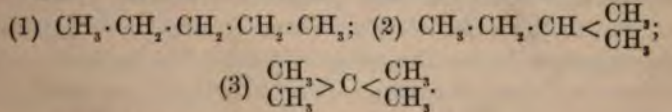
$$\underset{1}{CH_3}\cdot\underset{2}{CH_2}\cdot\underset{3}{CH_2}\cdot\underset{4}{CH_3}.$$

Sometimes the terminal atom is denoted by ω, the one linked to it by α, and the succeeding one by β, etc.

Law of the Even Numbers of Atoms.—The number of hydrogen atoms in the saturated hydrocarbons must be an even one, since their formula is C_nH_{2n+2}. All other organic compounds may be regarded as being derived by the exchange of these hydrogen atoms for other elements or groups of atoms, or by the removal of an even number of hydrogen atoms, or by both causes simultaneously. It follows from this that the sum of the atoms with uneven valency (hydrogen, the halogens, nitrogen, phosphorus, etc.) must always be an even number. The molecule of a substance whose empirical composition is $C_3H_2NO_2$ must be at least twice as great as this, because 2H + 1N is uneven.

Number of Possible Isomers.

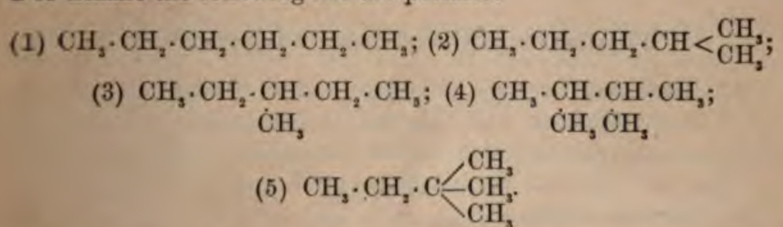
41. The tetravalency of the carbon atom, coupled with the principle of the formation of chains of atoms, not only enables us to account for the isomers which are known to exist, but also puts us in the position of being able to predict the existence of compounds. For a compound C_4H_{10}, for example, either the structure $CH_3\cdot CH_2\cdot CH_2\cdot CH_3$ or ${}^{CH_3}_{CH_3}{>}CH\cdot CH_3$ may be assumed, and in this case there are no further possibilities. Pentane may have the following structural formulæ:



$$(1)\ CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_3;\quad (2)\ CH_3\cdot CH_2\cdot CH{<}^{CH_3}_{CH_3};$$

$$(3)\ {}^{CH_3}_{CH_3}{>}C{<}^{CH_3}_{CH_3}.$$

For hexane the following five are possible:



$$(1)\ CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_3;\quad (2)\ CH_3\cdot CH_2\cdot CH_2\cdot CH{<}^{CH_3}_{CH_3};$$

$$(3)\ CH_3\cdot CH_2\cdot \underset{CH_3}{CH}\cdot CH_2\cdot CH_3;\quad (4)\ CH_3\cdot \underset{CH_3}{CH}\cdot \underset{CH_3}{CH}\cdot CH_3;$$

$$(5)\ CH_3\cdot CH_2\cdot C\begin{array}{l}\diagup CH_3\\ - CH_3\\ \diagdown CH_3\end{array}.$$

If the principles given above be assumed, it will be impossible to find structural formulæ other than those mentioned.

Should it be possible to actually obtain the same number of isomers as can be thus predicted, and no more, and should the products of synthesis or decomposition of the existing isomers necessitate the assumption of the same structural formulæ as those required by the theory, these facts constitute a very important confirmation of the correctness of the principles upon which the theory is based. This has in fact been proved to hold good in numerous instances, and therefore, on the other hand, affords an important means for determining the structure of a compound, because if all the structural formulæ which are possible for the compound according to the theory are considered, one of them will be found to be that of the substance.

In very many cases the number of isomers actually known is much smaller than that which is possible. This is due to the fact that the number of possible isomers increases very quickly with increase of the number of carbon atoms in the compound. CAYLEY has calculated that there are nine possible isomers for C_7H_{16}, eighteen for C_8H_{18}, thirty-five for C_9H_{20}, seventy-five for $C_{10}H_{22}$, one hundred and fifty-nine for $C_{11}H_{24}$, three hundred and fifty-four for $C_{12}H_{26}$, eight hundred and two for $C_{13}H_{28}$, etc. Chemists have not tried to prepare, for example, every one of the eight hundred and two possible isomers of the formula $C_{13}H_{28}$, because their attention has been occupied by more important problems. There can, however, be no doubt as to the possibility of obtaining all these compounds, because, as mentioned above, the methods for building them up are known, and there would therefore be no theoretical difficulties in the way of these experiments, though there might be hindrances of an experimental nature.

Physical Properties of Isomeric Compounds.

42. The normal compound has the highest boiling-point among the different isomers, and this rule holds good in general for homologous series other than that of the methane hydrocarbons.

Example. Normal hexane boils at 69°, and the boiling-points of the different isomers are:

Methyldiethylmethane: $(C_2H_5)_2CH \cdot CH_3$ B. P. 64°.
Ethylisobutyl: $C_2H_5 \cdot CH_2 \cdot CH(CH_3)_2$,, 62°.
Di-isopropyl: $(CH_3)_2CH \cdot CH(CH_3)_2$,, 58°.
Trimethylethylmethane: $(CH_3)_3 C \cdot C_2H_5$,, 46°.

ALCOHOLS, $C_nH_{2n+2}O$.

Methods of Formation and Constitution.

43. The members of this homologous series can be obtained by the action of silver hydroxide on the alkyl halides:

$C_nH_{2n+1}OH$

$$C_nH_{2n+1}I + AgOH = C_nH_{2n+2}O + AgI.$$

It is usual to bring an alkyl iodide in contact with moist oxide of silver, of which the portion dissolved in the water reacts like silver hydroxide ("Inorganic Chemistry," **246**). The preparation of the alcohol from the iodide can also be effected by heating it with excess of water at 100°:

C_2H_5OH

$$C_2H_5I + H_2O = C_2H_6O + HI.$$

When sodium reacts with an alcohol $C_nH_{2n+2}O$, one gramme-atom of free hydrogen is liberated from each gramme-molecule of the alcohol, and a compound called *sodium alcoholate* with the formula $C_nH_{2n+1}NaO$ is produced, which decomposes in presence of excess of water into NaOH and an alcohol. The sodium has thus replaced one atom of hydrogen, and neither it nor any other metal can replace more than one hydrogen atom; if excess of sodium is added, it remains unacted upon. It follows that there is only one hydrogen atom in the alcohol which is replaceable by sodium.

When an alcohol is treated with trichloride or pentachloride of phosphorus, an alkyl chloride is formed:

C_2H_5OH C_2H_5Cl

$$3C_nH_{2n+2}O + PCl_3 = 3C_nH_{2n+1}Cl + H_3PO_3.$$

We shall endeavour to deduce the constitution of the alcohols from these facts. Silver hydroxide can only have the structure Ag—O—H, its divalent oxygen atom being linked to its monovalent silver and hydrogen atoms. When silver hydroxide is brought into contact with an alkyl iodide, the reaction must be supposed to take place in such a way that on the one hand the iodine atom is set free from the alkyl-group, and on the other hand, the silver atom from the hydroxyl-group. The alkyl-group and the hydroxyl-group are thus afforded the opportunity of uniting with one another by means of the linking which has been set free in each of them:

$$C_nH_{2n+1}\boxed{I + Ag}OH \rightarrow C_nH_{2n+1}\text{—}OH.$$

This method of formation proves that the alcohols contain a hydroxyl-group; their preparation from alkyl iodides and water leads also to the same conclusion, which is further supported by the two properties of alcohols mentioned above. It is evident that if their structure is expressed by $C_nH_{2n+1}\cdot OH$, all the hydrogen atoms present, except one, are linked directly to carbon, while one hydrogen atom occupies a special position in the molecule, being attached to the oxygen atom, which in its turn is united through its second linking to a carbon atom. It is only natural to suppose that the special position occupied by this hydrogen atom is accompanied by a special property, that of being the only one of all the hydrogen atoms which is replaceable by alkali-metals. Moreover, sodium sets free hydrogen from another compound which without doubt contains a hydroxyl-group; this compound is water, for which no other constitution is possible than H—O—H.

The fact that the alcohols are converted into alkyl chlorides by the action of the chlorides of phosphorus is perfectly in accord with their containing a hydroxyl-group. It is seen at once from the empirical formulæ $C_nH_{2n+2}O$ and $C_nH_{2n+1}X$, that the halogen has replaced OH. It may be assumed that in this reaction the hydroxyl of the alcohol has changed places with the chlorine of the phosphorus compound:

$$\begin{tikzcd}[column sep=tiny] 3(C_nH_{2n+1}\cdot & OH \arrow[rr, bend left] &) + & Cl_3 \arrow[ll, bend left] & P. \end{tikzcd}$$

A consideration of the possible constitutional formulæ for substances having the general molecular formula $C_nH_{2n+2}O$ reveals the fact that on account of the way in which the oxygen atom is linked, only two formulæ are possible; thus, the compound C_2H_6O could be either

I. $CH_3\cdot CH_2\cdot OH$, or II. $CH_3\cdot O\cdot CH_3$.

Since all the hydrogen atoms in the second formula have the same value, it cannot be the one representing an alcohol, as it would not account for a very important property of these compounds, the action of the alkali-metals upon them. The action of silver hydroxide on an alkyl iodide, or that of PCl_3 on an alcohol, would accord equally ill with this formula, whereas formula I explains these reactions fully; it must therefore be adopted.

The constitutional formulæ of the alcohols have thus been deduced from their properties. Inversely, *the constitutional formulæ account for all the chemical properties of the compounds*, being simply a short way of expressing them. It is easy to see how valuable these formulæ are; because, if it is possible to derive a structural formula by studying some of the properties of a compound, it will be possible from this to deduce its other properties. The existence of properties indicated in this way has in numerous instances been established by experiment.

Nomenclature and Isomerism.

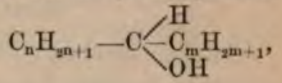
44. The alcohols of this series are named after the alkyl-groups contained in them; for example, *methyl*, *ethyl*, *propyl*, etc., *alcohol*.

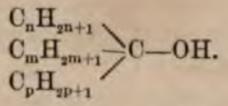
Isomerism may arise in three ways: by branching of the carbon chains, through the position of the hydroxyl-group, or through both these causes simultaneously.

This is seen from the following table of the isomeric alcohols C_3 to C_5:

Name.	Formula.	Boiling-point.	Specific Gravity at 20°. (d_4^{20}).
Propyl alcohols C_3H_8O			
1. Normal	$CH_3\cdot CH_2\cdot CH_2OH$	97°	0·804
2. Iso	$CH_3\cdot CHOH\cdot CH_3$	81°	0·789
Butyl alcohols $C_4H_{10}O$			
1. Normal primary	$CH_3\cdot CH_2\cdot CH_2\cdot CH_2OH$	117°	0·810
2. ,, secondary	$CH_3\cdot CH_2\cdot CHOH\cdot CH_3$	100°	
3. Iso	$(CH_3)_2CH\cdot CH_2OH$	107°	0·806
4. Trimethylcarbinol	$(CH_3)_3C\cdot OH$	83°	0·786
Amyl alcohols $C_5H_{12}O$			
1. Normal primary	$CH_3\cdot (CH_2)_3\cdot CH_2OH$	138°	0·815
2. Isobutylcarbinol	$(CH_3)_2CH\cdot CH_2\cdot CH_2OH$	131°	0·810
3. Secondary butylcarbinol	$CH_3\cdot CH(C_2H_5)\cdot CH_2OH$	128°	
4. Methylpropylcarbinol	$CH_3\cdot (CH_2)_2\cdot CHOH\cdot CH_3$	119°	
5. Methylisopropylcarbinol	$(CH_3)_2CH\cdot CHOH\cdot CH_3$	112·5°	
6. Diethylcarbinol	$C_2H_5\cdot CHOH\cdot C_2H_5$	117°	
7. Dimethylethylcarbinol	$(CH_3)_2C(OH)\cdot C_2H_5$	102°	
8. Tertiary butylcarbinol	$(CH_3)_3C\cdot CH_2OH$	112°	

The names containing carbinol have reference to the fact that all alcohols may be looked upon as methyl alcohol (*carbinol*), in which one or more of the hydrogen atoms, with the exception of the one in the hydroxyl-group, are replaced by alkyl-groups. In this way, isobutyl alcohol is called *isopropylcarbinol*, secondary butyl alcohol *methylethylcarbinol*, and normal butyl alcohol n-*propylcarbinol*, etc.

As is evident from the above examples, a *primary* alcohol is one in which the hydroxyl-group is linked to a primary carbon atom (**40**); while in a *secondary* or a *tertiary* alcohol the hydroxyl is linked to a secondary or a tertiary carbon atom respectively. Similarly, compounds which may be regarded as having been produced by replacement of hydrogen linked to a primary, secondary, or tertiary atom are called primary, secondary, or tertiary compounds. Thus primary alcohols are represented by the general formula $C_nH_{2n+1}—CH_2OH$, secondary by  $C_nH_{2n+1}—C\begin{cases} H \\ C_mH_{2m+1} \\ OH \end{cases}$, and tertiary by



$$\left.\begin{array}{l} C_nH_{2n+1} \\ C_mH_{2m+1} \\ C_pH_{2p+1} \end{array}\right\rangle C—OH.$$

General Properties of the Alcohols.

45. Some of the physical properties of the alcohols are given in the following table, which includes only normal primary compounds:

Name.	Formula.	Specific Gravity d_0^0.	Boiling-point.	Difference of the Boiling-points.
Methyl alcohol	CH_3OH	0·812	66°	
Ethyl ,,	C_2H_5OH	0·806 ?	78°	12°
Propyl ,,	C_3H_7OH	0·817	97°	19°
Butyl ,,	C_4H_9OH	0·823	117°	20°
Amyl ,,	$C_5H_{11}OH$	0·829	137°	20°
Hexyl ,,	$C_6H_{13}OH$	0·833	157°	20°
Heptyl ,,	$C_7H_{15}OH$	0·836	175°	18°
Octyl ,,	$C_8H_{17}OH$	0·839	191°	16°
Nonyl ,,	$C_9H_{19}OH$	0·842	213°	22°

It is seen that there is an increase in the boiling-point of about 20° for every additional CH_2 in the formulæ. A similar regularity is found in other homologous series. This table, together with that on page 51, shows that the normal compounds have the highest boiling-points; and this also holds good for the hydrocarbons (**42**).

The lower alcohols ($C_1 - C_4$) are mobile liquids, the middle ones ($C_5 - C_{11}$) are of a more oily nature, while the higher members are solid at the ordinary temperature; all are colourless, at least in thin layers. In thick layers they are slightly yellow, the colour becoming more marked with increase in the number of carbon atoms. The first members ($C_1 - C_3$) are miscible in all proportions with water, but the solubility of the higher members diminishes quickly as the number of carbon atoms increases.

The lower members have a spirituous smell, and the middle ones a disagreeable one, while the solid members are odourless. Their specific gravity is less than 1.

Methyl Alcohol, CH_3OH.

46. This substance is obtained on the large scale by the dry distillation of wood in iron retorts at as low a temperature as possible; or better, by treatment of wood with hot *producer-gas*, which is a mixture of carbon monoxide and nitrogen, obtained by passing air over coke at a white heat. To these methods of preparation the substance owes its name *wood-spirit*. The products of the distillation are gases, an aqueous liquid, and tar. The aqueous solution contains methyl alcohol, along with a number of other substances, of which the chief are acetic acid and acetone. The acetic acid is made to combine with lime, and the methyl alcohol purified by fractional distillation, and other methods. It is used in commerce in the preparation of aniline dyes and formaldehyde, for the *denaturation* of spirit so as to render it unfit for drinking purposes (**48**), etc.

Methyl alcohol burns with a pale-blue flame, and is miscible with water in all proportions, the mixing being accompanied by contraction and the development of heat. Its melting-point is − 93.9°; its other physical properties will be found in the table on page 52.

Ethyl Alcohol, C_2H_5OH.

47. This is ordinary alcohol, and is prepared artificially in enormous quantities. Its preparation depends upon a property possessed by *glucose*, a sugar with the formula $C_6H_{12}O_6$, of decomposing into carbon dioxide and alcohol in presence of *yeast-cells:*

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

About 95% of the glucose decomposes according to this equation; a number of higher alcohols of this series, chiefly *amyl alcohols*, $C_5H_{11}OH$, are formed as by-products, together with *glycerol*, *succinic acid*, etc.

In the technical manufacture of alcohol, this sugar itself is not used as a basis, owing to its being too costly. Some substance rich in starch, $(C_6H_{10}O_5)_x$, such as potatoes, grain, etc., is used instead. By the action of *enzymes*, the starch is almost completely converted into *maltose*, $C_{12}H_{22}O_{11}$, one molecule of this compound being then converted into two molecules of glucose by the action of one molecule of water:

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O = 2\underset{\text{Glucose}}{C_6H_{12}O_6}.$$

Enzymes are chemical compounds (unorganized ferments) which have the property, when certain substances are brought into contact with small quantities of them, of causing these substances to decompose, in most cases with addition of the elements of water. Their constitution and the way in which they act are both unknown (**222**).

The particular enzyme which is used in the technical manufacture of maltose from starch is called *diastase;* it is present in sprouting barley. The reaction to which it gives rise is called *saccharification*. When potatoes are used, they are first made into a thin, homogeneous pulp by treatment with steam under pressure at 140° to 150°, sprouting barley being then added after cooling. At a temperature of 60° to 62°, the decomposition into maltose is completed in twenty minutes.

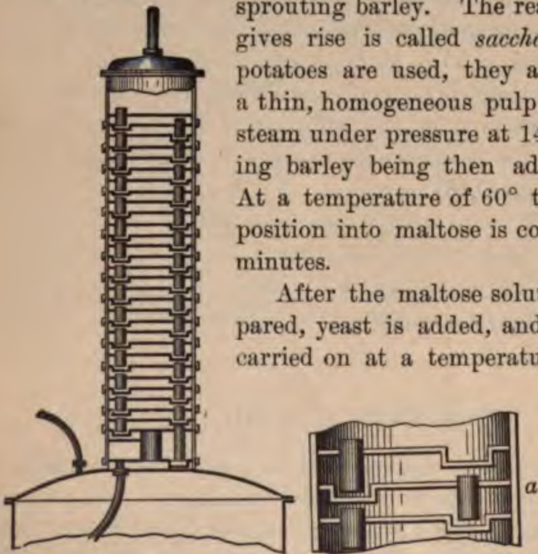


FIG. 23.—FRACTIONATING-COLUMN.

After the maltose solution has been prepared, yeast is added, and the fermentation carried on at a temperature *below* 33°. In order to separate the resulting alcohol from the other substances which are present, the product is submitted to distillation; by using a *fractionating-column* (Fig. 23), alcohol of

90% strength can be obtained, although the concentration of the alcohol in the fermented liquid does not exceed 18%.

The thin liquid residue remaining in the still is called *spent wash*, and is used for feeding cattle; it contains, amongst other things, almost all the albuminous substances present in the material from which the spirit has been manufactured.

The crude spirit (*low wines*) so prepared is again carefully fractionated, when alcohol of 96% by volume (*spirits*) is obtained. The fractions of higher boiling-point consist of an oily liquid with an unpleasant smell, which is called *fusel oil*, and contains chiefly amyl alcohols and other homologues. The residue is called *spent lees*.

Alcoholic beverages have long been known. They are classified into two main divisions, those that have been distilled and those that have not. To the first class belong *brandy* (40–50% alcohol), *gin* (alcohol distilled with juniper berries), *cognac* (obtained by distilling wine, above 50% alcohol), etc. The second class includes *beer* (3–4% alcohol), *wine* (8·5–10% alcohol), *madeira* (up to 21% alcohol), etc.

48. The alcohol of commerce (*spirits of wine*) always contains water. In order to obtain anhydrous or *absolute* alcohol from this, lumps of quicklime are added to spirit containing a high percentage of alcohol, until the quicklime shows itself above the surface of the liquid. The latter is then allowed to stand for some days, or boiled for several hours under a reflux-condenser (**18**), after which it is distilled. The preparation is much facilitated, and the loss, which is rather large by this method, is reduced to a minimum, by introducing a spirit of high percentage along with a little quicklime into a vat, which is then closed by a screw top, and heated some hours at 100° in a water-bath; the spirit is then distilled. In order to prepare absolute alcohol from dilute alcohol, the latter must first be concentrated by distilling it from a water-bath. This can also be effected by the addition of solid potassium carbonate, which causes the liquid to separate into two layers, the aqueous one below and the alcoholic one above; alcohol of 91·5% by weight is thus obtained.

Absolute alcohol is a mobile, colourless liquid, with a characteristic smell. It solidifies at − 112·3°, and burns with a pale-blue, non-luminous flame. It is very hygroscopic, being miscible with water in all proportions with contraction and rise in temperature. The maximum contraction is obtained by mixing 52 volumes of alcohol with 48 volumes of water, the volume of the resulting mixture at 20° being 96·3 instead of 100.

A test for absolute alcohol is its behaviour with anhydrous copper sulphate, which remains perfectly colourless when in contact with it, whereas if the slightest trace of water is present, the copper sulphate develops a light-blue colour after several hours. The specific gravity, a physical constant which is often used to ascertain the purity of liquid compounds, may also be employed for the same purpose.

On account of the great importance which a knowledge of the amount of alcohol in mixtures of water and alcohol has for industrial and fiscal purposes, it is necessary to have a method for quickly and easily determining this. Different chemists, among them VON BAUMHAUER, have shown that the determination of the specific gravity and the temperature of such a mixture, affords the easiest method of effecting this. For this purpose a table has been prepared with great accuracy, showing the specific gravities of mixtures of alcohol and water from 0% to 100%, at temperatures between 0° and 30°. When the specific gravity and temperature of a given mixture have been determined, the percentage of alcohol may be found by reference to the table. The specific gravity is usually determined in practice with a delicate hydrometer.

In commerce and in the arts, the amount of alcohol is usually expressed on the Continent of Europe in *volume-percentage*, or the number of litres of absolute alcohol contained in 100 litres of the aqueous solution.* For scientific purposes it is usually expressed in

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* In Great Britain the standard is *proof-spirit*. This name is derived from the old method of testing spirit by moistening gunpowder with it, and then bringing the mixture into contact with a lighted match. If the alcohol were "under proof," the powder did not take fire, but if there were sufficient alcohol present, the application of the light ignited the gunpowder, the spirit being then "over proof." When the proportions of alcohol and water were such that it was just possible to set fire to the powder, the sample was described as "proof-spirit." When the spirit is weaker than proof-spirit it is said to be *under proof*, and when stronger than proof-spirit is said to be *over proof;* for example, a spirit which is 5° under proof would contain in each 100 volumes the same quantity of alcohol as that contained in 95 volumes of proof-spirit, and a spirit 5° over proof would need 5 volumes of water added to each 100 volumes to convert it into proof-spirit. By act of Parliament "proof-spirit" is defined as "such a spirit as shall at a temperature of 51° F weigh exactly $\frac{12}{13}$ of an equal measure of distilled water." This corresponds to a spirit containing 57·1% of alcohol by volume, or 49·3% by weight.—TRANSLATOR.

percentage by weight, or the number of grammes of alcohol contained in 100 grammes of the aqueous solution. These percentage-numbers are not the same, because contraction takes place when alcohol and water are mixed, so that the percentages by weight are smaller than those by volume for a spirit of any given concentration.

The greater part of the alcohol produced is consumed in the form of beverages, the detrimental physiological effects of which are augmented by the impurities, especially fusel oil, which they contain. Alcohol is used in commerce for the preparation of lacquers, varnishes, dyes, important pharmaceutical preparations (chloroform, chloral, iodoform, etc.); it is also employed for the preservation of anatomical specimens. Alcohol is a good solvent for many organic compounds, and is widely employed in laboratory work for this purpose.

On account of the extensive use of alcohol for manufacturing-processes, the industries in which it is employed would be paralyzed if the necessary spirit were subject to the same excise duty as alcohol intended for consumption. The alcohol used in manufactures in some countries* is accordingly made unfit for drinking (*denatured* or *methylated*) by the addition of materials which impart to it a nauseous taste, and is sold duty-free. On the continent of Europe crude wood spirit is used for this purpose, and in Great Britain this is supplemented by the addition of a small quantity of paraffin oil.

A test for ethyl alcohol is the formation of iodoform on the addition of iodine and caustic potash (**152**).

Propyl Alcohols.

49. Two propyl alcohols are known, one boiling at 97° and having a specific gravity of 0·804, the other boiling at 81° and having a specific gravity of 0·789. In accordance with the principles which have been stated, only two isomers are possible:

$$\underset{\text{Normal propyl alcohol}}{CH_3\cdot CH_2\cdot CH_2OH}, \quad \text{and} \quad \underset{\text{Isopropyl alcohol}}{CH_3\cdot CH(OH)\cdot CH_3}.$$

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* The sale of duty-free alcohol is not permitted in the United States; a tax is levied of $1.10 per proof gallon (50% alcohol by volume), or $2.07 per standard gallon (231 cubic inches of 94% alcohol by volume), and is a heavy burden on many industries. The duty is much higher in Great Britain, being 11*s.* per gallon of proof-spirit (British standard, p. 56), but this disadvantage is in some measure counterbalanced by the sale of duty-free methylated spirit for manufacturing purposes.—TRANSLATOR.

Which structure has to be assigned to the substance with the higher boiling-point, and which to that with the lower, may be determined by submitting the substances to oxidation. From each of these alcohols is thus obtained a compound with the formula C_3H_6O, but these oxidation-products are not identical. When they are further oxidized, the compound C_3H_6O (propionaldehyde), obtained from the alcohol of higher boiling-point, yields an acid $C_3H_6O_2$, called propionic acid; whereas the substance C_3H_6O (acetone), obtained from the alcohol with the lower boiling-point, is converted into carbon dioxide and acetic acid, $C_2H_4O_2$:

C_3H_8O (propyl alcohol B.P. 97°) $\rightarrow C_3H_6O$ (propionaldehyde) $\rightarrow$
$\rightarrow C_3H_6O_2$ propionic acid.

C_3H_8O (isopropyl alcohol B.P. 81°) $\rightarrow C_3H_6O$ (acetone) $\rightarrow$
$\rightarrow CO_2 + C_2H_4O_2$ acetic acid.

Propionic acid has the constitution $CH_3 \cdot CH_2 \cdot COOH$, and acetone $CH_3 \cdot CO \cdot CH_3$, as will be shown later. It will be observed that the normal alcohol alone is capable of forming propionic acid, because the production of this substance must be due to the replacement of two hydrogen atoms by one oxygen atom, which in the normal alcohol can only give rise to a compound having the structure assigned to propionic acid. On the other hand, the formation of a substance having the structure of acetone by removal of two hydrogen atoms from a compound C_3H_8O is only possible when it has the constitution of isopropyl alcohol. The alcohol of higher boiling-point must therefore have the normal structure, and that boiling at the lower temperature must be isopropyl alcohol.

Oxidation affords a general method for distinguishing between primary and secondary alcohols. By referring to the formulæ given in **44**, it is seen that all primary alcohols contain the group $—CH_2OH$, which is converted by oxidation into the carboxyl-group $—C\lessgtr^{O}_{OH}$, the characteristic group of organic acids; further, all secondary alcohols contain the group $H \cdot \overset{|}{\underset{|}{C}} \cdot OH$, removal of the two hydrogen atoms from which yields the group $\overset{|}{\underset{|}{C}} : O$, characteristic of the *ketones*, the homologues of acetone.

The oxidation of a primary and of a secondary alcohol produces respectively an acid and a ketone with the same number of carbon atoms as the original alcohol.

A further deduction may be made from the facts above stated. In the conversion of normal propyl alcohol into propionic acid, as well as of isopropyl alcohol into acetone, the oxidation occurs at the carbon atom which is already linked to oxygen. This is always the case, and the general rule may be stated as follows. *When an organic compound is submitted to oxidation, the molecule is attacked at the part which already contains oxygen—that is, where oxidation has already begun.*

Normal propyl alcohol is obtained from fusel oil by fractionation, and is a colourless liquid with an agreeable odour. It is miscible with water in all proportions. Isopropyl alcohol is also a liquid; it does *not* occur in fusel oil, but may be obtained by the reduction of acetone (**120** and **156**).

Butyl Alcohols.

50. Four butyl alcohols are known (*cf.* Table, page 51), which is the number possible according to the theory. We shall here consider whether these theoretically possible formulæ are really in agreement with the properties of the four isomers. Two of the alcohols, those boiling at 117° and 107° respectively, yield on oxidation acids with the same number of carbon atoms. They must therefore have the structures 1 and 3 (*Ibid.*), since the group —CH_2OH is present in both. For reasons which will be referred to later, the alcohol boiling at 117° is considered to have the normal structure (1), and that boiling at 107° the structure (3). A third butyl alcohol, boiling at 100°, is converted by oxidation into a ketone with the same number of carbon atoms, showing that it must be a secondary alcohol corresponding to structure (2). Lastly, the fourth is solid at ordinary temperatures, melting at 25·5° and boiling at 83°. Since three of the theoretically possible structural formulæ have been assigned to the other isomers, there remains for this alcohol only the fourth, which is that of a tertiary alcohol. This structure for the alcohol melting at 25·5°, which has been thus arrived at by elimination, is in fact in accordance with its chemical behaviour. On oxidation, for example, it yields neither an acid nor a ketone with four carbon atoms, but the molecule is at once split up into substances containing a smaller number of carbon atoms. Remembering that an alcohol must contain the group $—CH_2OH$ in order to yield on oxidation an acid with the same number of carbon atoms, and that it must contain a group $H\cdot\overset{|}{\underset{|}{C}}\cdot OH$ in order to produce a ketone containing the same number of carbon atoms, it is evident that neither of these can be obtained from a tertiary alcohol. If the oxidation takes place in this, as in every other case, at the carbon atom which is already linked to oxygen, it must result in the decomposition of the molecule.

What has been said above holds good for tertiary alcohols in general, so that oxidation affords a means of distinguishing between primary, secondary, and tertiary alcohols. The experimental proof can be summed up as follows.

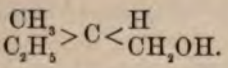
A primary alcohol yields on oxidation an acid with the same number of carbon atoms; a secondary alcohol yields on oxidation a ketone with the same number of carbon atoms; while oxidation of a tertiary alcohol at once splits up the molecule, yielding compounds containing a smaller number of carbon atoms.

Amyl Alcohols.

51. The alcohols containing five carbon atoms are called *amyl* alcohols. There are eight possible isomers, and all are known (*cf.* Table, page 51). They are liquids with a disagreeable smell, like that of fusel oil. Isobutylcarbinol, $(CH_3)_2CH\cdot CH_2\cdot CH_2OH$, is the principal constituent of fusel oil (**47**).

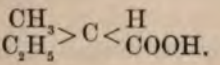
One of these alcohols, secondary butylcarbinol, affords a very remarkable case of isomerism. It has been shown how the arrangement of the atoms in a molecule accounts for the phenomenon of isomerism. A careful study of the properties of a compound makes it possible to assign to it a structural formula, to the exclusion of all the other formulæ which are possible for its known molecular composition. On the other hand, any given structural formula represents only *one* compound, since such a formula is the expression of a very definite set of properties; when these are unlike for two compounds, this must be indicated by their structural formulæ.

Nevertheless, there are three isomeric amyl alcohols which have been shown by careful examination to have the same structural formula:



$$\begin{matrix}CH_3\\C_2H_5\end{matrix}>C<\begin{matrix}H\\CH_2OH.\end{matrix}$$

That they have this constitution is proved by the fact that on oxidation they yield an acid



$$\begin{matrix}CH_3\\C_2H_5\end{matrix}>C<\begin{matrix}H\\COOH.\end{matrix}$$

the structure of which can easily be proved by synthesis (**166**).

The three amyl alcohols with this constitution have identical chemical properties; their physical constants are also almost all the same, but one of the latter serves to distinguish them from one another. When a beam of plane polarized light is passed through layers of these alcohols, the plane of polarization is rotated by one isomer to the left, and by the other to the right, while the third alcohol produces no rotation. The first two are said to be *optically active* (**27**, 2).

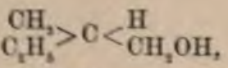
Since the difference between optically active compounds depends only upon a physical constant, while their chemical properties are identical, it may be asked whether this difference is not a purely *physical* one, arising from differences in the arrangement of the *molecules*, such as is supposed to exist in the case of dimorphous substances. There are two reasons opposed to this view.

First, differences in the arrangement of the molecules can only be supposed to exist in the case of *solid* substances, because it is only in these that the molecules have a fixed position in relation to one another. It is assumed that the molecules of liquids and gases are free to move; but they, too, afford examples of optical activity. In the case of liquids there is still a possibility that not the molecules themselves, but conglomerations of them, arranged in a definite manner, may be free to move. Were this the cause of optical activity, optically active liquids when converted into the gaseous state should, their vapour densities being normal, produce no rotation in the plane of polarization. That they actually do produce this rotation was proved by BIOT, and later by GERNEZ. In this case the phenomenon cannot be attributed to a difference in the arrangement of the molecules, because in a vapour of normal density each molecule is capable of independent motion.

Second, the optical activity shows itself in derivatives of optically active substances.

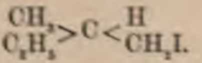
Hence it follows that *an explanation of the rotation of the plane of polarization in the case of liquids and of dissolved substances must be sought for in the structure of the molecules themselves.*

The question now arises as to what peculiarity in the structure of the molecules is the cause of this phenomenon. The following considerations will show how an insight may be obtained into it. The *lævo-rotatory amyl alcohol*, the constitution of which has been given above as



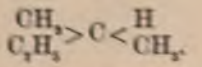
$$\begin{matrix}CH_3\\C_2H_5\end{matrix}>C<\begin{matrix}H\\CH_2OH,\end{matrix}$$

is converted by the action of gaseous hydriodic acid into *amyl iodide*, with the constitution



$$\begin{matrix}CH_3\\C_2H_5\end{matrix}>C<\begin{matrix}H\\CH_2I.\end{matrix}$$

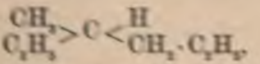
This compound is *optically active*. By treating it with nascent hydrogen, the iodine atom is replaced by hydrogen, with formation of *pentane*,



$$\begin{matrix}CH_3\\C_2H_5\end{matrix}>C<\begin{matrix}H\\CH_3.\end{matrix}$$

This compound is *optically inactive.*

If amyl iodide is subjected to the action of ethyl iodide in the presence of sodium, there results a *heptane*,



$$\begin{matrix}CH_3\\C_2H_5\end{matrix}>C<\begin{matrix}H\\CH_2\cdot C_2H_5.\end{matrix}$$

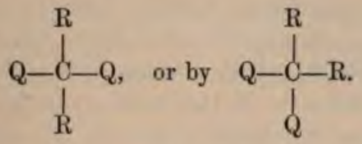
and this substance is *optically active.*

An examination of these three optically active substances shows that they differ from optically inactive pentane in the following way. In the latter there are two similar groups (methyl) linked to the central carbon atom, whereas in the others the four groups linked to this carbon atom are all different.

32. VAN 'T HOFF has shown that *optically active compounds in general contain at least one carbon atom linked to four different*

atoms or groups; and he has designated a carbon atom so linked an "asymmetric" carbon atom.

It has been stated above that there are three amyl alcohols having the same constitutional formula, of which one is dextro-rotatory, the second lævo-rotatory, and the third optically inactive. Three such isomers always exist in connection with one asymmetric carbon atom in the molecule, and of the two optically active substances one causes exactly the same amount of dextro-rotation as the other of lævo-rotation. VAN 'T HOFF has shown that the existence of this number of isomers is a necessary consequence of the occurrence of one asymmetric carbon atom in a molecule, provided certain assumptions are made regarding the relative positions of the atoms in space. These are as follows. The tetravalency of the carbon atom has its origin in four points of attraction, situated on its outer surface, so that it is able to link itself to atoms or groups of atoms in four directions. Concerning these directions various assumptions can be made. They may, for example, be supposed to lie in one plane. But this assumption is untenable, as will be seen by considering a compound CR_2Q_2, in which R and Q represent any dissimilar atoms or groups of atoms. If the four linkings lie in one plane, such a compound may be represented by the formula



$$\begin{array}{c} R \\ | \\ Q-C-Q, \\ | \\ R \end{array} \quad \text{or by} \quad \begin{array}{c} R \\ | \\ Q-C-R. \\ | \\ Q \end{array}$$

These are different, because in the first case the like groups are separated from one another by the unlike, while in the second case, the like groups are adjacent to one another. It follows from this that *in general* two isomers must exist in the case of all compounds CR_2Q_2. Experience teaches that this is not the case, because among the many hundreds of compounds of this type there is no instance known of the occurrence of two isomeric forms. The particular assumption that the directions of all four linkings lie in the same plane must therefore be abandoned, being at variance with the facts.

The most general assumption that can be made in regard to these directions is that each pair of them lies in the same plane.

They are then distributed in space in such a way that if the carbon atom be regarded as situated inside an irregular tetrahedron, the directions of the linkings will be toward the angles of the figure.*

53. We shall now ascertain whether this mode of representation is in accordance with the facts. If the directions of the linkings make different angles with one another, there still remains possible a difference in the structural arrangement of compounds CR_2Q_2, because it is just as easy to imagine that the groups R are connected with the linkings which have the smallest angle between them as to imagine that they are joined with those which make the greatest angle with one another. In the case of compounds CR_2Q_2 there is, however, only one arrangement possible when the directions of the linkings meet at equal angles. *This is the case when the carbon atom is regarded as being situated at the centre of a regular four-sided figure (tetrahedron), with its linkings directed towards the angles* (Fig. 24). By putting the groups R and Q in different positions in two atom models, it is always possible by rotating the models to bring them into such a position that the like groups coincide, showing that the two forms are identical.

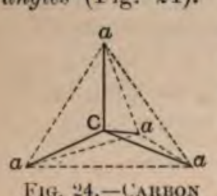


FIG. 24.—CARBON TETRAHEDRON.

This representation of the direction of the linkings explains how it is that there are no isomers of a compound CR_2Q_2. In the case of compounds C·RPQS, which contain four different groups, and therefore an asymmetric carbon atom, it indicates the possibility of the existence of two isomeric forms. It is seen from Figs. 25 and 26 (and still better from models) that for these four groups there are possible two arrangements which cannot be made to coincide with one another in any position, although they resemble one another in the same way that an object resembles its reflection in

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* The comprehension of what follows will be considerably facilitated by the construction of several models of carbon atoms with their linkings. This is easily done by cutting out a sphere from a cork to represent the carbon atom, the linkings being represented by moderately thick iron wires about ten centimetres long, the ends of which have been filed to a point. These wires are fixed in the cork sphere in the manner shown in Fig. 24. To show the linking of the atoms or groups of atoms, cork spheres of different colours are fastened to the ends of these iron wires, the different colours indicating that the groups are dissimilar.

a mirror. A figure of this kind has no plane of symmetry, hence the name "asymmetric carbon atom."

This makes it possible to understand how one isomer is just as much dextro-rotatory as the other lævo-rotatory (**52**). It is, in fact, the arrangement of the groups relative to the asymmetric carbon atom which is the cause of the rotation of the plane of polarization. If the arrangement of the groups in Fig. 25 produces dextro-rotation, then the inverse arrangement in the isomer in Fig. 26 must of necessity cause an equal rotation, but in an opposite direction.

FIG. 25. FIG. 26.

ASYMMETRIC C-ATOMS.

It has been stated above that not merely two, but three, isomers occur when there is one asymmetric carbon atom present in the molecule: a dextro-rotatory, a lævo-rotatory, and an optically inactive isomer. It has been proved that the optically inactive substance is composed of equal parts of the dextro-rotatory and of the lævo-rotatory compounds. Since these rotations are equal in amount, but different in direction, their sum has no effect upon the plane of polarization.

This isomerism in space, which is called *stereochemical isomerism* or *stereoisomerism*, is not indicated in the ordinary structural formulæ, which are written in one plane; hence the apparent contradiction that a single structural formula may represent two different compounds. VAN 'T HOFF's theory, however, supports the fundamental principle that isomerism has its origin in a difference in the arrangement of the atoms in the molecule.

In addition to the explanation of optical isomerism which has just been given, two others might be suggested, both of which, however, can be shown to be untenable. It might, for example, be supposed that the four linkings of the carbon atom are unequal in value; then a compound such as CP_2Q could exist in isomeric forms. Experience shows that this is not the case.

It might also be supposed that this phenomenon is due to a difference in the motion of the atoms in the molecule. If it were so, isomerism could no longer exist at absolute zero, since atomic motion ceases at this point; thus a falling temperature should cause a marked diminution in the difference between the optical isomers. There is, however, not the slightest indication of such behaviour.

Higher Alcohols, $C_nH_{2n+2}O$.

54. Their properties have already been mentioned (**45**). In addition may be cited *cetyl alcohol*, $C_{16}H_{33}OH$, obtained from spermaceti, and *myricyl alcohol*, $C_{30}H_{61}OH$, obtained from wax. The number of isomers of these higher compounds possible is very great, while the number actually known is but small. Of the higher members of the series, only the normal primary compounds are known.

Alcoholates.

55. Alcoholates are compounds obtained from alcohols by exchange of the hydroxyl-hydrogen atom for metals (**43**). The best known are *sodium methylate* or *methoxide*, $CH_3 \cdot ONa$, and *sodium ethylate* or *ethoxide*, $C_2H_5 \cdot ONa$. These are both white powders, which yield crystalline compounds with the alcohol corresponding to them. They are easily soluble in the alcohols, and, as will be seen later, are constantly used in syntheses. It was formerly supposed that the addition of water to a solution of an alcoholate converted it completely into NaOH, and liberated an equivalent quantity of alcohol; but LOBRY DE BRUYN has shown that this is only partly true, and that an equilibrium is reached in the reaction:

$$C_2H_5ONa + H_2O \rightleftarrows C_2H_5OH + NaOH.$$

(A proof of this will be found in **62**.) It follows that a solution of sodium hydroxide in alcohol partly decomposes into water and sodium alcoholate.

The alcoholic solution of sodium ethylate, which is usually obtained by dissolving pieces of sodium in absolute ethyl alcohol, gradually becomes brown, in consequence of an oxidation process (formation of aldehyde, **115**). On the other hand, the solution of sodium methylate in methyl alcohol remains unaltered, for which reason it is much more extensively used in syntheses than sodium ethylate.

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ALKYL HALIDES, ESTERS, AND ETHERS.

56. Many compounds containing a hydroxyl-group are known in inorganic chemistry; they are called bases, and resemble one another closely in their properties. This similarity may be attributed to their common possession of the group OH, which is present in their aqueous solution as an ion.

An aqueous solution of alcohol does not conduct an electric current, so that the alcohol is not ionized. This also follows from the fact that such a solution is not alkaline, and therefore contains no OH-ions. The question accordingly arises whether, notwithstanding this fact, the alcohols possess some of the properties of bases.

The answer to this is in so far affirmative that they are able to combine with acids, with elimination of water, in the same way as basic compounds:

$$\underset{\text{Alcohol}}{\mathrm{M}\cdot\boxed{\mathrm{OH}+\mathrm{H}}}\underset{\text{Acid}}{\cdot\mathrm{R}}=\underset{\text{Ester}}{\mathrm{M}\cdot\mathrm{R}}+\mathrm{HOH}.$$

These substances, which are comparable with the salts of inorganic chemistry, are called *compound ethers* or *esters*. The difference between the nature of bases and that of alcohols shows itself, however, in the way in which salts are formed, which is quite unlike that in which esters are produced. The formation of a salt from an acid and a base takes place instantaneously; it is a reaction of the ions, because the hydrogen ion of the acid unites with the hydroxyl-ion of the base ("Inorganic Chemistry," **66**):

$$\underset{\text{Base}}{[\dot{\mathrm{B}}+\mathrm{OH}']}+\underset{\text{Acid}}{[\dot{\mathrm{H}}+\mathrm{Z}']}=\underset{\text{Salt}}{[\dot{\mathrm{B}}+\mathrm{Z}']}+\mathrm{H_2O}.$$

The formation of esters, on the other hand, takes place very slowly, especially at ordinary temperatures. In this case the reaction is between the non-ionized alcohol and the acid:

$$\underset{\text{Alcohol}}{\mathrm{R}\cdot\mathrm{OH}}+\underset{\text{Acid}}{[\dot{\mathrm{H}}+\mathrm{Z}']}=\underset{\text{Ester}}{\mathrm{R}\cdot\mathrm{Z}}+\mathrm{H_2O}.$$

Generally, reactions between ions take place instantaneously, those between molecules slowly.

Many bases can lose water, with formation of anhydrides or oxides; so also can alcohols. By the splitting off of one molecule of water from two molecules of an alcohol, there are formed compounds with the general formula $C_nH_{2n+1}—O—C_nH_{2n+1}$, called *ethers;* when the elimination of water takes place between two different alcohols, the compounds produced have the general formula $C_nH_{2n+1}—O—C_mH_{2m+1}$, and are called *mixed ethers*.

Alkyl Halides.

57. The alkyl halides may be looked upon as being the haloid acid esters of the alcohols, as is shown by their formation from alcohol and a haloid acid:

$$C_nH_{2n+1}\boxed{OH + H}X = C_nH_{2n+1}X + H_2O.$$

In preparing alkyl halides by this method, the alcohol is saturated with the dry halogen acid, and then heated in a sealed tube or under a reflux-condenser. The reaction may also be carried out by heating the alcohol with sulphuric acid and sodium or potassium halide:

$$C_2H_5OH + H_2SO_4 + KBr = C_2H_5Br + KHSO_4 + H_2O.$$

Two other methods of formation for alkyl halides have already been alluded to (**30** and **43**); these are more fully treated below.

Action of Phosphorus Halides on Alcohols.—These sometimes react together very energetically. In preparing alkyl bromides and iodides, it is usual to employ phosphorus with bromine or iodine instead of the bromide or iodide of phosphorus itself. For example, in the preparation of ethyl bromide, amorphous phosphorus is added to strong alcohol, which does not dissolve it. Bromine is then added in drops, the temperature of the liquid being kept from rising by a cooling-agent. Each drop of bromine unites with phosphorus to form PBr_3, which reacts with the alcohol, producing ethyl bromide:

$$PBr_3 + 3C_2H_5OH = P(OH)_3 + 3C_2H_5Br.$$

The careful addition of bromine is continued until a quantity has been used corresponding to that required by the equation. The mixture is then allowed to stand for several hours, in order that the reaction may be as complete as possible, the final product consisting *chiefly* of phosphorous acid and ethyl bromide. Since the latter boils at 38·4°, and the acid is not volatile, it is possible to separate them by distillation. To effect this, the flask containing the mixture is immersed in a water-bath heated above the temperature mentioned.

It has just been mentioned that the reaction-mixture consists chiefly of phosphorous acid and ethyl bromide, whereas the above equation indicates that *only* these two substances are formed. Reactions in organic chemistry are seldom quantitative; in addition to the *main reaction* there are, in the great majority of cases, one or more secondary reactions. The explanation of this must be sought in the ease with which organic compounds undergo decomposition and react with one another. These secondary reactions frequently give rise to the formation of dark-coloured, amorphous substances called *resins*. It is seldom possible to obtain any individual compound out of them. Sometimes, however, the secondary products of a reaction can be isolated, as, for example, in the process described above, in which the ethyl ester of phosphorous acid is formed along with ethyl bromide:

$$PBr_3 + 3C_2H_5OH = P(OC_2H_5)_3 + 3HBr.$$

58. *Action of Halogens on Hydrocarbons.*—Only chlorides and bromides can be obtained in this way, because iodine does not react with hydrocarbons. The method is seldom used for the preparation of alkyl halides, since, for two reasons, mixtures of alkyl halides are obtained which are sometimes very difficult to separate; whereas, by employing the other methods, these compounds are produced without admixture of similar substances.

One of these causes is, that whenever one molecule of a hydrocarbon C_nH_{2n+2} is brought into contact with one molecule of chlorine or bromine, the reaction does not take place merely in accordance with the equation

$$C_nH_{2n+2} + Cl_2 = C_nH_{2n+1}Cl + HCl,$$

but that at the same time compounds $C_nH_{2n}Cl_2$, $C_nH_{2n-1}Cl_3$, etc., are formed, a portion of the hydrocarbon remaining unacted on.

It is possible to avoid the formation of these higher substitution-products by causing the halogens to react with the *vapour* of the boiling hydrocarbons.

The other cause is that the halogen replaces hydrogen in different positions in the molecule. Thus, chlorine reacts with normal pentane to form simultaneously primary and secondary alkyl chlorides,

$$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2Cl \quad \text{and} \quad CH_3 \cdot CH_2 \cdot CH_2 \cdot CHCl \cdot CH_3.$$

This can be proved by converting these chlorides into the corresponding alcohols and oxidizing the latter (**49**).

59. The following table gives some of the *physical properties of the alkyl halides.*

Formula of Alkyl.	Name.	Chloride.		Bromide.		Iodide.	
		Boiling-point.	Specific Gravity.	Boiling-point.	Specific Gravity.	Boiling-point.	Specific Gravity.
CH_3	Methyl	– 23·7°	0·952(0°)	4·5°	1·732(0°)	45°	2·293(18°)
C_2H_5	Ethyl	12·2°	0·918(8°)	38·4°	1·468(13°)	72·3°	1·944(14°)
C_3H_7	*n*–Propyl	46·5°	0·912(0°)	71°	1·383(0°)	102·5°	1·786(0°)
C_4H_9	*n*–Prim. butyl	78°	0·907(0°)	101°	1·305(0°)	130°	1·643(0°)
C_5H_{11}	*n*–Prim. amyl	107°	0·901(0°)	129°	1·246(0°)	156°	1·543(0°)

It will be noticed that only the lower chlorides and methyl bromide are gaseous at the ordinary temperature, most of the others being liquids, and the highest members solids. The specific gravities of the chlorides are in all cases less than 1, and diminish as the number of carbon atoms increases. The specific gravities of the bromides and iodides are considerably greater than 1 for the lowest members, although they also diminish with increase in the number of the carbon atoms, so that the highest terms of the homologous series are specifically lighter than water. They are all very slightly soluble in water, but dissolve readily in many organic solvents. The lowest members have a pleasant ethereal odour.

Chemical Properties.—In their action upon silver nitrate the alkyl halides are very different from the halides of the metals. In aqueous or alcoholic solution the latter at once yield a precipitate of silver halide, the reaction being quantitative. On the other hand, silver nitrate either does not precipitate silver halide from a solution of the alkyl halides, or the reaction only takes place slowly. The explanation is the same as that given in **56**, that in the first case the action is one between the ions, and in the second between the molecules. This proves that there are either no halogen ions present in an alkyl halide solution, or at least that their number is very small.

The halogen compounds can be converted into one another; for example, alkyl iodides can be obtained by heating the corresponding chlorides with KI or CaI_2. These reactions are often incomplete.

The alkyl iodides are chiefly used for introducing alkyl-groups into organic compounds.

Alkyl fluorides are also known, and are more volatile than the corresponding chlorine compounds. They are obtained by the action of silver fluoride on an alkyl iodide, and in other ways.

Esters of Other Mineral Acids.

60. Esters of a great number of mineral acids are known. The general methods for their preparation are as follows:

1. By the action of the acid on absolute alcohol:

$$\underset{\text{Alcohol}}{C_2H_5\cdot}\boxed{OH + H}\underset{\text{Nitric acid}}{ONO_2} = H_2O + \underset{\text{Ethyl nitrate}}{C_2H_5\cdot ONO_2}.$$

2. By the action of an alkyl halide on a silver salt:

$$SO_4\boxed{Ag_2 + 2I}C_2H_5 = \underset{\text{Ethyl sulphate}}{SO_4(C_2H_5)_2} + 2AgI.$$

3. By the action of mineral acid chlorides on alcohols or alcoholates:

$$\underset{\text{Phosphorus oxychloride}}{PO\boxed{Cl_3 + 3Na}}OC_2H_5 = \underset{\text{Neutral ethyl phosphate}}{PO(OC_2H_5)_3} + 3NaCl.$$

The acid esters of sulphuric acid, which are usually called *alkyl-sulphuric acids*, are of some importance. *Ethylsulphuric acid*, or *ethyl hydrogen sulphate*, $C_2H_5O\cdot SO_2\cdot OH$, is obtained by mixing alcohol with concentrated sulphuric acid. The formation of this compound is never quantitative, owing to the fact that an equilibrium is reached in the reaction (**99**). The ethylsulphuric acid is separated from the excess of sulphuric acid by means of the barium (or the strontium or calcium) salts of the alkyl-sulphuric acids, these compounds being easily soluble in water, while the sulphates are insoluble, or nearly so. It is only necessary to neutralize the mixture of sulphuric acid and alkyl-sulphuric acid with barium carbonate, the product being a solution of barium ethyl sulphate, $\genfrac{}{}{0pt}{}{ba}{C_2H_5}\!>SO_4$. The free ethylsulphuric acid is then obtained by the addition of the calculated quantity of sulphuric acid to this solution. At ordinary temperatures it is an odourless, oily, strongly acid liquid, miscible with water in all proportions; the aqueous solution decomposes into sulphuric acid and alcohol, slowly at the ordinary temperature, but quickly when heated to the boiling-point.

The barium salts of the amylsulphuric acids, obtained from the amyl alcohols and sulphuric acid, have different solubilities in water, and can be partially separated by fractional crystallization. By this means PASTEUR was able to separate the optically active amyl alcohol from isobutylcarbinol, $\begin{matrix} CH_3 \\ CH_3 \end{matrix} > CH \cdot CH_2 \cdot CH_2 \cdot OH$, both of which are present in the mixture of amyl alcohols boiling at 131°–132° obtained by the fractional distillation of fusel oil. Isobutylcarbinol is the chief constituent of the mixture of amyl alcohols boiling at this temperature.

Ethylsulphuric acid forms well crystallized salts; its potassium salt is used in the preparation of ethyl compounds. For example, ethyl bromide is readily prepared by the dry distillation of a mixture of potassium bromide and potassium ethyl sulphate:

$$\underset{\text{Potassium ethyl sulphate}}{KO \cdot SO_2 \cdot O\boxed{C_2H_5 + Br}}K = \underset{\text{Potassium sulphate}}{KO \cdot SO_2 \cdot OK} + \underset{\text{Ethyl bromide}}{C_2H_5Br.}$$

When free ethylsulphuric acid is heated, the neutral ethyl ester of sulphuric acid and free sulphuric acid are formed:

$$SO_2 < \begin{matrix} OC_2H_5 \\ OH \end{matrix} + SO_2 < \begin{matrix} OH \\ OC_2H_5 \end{matrix} = SO_2 < \begin{matrix} OH \\ OH \end{matrix} + SO_2 < \begin{matrix} OC_2H_5 \\ OC_2H_5 \end{matrix}.$$

Esters of the following mineral acids are also known: hypochlorous acid, perchloric acid, sulphurous acid, sulphuric acid, hyponitrous acid, nitrous acid, nitric acid, phosphorous acid, hypophosphoric acid, phosphoric acid, arsenious acid, arsenic acid, boric acid, and silicic acid.

Saponification.

61. When esters are boiled with dilute acids or alkalis, or when heated to a high temperature with water, they decompose into alcohol and acid, taking up one molecule of water. This process is called "saponification," because it resembles the preparation of soap from alkali and fat (**91**). The formation of an ester from an alcohol and an acid is called *esterification*.

Ethers.

62. The constitution of these compounds, which are isomeric with the alcohols, is proved by WILLIAMSON's synthesis, the action of an alcoholate on an alkyl halide:

$$C_nH_{2n+1} \cdot O\boxed{Na + I} \cdot C_mH_{2m+1} = C_nH_{2n+1} \cdot O \cdot C_mH_{2m+1} + NaI.$$

This synthesis affords confirmation of the constitution of the alcoholates indicated in **43**, that the metal occupies the place of the hydroxyl-hydrogen. For, supposing this were not the case, and that the metal had replaced a hydrogen atom directly linked to carbon, then sodium methylate, for example, would have the formula $Na\cdot CH_2\cdot OH$; this would yield propyl alcohol when treated with ethyl iodide:

$$C_2H_5\boxed{I + Na}\cdot CH_2OH = C_2H_5\cdot CH_2OH + NaI.$$

This reaction does not take place. There is produced instead methylethyl ether, which has the empirical formula of an alcohol, but none of its properties.

WILLIAMSON'S synthesis is also possible when the alcoholate is dissolved in dilute alcohol (50%). Though so much water is present, the reaction is almost a quantitative one, from which it follows that the greater part of the sodium alcoholate must be present as such, and therefore is not decomposed by the water into alcohol and sodium hydrate (**55**), because in that case the formation of the ether would necessarily be prevented.

63. The best known compound of the homologous series of ethers is the diethyl ether, $C_2H_5\cdot O\cdot C_2H_5$, which is usually called *ether*. This compound is manufactured, and also prepared in the laboratory, from sulphuric acid and ethyl alcohol. For this purpose a mixture of five parts of alcohol (90%) * is heated with nine parts of concentrated sulphuric acid at 130°–140°. Ether and water distil over, and as soon as distillation has commenced, alcohol is allowed to flow into the distilling-flask at such a rate as to keep the volume of liquid in it constant. Ether passes continually over, but after about six times as much alcohol has been added as was in the first instance mixed with the sulphuric acid, the distillate becomes richer and richer in alcohol, until finally the formation of ether stops altogether.

The explanation of this process is as follows. The alcohol and sulphuric acid in the first instance form ethylsulphuric acid (**60**).

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* Methylated spirit may be substituted for pure spirit, the product being called "methylated ether."—TRANSLATOR.

When ethylsulphuric acid is heated with water, it is saponified, with regeneration of the acid and alcohol:

$$C_2H_5 \cdot \boxed{OSO_3H + H}OH = C_2H_5 \cdot OH + H_2SO_4.$$

When, however, instead of water, ethyl alcohol reacts on ethylsulphuric acid, ether and sulphuric acid are formed in an exactly analogous manner:

$$C_2H_5\boxed{O \cdot SO_3H + H}O \cdot C_2H_5 = C_2H_5 \cdot O \cdot C_2H_5 + H_2SO_4.$$

The production of ether depends upon the formation of ethylsulphuric acid, and subsequent decomposition of this compound into ethyl ether and sulphuric acid by the addition of more alcohol. Since the sulphuric acid is again formed (regenerated) in this reaction, it yields a fresh quantity of ethylsulphuric acid, so that the process is a continuous one. This would lead to the expectation that a small quantity of sulphuric acid would be able to convert an unlimited amount of alcohol into ether, but this is not borne out by experience. The explanation is that in the formation of ethylsulphuric acid from alcohol and sulphuric acid, water is formed as a by-product:

$$C_2H_5\boxed{OH + H}SO_4H = C_2H_5 \cdot SO_4H + H_2O.$$

This water partly distils over along with the ether, but partly remains behind in the flask, decomposing the ethylsulphuric acid, as soon as it is formed, into alcohol and sulphuric acid. When the amount of water in the reaction-mixture exceeds a certain limit, it prevents the formation of ethylsulphuric acid altogether, and in this way puts an end to the production of ether.

When another alcohol is allowed to flow into the original mixture instead of ethyl alcohol, shortly before the distillation begins, a mixed ether is obtained:

$$C_2H_5 \cdot \boxed{SO_4H + H}O \cdot C_5H_{11} = C_2H_5 \cdot O \cdot C_5H_{11} + H_2SO_4.$$

This is a proof that the formation of ether really takes place in the two stages mentioned above.

The crude ether obtained in this manner contains water, alcohol, and small quantities of sulphur dioxide. It is left in contact with quicklime for several days, the water, sulphur dioxide, and part of the alcohol being thus removed; it is then distilled from a water-bath heated to about 55°. To remove the small quantity of alcohol remaining, it is shaken up several times with small volumes of water, and the water run off. The ether is separated from dissolved water by distillation, first over calcium chloride and finally over sodium.

Diethyl ether is a colourless, very mobile liquid, boiling at 35·4°, and solidifying at −113·1°. It has an agreeable odour; prolonged breathing of it produces unconsciousness, followed by but slightly disagreeable consequences on awakening. Ether is therefore used in surgery as an anæsthetic. It is slightly soluble in water, one volume dissolving in 11·1 volumes of water at 25°; on the other hand, water dissolves slightly in ether (2% by volume at 12°). On account of its low boiling-point, ether is very volatile, and as its vapour is highly combustible, burning with a luminous flame, and producing an explosive mixture with air, it is a substance which must be very carefully handled. Intense cold is produced by its evaporation, the outside of a flask containing it becoming coated with ice when the evaporation of the ether is promoted by the introduction of a rapid stream of air.

In the laboratory, ether is an invaluable solvent and crystallizing-medium for many compounds, in addition to its use for extracting aqueous solutions (**24**). It is also of great utility in many manufacturing-processes.

Homologues.

64. *Dimethyl ether*, $CH_3\cdot O\cdot CH_3$, is obtained in the same way as ordinary ether, and is a gas liquefying at − 20°. The higher homologues are liquids, the highest being solid crystalline substances; all have a specific gravity considerably less than 1, the majority between 0·7 and 0·8.

The ethers are comparatively stable towards chemical reagents. Dilute acids, alkalis, and phosphorus pentachloride have no action on them at ordinary temperatures; sodium is unable to displace any of their hydrogen. When, however, they are heated with haloid acids, halogen compounds are formed. In this way gaseous hydriodic acid, when passed into an ether at the ordinary temperature, produces alcohol and alkyl iodide:

$$C_nN_{2n+1}\cdot\boxed{O\cdot C_mH_{2m+1}+H}I = C_nH_{2n+1}I + C_mH_{2m+1}OH;$$

at higher temperatures water and alkyl iodide are formed:

$$C_nH_{2n+1}\underbrace{\boxed{O}\cdot C_mH_{2m+1} + \boxed{2H}}I = C_nH_{2n+1}I + C_mH_{2m+1}I + H_2O.$$

Isomerism.—This may be caused, as in the case of the alcohols, by branching of the carbon chains, by the alteration of the position of the oxygen atom in the molecule, or by both causes simultaneously.

ALKYL-RADICLES LINKED TO SULPHUR.

65. Those elements which are grouped in the same column of the periodic system ("Inorganic Chemistry," **211–221**) yield similar compounds, a fact traceable to their having equal valencies; they further resemble one another in their chemical properties. Experience has shown that organic compounds containing elements of such a group display the properties of their inorganic analogues in every variety of similarity and dissimilarity, their points of resemblance and of difference being sometimes even more marked than those of the inorganic compounds. A comparison of the oxygen compounds, which have been dealt with up to this point, with the sulphur compounds of similar structure, will serve as an example of this.

The alcohols and ethers may be regarded as being derived from water by the replacement of one or both of its hydrogen atoms by alkyl. The corresponding sulphur compounds are derived in the same way from sulphuretted hydrogen; they are represented thus:

$$C_nH_{2n+1}\cdot SH \quad \text{and} \quad C_nH_{2n+1}\cdot S\cdot C_mH_{2m+1}.$$

The first are called *mercaptans*, and the second *thioethers*.

The resemblance of these compounds to the alcohols and ethers is chiefly noticeable in their methods of formation, for if KSH instead of KOH reacts with an alkyl halide, a mercaptan is formed:

$$C_nH_{2n+1}\cdot \boxed{X + K}\cdot SH = C_nH_{2n+1}\cdot SH + KX.$$

The property possessed by alcohols, of having one hydrogen atom in the molecule distinguished from all the others in being replaceable by metals, is also found in mercaptans. It is therefore reasonable to suppose that the hydrogen atom, thus distinguished from all the others, is linked to sulphur, the rest of the hydrogen atoms being linked to carbon.

Just as the ethers are formed by the action of alkyl halides on alcoholates, so the thioethers are obtained by treating the metallic compounds of the mercaptans, the *mercaptides*, with alkyl halides:

$$C_nH_{2n+1}\cdot S\boxed{Na + I}C_mH_{2m+1} = C_nH_{2n+1}\cdot S\cdot C_mH_{2m+1} + NaI.$$

Water is a neutral compound, and sulphuretted hydrogen is a weak acid; corresponding to this, alcohol does not form alcoholates with the bases of the heavy metals, while mercaptans yield mercaptides with them. An alcohol such as amyl alcohol, which is soluble with difficulty in water, does not dissolve in alkalis; but the mercaptans, which are all insoluble in water, are on the other hand easily soluble in alkalis, with formation of mercaptides. They therefore possess an acid character.

Mercaptans.

66. In addition to the methods of formation already mentioned, mercaptans can be obtained by the action of phosphorus pentasulphide upon alcohols:

$$5C_nH_{2n+1}\cdot OH + P_2S_5 \rightarrow 5C_nH_{2n+1}\cdot SH;$$

or by distilling a solution of potassium alkyl sulphate with potassium hydrogen sulphide:

$$C_2H_5\boxed{O\cdot SO_3K + K\cdot}SH = C_2H_5\cdot SH + K_2SO_4.$$

They are liquids almost insoluble in water, with boiling-points markedly lower than those of the corresponding alcohols. Thus, *methyl mercaptan* boils at 6°, methyl alcohol at 66°. They are characterized by the possession of an *exceedingly disagreeable smell*, which they have in common with almost all volatile sulphur compounds. Our organs of smell are very sensitive to mercaptans, and can detect the merest traces of them, even when they are so slight as to be quite unrecognizable by chemical means.

Many metallic compounds of the mercaptans are known, some of them in a well crystallized form. The mercury mercaptides furnish an example of these bodies, and are produced by the action of mercaptans on mercuric oxide, whence the name of these compounds is derived (by shortening *corpus mercurio aptum* to *mercaptan*). Many of the other heavy metals, such as lead, copper, and bismuth, yield mercaptides; the lead compounds have a yellow colour. The mercaptan is set free from all mercaptides by the addition of mineral acids.

Thioethers.

67. In addition to the methods given in **65** for the preparation of these compounds, the action of potassium sulphide, K_2S, upon the salts of alkyl-sulphuric acids may be employed :

$$\underset{\text{Potassium ethyl sulphate}}{2C_2H_5\boxed{O\cdot SO_3K + K_2}}S = (C_2H_5)_2S + 2K_2SO_4.$$

The thioethers are neutral compounds with an exceedingly offensive smell. They are liquids insoluble in water, and yield double compounds with metallic salts, e.g. $(C_2H_5)_2S\cdot HgCl_2$.

The mercaptans resemble sulphuretted hydrogen in being slowly oxidized by contact with air, whereby they are converted into disulphides; for example, diethyl disulphide,

$$C_2H_5\cdot S\cdot S\cdot C_2H_5.$$

Here the hydrogen which is linked to sulphur is removed by oxidation, so that the disulphides have the constitution given above, the proof of this being that they are also obtained by heating potassium ethyl sulphate with K_2S_2.

Numerous compounds containing oxygen and sulphur occur among inorganic bodies : substances of this kind are also known in organic chemistry.

The *sulphoxides*, $\begin{matrix}C_nH_{2n+1}\\C_nH_{2n+1}\end{matrix}\!>SO$, are formed by the oxidation of thioethers with nitric acid. Their constitution is indicated by the fact that they are very easily reduced to thioethers. If the oxygen were linked to carbon, they would not behave in this manner, because neither alcohols nor ethers lose their oxygen by gentle reduction.

The *sulphones* are compounds with the constitution $\begin{matrix}C_nH_{2n+1}\\C_nH_{2n+1}\end{matrix}\!>SO_2$, as shown in **68**. They are formed by strongly oxidizing the thioethers, and also by the oxidation of sulphoxides. Nascent hydrogen is unable to effect their reduction.

Sulphonic Acids.

68. The *sulphonic acids* result when mercaptans undergo vigorous oxidation (with nitric acid). They have the formula $C_nH_{2n+1}\cdot SO_3H$. The alkyl-group remains intact during this oxidation, for the salts of these sulphonic acids are also formed when an alkyl iodide reacts with a sulphite :

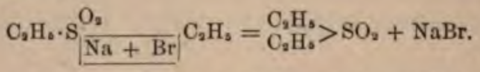
$$C_2H_5\boxed{I + K}SO_3K = KI + C_2H_5SO_3K.$$

Since the sulphur in mercaptans is directly linked to carbon, the same holds good for the sulphonic acids. This is further proved by the fact that the latter yield mercaptans on reduction. The structure of ethylsulphonic acid is therefore

$$CH_3\cdot CH_2\cdot SO_3H.$$

The group SO_3H must contain a hydroxyl-group, because PCl_5 yields with a sulphonic acid a compound $C_nH_{2n+1}\cdot SO_2Cl$, from which the sulphonic acid may be regenerated by the action of water. The structure of the compound is therefore $CH_3\cdot CH_2\cdot SO_2\cdot OH$, which leaves it still doubtful whether the group SO_2 contained in it has the structure $S<\begin{matrix}O\\|\\O\end{matrix}$ or $S\leqslant\begin{matrix}O\\O\end{matrix}$; that is, whether the sulphur in sulphonic acids is tetravalent or hexavalent. The alkyl-sulphonic acids are strongly acid, very hygroscopic, crystalline substances, and very soluble in water.

In the above-mentioned compounds $C_nH_{2n+1}\cdot SO_2Cl$, called *sulphonic chlorides*, chlorine can be replaced by hydrogen when it acts on them in the nascent state; the bodies thus obtained have the formula $C_nH_{2n+1}\cdot S\begin{matrix}O_2\\H\end{matrix}$, and are called *sulphinic acids*. When an alkyl halide reacts with the sodium salt of a sulphinic acid, a sulphone is formed (67):



$$C_2H_5\cdot S\begin{matrix}O_2\\\boxed{Na + Br}\end{matrix}C_2H_5 = \begin{matrix}C_2H_5\\C_2H_5\end{matrix}>SO_2 + NaBr.$$

This mode of preparation is a proof of the constitution of the sulphones.

Analogous *selenium* and *tellurium* compounds are known, corresponding to the majority of the sulphur compounds just described. These also have a most offensive smell.

ALKYL-RADICLES LINKED TO NITROGEN.

I. AMINES.

69. At the beginning of the previous section (**65**) it is stated that the properties possessed by inorganic compounds are even more marked in their organic derivatives. The compounds to be described in this section afford another striking example of this phenomenon.

The term *amines* is applied generally to substances which may be regarded as derived from ammonia by exchange of hydrogen for alkyl-radicles. The most characteristic property of ammonia is its power of combining with acids to form salts by direct addition:

$$NH_3 + H \cdot X = NH_4 \cdot X.$$

Trivalent nitrogen is thereby made pentavalent, a change apparently intimately connected with its basic character. This property is also found among the alkylamines. They are, at least those low in the series, better conductors of electricity, for the same molecular concentration of their aqueous solutions, and are therefore more strongly basic than ammonia ("Inorganic Chemistry," **66** and **238**). This applies also to the organic compounds corresponding to NH_4OH, ammonium hydroxide. The last-named substance is not known in the free state, but it exists in the aqueous solution of ammonia. It is very unstable, being completely decomposed into water and ammonia when its solution is boiled. It has only weakly basic properties, because there are but few NH_4-ions and OH-ions in its aqueous solution, apparently because the compound NH_4OH has a very strong tendency to break up into NH_3 and H_2O. Such a decomposition is, however, no longer possible for compounds containing four alkyl-groups in the place of the four hydrogen atoms of the NH_4-group; experience has shown that these compounds possess great stability. Since the nitrogen cannot revert to the trivalent condition, their basic character, in comparison with that of NH_4OH, is so strengthened that they are ionized to the same degree as the alkalis; they are almost completely split up in solutions whose dilution is $\frac{1}{100}$ of the normal.

The amines yield complex salts fully analogous to the platinum salt, $(NH_4)_2PtCl_6$, and the gold salt, NH_4AuCl_4, of ammonia.

unites with the alkyl halide, yielding the halogen salt of a quaternary ammonium base:

$$\text{IV.}\quad (C_nH_{2n+1})_3N + C_nH_{2n+1}\cdot Cl = (C_nH_{2n+1})_4N\cdot Cl.$$

It is assumed in the foregoing that excess of ammonia is employed; but even when this is not the case, and in general for every proportion of alkyl halide and ammonia, the reaction takes place in these four phases. The final result is, therefore, that the primary, secondary, and tertiary amines, and the ammonium base, are formed together. It is often possible, however, so to adjust the proportion of ammonia and alkyl halide, together with the duration of the reaction, etc., that a given amine is the main product, and the quantities of the other amines are small. The nature of the alkyl-group also exercises a great influence upon the character of the reaction-product.

The *separation of the mixture of amines* so obtained is often difficult, there being no method generally applicable. The separation of the ammonium bases from the ammonia and amines is simple, because while the amines are liquids volatilizing without decomposition, the lower members being even gases, the ammonium bases are not volatile. When, therefore, the mixture of the amine hydrohalides and the ammonium bases is distilled after addition of caustic potash, the free amines only pass over.

In order to separate the primary from the mixture of the hydrohalides of the three amines, fractional crystallization is largely made use of in their preparation, at least in the case of the lowest members, methylamine, dimethylamine, etc. The higher members. terms, beginning with the propylamines, can be separated by fractional distillation.

Various methods of preparing primary amines unmixed with secondary or tertiary are known (**85**, **104**, **244**, **254**, and **328**).

The *velocity of the formation of tetraalkylammonium iodides* from triethylamine and an alkyl iodide or bromide has been investigated by MENSCHUTKIN. It is apparently a bimolecular reaction ("Inorganic Chemistry," **50**), and therefore takes place according to the equation

$$s = \frac{dx}{dt} = k(a - x)(b - x),$$

where s is the velocity, k the constant of the reaction, a and b the quantities of amine and iodide by unit volume expressed in moleteristic odour, and are slightly soluble in water. They are easily reconverted into secondary amines by the action of concentrated hydrochloric acid (**285**); this is a proof of the structure given above, because if the nitroso-group were directly linked to a carbon atom either by its oxygen or by its nitrogen, it would not be possible thus to reconvert it into a secondary amine.

Tertiary amines are unacted upon by nitrous acid.

Their behaviour with nitrous acid is therefore a means of distinguishing the three classes of amines from one another. It also serves as a basis for the separation of the secondary and tertiary amines in the pure state from a mixture of the two. When a concentrated solution of sodium nitrite is added to a hydrochloric acid solution of a mixture of the two amines, the secondary amine is converted into a nitrosamine, which collects as an oily layer on the surface of the aqueous solution, and can be removed by means of a separating-funnel. The tertiary amine is not attacked, but remains in the aqueous solution in the form of a salt; it can be obtained by distilling with caustic potash. It should be mentioned that any primary amine which may be present is decomposed during the process.

Another method of distinguishing between primary, secondary, and tertiary amines consists in the determination of the number of alkyl-groups with which the amine can combine. For example, if a compound C_3H_9N is propylamine, $C_3H_7NH_2$, it should yield, when heated with excess of methyl iodide, a compound

$$\begin{matrix} C_3H_7 \\ (CH_3)_3 \end{matrix} NI = C_6H_{16}NI;$$

if $C_3H_9N = \begin{matrix} C_2H_5 \\ CH_3 \end{matrix} > NH$, the same treatment should yield $\begin{matrix} C_2H_5 \\ (CH_3)_3 \end{matrix} NI = C_5H_{14}NI$; lastly, if $C_3H_9N = (CH_3)_3N$, there would be obtained $(CH_3)_4NI = C_4H_{12}NI$. A titration of the iodine ion of the quaternary ammonium iodide formed is sufficient to determine whether C_3H_9N is primary, secondary, or tertiary.

Individual Members.

73. The lower members are inflammable gases which are very soluble in water; thus, 1150 volumes of methylamine dissolve in one volume of water at 12·5°. The succeeding members have low boiling-points, and are miscible with water in all proportions. Both they and the lowest members have a characteristic ammoniacal smell, like boiled lobsters. The highest members are odourless and insoluble in water. The specific gravities of the amines are appreciably less than 1, that of methylamine being only 0·699 at − 11°. The following table indicates the variations of their boiling-points:

Alkyl-Radicle.	Primary.	Secondary.	Tertiary.
Methyl	− 6°	7°	3·5°
Ethyl	19°	56°	90°
n-Propyl	49°	98°	156°
n-Butyl	76°	160°	215°
n-Octyl	180°	297°	366°

Methylamine occurs in *Mercurialis perennis, dimethylamine* and *trimethylamine* in herring-brine.

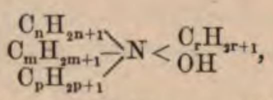
Tetramethylammonium hydroxide is obtained, like all its homologues, by treatment of its haloid acid salt with moist silver oxide, Ag·OH; it is a white, crystalline mass, and is very hygroscopic. It is decomposed by heat into trimethylamine and methyl alcohol:

$$(CH_3)_4N \cdot OH = (CH_3)_3N + CH_3OH.$$

The higher ammonium bases are converted by heat into a trialkylamine, water, and a hydrocarbon C_nH_{2n}:

$$(C_2H_5)_4N \cdot OH = \underset{\text{Triethylamine}}{(C_2H_5)_3N} + \underset{\text{Ethylene}}{C_2H_4} + H_2O.$$

The structure of the ammonium bases is thus explained. The nitrogen atom is the only one in the molecule which is able to link itself to the four monovalent alkyl-groups, and to the monovalent hydroxyl-group. It must be assumed to be pentavalent in these compounds, and the constitution of the ammonium bases is therefore



$$\left.\begin{array}{l}C_nH_{2n+1}\\C_mH_{2m+1}\\C_pH_{2p+1}\end{array}\right\rangle N < \begin{array}{l}C_rH_{2r+1}\\OH\end{array},$$

in which n, m, p, and r may be like or unlike.

Alkyl-derivatives of *hydrazine* or *diamide*, $H_2N \cdot NH_2$, are also known. Among the methods for their preparation may be mentioned the direct introduction of an alkyl-group into hydrazine, and the careful reduction of nitrosamines (**72**). They have little power of resistance towards oxidizing-agents, an alkaline copper solution, for example, being reduced by them at the ordinary temperature.

74. *Triethylamine* is soluble in water, although at about 20° this solution separates into two layers. The upper of these consists of a solution of water in the amine, and the lower of a solution of the amine in water. In the neighbourhood of 20° a slight rise in temperature is able to effect this separation into two layers, merely holding the tube for a moment in the warm hand being sufficient.

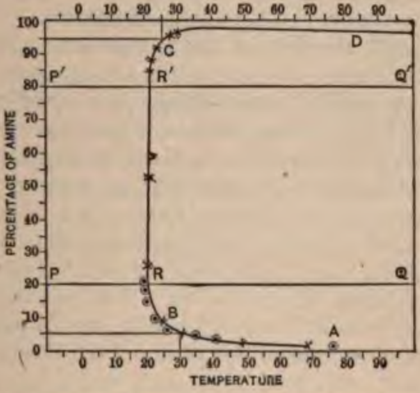


FIG. 27.—SOLUBILITY CURVE FOR TRIMETHYLAMINE AND WATER.

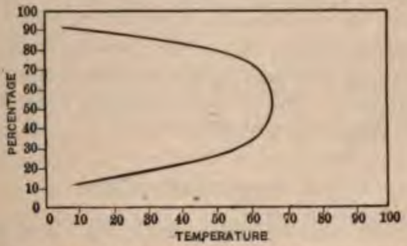


FIG. 28.—USUAL FORM OF SOLUBILITY CURVE FOR TWO LIQUIDS.

Why this separation takes place, and at what temperature, is most easily understood by a consideration of the curve of solubility of the system amine + water. This amine (Fig. 27) is less soluble in warm water than in cold, and below 20° is miscible with water in all proportions. If, for example, increasing quantities of the amine be added to water at 30°, it dissolves until the amount of amine reaches about 5% (*cf.* Fig. 27). The solution is then saturated, and addition of more of the amine produces a second layer of liquid. On the other hand, when water is added to trimethylamine at 25°, it dissolves until the amount of water reaches about 5% (*cf.* Fig. 27); beyond this point two layers are formed. The line *DC* is the solubility curve for water dissolved in trimethylamine, and the line *AB* that for trimethylamine in water. When the temperature falls, the solubility of the water in the amine increases on the one hand, and on the other, that of the amine in the water, so that the solubility lines meet one another between *B* and *C*. The whole area is then divided into two parts by the solubility curves. All the points within *ABCD* correspond to two layers of liquid, and all the points outside it to a homogeneous mixture.

If, for example, the abscissa *PQ* is drawn for a mixture of 20% of amine and 80% of water, the mixture is homogeneous for all temperatures up to the point *R*, and heterogeneous above that temperature. Along the very steep portion of the curve, represented in this special case by the part *BC*, a slight rise in temperature must evidently result in separation of the liquid; because although at about 20° (the point *R*) two liquid layers are just about to form, of which the aqueous layer would contain 20% of amine, at *R'*, corresponding to an increase of temperature of less than 1°, the latter contains 80% of amine, when the liquids must separate into two layers. It follows that in this part of the curve a small rise of temperature must cause a separation of water sufficient to alter the composition of one of the layers from 20% to 80% of amine.

It has been already mentioned that the relative solubility curve for the system water + triethylamine has a special path in the portion *BC*. The whole curve differs, however, from those obtained in ordinary cases. The solubility of liquids which are partially miscible with one another usually increases with the temperature, just as in the case of solids and liquids. The curve is therefore exactly reversed, so that it is usually as represented in Fig. 28.

II. NITRO-COMPOUNDS.

75. When silver nitrite reacts with an alkyl iodide, two compounds are formed, both of which have the empirical formula $C_nH_{2n+1}NO_2$. They have different boiling-points, there being obtained from ethyl iodide, for example, a substance $C_2H_5NO_2$, boiling at 17°, and another boiling at 113°–114°. The two isomers are therefore easily separated by fractionation.

The compound of lower boiling-point is decomposed into alcohol and nitrous acid by the action of caustic potash; it must therefore be looked upon as an ester of nitrous acid, being formed in accordance with the following equation:

$$C_nH_{2n+1}\boxed{I + Ag}\cdot ONO = C_nH_{2n+1}\cdot ONO + AgI.$$

When these esters, or *alkyl nitrites*, are reduced, they are converted into an alcohol and ammonia.

The compound boiling at the higher temperature behaves quite differently. It is not converted into a nitrite and alcohol by the action of alkalis, and on reduction its two oxygen atoms are replaced by two hydrogen atoms, with the formation of a primary amine:

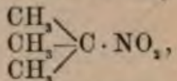
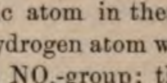
$$C_nH_{2n+1}NO_2 \rightarrow C_nH_{2n+1}NH_2.$$

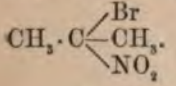
The last reaction shows that the nitrogen in this class of compounds is directly linked to carbon, because this is the case with the amines. The oxygen atoms cannot be linked otherwise than to the nitrogen, because the reduction to amine takes place at the ordinary temperature; it is not possible under these conditions to replace oxygen which is linked directly to carbon, for neither from alcohols nor from ethers is it possible to obtain, by reduction at low temperatures, substances which do not contain oxygen. This leads to the conclusion that these substances, which are called *nitro-compounds*, must have the constitution $C_nH_{2n+1}—NO_2$.

Nitro-compounds therefore contain a group NO_2, the nitrogen atom of which is directly linked to carbon; the group $—NO_2$ is called the nitro-group.

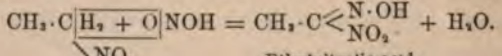
The names of these compounds are formed from those of the saturated hydrocarbons by the addition of the prefix *nitro*. The compound CH_3NO_2 is thus *nitromethane;* $C_2H_5NO_2$ is *nitroethane;* etc. *Nitroparaffins* is the general name of the members of this homologous series. They are colourless liquids of ethereal odour, the lower terms being slightly soluble in water; they distil without decomposition.

76. The nitro-derivatives have a number of characteristic properties. One of these is their possessing one hydrogen atom replaceable by alkali-metals, especially sodium. This sodium compound is most easily obtained by the action of sodium ethylate or methylate upon the nitro-compound in alcoholic solution. A fine, white, crystalline precipitate is thus formed, which in the case of nitroethane, for example, has the composition $C_2H_4NaNO_2$. The insolubility of these sodium compounds in absolute alcohol can sometimes be made use of to separate the nitro-paraffins from other substances.

This power of exchanging hydrogen for sodium only exists when there is at least one hydrogen atom linked to the carbon atom to which the nitro-group is attached. In the same way as from nitroethane, a metallic compound is also obtained from secondary nitropropane, $CH_3 \cdot CH < {CH_3 \atop NO_2}$; but nitrobutane,  $(CH_3)_3C \cdot NO_2$, does *not* yield any corresponding metallic derivative. It was formerly supposed that the metallic atom in these sodium compounds occupied the position of a hydrogen atom which was linked to the carbon atom attached to the NO$_2$-group; thus $C_2H_4NaNO_2$ was supposed to have the structure  $CH_3 \cdot C(NO_2)(H)(Na)$. It has been shown that this is not the case, as will be indicated in the section dealing with the *pseudo-acids* (**281**).

When an alkaline solution of a nitro-compound is brought into contact with bromine, one or more of its hydrogen atoms, when linked to the same carbon atom as the nitro-group, is replaced by bromine. This reaction is analogous to the above-mentioned substitution by metals, it being still possible, for example, to introduce one bromine atom into $CH_3 \cdot CHBrNO_2$, but not into  $CH_3 \cdot C(Br)(CH_3)(NO_2)$.

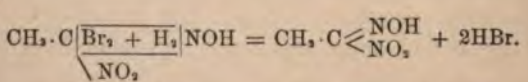
77. The behaviour of nitro-compounds with nitrous acid is very characteristic, and affords a method of distinguishing primary, secondary, and tertiary nitro-derivatives from one another. The reaction is carried out by adding sodium nitrite to an alkaline solution of the nitro-compound, and acidifying with dilute sulphuric acid. In the case of a primary nitro-compound, an *alkyl-nitrolic acid* is formed:



$$CH_3 \cdot C\boxed{H_2 + O}NOH \,(\searrow NO_2) = CH_3 \cdot C \lessgtr {N \cdot OH \atop NO_2} + H_2O.$$

Ethylnitrolic acid

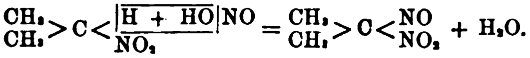
The constitution of these compounds is indicated by their production from a dibromonitro-compound by the action of hydroxylamine, H_2NOH:



$$CH_3 \cdot C\boxed{Br_2 + H_2}NOH \,(\searrow NO_2) = CH_3 \cdot C \lessgtr {NOH \atop NO_2} + 2HBr.$$

The alkyl-nitrolic acids dissolve in alkalis, yielding metallic compounds with a blood-red colour, this reaction affording a characteristic test for them. They crystallize well, but are by no means stable.

The secondary nitro-compounds yield *pseudonitrols* when similarly treated. They contain the group $= C<\begin{matrix}NO\\NO_2\end{matrix}$:



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>C<\begin{matrix}\overline{|H + HO|}NO\\NO_2\end{matrix} = \begin{matrix}CH_3\\CH_3\end{matrix}\!>C<\begin{matrix}NO\\NO_2\end{matrix} + H_2O.$$

Propyl pseudonitrol

The pseudonitrols are colourless, crystalline substances, which have an intense blue colour in the fused state or in solution; this characteristic serves as a test for them.

Lastly, the tertiary nitro-compounds are not acted upon by nitrous acid.

Among the other properties of nitro-compounds may be mentioned their decomposition into the acid containing the same number of carbon atoms, and hydroxylamine, when heated with hydrochloric acid:

$$\underset{\text{Nitroethane}}{CH_3\cdot CH_2\cdot NO_2} + H_2O = \underset{\text{Acetic acid}}{CH_3\cdot COOH} + \underset{\text{Hydroxylamine}}{H_2NOH}.$$

ALKYL-RADICLES LINKED TO OTHER ELEMENTS.

I. ALKYL-RADICLES LINKED TO ELEMENTS OF THE NITROGEN GROUP.

78. Ammonia unites readily with acids, with formation of salts. Phosphoretted hydrogen also possesses this property, although the phosphonium salts, PH_4X, are decomposed even by water into an acid and phosphoretted hydrogen.

The basic character has wholly disappeared in the case of arseniuretted hydrogen and antimoniuretted hydrogen; bismuth does not yield a hydride, and possesses, in fact, only very slight traces of the characteristics of metalloids.

Ammonia cannot be easily oxidized, and is unacted upon by the oxygen of the atmosphere at ordinary temperatures. On the other hand, the hydrides of phosphorus, arsenic, and antimony are easily oxidized.

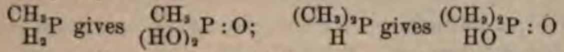
All the above-mentioned properties are displayed by the compounds which these elements form with alkyl-radicles.

Phosphines.

79. The amines yield stronger bases than ammonia; in the same way the *phosphines* yield stronger bases than PH_3, this becoming more marked with increase in the number of alkyl-groups which have replaced hydrogen atoms. The salts of the monoalkyl-phosphines, for example, are decomposed by water, whereas those of the dialkyl-phosphines and trialkyl-phosphines are not. The *quaternary phosphonium bases*, PR_4OH, are as strongly basic as the ammonium bases. When a phosphonium base is heated, it does not, like an ammonium base, split up into an alcohol (or $C_nH_{2n} + H_2O$) and a trialkyl base, but into a hydrocarbon C_nH_{2n+2} and an oxygen compound:

$$(C_2H_5)_4P \cdot OH = C_2H_6 + (C_2H_5)_3 \cdot PO.$$

This substance is called *triethylphosphine oxide*. In this reaction, the great affinity between phosphorus and oxygen plays an important part, this affinity being also indicated by the ease with which the phosphines undergo oxidation, a change effected even by the action of the air. Nitric acid oxidizes PH_3 to phosphoric acid, $OP(OH)_3$; in an analogous manner the phosphines take up one oxygen atom, and in addition as many oxygen atoms as there are hydrogen atoms directly linked to phosphorus:



$$\begin{matrix}CH_3\\H_2\end{matrix}P \text{ gives } \begin{matrix}CH_3\\(HO)_2\end{matrix}P:O; \qquad \begin{matrix}(CH_3)_2\\H\end{matrix}P \text{ gives } \begin{matrix}(CH_3)_2\\HO\end{matrix}P:O$$

Monomethylphosphinic acid — Dimethylphosphinic acid

$$\text{and } (CH_3)_3 \equiv P \text{ gives } (CH_3)_3 \equiv P:O.$$

Trimethylphosphine oxide

The constitution of these compounds is proved in various ways; for instance, by the fact that the *monoalkyl-phosphinic acids* are dibasic, that the *dialkyl-phosphinic acids* are monobasic, and that the *trialkyl-phosphine oxides* have no acid properties.

The phosphines are colourless liquids with a penetrating, stupefying odour. Methylphosphine, CH_3PH_2, is a gas; triethylphosphine in very small quantities has an odour of hyacinths.

Methods of Formation.—Only tertiary phosphines and phosphonium compounds are formed by the action of alkyl halides upon PH_3. Primary and secondary phosphines are obtained by heating phosphonium iodide, PH_4I, with an alkyl iodide and zinc oxide.

Arsines.

80. The primary and secondary arsines, H_2AsCH_3 and $HAs(CH_3)_2$, are obtained by reduction of monomethylarsenic and dimethylarsenic acid, $(CH_3)HAsO{\cdot}OH$ and $(CH_3)_2AsO{\cdot}OH$, by amalgamated zinc-dust and hydrochloric acid. Both are immediately oxidized by the air. Tertiary arsines do not yield bases with water. They are formed by the action of a zinc-alkyl on $AsCl_3$, and from sodium arsenide and an alkyl iodide:

$$AsNa_3 + 3C_2H_5I = As(C_2H_5)_3 + 3NaI.$$

Quaternary arsonium bases, however, have strongly marked basic properties. They are formed by the addition of alkyl halides to tertiary arsines, and treatment of the resulting halide with silver hydroxide.

The most studied arsenic derivatives containing alkyl-radicles are the *cacodyl compounds*. They were investigated by Bunsen, who gave them this name in consequence of their offensive smell. They are very poisonous. The name cacodyl is applied to the monovalent group $\begin{matrix}CH_3\\CH_3\end{matrix}\!>As-$. *Cacodyl oxide*, $[(CH_3)_2As]_2O$, is formed by distilling arsenic trioxide with the acetate of an alkali-metal. All the other cacodyl compounds are obtained from cacodyl oxide; thus *cacodyl chloride*, $(CH_3)_2AsCl$, is prepared by heating the oxide with hydrochloric acid. This chloride, and *cacodyl*, $(CH_3)_2As{\cdot}As(CH_3)_2$, are both spontaneously inflammable when brought into contact with air.

$$\begin{matrix}CH_3\\CH_3\end{matrix}\Big\rangle As-As\Big\langle\begin{matrix}CH_3\\CH_3\end{matrix}$$

Stibines.

The *tertiary stibines* and the *quaternary stibonium bases* have been obtained from antimony. The first named are very readily oxidized, taking fire spontaneously in the air. The stibonium bases are quite as basic in their character as the corresponding N, P, and As derivatives. The pentamethyl-derivative $Sb(CH_3)_5$ is also known.

Bismuthines.

Bismuth does not yield a hydride, but *tertiary bismuthines*, such as $(C_2H_5)_3Bi$, are known. They are very unstable, and explode when heated. They do not form addition-products with alkyl halides, so that the "bismuthonium bases" are not known.

II. ALKYL-RADICLES LINKED TO THE ELEMENTS OF THE CARBON GROUP.

81. The elements in each group or column of the periodic system are divided into two sub-groups, in one of which the elements are of an electro-positive, base-forming character, and in the other of an electro-negative, acid-forming character ("Inorganic Chemistry," **213**). The first division of the carbon group contains titanium, zirconium, and thorium, and the second, carbon, silicon, germanium, tin, and lead. It has generally been observed, not merely of the carbon group, but also of the other groups, that *only elements belonging to electro-negative sub-groups are capable of yielding alkyl-compounds*. For this reason, MENDELEJEFF predicted in 1870 that the then unknown element germanium would, in accordance with its position in the periodic system, yield alkyl-derivatives; this prediction was confirmed by the researches of WINKLER, to whom we are indebted for the discovery of this element. Titanium being an element belonging to the electro-positive sub-group, and in many respects resembling silicon, it has not been found possible to prepare its alkyl-derivatives.

The elements silicon, germanium, tin, and lead, like carbon, are tetravalent. Numerous attempts have been made to prepare compounds containing chains of silicon atoms resembling the carbon chains. They have not been successful, no compounds containing a chain of more than three silicon atoms having been prepared. As far, therefore, as is at present known, silicon lacks the power of linking itself together in chains to the same extent as carbon. On account of this defect, a "Chemistry of Silicon", analogous to the "Chemistry of Carbon", is not possible.

The silico-alkyls have a character analogous to that of the similarly constituted carbon-alkyl compounds. For example, *silicon tetraethyl*, $Si(C_2H_5)_4$, and *carbon tetraethyl*, $C(C_2H_5)_4$, are known; both are liquids, and are not acted upon by either fuming nitric or fuming sulphuric acid at the ordinary temperature, but they both yield substitution-products with chlorine. *Silicoheptane*, $(C_2H_5)_3SiH$, has a petroleum-like odour, in which it resembles *triethylmethane*, $(C_2H_5)_3CH$.

Organic compounds of tin have been prepared by Pope, which contain the Sn-atom linked to four dissimilar groups and therefore possess an *asymmetric Sn-atom*. He has also succeeded in splitting these up into their optically-active components.

III. ALKYL-RADICLES LINKED TO METALS.

82. When ethyl iodide is warmed with zinc, a white crystalline compound, C_2H_5ZnI, is formed, and when this is more strongly heated, ZnI_2 and $Zn(C_2H_5)_2$ result:

$$2C_2H_5ZnI = Zn(C_2H_5)_2 + ZnI_2.$$

Zinc-ethyl can be separated by distillation, which must be performed in an apparatus free from air, because it burns spontaneously when exposed to it, as do also the other zinc-alkyls.

The metallo-alkyls are colourless liquids, heavier than water. Zinc-methyl boils at 46°, zinc-ethyl at 118°, and zinc-propyl at 146°.

When alkyl iodides react with zinc-alkyls, *saturated hydrocarbons* are formed (**29**):

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\boxed{Zn+\begin{matrix}I\\I\end{matrix}}\begin{matrix}\cdot CH_3\\\cdot CH_3\end{matrix} = ZnI_2 + 2CH_3\cdot CH_3.$$

The halogens react very energetically with zinc-alkyls, yielding alkyl halides.

Sodium-alkyl and *potassium-alkyl* are formed by the action of sodium and potassium respectively upon zinc-alkyl. These metals dissolve in the zinc-alkyl, an equivalent quantity of zinc separating out. Sodium-alkyl and potassium-alkyl have not been obtained in the pure state, but only in solution in zinc-alkyl.

Very remarkable compounds of magnesium have recently been obtained by Grignard. When magnesium-turnings are brought into contact with an ethereal solution of an alkyl iodide, one molecule of the latter being employed for each atom of metal, a reaction occurs, the heat evolved thereby raising the ether to the boiling-point. When a sufficient quantity of ether is used, all the magnesium enters into solution, forming a compound $C_nH_{2n+1}\cdot Mg\cdot I$. This is combined with one molecule of ether, because on distilling off the ether the residue still contains one molecule of that substance for every molecule of the metallic compound. Further, in a solvent other than ether, magnesium alkyl halide is not formed. The ethereal solution so obtained can be used with great advantage for the synthesis of secondary and tertiary alcohols, and for other purposes (**97** and **111**).

Mercury-alkyls are prepared similarly to the zinc compounds. They do not take fire in the air, and are dangerously poisonous. Such compounds as $C_2H_5\cdot Hg\cdot OH$ are strong bases.

In addition to the compounds mentioned above, alkyl-derivatives of beryllium, magnesium, cadmium, aluminium, thallium, and lead have been obtained.

NITRILES AND ISONITRILES.

83. When potassium ethyl sulphate is distilled with potassium cyanide or anhydrous potassium ferrocyanide, "yellow prussiate of potash," $K_4Fe(CN)_6$, a liquid of exceedingly unpleasant odour is obtained. By means of fractional distillation it can be separated into two portions, both of which have the formula C_3H_5N. One of these, which is called *ethylcarbylamine*, is only present in small quantities; it boils at 82°, and has the same disagreeable smell as the original mixture. The other, which constitutes the main portion, is called *ethyl cyanide;* it boils at 97°, and after purification, has an odour by no means disagreeable, and much less penetrating than that of the other compound.

These isomers behave quite differently when acted upon by inorganic acids. Ethylcarbylamine is attacked by them at ordinary temperatures; its disagreeable odour disappears, and the substance itself, which at first floated upon the acid in the form of an oily layer, goes wholly into solution. *Formic acid,* CH_2O_2, can be obtained from this solution by distillation; and on addition of caustic potash to the residue in the distilling-flask and subsequent distillation, ethylamine, $C_2H_5NH_2$, passes over, showing that the nitrogen in ethylcarbylamine, C_3H_5N, is directly linked to the ethyl-group:

$$\underset{\text{Ethylcarbylamine}}{C_3H_5N} + 2H_2O = \underset{\text{Formic acid}}{CH_2O_2} + \underset{\text{Ethylamine}}{C_2H_5NH_2}.$$

Ethyl cyanide is only slowly attacked by inorganic acids at ordinary temperatures, but more quickly on heating. The reaction is carried out in a flask with a reflux-condenser, and if after its completion the liquid is distilled, *propionic acid,* $C_3H_6O_2$, passes over. This acid contains the same number of carbon atoms as the original compound C_3H_5N. On making the residue in the flask alkaline, and distilling again, a volatile base, *ammonia,* is found in the distillate. The nitrogen in ethyl cyanide *cannot,* therefore, be directly linked to the ethyl-radicle:

$$\underset{\text{Ethyl cyanide}}{C_3H_5N} + 2H_2O = \underset{\text{Propionic acid}}{C_3H_6O_2} + NH_3.$$

It must be concluded from these facts that the nitrogen of the compound with the lower boiling-point is directly linked to the ethyl-groups, and the three carbon atoms are not directly linked to each other, in view of the ease with which one of the carbon atoms can be split off as formic acid; on the other hand, there must be a chain of three carbon atoms present in the compound of the higher boiling-point, since such a chain is found in propionic acid (**87**), and the nitrogen is not directly linked to the ethyl-group. These properties are expressed by the following constitutional formulæ:

$$\text{I. } \underset{\text{Carbylamine}}{C_2H_5\text{—}NC.} \qquad \text{II. } \underset{\text{Cyanide}}{C_2H_5\text{—}CN.}$$

On account of their method of formation, each must contain the group CN.

Compounds having a structural formula like I are called *carbylamines* or *isonitriles;* those having a structural formula like II are called *cyanides* or *nitriles.* The former are called after the alkyl-radicle which they contain, thus: *methylcarbylamine*, *ethylcarbylamine*, etc. The latter are called in an analogous manner *methyl cyanide*, *ethyl cyanide*, etc., although the word nitrile is more frequently used, when they are named after the acid from which they may be regarded as derived. Thus, $CH_3 \cdot CN$ is *acetonitrile*, and $C_2H_5 \cdot CN$ *propionitrile*, etc.

The constitution of the groups —CN and —NC requires further consideration. They are represented as $-C \equiv \overset{III}{N}$ and $-\overset{V}{N} \equiv C$, there being in one case a triple bond, and in the other a quadruple bond, between C and N. The reason for adopting these formulæ in preference to such a one, for example, as $-\underset{\|}{C}-N=$, in which free linkings are present, will appear later (**128**).

The existence of a divalent carbon atom in the carbylamines, that is to say, a group $-\overset{III}{N} = \overset{II}{C}$, is assumed by NEF and some other chemists.

Carbylamines.

84. These compounds are the principal product of the reaction of alkyl iodides with silver cyanide. They can also be formed by the action of caustic potash and chloroform, $CHCl_3$, upon primary amines, when they are obtained free from nitriles:

$$C_2H_5N|\overline{H_2}|\underline{+\ C}|\overline{HCl_3}| + 3KOH = 3KCl + 3H_2O + C_2H_5 \cdot NC.$$

On account of the extraordinary and characteristic odour of the carbylamines, this reaction affords an *exceedingly delicate test for primary amines*, since secondary and tertiary amines could not yield carbylamines by the reaction represented in the above equation, for this requires *two* hydrogen atoms to be directly linked to the nitrogen of the amine.

The carbylamines are colourless liquids, very stable towards alkalis, but readily converted by acids into a primary amine and formic acid. They yield unstable addition-products, such as $2CH_3NC \cdot 3HCl$, by the action of dry HCl in ethereal solution, and may therefore be looked upon as possessing weak basic properties.

Nitriles.

85. These constitute the chief product obtained when potassium cyanide reacts with alkyl iodides, or when it is submitted to dry distillation along with an alkyl potassium sulphate. It is sometimes an advantage to use anhydrous potassium ferrocyanide, $K_4Fe(CN)_6$, instead of potassium cyanide.

In addition to being obtainable by methods to be described in **110**, 3, nitriles may be prepared by the action of an alkaline bromine solution (German, *Bromlauge*) on primary amines, in accordance with the following equations:

$$C_7H_{15}CH_2 \cdot NH_2 + 2Br_2 + 2NaOH = C_7H_{15}CH_2 \cdot NBr_2 + 2NaBr + 2H_2O.$$

$$C_7H_{15}C|\overline{H_2}|\underline{N}|\overline{Br_2}| + 2NaOH = C_7H_{15}CN + 2NaBr + 2H_2O.$$

This reaction is only applicable with advantage to the higher primary amines.

The nitriles are liquids of characteristic odour, and have specific gravities about 0·8. They are soluble in water. They are converted not only by acids, but also by warming with alkalis, into ammonia, and fatty acids containing the same number of carbon atoms. This process is called *saponification* of nitriles. They have the power of forming addition-products with many substances, the triple bond between nitrogen and carbon being thereby broken and converted into a single bond. An example of this class of reactions is the addition of hydrogen:

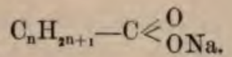
$$C_2H_5 \cdot CN + 4H = C_2H_5 \cdot CH_2 \cdot NH_2.$$

This results in the formation of a primary amine with the same number of carbon atoms. The reaction gives a particularly good yield for the higher members, when sodium is brought into contact with a mixture of the nitrile and absolute alcohol heated to boiling.

A description of a number of other addition-products of the nitriles will be found in **105.**

ACIDS, $C_nH_{2n}O_2$.

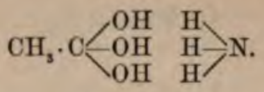
86. It was stated in **82** that a solution of sodium-alkyl in zinc-alkyl is obtained when sodium reacts with the latter. When a stream of dry carbon dioxide is passed into this solution, there is formed the sodium salt of an acid which contains one carbon atom in the molecule more than the alkyl-group. Thus, sodium-methyl, CH_3Na, yields sodium acetate, $C_2H_3O_2Na$. This reaction may be explained by assuming that the sodium atom is released from the alkyl-group, and reacts with CO_2, becoming linked to one of its oxygen atoms, for which it possesses great affinity. In this way $\mathrm{C}\ll^{\mathrm{O}}_{\mathrm{O}}$ is converted into $-\mathrm{C}\ll^{\mathrm{O}}_{\mathrm{ONa}}$. Since this group, and also the alkyl-radicle from which the sodium atom has been separated, have one free carbon bond apiece, it may be assumed that the two groups unite, forming a compound



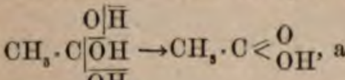
$$C_nH_{2n+1}-\mathrm{C}\ll^{\mathrm{O}}_{\mathrm{ONa}}.$$

In accordance with this reaction the acids $C_nH_{2n}O_2$ contain the group $-\mathrm{C}\ll^{\mathrm{O}}_{\mathrm{OH}}$ linked to an alkyl-radicle. This view is supported by the formation of these compounds by other methods.

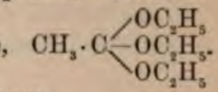
Among such reactions may be mentioned, first, the synthesis of the acids from the interaction of an alkyl iodide and potassium cyanide, and saponification of the resulting nitrile. This saponification consists in the adding on of water, and entails breaking the bonds between carbon and nitrogen in the group $-C\equiv N$. If the bond in a nitrile $CH_3\cdot CH_2\cdot CH_2\cdot\ldots CN$ were broken at any other point, it would involve a breaking of the carbon chain, and prevent the formation of an acid containing the same number of carbon atoms as the nitrile. The saponification of the nitrile, in which an acid and ammonia are formed, may therefore be regarded as taking place in the following manner. The molecules of water split up into H and OH, the hydroxyl uniting with the carbon, and the hydrogen with the nitrogen. If this happens three times, the nitrogen is converted into ammonia, the three bonds between carbon and nitrogen, in the nitrile, being broken:



$$CH_3\cdot C\begin{cases}OH\\ OH\\ OH\end{cases}\begin{matrix}H\\ H\\ H\end{matrix}\Big\rangle N.$$



The formula of the acid formed is not $CH_3\cdot CO_3H_3$, but $CH_3\cdot CO_2H$, containing one molecule of water less. When one molecule of water is split off from $CH_3\cdot CO_3H_3$, there results $CH_3\cdot C\begin{matrix}O|\overline{H}\\ |\overline{OH}\\ \overline{OH}\end{matrix}\rightarrow CH_3\cdot C\lessgtr{}^{O}_{OH}$, a substance containing the *carboxyl-group.*



In this explanation of the formation of acids, the existence of an intermediate compound containing three hydroxyl-groups is assumed. Such substances are not known, but the assumption seems by no means improbable, because compounds exist containing three alkoxyl-groups; for example, $CH_3\cdot C\begin{cases}OC_2H_5\\ OC_2H_5\\ OC_2H_5\end{cases}$. Substances of this kind are called *ortho-esters* (**155**).

The acids $C_nH_{2n}O_2$ can also be formed by the action of carbon monoxide on metallic alkoxides under the influence of heat:

$$CH_3\cdot ONa + CO = CH_3\cdot COONa.$$

The formation of an addition-product between $CH_3\cdot ONa$ and CO can be explained by the assumption that the alcoholate first decomposes into CH_3 and ONa.

It was mentioned in **49** and **50** that primary alcohols are converted by oxidation into acids with the general formula $C_nH_{2n}O_2$, containing the same number of C-atoms in the molecule. In this reaction the group $—CH_2OH$ is oxidized to $—COOH$.

The higher primary alcohols can also be converted into the corresponding acids by heating them with soda-lime, free hydrogen being formed as a by-product:

$$\underset{\text{Stearyl alcohol}}{C_{17}H_{35}\cdot CH_2OH} + NaOH = \underset{\text{Sodium stearate}}{C_{17}H_{35}\cdot COONa} + 2H_2.$$

A proof of the presence of hydroxyl in the carboxyl-group is afforded by the action of the chlorides of phosphorus, which effect the replacement of the OH-group by Cl in the same way as with the alcohols.

The acids of this series contain one hydrogen atom replaceable by metals. Since the hydrogen atom in the carboxyl-group occupies a special position, being the only one directly linked to oxygen, it is natural to suppose that it is *this* hydrogen atom which is replaceable. This is easily proved by treating silver acetate, $C_2H_3O_2Ag$, with ethyl iodide. Ethyl acetate is formed, and not butyric acid, as would be the case if the Ag-atom were present in the methyl-group; thus, $CH_2Ag \cdot COOH$.

87. The lower members of this series of acids are liquid at ordinary temperatures. They can be distilled without decomposition, and, when pure, have a very irritating and strongly acid odour. They are miscible in all proportions with water. The middle members (C_4—C_9) have a disagreeable rancid smell. They are of an oily nature, and do not mix with water in all proportions. The higher members, beginning at C_{10}, are solid at ordinary temperatures, are without odour, and resemble paraffin in character. They are almost insoluble in water, and cannot be distilled at the atmospheric pressure without decomposition. All the acids of this series dissolve readily in alcohol and ether. With the exception of the first member, they are very stable towards oxidizing-agents.

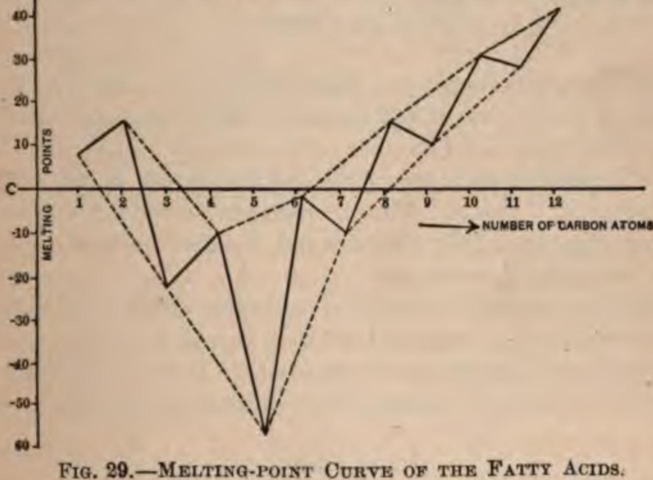


FIG. 29.—MELTING-POINT CURVE OF THE FATTY ACIDS.

The acids of the series $C_nH_{2n}O_2$ are called the *fatty acids*, on account of the fact that the higher members were first obtained from fats.

Many of the fatty acids occur in nature, either in the free state, or as esters. They are of great theoretical and technical importance. The following table contains the names, formulæ, and certain physical constants of the normal-chain acids belonging to the series $C_nH_{2n}O_2$:

Name.	Formula.	Melting-point.	Boiling-point.	Specific Gravity.
Formic Acid.........	CH_2O_2	8·3°	101°	1·2310 (10°)
Acetic Acid...........	$C_2H_4O_2$	16·598°	118°	1·0515 (15°)
Propionic Acid........	$C_3H_6O_2$	− 22°	141°	0·9985 (14°)
Butyric Acid..........	$C_4H_8O_2$	− 7·9°	162°	0·9599 (19·1°)
Valeric Acid..........	$C_5H_{10}O_2$	− 58·5°	186°	0·9560 (0°)
Caproïc Acid..........	$C_6H_{12}O_2$	− 1·5°	205°	0·9450 (0°)
Heptylic Acid........	$C_7H_{14}O_2$	− 10·5°	223°	0·9186 (17·2°)
Caprylic Acid.........	$C_8H_{16}O_2$	16·5°	237·5°	0·9100 (20°)
Nonylic Acid..........	$C_9H_{18}O_2$	12·5°	254°	0·9110 (M.P)
Capric Acid...........	$C_{10}H_{20}O_2$	31·4°	269°	0·9300 (37°)
Palmitic Acid.........	$C_{16}H_{32}O_2$	62·618°		
Margaric Acid.... ...	$C_{17}H_{34}O_2$	60°		
Stearic Acid..........	$C_{18}H_{36}O_2$	69·32°		

Although the boiling-point rises regularly for every increase in the number of C-atoms in the molecule, the melting-points of the acids containing an even number of C-atoms are higher than those of the acids immediately preceding and succeeding them, with an odd number of C-atoms. This is distinctly seen from the curve shown in Fig. 29. This phenomenon has also been observed in some other homologous series.

It is often necessary to consider the group which remains when the hydroxyl-group is supposed to be removed from a fatty acid. This group is not known in the free state. It is named after the corresponding acid by changing the termination "ic" into "yl"; thus,

$H\cdot CO$ Formyl,
$CH_3\cdot CO$ Acetyl,
$C_2H_5\cdot CO$ Propionyl,
$C_3H_7\cdot CO$ Butyryl,
$C_4H_9\cdot CO$ Valeryl,
etc.

Formic Acid, $H\cdot COOH$.

88. This compound derives its name from the fact that it occurs in the bodies of ants (Latin, *formica*). It can be obtained by passing carbon monoxide over soda-lime at 210°, the yield being good (**86**). It is, however, usually prepared by another method (**158**). It may also be obtained by the oxidation of methyl alcohol. A peculiar method for its formation is to submit carbon monoxide and steam, or carbon dioxide and hydrogen, to a silent electric discharge.

Pure formic acid is a colourless liquid with an irritating odour. Its salts are called *formates*, and are soluble in water, some of them only with difficulty.

Formic acid is distinguished from its homologues: first, by the ease with which it undergoes oxidation, it being therefore a good reducing agent; second, in being easily decomposed into CO and H_2O. When mercuric oxide is added to a solution of formic acid, a solution of mercuric formate is obtained. If this be filtered and warmed, mercurous formate is precipitated with evolution of CO_2, and on further warming, metallic mercury is obtained:

$$\mathrm{Hg}\underset{\text{Mercuric formate}}{\underline{\frac{\mathrm{OOCH}\quad\mathrm{HCOO}}{|\mathrm{OOCH}+\mathrm{H}|\mathrm{COO}|}}}\mathrm{Hg} = \underset{\substack{\text{Mercurous}\\ \text{formate}}}{2\mathrm{HgOOCH}} + \mathrm{CO_2} + \mathrm{HCOOH};$$

$$\mathrm{Hg}\underset{\text{Mercurous formate}}{\underline{\overline{|\mathrm{OOCH}+\mathrm{H}|\mathrm{COO}|}}}\mathrm{Hg} = 2\mathrm{Hg} + \mathrm{CO_2} + \mathrm{HCOOH}.$$

In this process half the formic acid in the salt is set free, and half is oxidized. An exactly analogous reaction takes place when a solution of silver formate is warmed; metallic silver is precipitated, carbon dioxide evolved, and half of the acid set free.

When formic acid is warmed with concentrated sulphuric acid, water and carbon monoxide are formed:

$$|\overline{\mathrm{H}}\underline{|\mathrm{CO}|}\overline{\mathrm{OH}}| = \mathrm{H_2O} + \mathrm{CO}.$$

The same effect is produced by the introduction of finely powdered metallic rhodium into an aqueous solution of the acid, when the decomposition takes place even at ordinary temperatures. The rhodium acts as an accelerating, catalytic agent. Since reactions which of themselves would not take place cannot be brought about by catalysis ("Inorganic Chemistry," **25**), it follows that formic acid decomposes of itself in the above sense, although so slowly as to seem perfectly stable. This applies to a large number of organic compounds (*Ibid.*, **104**).

It will have been noticed that the general properties of formic acid differ in some respects from those of the other acids of the homologous series in which it is the lowest member. As will be seen later, this phenomenon is of frequent occurrence.

Acetic Acid, $CH_3 \cdot COOH$.

89. This substance has been known longer than any other acid. It is manufactured by two different methods.

a. By allowing dilute alcohol, wine, beer, etc., to become oxidized by exposure to the air, with production of vinegar. The oxygen of the atmosphere acts upon the alcohol with the aid of bacteria, and the process must be so regulated that these bacteria produce the greatest possible effect. To this end it is important that the temperature should be kept about 35°.

In the "quick process" for the preparation of vinegar (Fig. 30), dilute alcohol (6–10%) is allowed to drop on beech-wood shavings contained in a vat with a perforated false bottom, *a*. Holes are bored in the sides of the vat near the bottom, serving to admit an ascending stream of air, opposite in direction to that of the alcohol. The shavings of beech-wood have the effect of distributing the liquid over a very large surface, and so facilitating the oxidizing action of the air, while at the same time they serve as a feeding-ground for the bacteria.

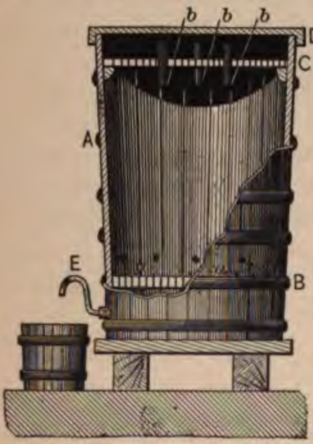


FIG. 30.—PREPARATION OF VINEGAR BY THE "QUICK PROCESS."

b. It has been mentioned (**46**) that acetic acid is obtained in the distillation of wood. By treatment with quicklime, the acid is converted into calcium acetate, which is freed from tarry impurities by heating it to 200° in the air. The acetic acid is then set free by distilling with an equivalent quantity of concentrated hydrochloric acid. It can be purified by distillation over potassium bichromate, being very stable towards oxidizing-agents.

Anhydrous acetic acid is solid at temperatures below 16·6°, when it has much the appearance of ice; hence the name *glacial acetic acid*. It has a very penetrating odour, and is obtained by allowing a very concentrated solution of acetic acid to solidify, pouring off the liquid residue, melting the solidified acid, again allowing it to crystallize, etc., these operations being repeated until the melting-point is constant. A rise of temperature and contraction of volume occur when glacial acetic acid is mixed with water, the maximum rise and contraction being obtained by mixing in the proportion of one gramme-molecule of acetic acid to one gramme-molecule of water. This fact is evidence of the existence of a compound called *ortho-acetic acid* (**86**), with the formula $CH_3 \cdot COOH \cdot H_2O = CH_3 \cdot C(OH)_3$.

A 55 per cent. solution of glacial acetic acid in water has the same specific gravity as the pure, anhydrous acid. When water is added to glacial acetic acid, the specific gravity of the mixture first rises; further addition of water causes it to fall. This circumstance makes it impossible to determine the amount of acid present in such mixtures by the simple use of the hydrometer.

The strength of very concentrated acetic acid is best determined by an observation of its melting-point, a thermometer graduated in tenths of a degree being used. In accordance with the formula given in **14**,

$$AM = \text{Constant};$$

the presence of 1% of water (molecular weight 18) would, since the constant for glacial acetic acid is 39, cause a lowering of the freezing-point (A) of $\frac{39}{18}$, or 2·16°. Since a thermometer graduated in tenths can easily be read to within one-twentieth of a degree, the amount of water can be determined to within $\frac{1}{2 \cdot 16 \times 20}$, or 0·025%. This is a degree of accuracy unattainable by titration.

When either no very great accuracy is required, or the acetic acid is dilute, it is best to determine the strength by titrating a weighed quantity of the solution with a standard solution of alkali.

The vapour density of acetic acid at temperatures slightly above its boiling-point is twice as great as that corresponding to the formula $C_2H_4O_2$. At about 200°, however, the vapour density is normal. A similar phenomenon has been observed in the case of many other fatty acids.

The *acetates*, or salts of acetic acid, are generally soluble in water, the silver salt dissolving with difficulty. When ferric chloride is added to the solution of an acetate, such as sodium acetate, a blood-red colour is produced, owing to the formation of ferric acetate (the salts of formic and propionic acids produce the same result). When this solution is sufficiently dilute, a brown-red precipitate of basic ferric acetate, $Fe\begin{matrix}C_2H_3O_2\\(OH)_2\end{matrix}$, is produced on boiling, acetic acid being liberated at the same time.

A very delicate test for acetic acid is the formation of cacodyl oxide (**80**). Owing to the extremely poisonous nature of this substance, great care must be exercised in applying this test. Among the acetates of technical importance are *lead acetate* ("sugar of lead"), *basic lead acetate*, and *aluminium acetate*. The first two are used in the manufacture of white lead, and the third as a mordant in calico-printing (**321**).

Butyric Acids, $C_4H_8O_2$.

90. Two isomeric acids with the formula $C_4H_8O_2$ are known. They are *normal butyric acid*, $CH_3\cdot CH_2\cdot CH_2\cdot COOH$, and *isobutyric acid*, $\begin{matrix}CH_3\\CH_3\end{matrix}\!>CH\cdot COOH$. The constitution of these acids is proved by their synthesis, the normal compound being obtained from *n*-propyl iodide, and the iso-acid from isopropyl iodide:

$$CH_3\cdot CH_2\cdot CH_2I \rightarrow CH_3\cdot CH_2\cdot CH_2\cdot CN \rightarrow CH_3\cdot CH_2\cdot CH_2\cdot COOH.$$

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>CHI \rightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!>CH\cdot CN \rightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!>CH\cdot COOH.$$

The normal compound is also called *fermentation butyric acid*, from the fact that it can be obtained by the fermentation under certain conditions of such substances as sugar. It has an extremely disagreeable odour, and can only be oxidized with difficulty.

Butter contains about 4–5% of *n*-butyric acid, along with smaller quantities of other volatile acids of the fatty series, such as caproïc acid. These are probably present in the form of esters. Since "volatile fatty acids" are not obtained by saponification of other fats, whether animal or vegetable, their presence furnishes the most characteristic distinction between butter and margarine, which is a mixture of animal and vegetable fats. Since the percentage of volatile fatty acids in butter is not a constant quantity, but may vary between wide limits, it is impossible in certain cases to identify a mixture of butter and margarine by a determination of the amount of these acids present. By the application of other tests, it is sometimes possible to obtain reliable results in doubtful cases.

Isobutyric acid also has a very disagreeable smell. It is a compound containing a tertiary hydrogen atom, and experience has shown that such compounds are very easily oxidized, so that oxidation affords a method of distinguishing between the normal acid and the iso-acid.

The calcium salts of these acids also exhibit a remarkable difference in properties, that of the normal acid being less soluble in hot water than in cold, while that of the iso-acid follows the ordinary rule, and is more soluble in hot than in cold water. A solution of normal calcium butyrate saturated at 0° deposits considerable quantities of the salt when heated to about 80°.

In accordance with the *principle of mobile equilibrium* ("Inorganic Chemistry," **235**), normal calcium butyrate should dissolve in water with slight evolution of heat, and the calcium salt of isobutyric acid with slight absorption of heat. This view is fully supported by the results of experiment.

Higher Fatty Acids, $C_nH_{2n}O_2$.

91. Many of these occur in nature, chief among them being *palmitic acid*, $C_{16}H_{32}O_2$, and *stearic acid*, $C_{18}H_{36}O_2$, both of which contain normal carbon chains, as will be shown later (**144**). They are found in very large quantities as esters of glycerol (**159**), being the principal constituent of most animal and vegetable fats. They are obtained from these by saponification, a process carried out by heating either with slaked lime (**101**), or with concentrated sulphuric acid. Sulphuric acid causes slight carbonization, with the result that the fatty acids have a dark colour imparted to them. They can be purified by distillation with superheated steam. By saponification of fats in this way, a mixture of fatty acids is obtained, which is semi-solid at ordinary temperatures. It contains the two acids mentioned above, which, when pure, melt at 62° and 69° respectively; when mixed, each lowers the melting-point of the other (**14**). Moreover, the liquid oleic acid, which belongs to another homologous series, is also present; it can be pressed out of the mixture, leaving a white, solid substance used in the manufacture of "stearine" candles. For this purpose it is melted, and a little paraffin wax added to prevent the crystallization of the fatty acids, which would make the candles very brittle; the molten mass is then poured into moulds, in the middle of which wicks are fastened.

Soaps are the alkali-salts of the fatty acids. They are prepared by saponifying the fats with solutions of caustic soda or caustic potash heated to the boiling temperature. The potassium-soap is called "soft soap," and usually has a yellow colour. In some countries the colour is changed to green by the addition of a little indigo, the soap being then known as "green soap." Potassium-soap contains not only the potassium salt of the fatty acid, but also the glycerol produced in the reaction, and a considerable proportion of water. Sodium-soap is hard; it is separated from the reaction-mixture, after saponification is complete, by "salting-out," which consists in the addition of common salt in the solid state to the mixture at the boiling temperature. Since the sodium salt of the fatty acid is insoluble in a concentrated solution of sodium chloride, it separates out in the molten state, forming a layer on the surface of the brine. The glycerol remains dissolved in the latter; the soap obtained in this way consists of the sodium salt of the fatty acid, together with a small percentage of water.

92. The cleansing action of soap may be explained in the following way. As early as the beginning of the nineteenth century it was pointed out by CHEVREUL that when an alkali-salt of one of the higher fatty acids is brought into contact with a large excess of water, it decomposes with formation of free alkali. The acid thus liberated unites with a second molecule of the salt, forming an insoluble substance, which with the water produces the lather. The presence of free alkali in dilute soap-solutions can be readily shown as follows. A concentrated soap-solution is only very slightly coloured by phenolphthaleïn; but the addition of a large quantity of water causes the development of the red colour, due to the action of the base thus liberated on the phenolphthaleïn. The soap has therefore undergone hydrolytic dissociation ("Inorganic Chemistry," **239**), owing to the weak acid properties of the higher fatty acids.

The soiling of the skin, clothing, etc., is usually due to substances of a fatty nature. When a fat is brought into contact with an alkaline liquid, and the mixture shaken, a part is saponified, and dissolves. The greater portion, however, remains suspended in the liquid in the form of minute drops, which give it a milky appearance. The product is called an emulsion. The alkali liberated from the soap has therefore both a saponifying and an emulsifying action on the substance to which the soiling is due.

If the correctness of this explanation is admitted, the question arises as to why free alkali should not be used instead of soap for washing-purposes. It is because the use of soap prevents the presence of an excessive proportion of free alkali. The proportion of alkali liberated from soap is small with a small quantity of water, and large with a large quantity. But the addition of a large quantity of water does not very much affect the concentration—the amount of free alkali in unit volume of liquid—since, although it produces much free alkali, it simultaneously dilutes it. The use of soap has therefore the effect of automatically regulating the amount of free alkali present in the water, and keeping the solution very dilute. This would not be the case if free alkali were employed instead of soap, and the latter possesses the further advantage of forming a lather, which takes up the dirt and facilitates its removal.

When water contains a certain percentage of calcium salts, it is said to be *hard* ("Inorganic Chemistry," **259**). Such water does not lather with soap, but causes the formation of a white, flocculent substance, consisting of insoluble calcium salts of the fatty acids. Hard water is therefore unsuitable for washing because it prevents the formation of a lather, and also because the alkali combines with the acid of the calcium salts (sulphate and carbonate) present.

Electrolytic Dissociation.

93. It is fully explained in "Inorganic Chemistry," **65** and **66**, why molecules of acids, bases, and salts are assumed to split up in aqueous solution into particles called ions, charged with opposite kinds of electricity. In such a solution, an acid is either wholly or partly split up into positively charged hydrogen ions, H (cations), and negatively charged anions: for acetic acid, $H^{\cdot}$ (positive), and $(C_2H_3O_2)'$ (negative). Bases yield a positively charged metallic ion, and a negatively charged OH'-ion; salts a positively charged metallic ion, and a negatively charged acid-radicle ion.

It is further stated (*Ibid.*, **66**) that in the solution of a partly ionized substance an equilibrium exists which can be expressed in the case of a monobasic acid by

$$ZH \rightleftarrows Z' + H^{\cdot},$$

where Z' represents the acid radicle. If v is the volume in litres containing one gramme-molecule of the acid, and α is the portion ionized, then the concentration of the ions is $\frac{\alpha}{v}$, and that of the un-ionized portion is $\frac{1-\alpha}{v}$. The equation representing the state of equilibrium in the case of the above example of a monobasic acid is therefore (*Ibid.*, **49**)

$$k\frac{1-\alpha}{v} = \left(\frac{\alpha}{v}\right)^2, \text{ or } \frac{\alpha^2}{v(1-\alpha)} = k.$$

In this equation k is constant, and is called the *ionization constant*. It has been shown that this equation affords an exact measure of the amount of ionization in the case of the very weak organic acids; that is, expresses accurately the connection between the dilution v and the ionization α. For this reason it is called the *law of dilution*. It was discovered by Ostwald, who dissolved one gramme-molecule of an acid in different quantities of water, v, and ascertained the ionizations α by a determination of the electric conductivity. On substituting the values obtained for α and v respectively in the expression $\frac{\alpha^2}{v(1-\alpha)}$, the latter was always found to have the same value, as it must if k is constant.

As the constant is a very small number, it is usual to multiply it by 100, and to denote this quantity by K, so that $K = 100k$.

The accuracy of this law will be seen from the examples in the following table:

Acetic Acid.			Propionic Acid.			n-Butyric Acid.		
v	$100a$	$100k$	v	$100a$	$100k$	v	$100a$	$100k$
8	1·193	0·00180	8	1·016	0·00130	8	1·068	0·00144
16	1·673	0·00179	16	1·452	0·00134	16	1·536	0·00150
32	2·380	0·00182	32	2·050	0·00134	32	2·165	0·00149
64	3·33	0·00179	64	2·895	0·00135	64	3·053	0·00150
128	4·68	0·00179	128	4·04	0·00133	128	4·292	0·00150
1024	12·66	0·00177	1024	10·79	0·00128	1024	11·41	0·00144

94. The property of acids, usually called their "strength," depends upon their degree of ionization, strong acids undergoing considerable, and weak acids but slight, ionization. Since the constant K rises or falls in value simultaneously with α and is independent of the concentration, it affords a convenient measure of the strength of an acid.

The following shows the value of K for certain fatty acids:

Formic Acid.	Acetic Acid.	Propionic Acid.	n-Butyric Acid.	Valeric Acid.
0·0214,	0·0018,	0·0013,	0·0015,	0·0016.

It will be noticed that formic acid has a greater value for K, and is therefore stronger, than its homologues, a fact which affords another example of the difference in properties existing between it and the other members of the series.

A consideration of the degrees of ionization for equal concentrations shows that these acids are very weak compared with strong mineral acids like hydrochloric and sulphuric. When $v = 16$, then for hydrochloric acid $100\alpha = 95 \cdot 55$, and for acetic acid only $1 \cdot 673$. It is obvious that 100α is the amount ionized, expressed in percentage.

Although the law of dilution is generally applicable to the weak organic acids, it does not hold good for the strong mineral acids. It has not yet been possible to give a perfectly satisfactory explanation of this phenomenon.

DERIVATIVES OF THE FATTY ACIDS OBTAINED BY MODIFYING THE CARBOXYL-GROUP.

95. The carboxyl-group may be modified by the exchange of its oxygen atoms or hydroxyl-group for other elements or groups. This is the case in the classes of compounds described in this section.

I. Acid Chlorides.

These are derived from the acids by replacement of the hydroxyl-group by chlorine, so that they contain the group —COCl. They are obtained from the acids by the action of the chlorides of phosphorus, PCl_5 and PCl_3, or of phosphorus oxychloride, $POCl_3$:

$$3C_nH_{2n+1}\cdot COOH + PCl_3 = 3C_nH_{2n+1}\cdot COCl + P(OH)_3.$$

The ease with which the acid chlorides are converted into the corresponding acids is a proof that the chlorine atom has replaced the hydroxyl-group. In the case of the lower members this can be effected by merely bringing them into contact with water. If the chlorine atom had entered the alkyl-group, this would not take place, because an alkyl chloride is not decomposed by water at ordinary temperatures.

The acid chlorides of this series, at least the lower members, are liquids with a suffocating, irritating odour. The chloride corresponding to formic acid is not known. *Acetyl chloride*, CH_3COCl, fumes in the air, and can be distilled without decomposition. It boils at 55°, and its specific gravity is 1·13 at 0°.

The acid chlorides, especially acetyl chloride, are of great service in determining whether organic compounds contain hydroxyl, because with such compounds they yield acetyl-derivatives. In this way they react with alcohols, forming esters:

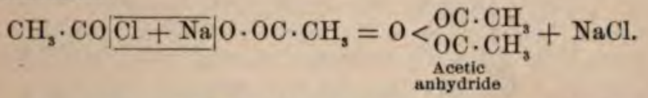
$$R\cdot O\boxed{H + Cl}OC\cdot CH_3 = RO\cdot OC\cdot CH_3 + HCl.$$

The compound in which the presence of hydroxyl is suspected is tested by allowing it to remain for some time in contact with acetyl chloride, either at the ordinary temperature or under the influence of slight heat. To ascertain whether an acetyl-compound has been formed, the product is submitted to analysis, or is saponified. In the latter case, the presence of acetic acid proves that an acetyl-derivative was present.

The acid chlorides also react with the mercaptans, with the formation of acetyl-compounds.

II. Acid Anhydrides.

96. These are formed by treating the alkali-salts of acids with acid chlorides:



$$CH_3\cdot CO\boxed{Cl + Na}O\cdot OC\cdot CH_3 = \underset{\text{Acetic anhydride}}{O<\begin{matrix}OC\cdot CH_3\\ OC\cdot CH_3\end{matrix}} + NaCl.$$

Higher anhydrides are best obtained by heating the sodium salts of the higher acids with acetic anhydride.

The acid chlorides may be looked upon as the mixed anhydrides of hydrochloric acid and an acid, a view which is supported by their formation from these two acids in presence of phosphorus pentoxide as a dehydrating-agent.

Mixed anhydrides of the fatty acids themselves exist, although when distilled they decompose into the anhydrides of the two acids.

The lower members of this series are liquids with a disagreeable, suffocating odour. They are immiscible with water, and partly on this account decompose but slowly when in contact with it. *Acetic anhydride* boils at 137°, and has a specific gravity of 1·073 at 20°. Like acetyl chloride it is used in testing for the presence of the hydroxyl-group. No anhydride of formic acid is known.

III. Esters.

97. These result from the interaction of acid chlorides, or anhydrides, and alcohols:

$$CH_3\cdot CO\boxed{Cl + H}OC_2H_5 = CH_3\cdot COOC_2H_5 + HCl.$$

They are also formed by direct treatment of the alcohol with the acid, although extremely slowly at ordinary temperatures:

$$CH_3\cdot COOH + HOC_2H_5 = CH_3\cdot COOC_2H_5 + H_2O.$$

The speed of the reaction is much increased under the influence of heat. Esters are further obtained by acting upon the silver salt of an acid with an alkyl iodide.

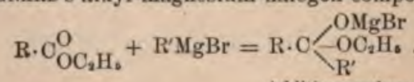
The following is a characteristic and frequently used method for the preparation of these compounds. Dry hydrochloric-acid gas is led through a mixture of absolute alcohol and the anhydrous organic acid. After some time the reaction-mixture is poured into water, whereupon the ester separates out, owing to its slight solubility. The formation of esters in this way may be explained on the assumption that a very small quantity of the hydrochloric acid unites with the organic acid, water being eliminated, and a minute quantity of the acid chloride formed:

$$CH_3 \cdot COOH + HCl = CH_3 \cdot COCl + H_2O.$$

It is true that, for each molecule of acid chloride formed in accordance with this equation, an equivalent quantity of water is produced, sufficient to reconvert the chloride into the acid and hydrochloric acid. There is, however, such an infinitely greater number of molecules of alcohol than of water with which the chloride can react, that the *probability* of the formation of an ester is very much greater than that of the regeneration of the acid. This state of things continues as long as the amount of alcohol present greatly exceeds that of the water formed; it is made to do so by dissolving the organic acid in a large excess of alcohol, when the object is to obtain the maximum yield of ester. The formation of esters is called *esterification*.

The esters are colourless liquids of neutral reaction, and do not mix with water in all proportions. They are lighter than water, most of them having a specific gravity between 0·8 and 0·9. The majority are characterized by the possession of a very agreeable odour, resembling that of fruits, a fact which finds practical application in their employment in the manufacture of fruit essences. For example, *isoamyl-isovalerate* (B.P. 196°) has an odour of apples, *ethyl butyrate* (B.P. 121°) of pineapple, and *isoamylacetate* (B.P. 148°) of pears, and so on.

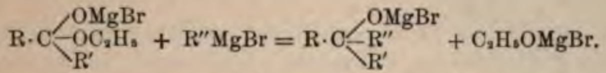
Tertiary alcohols can easily be synthesized from the esters by means of GRIGNARD's alkyl-magnesium-halogen compounds (**82**):



$$R \cdot C\begin{matrix}O \\ OC_2H_5\end{matrix} + R'MgBr = R \cdot C\begin{matrix}OMgBr \\ -OC_2H_5 \\ R'\end{matrix}.$$

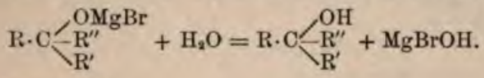
Addition-product

The addition-product so obtained reacts with a second molecule of the magnesium compound:



$$\mathrm{R\cdot C}\begin{array}{l}\diagup\mathrm{OMgBr}\\ -\mathrm{OC_2H_5}\\ \diagdown\mathrm{R'}\end{array} + \mathrm{R''MgBr} = \mathrm{R\cdot C}\begin{array}{l}\diagup\mathrm{OMgBr}\\ -\mathrm{R''}\\ \diagdown\mathrm{R'}\end{array} + \mathrm{C_2H_5OMgBr}.$$

Decomposition with water then yields the tertiary alcohol:



$$\mathrm{R\cdot C}\begin{array}{l}\diagup\mathrm{OMgBr}\\ -\mathrm{R''}\\ \diagdown\mathrm{R'}\end{array} + \mathrm{H_2O} = \mathrm{R\cdot C}\begin{array}{l}\diagup\mathrm{OH}\\ -\mathrm{R''}\\ \diagdown\mathrm{R'}\end{array} + \mathrm{MgBrOH}.$$

R, R′, and R″ = alkyl.

98. The formation of esters has been carefully investigated by several chemists, first of whom were Berthelot and Péan de St. Gilles. Their researches have shown that the reaction between the acid and the alcohol is never complete, some of both remaining uncombined, no matter how long the process has been carried on. When equivalent quantities of acetic acid and ethyl alcohol, for example, are used, the final product is such that from each gramme-molecule of alcohol and acid used, only two-thirds of a gramme-molecule of an ester and of water are formed, while one-third of a gramme-molecule of the alcohol and of the acid respectively remain uncombined. The same limiting point is reached when an ester and water are brought into contact in equivalent quantities. A *state of equilibrium* is ultimately reached between the four substances, alcohol, acid, ester, and water, due to the *reversibility* of the reaction ("Inorganic Chemistry," **49**). It may be represented as follows:

$$\mathrm{C_2H_5\cdot OH + CH_3\cdot CO\cdot OH \rightleftarrows CH_3\cdot CO\cdot OC_2H_5 + H_2O.}$$

The equation of equilibrium deduced in *Ibid.*, **49** and **50**, may be applied to the formation and decomposition of esters. It is

$$k(p-x)(q-x) = k'x^2, \quad \text{or} \quad (p-x)(q-x) = Kx^2,$$

where p is the concentration of the alcohol in the first instance, and q that of the acid, while x represents the quantities of water and of ester respectively present when the state of equilibrium is attained. All these are expressed in gramme-molecules, and K is a constant. There are here two reactions, with opposite effects, taking place simultaneously, so that all the statements already made

(*Ibid.*) are equally applicable in the present instance. When p, q, and K are known, the unknown quantity x may be calculated.

> Numerous observations have proved that K is equal to 0·25 for the system ethyl alcohol + acetic acid. When one gramme-molecule of alcohol (46 g.) and one gramme-molecule of acetic acid (60 g.) are brought into contact, in this case both p and q being equal to 1, the equation is
>
> $$(1-x)^2 = 0\cdot25x^2, \quad \text{or} \quad x^2 - \tfrac{8}{3}x + \tfrac{4}{3} = 0,$$
>
> from which it follows that
>
> $$x = \tfrac{2}{3}.$$
>
> It follows that this system in the state of equilibrium contains $\frac{1}{3}$ gramme-molecule alcohol + $\frac{1}{3}$ gramme-molecule acetic acid + $\frac{2}{3}$ gramme-molecule water + $\frac{2}{3}$ gramme-molecule ester.

99. Several deductions can be drawn from the equation

$$(p-x)(q-x) = Kx^2,$$

which had been established by experiment long previous to these theoretical developments.

1. The esterification is approximately quantitative only when a large excess of the alcohol is mixed with a very small quantity of the acid, or when a small proportion of the alcohol is brought into contact with a large amount of the acid.

Putting the equation in the form

$$\frac{p-x}{x} = K\frac{x}{q-x},$$

it is evident that, the quantity of the alcohol (p) being infinitely great, the right-hand side $= \infty$. This holds good when $q = x$, that is, when all the acid has been converted into ester. It is also true when the ratio of the quantity of acid to alcohol is infinitely great, the whole of the alcohol changing into ester.

2. The alcohol and the acid exercise the same influence on the formation of esters; that is, if one mixture is made containing a certain number of acid molecules and n times as many alcohol molecules, and another in which the proportions of acid and alcohol are reversed, then the number of molecules of acid converted into ester in the first case is equal to that of the molecules of alcohol converted in the second.

When p gramme-molecules of alcohol are mixed with np gramme-molecules of acid, the equation becomes

$$\frac{p-x}{x} = K\frac{x}{np-x}.$$

Inversely, when np gramme-molecules of alcohol are added to p gramme-molecules of acid, we have

$$\frac{np-x}{x} = K\frac{x}{p-x}.$$

But these two equations are identical, the first being converted into the second by multiplying across by $\frac{np-x}{p-x}$.

3. The addition of a quantity of the ester to the mixture of the alcohol and the acid at the beginning of the experiment has the same effect on the formation of ester as would be exerted by an equivalent quantity of water.

When r gramme-molecules of water or of ester are added to a mixture containing p gramme-molecules of alcohol and q gramme-molecules of acid, then in both cases the equation becomes

$$(p-x)(q-x) = Kx(x+r).$$

It follows from this that the equilibrium is influenced to the same extent by the addition of water and of ester in equivalent quantities.

100. A typical application of the principle of mobile equilibrium ("Inorganic Chemistry," **235**) may be made in the case of the formation of esters. Although the velocity of formation and decomposition of esters depends greatly upon the temperature, a change in the latter has but very slight effect upon the equilibrium. At 10° the limit of esterification is 65·2%, at 220° it is 66·5%. In accordance with the principle just mentioned, this would not be the case unless the heats of formation of the esters were very small. That they actually are so has been established by experiment.

101. The saponification of esters under the influence of acids takes place in accordance with the following equation:

$$CH_3{\cdot}COOC_2H_5 + H_2O = CH_3{\cdot}COOH + C_2H_5OH.$$

The action of the acid which is here added is therefore only catalytic. It may thus be noted that the presence of mineral acid only accelerates the saponification, and that the same result would be obtained without this acid, though in a space of time incomparably longer (**88**). If the concentration of the ester be C_1, that of the water be C_2, and x the quantity of ester which has undergone saponification during the time t, then the velocity of saponification for each moment can be represented by the equation for bimolecular reactions ("Inorganic Chemistry," **50**):

$$\frac{dx}{dt} = k(C_1 - x)(C_2 - x). \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If the ester is dissolved in a very large quantity of water, the concentration C_2 of the water is only very slightly altered by the saponification, so that it may be included in the constant. The equation is therefore simplified to that for a unimolecular reaction:

$$\frac{dx}{dt} = k_1(C_1 - x). \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The saponification of esters by bases may be represented as follows:

$$CH_3 \cdot COOC_2H_5 + NaOH = CH_3 \cdot COONa + C_2H_5OH.$$

Since in this case the reaction is a bimolecular one, equation (1) holds good for it.

The velocity of saponification of esters by acids depends largely on the particular one used. With strong acids the process is rapid, and slow with weak ones. It has been shown that the velocity of saponification is conditional upon the amount of electrolytic dissociation of the acid employed. From this fact it may be concluded that the saponifying action is due to the hydrogen ion, since this is common to all acids. The velocity is very much greater for bases than for acids; thus, for dilute (decinormal) solutions of caustic potash and hydrochloric acid, the ratio of the velocity constants K for the saponification of methyl acetate is 1350:1. The velocity of saponification in the case of bases also depends upon their electrolytic dissociation. Ammonium hydroxide, for example, which is considerably less ionized than caustic potash or caustic soda, saponifies much more slowly than the latter. It is therefore the hydroxyl-ion, common to all the bases, which causes saponification.

In the technical saponification of fats with slaked lime (**91**) a much smaller amount of this base is used than the equivalent of the quantity of acid obtained; the saponification is nevertheless complete. This is due to the fact that the higher fatty acids are very weak, in consequence of which their salts undergo partial hydrolytic dissociation. Thus, notwithstanding the excess of acid, there is always some free base (hydroxyl-ions) present, by which the saponification is effected.

Esterification of Primary, Secondary, and Tertiary Alcohols.

102. Menschutkin has investigated the quantity of ester formed when primary, secondary, and tertiary alcohols respectively are heated with an equivalent quantity of acetic acid in sealed tubes for one hour at 154°. He has shown that the percentage-numbers obtained for all the members of each class of alcohols are nearly the same, although they differ widely for the classes themselves. Thus about 47% of primary, about 22% of secondary, and only about 1.5% of tertiary alcohols are converted into esters. This affords a means of determining to which of the three classes a given alcohol belongs.

IV. Thio-acids. $R\cdot CO\cdot SH$.

103. The thio-acids are formed by the interaction of acid chlorides and potassium sulphydrate, KSH, a method of formation which is a proof of the constitution indicated above. They are liquids with a most disagreeable smell, and when heated with salts of heavy metals readily yield acetic acid and the corresponding metallic sulphide.

V. Acid Amides, $C_nH_{2n+1}\cdot CONH_2$.

104. Acid amides are formed by the action of ammonia on acid chlorides or anhydrides, a method which affords a proof of their constitution:

$$C_nH_{2n+1}\cdot CO\boxed{Cl+H}NH_2 = C_nH_{2n+1}\cdot CONH_2 + HCl;$$

$$\begin{matrix} C_nH_{2n+1}\cdot CO \\ C_nH_{2n+1}\cdot CO \end{matrix}\!>\boxed{O+\begin{matrix} H \\ H \end{matrix}}\begin{matrix} NH_2 \\ NH_2 \end{matrix} = 2C_nH_{2n+1}\cdot CONH_2 + H_2O.$$

Acid amides are also formed when the ammonium salts of the fatty acids are strongly heated, or when the sodium salts are distilled with ammonium chloride, one molecule of water being split off:

$$C_nH_{2n+1}\cdot CO|\overline{O}|\underline{NH_2}|\overline{H_2}| = C_nH_{2n+1}\cdot CONH_2 + H_2O.$$

It has already been mentioned (**86**) that when the nitriles are warmed with acids, two molecules of water are taken up, with formation of the corresponding acids. This reaction can be so carried out—for example by dissolving the nitrile in concentrated sulphuric acid—that only one molecule of water is added on. By this means, amides are obtained:

$$C_nH_{2n+1}\cdot CN + H_2O = C_nH_{2n+1}\cdot CONH_2.$$

The acid amides are therefore intermediate products in the conversion of nitriles into acids. Amides yield, on the one hand, nitriles by elimination of water, by distilling with phosphorus pentoxide for example; and on the other, the corresponding acids by addition of the elements of water, on boiling with dilute acids or alkalis.

The acid amides are also formed by the action of ammonia upon esters:

$$CH_3\cdot CO|\overline{\underline{OC_2H_5 + H}}|NH_2 = CH_3\cdot CONH_2 + C_2H_5OH.$$

The acid amides are solid, crystalline compounds, with the exception of *formamide*, $H\cdot CONH_2$, which is liquid. The lower members are soluble in water, and odourless when pure. *Acetamide*, $CH_3\cdot CONH_2$, melts at 82°, and distils at 222°. Some specimens have a strong odour suggestive of the excrement of mice, due to slight traces of impurities. The remarkably high boiling-point of this substance is worthy of notice.

There is a great difference between the behaviour of the acid amides and the amines. The bond between carbon and nitrogen in the group $-C\!\!<\!\!\begin{array}{l}O\\NH_2\end{array}$ of the amides is easily broken by boiling with acids or alkalis, which is not the case with the bond between carbon and nitrogen in the amines. Further, the basic properties of ammonia are greatly weakened by the exchange of one of its hydrogen atoms for an acid radicle; and although salts of acid amides do exist, they are decomposed by water. This is the case, for example, with acetamide hydrochloride, $CH_3\cdot CO\cdot NH_2HCl$, which is formed by passing dry hydrochloric-acid gas through an ethereal solution of acetamide. The acid amides even possess acid properties; thus, an aqueous solution of acetamide dissolves mercuric oxide, forming a compound with the formula $(CH_3\cdot CONH)_2Hg$.

The behaviour of the amides and amines towards nitrous acid is analogous, the corresponding acids and alcohols respectively being produced by exchange of NH_2 for OH (**72**).

The amides can be converted into the amines with one carbon atom less in the molecule, by treatment with bromine and caustic potash, or by distilling with bleaching-powder and slaked lime, a good method of preparing the primary amines free from the corresponding secondary and tertiary derivatives. In this way, *butyramide*, $CH_3\cdot CH_2\cdot CH_2\cdot CONH_2$, yields *propylamine*, $CH_3\cdot CH_2\cdot CH_2\cdot NH_2$. The theory of this reaction will be explained later (**244**).

105. In addition to the derivatives already described, there are others which can be obtained from the acids by substitution in the carboxyl-group, some of which are described below.

Amido-chlorides are formed by the action of phosphorus pentachloride on the acid amides:

$$R\cdot CONH_2 + PCl_5 = R\cdot CCl_2\cdot NH_2 + POCl_3.$$

These compounds are only stable when one or both of the hydrogen atoms of the amido-group, NH_2, are replaced by alkyl-radicles. They yield *imino-chlorides*, $R\cdot CCl{:}NH$, by the splitting off of one molecule of HCl; the same compounds are formed by the addition of HCl to nitriles.

Imino-ethers have the constitution $R\cdot C{<}\genfrac{}{}{0pt}{}{NH}{OR}$, derived by replacement of the doubly-linked oxygen of the carboxyl-group with the imido-group, NH. They are obtained by combination of alcohols and nitriles under the influence of dry hydrochloric-acid gas:

$$RC\equiv N + \genfrac{}{}{0pt}{}{H}{\dot{O}R} = R\cdot C{<}\genfrac{}{}{0pt}{}{NH}{OR}.$$

The imino-ethers form well-crystallized salts with hydrochloric acid, which are converted by treatment with ammonia into the hydrochlorides of the *amidines:*

$$R\cdot C{<}\genfrac{}{}{0pt}{}{NH\cdot HCl}{OC_2H_5} + NH_3 = R\cdot C{<}\genfrac{}{}{0pt}{}{NH\cdot HCl}{NH_2} + C_2H_5\cdot OH.$$

The amidines are unstable in the free state, but are strongly monobasic, and form stable salts.

Amidoximes are addition-products of the nitriles with hydroxylamine, NH_2OH:

$$R\cdot CN + H_2NOH = R\cdot C\begin{matrix}\leqslant NOH \\ < NH_2\end{matrix}.$$

They yield salts with both acids and bases, and, with an alkaline solution of a copper salt, give a flocculent, muddy-brown or green precipitate. The latter affords a characteristic test for them.

Acid hydrazides are formed by the action of hydrazine, $H_2N—NH_2$, on acid chlorides or esters, and therefore have the constitution $R\cdot CONH\cdot NH_2$. They are converted by the action of nitrous acid into *acid azides*:

$$R\cdot CONH\cdot NH_2 + HNO_2 = R\cdot CON_3 + H_2O.$$

These are volatile, explosive substances, some of which crystallize well.

ALDEHYDES AND KETONES.

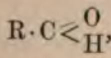
106. The aldehydes and ketones have the general formula $C_nH_{2n}O$. They are formed by the oxidation of primary and secondary alcohols respectively. Both these classes of alcohols have the general formula $C_nH_{2n+2}O$, so that the reaction in each case consists in the removal of two hydrogen atoms.

On further oxidation, the aldehydes take up one oxygen atom, forming the corresponding acids containing the same number of carbon atoms. Thus $C_nH_{2n}O$ is converted into $C_nH_{2n}O_2$, so that an aldehyde is an intermediate product in the oxidation of an alcohol to an acid:

$$\underset{\text{Primary Alcohol}}{C_nH_{2n+2}O} \longrightarrow \underset{\text{Aldehyde}}{C_nH_{2n}O} \longrightarrow \underset{\text{Acid}}{C_nH_{2n}O_2}.$$

The constitutional formula of a primary alcohol is $C_nH_{2n+1}\cdot CH_2OH$; on oxidation this yields an acid $C_nH_{2n+1}\cdot COOH$. Since the alkyl-group C_nH_{2n+1} is not altered in this reaction, it must be present in the aldehyde. Hence, it follows that the two hydrogen atoms removed from the alcohol by oxidation must come from the group $—CH_2OH$.

There still remain two possible structural formulæ,

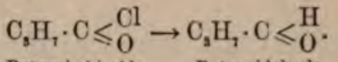


$$R\cdot C{<}^{O}_{H}, \quad \text{and} \quad R\cdot C—OH,$$

of which the second contains either a divalent carbon atom or two free linkings, which makes it very improbable that it is the correct formula (**17**). It should moreover be noticed that it contains a hydroxyl-group, whereas the aldehydes have none of the properties peculiar to substances containing this group. They do not, for example, yield esters or ethers; and phosphorus pentachloride does not replace OH by Cl, but causes the exchange of the oxygen atom for *two* chlorine atoms.

Since the second formula is not in agreement with the properties of the aldehydes, it follows that the first is the correct one.

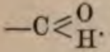
This view is supported by the fact that the aldehydes are formed when acid chlorides dissolved in moist ether are acted on with sodium, the chlorine atom being replaced by a hydrogen atom:



$$C_3H_7\cdot C\leqslant^{Cl}_{O} \rightarrow C_3H_7\cdot C\leqslant^{H}_{O}.$$

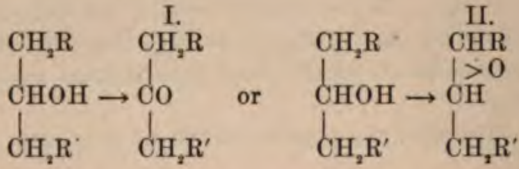
n-Butyryl chloride Butyraldehyde

The aldehydes are therefore compounds which contain the group



$$-C\leqslant^{O}_{H}.$$

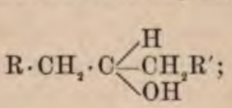
107. It was stated in **106** that the ketones are formed by the oxidation of the secondary alcohols. The ketones likewise lack the properties peculiar to hydroxyl-compounds, which proves that the hydrogen atom of the hydroxyl-group has been removed by the oxidation. Leaving out of account the possibility of the setting free of bonds, the removal of the second hydrogen atom can only take place in one of two ways—from the same carbon atom to which the oxygen is linked, or from the other carbon atom. This can be illustrated in the following way, R and R′ representing alkyl-groups:



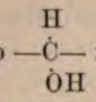
$$\begin{array}{l} CH_2R \\ | \\ CHOH \\ | \\ CH_2R' \end{array} \rightarrow \overset{\text{I.}}{\begin{array}{l} CH_2R \\ | \\ CO \\ | \\ CH_2R' \end{array}} \quad \text{or} \quad \begin{array}{l} CH_2R \\ | \\ CHOH \\ | \\ CH_2R' \end{array} \rightarrow \overset{\text{II.}}{\begin{array}{l} CHR \\ |>O \\ CH \\ | \\ CH_2R' \end{array}}$$

For reasons analogous to those stated in the case of the aldehydes, formula I is more probable than formula II. The products obtained by the oxidation of the ketones show that their constitution is in fact represented by formula I.

The general formula for a secondary alcohol is



$$R\cdot CH_2\cdot C\begin{cases} H \\ CH_2R' \\ OH \end{cases};$$

from such an alcohol two acids, $R\cdot CH_2\cdot COOH$ and $R'\cdot CH_2\cdot COOH$, are obtained by strong oxidation, the carbon chain being broken in some of the molecules to the right, and in others to the left, of the CHOH-group. A means of determining what alkyl-groups are linked to the group  $-\overset{H}{\underset{OH}{\dot{C}}}-$ in any secondary alcohol is afforded by this reaction. Since the same acids are obtained by oxidizing ketones, which are themselves produced by submitting secondary alcohols to gentle oxidation, it follows that the alkyl-groups of the secondary alcohols must exist unchanged in the ketone. Hence, such a structure as that represented by formula II is excluded, so that formula I must be the correct one.

Ketones therefore contain the group CO, called the *carbonyl-group, linked to two carbon atoms.*

Aldehydes may be looked upon as ketones in which an alkyl-group has been replaced by hydrogen.

Nomenclature.

108. The name aldehyde is derived from *al*(cohol) *dehyd*(rogenatus), that is, "alcohol from which hydrogen has been abstracted." The word ketone has its origin in the name of the first member of the series, *acetone*, $CH_3 \cdot CO \cdot CH_3$.

The aldehydes are named after the corresponding acids: *formaldehyde* $H \cdot CHO$, *acetaldehyde* $CH_3 \cdot CHO$, *propionaldehyde* $C_2H_5 \cdot CHO$, *valeraldehyde*, $C_4H_9 \cdot CHO$, etc.

The ketones derive their names from the alkyl-groups which they contain: *dimethylketone* $CH_3 \cdot CO \cdot CH_3$, *methylpropylketone* $CH_3 \cdot CO \cdot C_3H_7$, etc.

Methods of Formation.

109. There are several methods, other than the oxidation of alcohols, applicable to the preparation of both aldehydes and ketones.

1. Dry distillation of the salts of the fatty acids; calcium acetate yields acetone:

$$\begin{array}{l} CH_3 \cdot CO\boxed{Oca}^{*} \\ CH_3 \cdot \boxed{COOca} \end{array} = CH_3 \cdot CO \cdot CH_3 + CaCO_3.$$

---

[*] ca = ½Ca.

An aldehyde is produced by the distillation when an equivalent quantity of a formate is mixed with the salt of the other fatty acid:

$$\begin{array}{r|l|} \mathrm{C_3H_7\cdot CO} & \mathrm{ONa} \\ \mathrm{H} & \mathrm{COONa} \\ \end{array} = \mathrm{C_3H_7\cdot C}{<}\begin{smallmatrix}\mathrm{O}\\ \mathrm{H}\end{smallmatrix} + \mathrm{Na_2CO_3}.$$

Lastly, *mixed ketones* are obtained when a mixture of the salts of two different fatty acids, except formates, is distilled:

$$\begin{array}{r|l|} \mathrm{CH_3\cdot CO} & \mathrm{ONa} \\ \mathrm{C_2H_5\cdot} & \mathrm{COONa} \\ \end{array} = \underset{\text{Methylethylketone}}{\mathrm{CH_3\cdot CO\cdot C_2H_5}} + \mathrm{Na_2CO_3}.$$

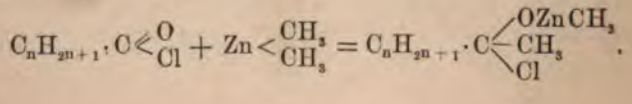
In the last two reactions the product contains the corresponding simple ketones in addition to the aldehyde or mixed ketone. Thus, in the example given above, dimethylketone and diethylketone are also formed.

Given the structure of the fatty acids, the method of formation just described could be put forward as a proof of the constitution of the aldehydes and ketones, if it were not that the reaction only takes place at high temperatures. Since under such conditions organic compounds frequently undergo changes of structure, more especially at the moment of formation, such *pyrogenetic* reactions cannot be regarded as furnishing conclusive evidence of the constitution of a compound.

2. Aldehydes or ketones can be obtained from compounds containing two halogen atoms linked to a single carbon atom, by heating them with water:

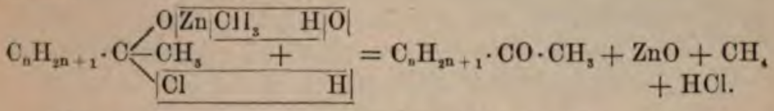
$$\underset{\text{Ethylidene chloride}}{\mathrm{CH_3\cdot CH}}\boxed{\mathrm{Cl_2 + H_2}}\mathrm{O} = \mathrm{CH_3\cdot CHO} + \mathrm{2HCl}.$$

3. An important method for the preparation of ketones, but not of aldehydes, is the interaction of acid chlorides and zinc-alkyls, or zinc alkides (**82**). When the two substances are brought together, an addition-product is first formed; this can only result through the changing of the double bond of the oxygen atom into a single one:



$$\mathrm{C_nH_{2n+1}\cdot C}{<}\begin{smallmatrix}\mathrm{O}\\ \mathrm{Cl}\end{smallmatrix} + \mathrm{Zn}{<}\begin{smallmatrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{smallmatrix} = \mathrm{C_nH_{2n+1}\cdot C}\begin{smallmatrix}\diagup\mathrm{OZnCH_3}\\ -\mathrm{CH_3}\\ \diagdown\mathrm{Cl}\end{smallmatrix}.$$

A ketone is formed when this addition-product is treated with water:

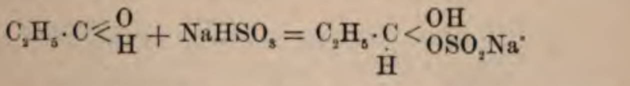


$$C_nH_{2n+1}\cdot C\left\langle\begin{array}{l} O\,|Zn|\,CH_3 \qquad H|O| \\ CH_3 \qquad\quad + \\ |Cl \qquad\qquad\quad H| \end{array}\right. = C_nH_{2n+1}\cdot CO\cdot CH_3 + ZnO + CH_4 + HCl.$$

110. Several properties common to the aldehydes and ketones depend on their *power of forming addition-products.* This power has its origin in the double bond of the oxygen atom, the conversion of which into a single bond sets free a carbon and an oxygen linking. This enables the aldehydes and ketones to form addition-products with the following elements and compounds.

1. *Hydrogen.*—An addition-product is formed by the action of sodium amalgam on an aqueous solution of the aldehydes or ketones; or, if they are insoluble, on a mixture of them with water. Primary alcohols are formed from aldehydes, and secondary from ketones.

2. *Sodium hydrogen sulphite.*—When aldehydes or ketones are shaken up with a very concentrated solution of this compound, a crystalline addition-product is obtained:



$$C_2H_5\cdot C\!<\!\begin{smallmatrix}O\\H\end{smallmatrix} + NaHSO_3 = C_2H_5\cdot\underset{H}{C}\!<\!\begin{smallmatrix}OH\\OSO_2Na\end{smallmatrix}.$$

To these compounds is assigned the constitution indicated by the above formula, because they are very easily converted by the action of dilute acids or sodium carbonate solution into the corresponding aldehydes or ketones; in the case of the higher members, mere solution in water effects this decomposition. For this reason, it is highly improbable that there is a direct bond between sulphur and carbon (**67**). The acid sulphite compounds—sometimes incorrectly called *bisulphite* compounds—dissolve readily in water, but are insoluble in very concentrated solutions of the acid sulphite itself.

The ketones do not all give these addition-products. They are most readily obtained from those containing one methyl-group directly linked to carbonyl, or methylketones.

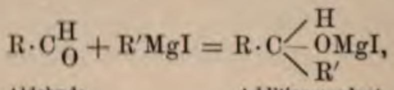
The use of acid sulphite is often exceedingly serviceable for the purification of aldehydes or ketones, or for separating them from reaction-mixtures.

3. *Hydrocyanic acid.*—When an aldehyde or ketone is brought into contact with an aqueous solution of hydrocyanic acid, combination takes place:

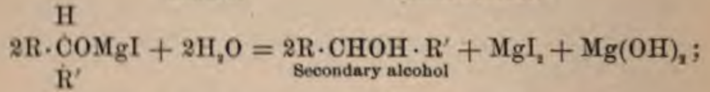
$$\begin{matrix}CH_3\\C_2H_5\end{matrix}>CO+HCN=\begin{matrix}CH_3\\C_2H_5\end{matrix}>C<\begin{matrix}OH\\CN\end{matrix}.$$

This is a very important synthesis, because the hydroxy-nitriles thus formed can be converted into hydroxy-acids by saponification. This affords a means of synthesizing compounds of the latter class (**182**, 5).

111. With GRIGNARD's alkyl magnesium halides (**82**), aldehydes and ketones form addition-products, which, on treatment with water, yield respectively secondary or tertiary alcohols:



$$\underset{\text{Aldehyde}}{R\cdot C\begin{matrix}H\\O\end{matrix}}+R'MgI=\underset{\text{Addition-product}}{R\cdot C\begin{matrix}H\\OMgI\\R'\end{matrix}},$$



$$2R\cdot\overset{H}{\underset{R'}{C}}OMgI+2H_2O=\underset{\text{Secondary alcohol}}{2R\cdot CHOH\cdot R'}+MgI_2+Mg(OH)_2;$$

$$\underset{\text{Acetone}}{\begin{matrix}CH_3\\CH_3\end{matrix}>CO}+CH_3MgBr=\underset{\text{Addition-product}}{\begin{matrix}CH_3\\CH_3\end{matrix}>C<\begin{matrix}OMgBr\\CH_3\end{matrix}},$$

$$2\begin{matrix}CH_3\\CH_3\end{matrix}>C<\begin{matrix}OMgBr\\CH_3\end{matrix}+2H_2O=\underset{\text{Trimethylcarbinol}}{2(CH_3)_3COH}+MgBr_2+Mg(OH)_2.$$

112. Other properties common to aldehydes and ketones depend upon the fact that the doubly-linked oxygen atom can be exchanged for other atoms or groups.

1. *Phosphorus pentachloride* replaces the oxygen atom by two chlorine atoms.

2. *Hydroxylamine* reacts in accordance with the following equation:

$$\begin{matrix}CH_3\\CH_3\end{matrix}>C\boxed{O+H_2}NOH\rightarrow\begin{matrix}CH_3\\CH_3\end{matrix}>C:NOH.$$

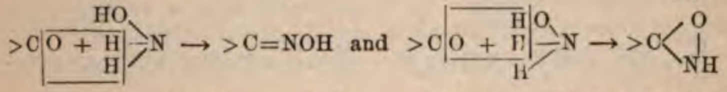
The compounds thus formed have the general name *oximes*, being called *aldoximes* when they are derived from aldehydes, and *ketoximes* when derived from ketones. This reaction is of very general application. The oximes are either crystalline compounds, or liquids, and possess both acid and basic properties. When treated with bases, the hydrogen of the hydroxyl-group is replaced by a metal; with acids, addition-products are formed, the reaction being similar to the production of ammonium salts:

$$(CH_3)_2C{=}NOH \cdot HCl.$$
Acetoxime hydrochloride

On boiling with dilute hydrochloric acid, the oximes take up one molecule of water, yielding hydroxylamine, and either an aldehyde or a ketone.

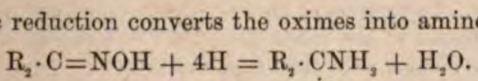
The following is a proof of the constitution given above for the oximes. There can be no doubt that when hydroxylamine acts on a ketone or an aldehyde, condensation takes place with elimination of the water formed by the union of the hydrogen of the hydroxylamine with the oxygen of the carbonyl-group, because, if the alkyl-groups took part in the reaction, the regeneration of the aldehyde or ketone would not be so readily effected. The possible structural formulæ for the oximes are therefore reduced to two:

I. II.

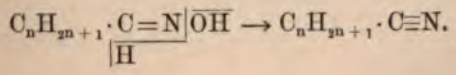


The oximes contain one hydrogen atom replaceable by an alkyl-group. When such an alkyl-oxime is boiled with hydrochloric acid, there is formed, in addition to the aldehyde or ketone, an alkyl-hydroxylamine. This has the constitution $H_2N \cdot O \cdot R'$, because on heating it with hydriodic acid, the alkyl-group is split off with formation of an alkyl iodide, a reaction which could not take place if the alkyl-group were directly linked to the nitrogen atom; since, if this were the case, an alkyl-amine would of necessity be formed. Formula II is therefore excluded, as replacement of the hydrogen atom in its NOH-group indicates the formation of a compound containing an alkyl-group directly linked to a nitrogen atom.

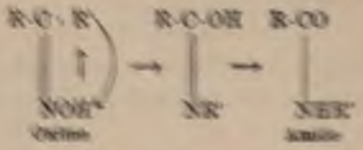
Energetic reduction converts the oximes into amines:


$$R_2 \cdot C{=}NOH + 4H = R_2 \cdot \underset{H}{C}NH_2 + H_2O.$$

The aldoximes are readily transformed into the corresponding nitriles by the action of dehydrating-agents, such as acetic anhydride:


$$C_nH_{2n+1} \cdot C{=}\underset{H}{N}\,\overline{OH} \rightarrow C_nH_{2n+1} \cdot C{\equiv}N.$$

Ketoximes undergo a very peculiar rearrangement of the atoms in the molecule, an *intramolecular transformation*, called, after its discoverer, "BECKMANN's transformation." This takes place, for example, on the addition of acetyl chloride. The ketoximes thus yield acid amides, with substituting-groups linked to the nitrogen atoms:



In accordance with the above formula, this reaction may be looked upon as due to the exchange of the hydroxyl-group of the oxime for an alkyl-group of the ketone-residue. The unstable product which is assumed to be first formed changes into the amide, the hydrogen atom of the OH-group becoming linked to the nitrogen atom.

Aldehydes and ketones react with *phenylhydrazine*, $C_6H_5NH \cdot NH_2$ (305), in a manner exactly analogous to their behaviour with hydroxylamine:

$$\frac{R}{R'}{>}C\boxed{O + H_2}N\cdot \underbrace{NH\cdot C_6H_5}_{\text{Phenylhydrazine}} = \underbrace{\frac{R}{R'}{>}C{=}N\cdot NH\cdot C_6H_5}_{\text{Phenylhydrazone}} + H_2O.$$

The substances formed, called *hydrazones*, are either well-defined crystalline compounds, or liquids. When heated with hydrochloric acid, they take up the elements of water, forming phenylhydrazine and the corresponding aldehyde or ketone. Phenylhydrazine and hydroxylamine are important reagents for detecting the presence of a carbonyl-group in a compound, because only substances containing this group react with them.

The constitution of the phenylhydrazones is established in the following way. Derivatives of phenylhydrazine obtained by replacement of the hydrogen of the imido-group, —NH, by an alkyl-group, react in the same manner with aldehydes and ketones. Thus the structure $R_2C{<}\begin{matrix}NH\\N\cdot C_6H_5\end{matrix}$ is excluded. This is rendered even more evident by the fact that only phenylhydrazines which contain an unsubstituted amido-group are capable of forming hydrazones.

ALDEHYDES.

113. In addition to those mentioned above (**110** to **112**), which they share with ketones, aldehydes possess the following properties peculiar to themselves.

1. They form addition-products with ammonia. Thus, acetaldehyde-ammonia is produced when ammonia reacts with acetaldehyde:

$$\underset{\text{Acetaldehyde}}{C_2H_4O} + NH_3 = \underset{\text{Acetaldehyde-ammonia}}{C_2H_4ONH_3}.$$

It is precipitated in the form of white crystals when dry ammonia-gas is passed into a solution of acetaldehyde in carefully dried ether, and is very soluble in water. Acids decompose the aldehyde-ammonia compounds into their components; caustic potash is unable to effect this decomposition.

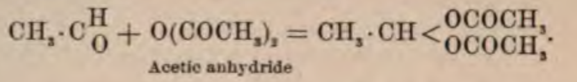
> The molecular formula of acetaldehyde-ammonia at ordinary temperatures is three times that of its empirical formula. When dried over sulphuric acid, it loses water easily, being converted into $(CH_3\cdot CHNH)_3$, which is a polymer of ethylidene-imine.

2. Reaction with alcohols. Aldehydes are capable of combination with two molecules of alcohols, with elimination of water:

$$CH_3\cdot C\begin{matrix}H|\\ \underline{|O}\end{matrix} + \begin{matrix}\overline{H}|OC_2H_5\\ \underline{H}|OC_2H_5\end{matrix} \rightleftarrows CH_3\cdot \underset{H}{C}<\begin{matrix}OC_2H_5\\ OC_2H_5\end{matrix} + H_2O.$$

These compounds are called *acetals*. They are readily formed by the addition of the aldehyde to a 1% solution of anhydrous HCl in alcohol. This reaction is not complete; it is limited by the reverse one, since water, acting on acetal, causes the formation of aldehyde and alcohol. Both formation and decomposition of acetal are considerably accelerated by the presence of a small quantity of a strong mineral acid, which acts here as a powerful catalytic agent. The acetals are liquids of aromatic odour, and distil without decomposition. They are not attacked by alkalis, but are split up by acids into the compounds from which they were produced. This latter property further establishes the structure given above, according to which the alkyl-groups are linked to the aldehyde-residue by means of oxygen, since a carbon bond could not usually be broken in this manner.

3. Addition-products are obtained with acid anhydrides:



$$CH_3\cdot C\begin{smallmatrix}H\\O\end{smallmatrix} + \underset{\text{Acetic anhydride}}{O(COCH_3)_2} = CH_3\cdot CH<\begin{smallmatrix}OCOCH_3\\OCOCH_3\end{smallmatrix}.$$

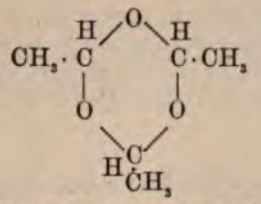
These compounds, which are analogous to the acetals, are easily decomposed by water, and still more easily by alkalis, into the corresponding acid and aldehyde.

114. The aldehydes further possess the power of combining with themselves. This takes place in two ways. When a few drops of concentrated sulphuric acid are added to acetaldehyde, a liquid boiling at 22°, it is observed that the mixture becomes warm, and even begins to boil violently. At the end of the reaction a colourless liquid is obtained, similar to the original one, but boiling about 100° higher, at 124°. The empirical formula of this compound is the same as that of aldehyde itself, C_2H_4O, but its vapour density is three times as great, so that it has the molecular formula $C_6H_{12}O_3$. This compound, *paraldehyde*, is readily converted into ordinary aldehyde by distillation with dilute sulphuric acid. This is another example of a reaction limited by the reverse one:

$$C_6H_{12}O_3 \rightleftarrows 3C_2H_4O.$$

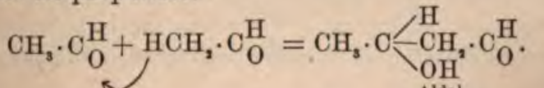
The equilibrium reached must be independent of the nature of the acid, that is, of the catalytic agent ("Inorganic Chemistry," **49**). This has been proved by experiment in this case. The same state of equilibrium must be reached without the aid of any catalytic agent, but the reaction then proceeds so slowly that it has not yet been possible to prove this experimentally. A direct linkage between the carbon atoms of the three aldehyde molecules which have united to form paraldehyde is improbable, but a linkage through the oxygen atoms must be assumed, because it accounts for the ease with which the molecule of paraldehyde can be split up. It is not attacked by sodium, and therefore cannot contain hydroxyl-groups. All the characteristics peculiar to aldehydes are wanting, showing that paraldehyde does not contain the group $-C\lessgtr\begin{smallmatrix}O\\H\end{smallmatrix}$.

The following constitutional formula best expresses these properties:



The linking together of two or more molecules of a substance, with formation of a body from which the original compound may be regenerated, is called *polymerization*.

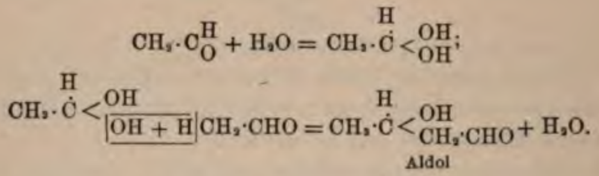
115. The union of the aldehyde molecules among themselves takes place in a different way when a dilute solution of an alkali is added to an aldehyde. When an aqueous solution of acetaldehyde is warmed with caustic potash, the liquid becomes yellow; after a short time, reddish-yellow, amorphous masses are precipitated. The aldehyde has *resinified*, and the reddish-yellow substance formed is called *aldehyde-resin*. When, however, dilute caustic potash (or sodium acetate, zinc chloride, etc.) is added to acetaldehyde, a substance is formed having the same empirical composition as acetaldehyde, but with double the molecular formula, $C_4H_8O_2$. This compound is called *aldol*; it is a liquid, distilling without decomposition under diminished pressure, and readily undergoing polymerization. It possesses the properties peculiar to the aldehydes, yielding on oxidation, for example, an acid with the same number of carbon atoms. The acid so obtained has the formula $C_4H_8O_3$, and on investigation proves to be an *n*-hydroxybutyric acid, that is, *n*-butyric acid in which one of the H-atoms of the alkyl-group has been replaced by hydroxyl. It can be converted into butyric acid, which contains a chain of four carbon atoms, proving the presence of such a chain in aldol. In this case, the linking together of the aldehyde molecules has been effected through the carbon bonds, a further proof of which is that aldol cannot be reconverted into aldehyde. The following equation represents the linking together of the aldehyde molecules to form aldol, the formula given for which accounts for its properties:



$$CH_3 \cdot C\genfrac{}{}{0pt}{}{H}{O} + HCH_2 \cdot C\genfrac{}{}{0pt}{}{H}{O} = CH_3 \cdot C\left\langle\begin{matrix} H \\ CH_2 \cdot C\genfrac{}{}{0pt}{}{H}{O} \\ OH \end{matrix}\right. .$$

Aldol

In addition to the above explanation of the formation of aldol by the combination of one of the hydrogen atoms of one aldehyde molecule with the oxygen atom of another to form hydroxyl, it might be explained by assuming that an aldehyde molecule united with a molecule of water, forming an addition-product which reacts with a second molecule of aldehyde with elimination of water:



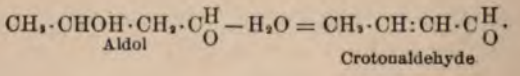
$$CH_3\cdot C^{H}_{O} + H_2O = CH_3\cdot \overset{H}{\dot{C}} < \begin{matrix}OH\\OH\end{matrix};$$

$$CH_3\cdot \overset{H}{\dot{C}} < \begin{matrix}OH\\ \boxed{OH + H}\end{matrix} CH_2\cdot CHO = \underset{\text{Aldol}}{CH_3\cdot \overset{H}{\dot{C}} < \begin{matrix}OH\\ CH_2\cdot CHO\end{matrix}} + H_2O.$$

The formation of such an addition-product with subsequent elimination of the water, is frequently assumed to take place, this assumption often affording an explanation of the course of reactions. This has been experimentally verified in a few cases.

Aldol is both an alcohol and an aldehyde, hence its name, *ald*(ehyde-alcoh)*ol*. The linking together of molecules through carbon bonds, as in the formation of aldol, with the production of compounds from which the original substance cannot be regenerated by any simple method. is called *condensation.*

It is probable that aldehyde-resin is a product resulting from continued condensation of the aldol molecules with elimination of water, just as aldol itself easily loses one molecule of water when heated, with formation of crotonaldehyde:



$$\underset{\text{Aldol}}{CH_3\cdot CHOH\cdot CH_2\cdot C^{H}_{O}} - H_2O = \underset{\text{Crotonaldehyde}}{CH_3\cdot CH:CH\cdot C^{H}_{O}}.$$

Tests for Aldehydes.

116. The following tests are used for the detection of aldehydes.

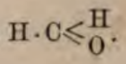
1. Resinification with alkalis.

2. Reduction of an ammoniacal silver solution. This solution is prepared by adding excess of caustic potash to a solution of silver nitrate, and then ammonia carefully until the silver oxide precipitated is just dissolved. When this liquid is brought into a dilute aqueous solution of an aldehyde, and the mixture warmed,

metallic silver is deposited on the sides of the tube in the form of a beautiful metallic mirror.

3. When aldehyde is added to a solution of magenta which has been decolourized with sulphurous acid, the red colour is restored by the formation of condensation-products.

Formaldehyde, $H \cdot C \lessgtr \begin{smallmatrix} H \\ O \end{smallmatrix}$.



$H \cdot C{<}\begin{smallmatrix} H \\ O \end{smallmatrix}$

117. It was mentioned in **88** that formic acid, the first member of the homologous series of fatty acids, has certain properties not possessed by the higher members. Formaldehyde affords a striking example of this phenomenon of disparity between the first and succeeding members in a homologous series.

Formaldehyde is obtained by the oxidation of methyl alcohol. This is effected by passing a mixture of air and methyl alcohol vapour over a hot spiral of platinum or copper. The heat produced by this reaction is sufficient to raise the temperature of the spiral to redness, and to maintain it at this point, provided the stream of gas is passed over it with sufficient velocity. The formaldehyde produced is absorbed in water in which it is readily soluble.

Formaldehyde is gaseous at ordinary temperatures. It has a very pungent odour. When cooled with solid carbon dioxide and ether, it liquefies, its boiling-point being − 20°. Even at this temperature polymerization begins, and at higher temperatures it polymerizes with explosive energy. When the aqueous solution is evaporated over concentrated sulphuric acid, only part of the formaldehyde is evolved as gas; the rest polymerizes, and remains behind in the form of a white, crystalline mass, called *oxymethylene*. The molecular weight of this polymer is not known, but on heating, it is reconverted into formaldehyde, which proves it to be a true polymer. Formaldehyde does not yield an aldehyde-ammonia on treatment with ammonia, but a complicated compound, $C_6H_{12}N_4$, *hexamethyleneamine*, a crystalline, basic substance. Formaldehyde does not resinify when treated with caustic potash, but is converted into methyl alcohol and formic acid:

$$2CH_2O + H_2O = CH_3OH + HCOOH.$$

The *oxime of formaldehyde* also readily undergoes polymerization. It is thus seen that formaldehyde and its derivatives display a much greater tendency towards polymerization than do the other aldehydes, and differ from them in their behaviour with ammonia and with caustic potash.

An aqueous solution containing 40% of formaldehyde is sold under the name "formalin." When diluted, this is used as a disinfectant, and in the preservation of anatomical specimens. It possesses the remarkable property of converting albuminous substances into a hard, elastic mass, quite insoluble in water. The contents of a hen's egg, for example, undergo this transformation when left in contact with formalin for half-an-hour; brain-substance attains the consistency of india-rubber, and a solution of gelatine is converted into a hard, transparent, insoluble, odourless mass, reducible to a fine powder, 25 drops being used for every 500 g. of dissolved gelatine.

The concentration of a formalin solution is determined by adding excess of a solution of sodium hydroxide of twice the normal strength, followed by hydrogen peroxide, which converts the formaldehyde completely into formic acid. The amount of alkali not taken up by this acid is estimated by titration, from the result of which the amount of formaldehyde can be calculated, since one molecule of the aldehyde yields one molecule of the acid.

Acetaldehyde, $CH_3 \cdot C \lesssim^{H}_{O}$.

118. Acetaldehyde may be regarded as the typical aldehyde of this series. It possesses the properties given above as general for this class of compounds. It is obtained by the oxidation of ethyl alcohol by means of potassium bichromate and sulphuric acid, and is a liquid with a disagreeable odour, at least in a dilute state; it boils at 22°, and solidifies at −120·6°. As already stated (**114**), it easily undergoes polymerization with formation of paraldehyde, $C_6H_{12}O_3$. Another compound having the formula $C_6H_{12}O_3$ also exists, called *metaldehyde;* it is a crystalline product, and must be likewise a polymer, since heating reconverts it into ordinary aldehyde. As in the case of paraldehyde, it does not give the ordinary aldehyde reactions; for example, it is not resinified by alkalis. Paraldehyde and metaldehyde are possibly stereoisomers.

KETONES.

119. The general properties of the ketones have been already mentioned (**110** to **112**). The first member of this homologous series cannot contain less than three carbon atoms.

Experience has shown that ketones, which may be represented by the general formula $R\cdot CO\cdot R'$, are always split up at the carbonyl-group on oxidation (**107**); that is, oxidation occurs at that point in the molecule at which oxygen is already present (**49**). This decomposition can, however, take place in two different ways:

$$R\cdot|CO\cdot R' \quad \text{or} \quad R\cdot CO\cdot|R'.$$

Methylnonylketone, $CH_3\cdot\underset{\mathrm{I}}{|}CO\cdot\underset{\mathrm{II}}{|}C_9H_{19}$, for example, can yield formic acid, CH_2O_2, and capric acid, $C_{10}H_{20}O_2$; or acetic acid, $C_2H_4O_2$, and pelargonic acid, $C_9H_{18}O_2$; according as the decomposition take splace at the points indicated by the lines I and II respectively. The oxidation is actually such that the decomposition takes place at both points simultaneously, so that four acids are obtained. Two of these may be identical; for example, the oxidation of methylethylketone, $CH_3\cdot CO\cdot C_2H_5$, produces acetic and acetic acid by decomposition at one point of the molecule, while if it takes place at the other point, formic and propionic acids are produced. In the majority of cases, one of these reactions predominates, usually that one which leaves the carbonyl linked to the smallest alkyl-residue. The oxidation of the ketones therefore affords a means of determining the position which the carbonyl-group occupies in the molecule.

The ketones are further distinguished from the aldehydes by their behaviour towards ammonia; this has been carefully investigated in the case of acetone, the first member of the series. By elimination of water it yields complicated substances, such as *diacetoneamine*, $C_6H_{13}NO$ $(2C_3H_6O + NH_3 - H_2O)$, *triacetoneamine*, $C_9H_{17}NO$ $(3C_3H_6O + NH_3 - 2H_2O)$, etc.

The ketones do not yield polymers, but are capable of forming condensation-products.

Acetone, $CH_3 \cdot CO \cdot CH_3$.

120. Acetone is prepared on the manufacturing scale from crude wood-spirit (**46**), and by the dry distillation of calcium acetate. It is present in very small quantities in normal urine, but in much greater amount as a result of pathological conditions, as in cases of *diabetes mellitus* and *acetonuria*. It is a liquid of peculiar, peppermint-like odour, boils at 56·3°, solidifies at − 94·9°, and has a specific gravity of 0·812 at 0°. It is an excellent solvent for many organic compounds, and is miscible in all proportions with water. It is converted by reduction into isopropyl alcohol, and yields a crystalline oxime melting at 69°.

Sulphonal, a compound important in medicine as a soporific, is prepared from acetone. In presence of hydrochloric acid, acetone unites with ethylmercaptan with elimination of water:

$$(CH_3)_2CO + 2HS \cdot C_2H_5 = \underset{\substack{\text{Dimethyldiethyl-}\\\text{mercaptole}}}{(CH_3)_2C(SC_2H_5)_2} + H_2O$$

Oxidation with potassium permanganate converts the two sulphur atoms of this compound into SO_2-groups, forming diethylsulphonedimethylmethane, $(CH_3)_2C(SO_2C_2H_5)_2$, or sulphonal. It crystallizes in colourless prisms, which dissolve with difficulty in cold water, and melt at 126°.

Thioaldehydes and Thioketones.

121. These are compounds containing sulphur in place of the oxygen of the aldehydes and ketones. Thioacetaldehyde is not itself known, but its polymer, *trithioacetaldehyde*, $C_6H_{12}S_3$, is obtained by leading sulphuretted hydrogen into acetaldehyde in presence of hydrochloric acid. Oxidation converts it into a trisulphone (**67**), each sulphur atom being oxidized to an SO_2-group.

Although acetone itself does not undergo polymerization, replacement of its oxygen atom by a sulphur atom confers this property on it in a high degree. This polymerization can be effected by the methods applied to aldehydes. Three molecules become linked together, forming *trithioacetone*, $C_9H_{18}S_3$.

UNSATURATED HYDROCARBONS.

I. ALKYLENES OR OLEFINES, C_nH_{2n}.

Methods of Formation.

122. 1. The *olefines* are obtained in the dry distillation of complicated carbon compounds, which accounts for their presence to the extent of 4–5% in coal-gas.

2. By elimination of the elements of water from the alcohols $C_nH_{2n+2}O$:

$$C_5H_{11}\cdot OH = C_5H_{10} + H_2O.$$

This can sometimes be brought about by mere heating, as in the case of tertiary alcohols, but it is usually necessary to heat the alcohol with a dehydrating-agent, such as concentrated sulphuric acid or zinc chloride. The elimination of water from the secondary and tertiary alcohols is more easily effected than from the corresponding primary compounds.

3. By splitting off a haloid acid from alkyl halides. This is carried out by heating the latter with alcoholic potash, a solution of caustic potash in alcohol:

$$C_nH_{2n+1}I + KOC_2H_5 = C_nH_{2n} + KI + C_2H_5OH.$$

Ether is formed at the same time (**62**):

$$C_nH_{2n+1}I + KOC_2H_5 = C_nH_{2n+1}OC_2H_5 + KI.$$

When alkyl iodides are used, the reaction takes place chiefly in accordance with the first of these two equations, the secondary and tertiary iodides being specially suited for the production of unsaturated hydrocarbons.

Name.	Formula.	Boiling-point.	Name.	Formula.	Boiling-point.
Ethylene......	C_2H_4	− 103°	Heptylene....	C_7H_{14}	98°
Propylene	C_3H_6		Octylene......	C_8H_{16}	124°
n-Butylene....	$CH_2:CH \cdot C_2H_5$	− 5°	Nonylene	C_9H_{18}	153°
n-Amylene....	C_5H_{10}	35°	Decylene.....	$C_{10}H_{20}$	172°
Hexylene....	C_6H_{12}	68°	Undecylene...	$C_{11}H_{22}$	195°

The names of the members of this series are derived from those of the saturated hydrocarbons by altering the termination "ane" to "ylene." These compounds are denoted by the general name *alkylenes* or *olefines*.

In order to indicate the position of the double linking in the molecule, the alkylenes are sometimes regarded as substituted ethylenes; thus, $CH_3 \cdot CH : CH \cdot CH_3$ is called *symmetrical dimethylethylene*, and $(CH_3)_2C : CH_2$, *asymmetrical dimethylethylene*.

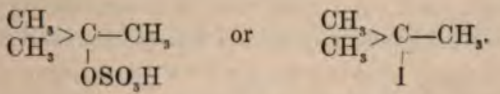
Properties.

123. The lowest members of this homologous series are gases, and are slightly soluble in water; the higher members are liquids or solids, insoluble in water, but soluble in alcohol and ether. At their melting-points the specific gravities of the lower members are about 0·63, rising with increase in the number of carbon atoms to about 0·79.

Their most important chemical property is the power of forming addition-products, on account of which they are said to be *unsaturated*. Addition-products are very readily obtained by the action of the halogens, especially bromine, on the olefines, and in general on substances containing a double bond, the presence of which can be detected by their power of decolourizing bromine-water. Another test for the presence of a double linking, suggested by BAEYER, is carried out by shaking the substance with a dilute solution of potassium permanganate and sodium carbonate. Owing to reduction in presence of a double carbon bond, the violet colour of the permanganate quickly disappears, with formation of a brown-red, flocculent precipitate of a hydrate of manganese dioxide. Various classes of compounds, for example aldehydes, react similarly with potassium permanganate, so that the test can only be applied, when they are absent, to hydrocarbons, unsaturated acids, and a few other substances.

The haloid acids react by addition with the olefines to form the alkyl halides. Hydriodic acid combines in this way very readily.

Concentrated sulphuric acid yields the alkyl-sulphuric acids by addition, it being sometimes necessary to employ the fuming acid. The addition of sulphuric acid, like that of the haloid acids, results in the union of the acid-residue with the unsaturated carbon atom linked to the smallest amount of hydrogen. For example, isobutylene, $\begin{matrix}CH_3\\CH_3\end{matrix}{>}C:CH_2$, treated with sulphuric or hydriodic acid yields



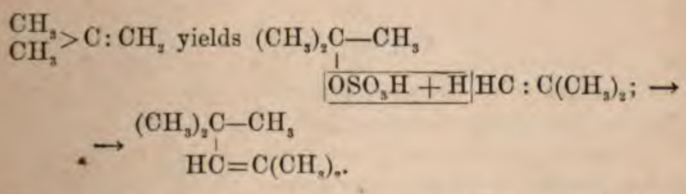
$$\begin{matrix}CH_3\\CH_3\end{matrix}{>}\underset{\displaystyle OSO_3H}{\overset{}{C}}{-}CH_3 \quad \text{or} \quad \begin{matrix}CH_3\\CH_3\end{matrix}{>}\underset{\displaystyle I}{C}{-}CH_3.$$

This reaction may be expressed in another way by stating that there is a tendency on the part of the methyl-groups to increase in number in addition-reactions of this kind.

Hypochlorous acid, Cl·OH, can also form addition-products, which are chlorinated alcohols:

$$\underset{\text{Ethylene}}{CH_2 = CH_2} + ClOH = \underset{\text{Glycolchlorhydrin}}{CH_2Cl\cdot CH_2OH.}$$

124. Olefines can also form condensation-products; for example, butylene and the amylenes yield them on treatment with moderately dilute sulphuric acid, although ethylene cannot be similarly condensed. The condensation may be explained by assuming that an addition-product with sulphuric acid, an alkyl-sulphuric acid, is first formed, which then reacts with a second molecule of the olefine:



$$\begin{matrix}CH_3\\CH_3\end{matrix}{>}C:CH_2 \text{ yields } (CH_3)_2\underset{\displaystyle \boxed{OSO_3H + H}HC:C(CH_3)_2;}{C}{-}CH_3 \rightarrow$$

$$\rightarrow \begin{matrix}(CH_3)_2C{-}CH_3\\ |\\ HC{=}C(CH_3)_2.\end{matrix}$$

The simplest member of this series, CH_2, *methylene*, has not been obtained. Various attempts have been made to prepare it:

for instance, by the removal of HCl from methyl chloride: these have always resulted in the formation, not of methylene, but of ethylene, two CH_2-groups uniting to form a single molecule.

Ethylene, C_2H_4.

125. Ethylene is a gas, and is usually prepared by heating a mixture of alcohol and sulphuric acid. Ethylsulphuric acid is first formed (**60**), and decomposes on further heating into ethylene and sulphuric acid:

$$C_2H_5SO_4H = C_2H_4 + H_2SO_4.$$

In the preparation of ether the temperature is not allowed to rise above a certain limit, and fresh alcohol is continually added, but in this reaction a higher temperature is employed, and no alcohol is added. As a result of this stronger heating, sulphur dioxide and carbon dioxide are produced, and are removed from the ethylene by washing it with dilute alkali. A purer product is obtained by dropping ethyl alcohol on phosphoric acid, heated to 200°, and subsequently raising the temperature to 220°.

Ethylene can also be readily prepared from ethylene bromide, $C_2H_4Br_2$, by removal of its two bromine atoms. This is effected by bringing it into contact with a copper-zinc couple (**29**).

Ethylene possesses a peculiar, sweetish odour, and burns with a luminous flame. It is slightly soluble in water and in alcohol. When passed into bromine it is quickly converted into ethylene bromide, $C_2H_4Br_2$. It is readily absorbed by concentrated sulphuric acid at 170°, with formation of ethylsulphuric acid. It is a remarkable fact, discovered by SABATIER, that a mixture of hydrogen and ethylene is changed completely into ethane when passed over finely-divided nickel, at temperatures of less than 300° (**29** and **133**).

Amylenes, C_5H_{10}.

126. A mixture of isomeric amylenes, together with pentane, is technically prepared by heating fusel oil (**47**) with zinc chloride.

The isomeric amylenes can be separated by two methods, which are also applicable in other similar cases. One of these is based on the solubility of some of them in a mixture of equal volumes of water and concentrated sulphuric acid at a low temperature, whereby amylsulphuric acid is formed, whereas the others are insoluble. This treatment, however, converts a part of the amylenes into condensation-products, called *diamylene* and *triamylene*. The other method of separation depends upon the different velocities with which the isomeric amylenes form addition-products with hydriodic acid.

The Nature of the Double Carbon Bond.

127. In the foregoing, the presence of a double carbon bond in the alkylenes has been arbitrarily assumed, although the linkage in unsaturated compounds can be represented in a variety of ways, which may be summarized as follows:

1. *Existence of divalent or trivalent carbon atoms:*

$$\mathrm{CH_3{-}\overset{II}{C}{-}CH_3}, \qquad \mathrm{\overset{III}{C}H_2{-}\overset{III}{C}H{-}CH_3}.$$

2. *Existence of free bonds,* for which there are two possibilities:

   a. Free bonds only on one carbon atom:

$$\mathrm{CH_3{-}\underset{\vdots\,\vdots}{C}{-}CH_3}.$$

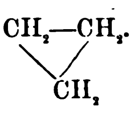
   b. Free bonds on different carbon atoms:

$$\mathrm{\underset{|}{C}H_2{-}\underset{|}{C}H{-}CH_3}.$$

3. *Existence of double carbon bond:*

$$\mathrm{CH_3{-}CH{=}CH_2}.$$

4. *Existence of a closed chain:*

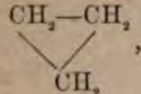


It was stated in **123** that unsaturated compounds are convertible into saturated compounds by addition of atoms or groups. The constitution of these addition-products, on the one hand, and the method of formation of the unsaturated products obtained by the splitting off of a haloid acid, etc., from the saturated compounds, on the other, allow a decision to be arrived at between these four possibilities.

It should be observed that the addition-product is the same, whether the existence of a divalent carbon atom, or of two free bonds on the same carbon atom, be assumed. For example, whether propylene be supposed to have the constitution $CH_3\cdot\overset{II}{C}\cdot CH_3$ or $CH_3\cdot\underset{\|}{C}\cdot CH_3$, the addition of bromine produces the same substance, $CH_3\cdot CBr_2\cdot CH_3$. Similarly, the assumption of trivalent carbon atoms, or of free bonds on different carbon atoms, leads to the same result; thus $\overset{III}{C}H_2\cdot\overset{III}{C}H_2$ with two trivalent carbon atoms, and $\underset{|}{C}H_2\cdot\underset{|}{C}H_2$, with free bonds, must yield the same addition-product with bromine, $CH_2Br\cdot CH_2Br$. It follows that for the present it is unnecessary to treat cases 1 and 2 separately.

It is easy to show that addition does not take place at one carbon atom alone of unsaturated compounds; for if this were so, ethylene chloride, $C_2H_4Cl_2$, would have the constitution $CH_3\cdot CHCl_2$, and ethylene itself, $CH_3\cdot CH$. Ethylene chloride would then be identical with the product obtained by the action of phosphorus pentachloride upon aldehyde, $CH_3\cdot CHO$, since the exchange of the oxygen atom in the latter for two chlorine atoms yields a compound of the formula $CH_3\cdot CHCl_2$. But ethylene chloride is different from the compound $C_2H_4Cl_2$ (*ethylidene chloride*) obtained from aldehyde. Similarly, propylene chloride, $C_3H_6Cl_2$, obtained by the addition of chlorine to propylene, is not identical with the reaction-product obtained by treating acetone with phosphorus pentachloride, $CH_3\cdot CCl_2\cdot CH_3$ (*chloroacetone*), nor with that from propionaldehyde, $CH_3\cdot CH_2\cdot CHCl_2$ (*propylidene chloride*). Ethylene therefore cannot have either the formula $CH_3\cdot\overset{\|}{C}H$ or $CH_3\cdot\overset{II}{C}H$, nor propylene any of the formulæ $CH_3\cdot\underset{\|}{C}\cdot CH_3$, $CH_3\cdot CH_2\cdot\underset{\|}{C}H$, $CH_3\cdot\overset{II}{C}\cdot CH_3$, or $CH_3\cdot CH_2\cdot\overset{II}{C}H$.

A further insight into the structure of the unsaturated compounds is derived from a consideration of the following facts. Propylene is obtained by the elimination of HI from *n*-propyl iodide, $CH_3\cdot CH_2\cdot CH_2I$. The same compound is obtained by the removal of HI from isopropyl iodide, $CH_3\cdot CHI\cdot CH_3$. Hence, it follows that propylene cannot have either the formula $\underset{|}{C}H_2\cdot CH_2\cdot\underset{|}{C}H_2$

or , and therefore the remaining possibilities are

$CH_3\cdot\underset{|}{C}H\cdot\underset{|}{C}H_2$, $CH_3\cdot\overset{III}{C}H\cdot\overset{III}{C}H_2$, and $CH_3\cdot CH:CH_2$.

Isobutylene, C_4H_8, is similarly obtained by the elimination of HI from both *isobutyl iodide*, $(CH_3)_2C\boxed{H}\overline{CH_2}\boxed{I}$, and *trimethylcarbinol iodide*, $(CH_3)_2C\boxed{I}\underline{\cdot CH_2}\boxed{H}$. Thus, isobutylene can only have one of the formulæ $(CH_3)_2\underset{|}{C}\cdot\underset{|}{C}H_2$, $(CH_3)_2\overset{III}{C}\cdot\overset{III}{C}H_2$, and $(CH_3)_2C:CH_2$. These two examples show that *the removal of haloid acid from an alkyl halide takes place in such a way that the halogen atom and the hydrogen atom respectively split off from two carbon atoms which are directly linked to each other.*

The following examples will serve to further illustrate this general rule. If HI be removed from pentyl iodide, $\begin{matrix}CH_3\\C_2H_5\end{matrix}>CH\cdot CH_2I$, the *amylene*, C_5H_{10}, thus formed should, in accordance with the rule, have the constitution $\begin{matrix}CH_3\\C_2H_5\end{matrix}>\underset{|}{C}\cdot\underset{|}{C}H_2$. This is in fact the case, because the addition-product obtained by the action of hydriodic acid on this amylene is not the original pentyl iodide, but one with the formula $\begin{matrix}CH_3\\C_2H_5\end{matrix}>CI\cdot CH_3$; this is proved by replacement of I by OH, and comparison of the tertiary alcohol thus obtained with that having the same formula prepared in accordance with the method of synthesis described in **111**.

The constitution of another pentyl iodide, $(CH_3)_2CH\cdot CH_2\cdot CH_2I$, which yields C_5H_{10} on elimination of HI, may be similarly established. This amylene yields with HI another pentyl iodide, $(CH_3)_2CH\cdot CHI\cdot CH_3$, the constitution of which is proved by its conversion into an alcohol which yields a ketone on oxidation, and is therefore a secondary alcohol.

BUTLEROW has shown that the splitting off of a haloid acid cannot take place when the halogen atom and hydrogen atom are not linked to carbon atoms in juxtaposition to one another. He started from isobutylene, $(CH_3)_2C:CH_2$, which yields, by addition of two bromine atoms, $(CH_3)_2CBr\cdot CH_2Br$. Elimination of HBr from this dibromide produces $(CH_3)_2C:CHBr$, the constitution of which follows from its conversion into acetone by oxidation:

$$(CH_3)_2C\,|\!:CHBr \longrightarrow (CH_3)_2CO.$$

It has not been found possible to again split off HBr from the compound $(CH_3)_2C:CHBr$, *monobromobutylene*, in which there is no hydrogen linked to the carbon atom directly connected to the CHBr-group.

128. It is seen from the foregoing that only three possible constitutional formulæ remain for the unsaturated hydrocarbons.

1. Two free bonds on two carbon atoms directly linked to one another: $R\cdot \underset{|}{C}H\cdot \underset{|}{C}H\cdot R'$.

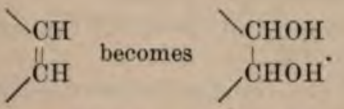
2. Trivalent carbon atoms directly linked to one another: $R\cdot \overset{III}{C}H\cdot \overset{III}{C}H\cdot R'$.

3. A double bond between two carbon atoms: $R\cdot CH : CH\cdot R'$.

The preference is given to the formula with the double bond for the following reasons. In the first place, it would be remarkable if free bonds or trivalent carbon atoms could only occur in juxtaposition to one another, that is, if carbon atoms which are not directly linked together could not have free bonds, or be trivalent. Second, experience has shown that unsaturated compounds containing an uneven number of free bonds or trivalent carbon atoms do not exist. Next to the saturated hydrocarbons C_nH_{2n+2}, come in order of the number of their hydrogen atoms, C_nH_{2n}, C_nH_{2n-2}, etc. Hydrocarbons, C_nH_{2n+1}, C_nH_{2n-1}, etc., in which one or three free bonds, or trivalent carbon atoms, could be supposed to be present, do not exist, all attempts to isolate methyl CH_3, ethyl C_2H_5, etc., having totally failed. Thus no support is to be found here for the assumption of either free bonds or of trivalent carbon atoms. On the other hand, both facts admit of a perfectly natural explanation when the existence of a double linking is assumed, since in this case the elimination of haloid acid must take place from the carbon atoms directly linked to one another, and compounds such as C_nH_{2n+1} could not occur. The assumption of the double bond is therefore the only one capable of giving expression to the observed facts.

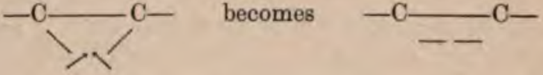
The non-existence of free bonds in the unsaturated hydrocarbons has led by analogy to the conclusion that they are also absent from other compounds containing atoms doubly linked, trebly linked, etc., such as nitrogen in the nitriles, oxygen in the ketones, etc.

129. The assumption of the existence of multiple bonds presents at first sight, however, certain difficulties when the power of forming addition-products possessed by all such compounds is considered. It has been stated several times that carbon bonds are only broken with difficulty (**40**), but in this case the double carbon bond is very easily converted into a single one by formation of an addition-product. It is still more remarkable that when a substance containing a double bond in its carbon chain is oxidized, the chain should always be broken at the position of the double bond. A satisfactory explanation of this is afforded by the fact that in many cases in which substances containing a double carbon bond are oxidized, it is possible to show that the breaking of the carbon chain at the point where the double bond is present, does not occur directly, but that an addition-product is first formed by the taking up of two OH-groups, it being often possible to isolate this product:



Since oxidation takes place—in accordance with the general rule in **49**—at a point where it has already begun, it follows that in this case further oxidation must result in a breaking of the carbon chain at the point where the double bond originally existed. Thus, the breaking of the unsaturated chain by oxidation depends on the formation of an intermediate addition-product, and it is therefore only necessary to find an explanation for the ease with which this is effected. This can be best arrived at by a consideration of the nature of the bonds between the atoms. An affinity or bond may be looked upon as an attraction exercised by one atom upon another. Should an atom possess more than one affinity, it is assumed that the attraction is exercised in more than one direction, and is concentrated at certain points of its surface, somewhat after the manner in which the attraction exercised by a magnet is concentrated at its two poles. Any other assumption, such as that the attracting force is equally distributed over the whole surface of an atom, would make it difficult to understand why each element should have a determinate valency. If the carbon atom is tetravalent, there must be on its surface four such points or "poles," situated at the angles of a regular tetrahedron (**53**). In the case of a single bond between two such poles on different carbon atoms, their mutual attraction would cause them to approach one another as closely as possible.

Baeyer has put forward the supposition that these poles on the surface of carbon atoms are movable. Such a movement results, however, in a certain "tension," which tends to bring back the poles to their original position. For example, when a single bond between two carbon atoms is converted into a double one, the directions of the affinities of each of the two carbon atoms must undergo an appreciable alteration:



The tension resulting from this is therefore a cause of the ease with which double bonds can be broken. We shall see later that Baeyer's *tension theory* also affords an explanation of other important phenomena (**262**).

It is seen from the foregoing that the double bond must not be regarded as a mere doubling of the single one, as the expression "double bond" would indicate.

II. POLYMETHYLENE COMPOUNDS, C_nH_{2n}.

130. Isomeric with the olefines is a series of compounds, C_nH_{2n}, chiefly distinguished from the former by the absence of, or at least a diminution in, the power of forming addition-products. Most of these compounds are very stable; thus pentamethylene, C_5H_{10}, bears a strong resemblance to *n*-pentane, C_5H_{12}. It will be seen later (**260–262**) that the methods for the formation of these compounds necessitate the assumption of a closed carbon chain in the molecule.

III. HYDROCARBONS, C_nH_{2n-2}.

131. A variety of structures is possible for these compounds, which contain four hydrogen atoms less than the corresponding paraffins. Thus, hydrocarbons containing two double bonds have the general formula C_nH_{2n-2}, for example,

$$CH_2:CH\cdot CH:CH_2.$$
Vinylethylene

Further, substances containing a *triple bond* have also the same empirical composition, for example,

$$\underset{\text{Allylene}}{CH_3\cdot C\equiv CH.}$$

The reasons for the assumption of a triple linking in these compounds are identical with those which led to the assumption of the double bond in the olefines (**128**).

A. HYDROCARBONS WITH TRIPLE BONDS.

Nomenclature.

132. The first member, C_2H_2, is called *acetylene*; the second, C_3H_4, *allylene*; the higher members are generally regarded as substituted acetylenes; thus C_4H_6 is called *ethylacetylene*, C_6H_{10} *butylacetylene*, etc.

Methods of Formation.

1. By the dry distillation of complex compounds; hence the occurrence of acetylene in coal-gas.

2. By the withdrawal of two molecules of haloid acid from compounds of the formula $C_nH_{2n}X_2$, where X represents the halogen atom, these compounds being formed by the addition of halogen to alkylenes:

$$\underset{\text{Ethylene bromide}}{CH_2Br—CH_2Br} - 2HBr = \underset{\text{Acetylene}}{CH\equiv CH.}$$

This is effected by heating with alcoholic potash.

A general method for the preparation of unsaturated compounds is furnished by this method of adding on halogen, followed by the removal of haloid acid. For example, starting with C_nH_{2n+2}, $C_nH_{2n+1}X$ is obtained by the action of chlorine or bromine. Heating with alcoholic potash converts this into C_nH_{2n}, from which $C_nH_{2n}Br_2$ is obtained by the action of bromine, and is converted into C_nH_{2n-2} by abstraction of 2HBr. This compound can again form an addition-product with bromine, and so on.

3. By the abstraction of 2HX from compounds of the formula $C_nH_{2n}X_2$, formed by the action of phosphorus pentahalide upon aldehydes or ketones:

$$\underset{\text{Ethylidene chloride}}{CH_3\cdot CHCl_2} - 2HCl = \underset{\text{Acetylene}}{CH\equiv CH.}$$

$$\underset{\text{Chloroacetone}}{CH_3\cdot CCl_2\cdot CH_3} - 2HCl = \underset{\text{Allylene}}{CH_3\cdot C\equiv CH.}$$

Acetylene, C_2H_2.

133. Acetylene is a colourless gas of disagreeable odour, is somewhat soluble in water, and condenses at 18° and 83 atmospheres to a liquid boiling at $-82 \cdot 4°$. It can be synthesized from its elements by means of an electric arc between carbon poles in an atmosphere of hydrogen, a small quantity of methane, and a trace of ethane, being simultaneously formed. Its presence can be detected by means of an ammoniacal solution of cuprous chloride, which yields a red precipitate of copper acetylene even when traces of acetylene are mixed with other gases. Acetylene is also obtained as a product of the incomplete combustion of many organic substances. It is prepared on the large scale by the action of water on calcium carbide, or calcium acetylene, CaC_2:

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2.$$

The reaction is somewhat violent, and is attended with evolution of considerable heat. Calcium carbide is prepared by heating carbon with quicklime, CaO, in an electric furnace. The calcium liberated by the action of the carbon on the quicklime enters into combination with the excess of carbon, under the influence of the high temperature, and forms calcium carbide, which is white when perfectly pure, but has usually a dark reddish-brown colour, due to the presence of small quantities of iron.

Acetylene can be prepared at a moderate cost by this method, and attempts have been made to use it for lighting purposes, as a stream of the gas, passed through a fine opening, burns with an intensely luminous flame. Up to the present, these attempts have been attended by difficulties, partly owing to the cost of production, but more to the nature of acetylene itself. It forms explosive copper acetylene with the copper of the gas-fittings; a mixture with air explodes with extreme violence, and is much more dangerous than a mixture of ordinary coal-gas and air. This is due to the fact that much heat is taken up in the formation of acetylene, this compound being strongly endothermic ("Inorganic Chemistry," **97**). In addition to this, the limits of explosion are much wider than for any other gas, an explosive mixture being formed with air by the admixture of 3-82% of acetylene, while in the case of coal-gas the limits are only 5-28%. The velocity of propagation of combustion is also much greater in the case of acetylene, and this augments considerably the force of the explosion.

Acetylene prepared from calcium carbide sometimes contains small quantities of sulphuretted hydrogen and phosphoretted hydrogen, to which it owes its disagreeable smell. It can be freed from the former by a solution of caustic alkali, and from the latter by a solution of corrosive sublimate in hydrochloric acid The removal of phosphoretted hydrogen is of special importance, since its presence may lead to the spontaneous ignition of the gas.

By the direct hydrogenation of acetylene in presence of reduced nickel (**29** and **125**), SABATIER and SENDERENS have obtained liquid mixtures of hydrocarbons which can be made to correspond either with American or Caucasian petroleum by varying the conditions of the experiment. To account for the formation of petroleum, they assume that there are in the interior of the earth free alkali-metals and metallic carbides, which in contact with water give rise to mixtures of hydrogen and hydrocarbons. These gases encounter finely-divided nickel, cobalt, or iron, and thus yield the mixtures of hydrocarbons constituting natural petroleum (**34**).

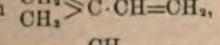
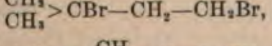
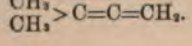
B. HYDROCARBONS WITH TWO DOUBLE BONDS.

134. Hydrocarbons with two double bonds have been comparatively little investigated. *Allene* is obtained from tribromopropane, $CH_2Br\cdot CHBr\cdot CH_2Br$, by removal of HBr by means of potash, and subsequent treatment of the dibromo-compound thus formed with zinc-dust, which removes the two remaining bromine atoms (**125**):

$$\underset{\text{Tribromopropane}}{CH_2Br\cdot CHBr\cdot CH_2Br} \rightarrow \underset{\text{Dibromopropylene}}{CH_2{:}CBr\cdot CH_2Br} \rightarrow \underset{\text{Allene}}{CH_2{:}C{:}CH_2.}$$

Its constitution follows from this method of preparation. It is a colourless gas, and unlike the isomeric allylene, $CH_3\cdot C\equiv CH$, does not yield metallic derivatives (**132**).

Diallyl, $CH_2{:}CH\cdot CH_2\cdot CH_2\cdot CH{:}CH_2$, is obtained by the action of sodium upon *allyl iodide*, $CH_2{:}CH\cdot CH_2I$ (**135**), from which it follows that it has the constitution indicated by the above formula.

A hydrocarbon of this series of theoretical importance is *isoprene*, C_5H_8. It is obtained by the dry distillation of caoutchouc, and is a liquid boiling at 37°. By the union of two or more molecules, it passes into terpenes, $C_{10}H_{16}$, $C_{15}H_{24}$, etc. It is converted by concentrated hydrochloric acid into a substance strongly resembling caoutchouc, perhaps identical with it. Isoprene is proved to have the constitution  $\begin{matrix}CH_2\\CH_3\end{matrix}\!\geqslant C\cdot CH{=}CH_2$, by the addition of 2HBr, which yields a dibromide,  $\begin{matrix}CH_3\\CH_3\end{matrix}\!>CBr{-}CH_2{-}CH_2Br$, identical with that obtained from dimethylallene,  $\begin{matrix}CH_3\\CH_3\end{matrix}\!>C{=}C{=}CH_2$.

SUBSTITUTION PRODUCTS OF THE UNSATURATED HYDROCARBONS.

I. UNSATURATED HALOGEN COMPOUNDS.

188. Since the saturated hydrocarbons themselves do not possess any salient characteristics, the properties of their compounds depend upon the nature of the substituting elements or groups. Hitherto we have only considered compounds whose properties are due to the presence in the molecule of a single group, hydroxyl, carbonyl, a multiple carbon bond, etc. We have now to consider compounds containing more than one characteristic group in the molecule.

When these groups are present simultaneously in the same molecule they generally exercise a modifying influence upon one another. The extent of this influence varies considerably, as will be seen from a consideration of the different classes of unsaturated halogen compounds.

Halogen derivatives of the type [illegible] are obtained by the substitution of halogen for hydrogen in the hydrocarbons [illegible] [illegible]

[illegible]

[illegible]

[illegible]

[illegible]

The methods by which these compounds are obtained indicate that the halogen atom in them is linked to a carbon atom having a double bond. Their properties differ widely from those of compounds, such as the alkyl halides, in which the halogen atom is linked to a carbon atom having only single bonds; and this rule is generally applicable to compounds of this kind. The halogen atom of the alkyl halides is especially suited for taking part in double decompositions, being replaceable by hydroxyl, an alkoxyl-group, an acid-residue, the amido-group, etc.

This aptitude for double decomposition is almost wholly wanting in compounds whose halogen atom is linked to a carbon atom with a double bond. Alkalis do not convert them into alcohols, nor alkoxides into ethers; but invariably, when a reaction does take place, a haloid acid is split off, with formation of hydrocarbons of the series C_nH_{2n-2}.

An isomer of α- and *β-chloropropylene,* which have been referred to above, is called *allyl chloride.* The halogen atom in this compound takes part in double decompositions as easily as that in an alkyl chloride. Allyl chloride is obtained by the action of phosphorus pentachloride upon allyl alcohol, which can be prepared by a method to be described later (**158**). This alcohol yields *n*-propyl alcohol by addition of hydrogen, and its hydroxyl-group must therefore be at the end of the carbon chain. Hence, the halogen atom in allyl chloride must also be attached to the end of the chain, since it takes the place of the hydroxyl-group. Given the constitutions of α- and β-propylene chloride, which are deduced from that of propionaldehyde and acetone, the allyl halides can only have the constitutional formula

$$CH_2=CH\cdot CH_2X.$$

Here the halogen atom is attached to a singly-linked carbon atom, and retains its normal character in spite of the presence of a double bond in the molecule.

This dependence of the character of a halogen atom on its position in the molecule of an unsaturated compound affords a means of determining whether it is attached to a singly-linked or doubly-linked carbon atom, by ascertaining whether it does or does not possess the power to take part in double decompositions.

The following are examples of individual members of the series.

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Halogen derivatives of the type $C_nH_{2n-1}X$ are obtained by the addition of halogen to the hydrocarbons C_nH_{2n}, and subsequent abstraction of one molecule of haloid acid:

$$CH_2{=}CH_2 + Br_2 = CH_2Br{-}CH_2Br.$$
$$\underset{\text{Ethylene bromide}}{CH_2Br{-}CH_2Br} - HBr = \underset{\text{Vinyl bromide}}{CH_2{=}CHBr.}$$

They are also formed by removal of one molecule of haloid acid from compounds containing two halogen atoms linked to the same carbon atom:

$$\underset{\text{Propylidene chloride}}{CH_3{\cdot}CH_2{\cdot}CHCl_2} - HCl = \underset{\alpha\text{-Chloropropylene}}{CH_3{\cdot}CH{=}CHCl.}$$
$$\underset{\text{Chloroacetone}}{CH_3{\cdot}CCl_2{\cdot}CH_3} - HCl = \underset{\beta\text{-Chloropropylene}}{CH_2{=}CCl{-}CH_3.}$$

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The following are examples of individual members of the series.

Vinyl chloride $CH_2:CHCl$ is a gas, *vinyl bromide* $CH_2:CHBr$ a liquid of ethereal odour. Both these compounds polymerize readily.

Allyl chloride, *allyl bromide*, and *allyl iodide*, boil respectively at 46°, 70°, and 103°. They are often used in syntheses for the introduction of an unsaturated group into a compound. They have a characteristic odour resembling that of mustard.

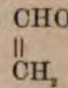
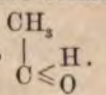
The *propargyl compounds*, $CH{\equiv}C\cdot CH_2X$, may be mentioned as a type of the series $C_nH_{2n-3}X$. Their constitution is inferred from the fact that they yield metallic derivatives, showing that they contain the group $C{\equiv}H$, and also because their halogen atom is capable of taking part in double decompositions, and is therefore attached to a singly-linked carbon atom. They are obtained from propargyl alcohol (**138**) by the action of phosphorus pentahalide, and are liquids possessing a pungent smell.

The compound $CHBr:C$, *bromoacetylidene*, which is assumed by NEF to contain a divalent carbon atom, can be obtained from acetylene bromide, $CHBr:CHBr$, by treatment with alcoholic potash. It is a gas, taking fire spontaneously in the air: its solution in alcohol is phosphorescent, owing to slow oxidation, and the gas itself has an odour very similar to that of phosphorus.

II. UNSATURATED ALCOHOLS.

136. The hydroxyl-group of the unsaturated alcohols may be attached to a singly-linked or doubly-linked carbon atom:

$$\underset{\text{Allyl alcohol}}{CH_2:CH\cdot CH_2OH,} \qquad \underset{\text{Vinyl alcohol}}{CH_2:CH\cdot OH.}$$

Very few compounds of the type of vinyl alcohol are known. In the majority of cases in which their formation might be expected, their isomers are obtained. Thus, when water is abstracted from glycol, $CH_2OH\cdot CH_2OH$, there results, not *vinyl alcohol*,  $\begin{matrix}CHOH\\ \|\\ CH_2\end{matrix}$, but an isomer, acetaldehyde,  $\begin{matrix}CH_3\\ |\\ C{<}^{H}_{O}\end{matrix}$.

When β-bromopropylene, $CH_3\cdot CBr:CH_2$, is heated with water, there is formed not β-hydroxypropylene, $CH_3\cdot C(OH):CH_2$, but the isomeric acetone, $CH_3\cdot CO\cdot CH_3$. It has been generally observed that in cases in which a grouping of the atoms in the

Allyl alcohol must therefore contain the group $—CH_2OH$, which is characteristic of primary alcohols.

Allyl alcohol is a liquid with an irritating odour, solidifying at − 50°, and boiling at 96·5°, and is miscible with water in all proportions. Its specific gravity at 0° is 0·872. It forms addition-products with the halogens and with [illegible]drogen, yielding with the latter *n*-propyl alcohol.

Many other compounds containing the allyl-grou[illegible] $CH_2:CH·CH_2—$, are known. Of these *allyl sulphide* $(CH_2:CH·CH_2)_2S$, the principal constituent of oil of garlic, may be mentioned. It is synthetically obtained by the action of potassium sulphide, K_2S, on allyl iodide.

We have seen that the influence of the double bond in the unsaturated halogen compounds and alcohols is very pronounced when it is situated in the immediate neighbourhood of halogen or hydroxyl, but that otherwise it is much less marked. The rule is that *when two groups are situated in immediate proximity to one another in the same molecule, each group exercises a strong influence upon the properties of the other.*

Propargyl Alcohol, $CH{\equiv}C·CH_2OH$.

138. *Propargyl alcohol* contains a triple bond, and is prepared in the following way. $CH_2Br·CHBr·CH_2Br$, tribromhydrin (**153**), is converted by treatment with caustic potash into $CH_2:CBr·CH_2Br$. When treated with potassium acetate and then saponified, this yields $CH_2:CBr·CH_2OH$, since only the terminal Br-atom is capable of taking part in a double decomposition (**135**). When this alcohol is again brought into contact with caustic potash, HBr is split off, with formation of propargyl alcohol, the constitution of which is indicated by this method of formation, and also by its properties. The presence of the group $\equiv CH$ is shown by the formation of metallic derivatives, and that it is a primary alcohol is proved by the fact that on oxidation it yields *propiolic acid*, $CH{\equiv}C·COOH$, an acid containing the same number of carbon atoms.

Propargyl alcohol is a liquid of agreeable odour, soluble in water, and boiling at 114°–115°; its specific gravity at 21° is 0·963. Its metallic derivatives are explosive.

MONOBASIC UNSATURATED ACIDS.

I. ACIDS OF THE OLEÏC SERIES, $C_nH_{2n-2}O_2$.

139. The acids of the oleïc series may be obtained from the saturated acids $C_nH_{2n}O_2$ by the general methods for converting saturated into unsaturated compounds.

1. Substitution of one hydrogen atom in the alkyl-group of a saturated acid by a halogen atom, and subsequent abstraction of haloid acid by heating with alcoholic potash.
2. Removal of the elements of water from the monohydroxy-acids:

$$\underset{\beta\text{-Hydroxybutyric acid}}{CH_3{\cdot}CHOH{\cdot}CH_2{\cdot}COOH} - H_2O = \underset{\text{Crotonic acid}}{CH_3{\cdot}CH{:}CH{\cdot}COOH.}$$

The acids of this series can also be prepared from unsaturated compounds by

3. Oxidation of the unsaturated alcohols and aldehydes.
4. The action of potassium cyanide on unsaturated halogen compounds, such as allyl iodide, and hydrolysis of the resulting nitrile.

Nomenclature.

140. The majority of the acids of the oleïc series are named after the substances from which they were first obtained, but a few of the middle members have names indicating the number of carbon atoms in the molecule. The first member, $CH_2{:}CH{\cdot}COOH$, is called *acrylic acid;* others are $C_4H_6O_2$ *crotonic acid*, $C_5H_8O_2$ *angelic and tiglic acids*, $C_{11}H_{20}O_2$ *undecylenic acid*, $C_{18}H_{34}O_2$ *oleïc acid*, $C_{22}H_{42}O_2$ *erucic acid*, etc.

It might be anticipated that in this case the splitting off of haloid acid also takes place as indicated in the second method, with the production of two double bonds:

$$CH_3 \cdot CCl_2 \cdot CH_3 - 2HCl = CH_2{=}C{=}CH_2,$$

or

$$CH_3 \cdot CHBr \cdot CHBr \cdot CH_3 - 2HBr = CH_2{=}CH \cdot CH{=}CH_2.$$

Experience has shown that this is not the case. The formula of the resulting product may be determined, for example, by a study of its bromine addition-products, and also from the reactions characteristic of compounds containing the group $\equiv CH$ (see below).

Some of the hydrocarbons prepared by the foregoing methods exhibit a peculiar behaviour towards an ammoniacal solution of cuprous chloride or of a silver salt, which affords a ready means of recognizing them. By replacement of hydrogen, they yield metallic derivatives, insoluble in the ammoniacal solution or in water, which separate out as a voluminous precipitate. These compounds are explosive, the copper yellow or red, and the silver white. Acetylene yields these metallic compounds, and of its higher homologues, those derived from the dihalogen compounds of the aldehydes also give them. Their method of formation shows that these homologues contain the group $\equiv CH$:

$$C_nH_{2n+1} \cdot CH_2 \cdot CHO \rightarrow C_nH_{2n+1} \cdot CH_2 \cdot CHCl_2 \rightarrow C_nH_{2n+1} \cdot C{\equiv}CH.$$

From this it may be concluded that *the group* $\equiv CH$ *must be present in the hydrocarbons which yield metallic derivatives;* it is the hydrogen of this group which is replaced by metals. In support of this view is the fact that only the dichloro-derivatives of the methylketones (**110**) can be transformed into hydrocarbons yielding metallic compounds:

$$C_nH_{2n+1} \cdot CO \cdot CH_3 \rightarrow C_nH_{2n+1} \cdot CCl_2 \cdot CH_3 \rightarrow \underset{\text{Yields metallic derivatives.}}{C_nH_{2n+1} \cdot C{\equiv}CH};$$

$$C_2H_5 \cdot CO \cdot C_2H_5 \rightarrow C_2H_5 \cdot CCl_2 \cdot CH_2 \cdot CH_3 \rightarrow \underset{\substack{\text{Does not yield metallic}\\ \text{derivatives.}}}{C_2H_5 \cdot C{\equiv}C \cdot CH_3}.$$

The isomeric hydrocarbons containing two double bonds (**134**) are also incapable of forming metallic compounds.

The hydrocarbons are readily prepared in the free state from their metallic derivatives by the action of dilute hydrochloric acid. This affords a means of isolating the members of the series

C_nH_{2n-2}, which yield such derivatives, from mixtures, and of obtaining them in the pure state.

The hydrocarbons of this series can add on four halogen atoms or two molecules of a haloid acid. In presence of mercury salts they can take up water, forming aldehydes or ketones:

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

In this reaction, mercury compounds are first formed by addition; thus, when allylene, C_3H_4, is passed into a solution of mercuric chloride, $HgCl_2$, a precipitate of the composition $3HgCl_2 3HgO \cdot 2C_3H_4$ is first formed, and is converted into acetone by the action of hydrochloric acid.

The hydrocarbons of the acetylene series also possess the power of yielding condensation-products. This sometimes takes place between three molecules; thus, acetylene, C_2H_2, condenses to benzene, C_6H_6; dimethylacetylene, C_4H_6, to hexamethylbenzene, $C_{12}H_{18}$, etc. The action of heat on acetylene, and of sulphuric acid on its homologues, effects this transformation.

A remarkable reaction, resulting in a change in the position of the triple bond, takes place when the hydrocarbons of the series C_nH_{2n-2} containing the group $\equiv CH$ are heated to a high temperature in a sealed tube with alcoholic potash:

$$\underset{\text{Propylacetylene}}{C_2H_5 \cdot CH_2 \cdot C{\equiv}CH} \text{ is converted into } \underset{\text{Ethylmethylacetylene}}{C_2H_5 \cdot C{\equiv}C \cdot CH_3}.$$

It is probable that in this reaction an addition-product is first formed at one part of the molecule, followed by a splitting off from another part. That the displacement of the triple linking does take place in the example given above, is proved by the fact that although propylacetylene yields metallic derivatives, the substance obtained by heating it with alcoholic potash does not, but is converted by oxidation into propionic and acetic acids. This determines the position of the triple bond, since, for reasons similar to those which apply to the double bond (**129**), the carbon chain is broken by oxidation at the point occupied by the multiple bond. The substance obtained must therefore have the formula given above, and be ethylmethylacetylene.

Acetylene, C_2H_2.

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$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2.$$

The reaction is somewhat violent, and is attended with evolution of considerable heat. Calcium carbide is prepared by heating carbon with quicklime, CaO, in an electric furnace. The calcium liberated by the action of the carbon on the quicklime enters into combination with the excess of carbon, under the influence of the high temperature, and forms calcium carbide, which is white when perfectly pure, but has usually a dark reddish-brown colour, due to the presence of small quantities of iron.

Acetylene can be prepared at a moderate cost by this method, and attempts have been made to use it for lighting purposes, as a stream of the gas, passed through a fine opening, burns with an intensely luminous flame. Up to the present, these attempts have been attended by difficulties, partly owing to the cost of production, but more to the nature of acetylene itself. It forms explosive copper acetylene with the copper of the gas-fittings; a mixture with air explodes with extreme violence, and is much more dangerous than a mixture of ordinary coal-gas and air. This is due to the fact that much heat is taken up in the formation of acetylene, this compound being strongly endothermic ("Inorganic Chemistry," **97**). In addition to this, the limits of explosion are much wider than for any other gas, an explosive mixture being formed with air by the admixture of 3–82% of acetylene, while in the case of coal-gas the limits are only 5–28%. The velocity of propagation of combustion is also much greater in the case of acetylene, and this augments considerably the force of the explosion.

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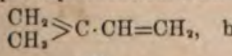
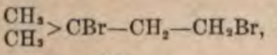
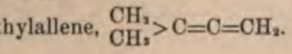
Its constitution follows from this method of preparation. It is a colourless gas, and unlike the isomeric allylene, $CH_3{\cdot}C{\equiv}CH$, does not yield metallic derivatives (**132**).

Diallyl, $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2$, is obtained by the action of sodium upon *allyl iodide*, $CH_2{:}CH{\cdot}CH_2I$ (**135**), from which it follows that it has the constitution indicated by the above formula.

A hydrocarbon of this series of theoretical importance is *isoprene*, C_5H_8. It is obtained by the dry distillation of caoutchouc, and is a liquid boiling at 37°. By the union of two or more molecules, it passes into terpenes, $C_{10}H_{16}$, $C_{15}H_{24}$, etc. It is converted by concentrated hydrochloric acid into a substance strongly resembling caoutchouc, perhaps identical with it. Isoprene is proved to have the constitution  $\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}{\geqslant}C{\cdot}CH{=}CH_2$, by the addition of 2HBr, which yields a dibromide,  $\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}{>}CBr{-}CH_2{-}CH_2Br$, identical with that obtained from dimethylallene,  $\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}{>}C{=}C{=}CH_2$.

SUBSTITUTION-PRODUCTS OF THE UNSATURATED HYDROCARBONS.

Begin

I. UNSATURATED HALOGEN COMPOUNDS.

135. Since the saturated hydrocarbons themselves do not possess any salient characteristics, the properties of their compounds depend upon the nature of the substituting elements or groups. Hitherto we have only considered compounds whose properties are due to the presence in the molecule of a single group, hydroxyl, carboxyl, a multiple carbon bond, etc. We have now to describe substances containing more than one characteristic group in the molecule.

When these groups are present simultaneously in the same molecule, they generally exercise a modifying influence upon one another. The extent of this influence varies considerably, as will be seen from a consideration of the different classes of unsaturated halogen compounds.

Halogen derivatives of the type $C_nH_{2n-1}X$ are obtained by the addition of halogen to the hydrocarbons C_nH_{2n}, and subsequent abstraction of one molecule of haloid acid:

$$CH_2{=}CH_2 + Br_2 = CH_2Br{-}CH_2Br.$$

$$\underset{\text{Ethylene bromide}}{CH_2Br{-}CH_2Br} - HBr = \underset{\text{Vinyl bromide}}{CH_2{=}CHBr.}$$

They are also formed by removal of one molecule of haloid acid from compounds containing two halogen atoms linked to the same carbon atom:

$$\underset{\text{Propylidene chloride}}{CH_3\cdot CH_2\cdot CHCl_2} - HCl = \underset{\alpha\text{-Chloropropylene}}{CH_3\cdot CH{=}CHCl.}$$

$$\underset{\text{Chloroacetone}}{CH_3\cdot CCl_2\cdot CH_3} - HCl = \underset{\beta\text{-Chloropropylene}}{CH_2{=}CCl{-}CH_3.}$$

The methods by which these compounds are obtained indicate that the halogen atom in them is linked to a carbon atom having a double bond. Their properties differ widely from those of compounds, such as the alkyl halides, in which the halogen atom is linked to a carbon atom having only single bonds; and this rule is generally applicable to compounds of this kind. The halogen atom of the alkyl halides is especially suited for taking part in double decompositions, being replaceable by hydroxyl, an alkoxyl-group, an acid-residue, the amido-group, etc.

This aptitude for double decomposition is almost wholly wanting in compounds whose halogen atom is linked to a carbon atom with a double bond. Alkalis do not convert them into alcohols, nor alkoxides into ethers; but invariably, when a reaction does take place, a haloid acid is split off, with formation of hydrocarbons of the series C_nH_{2n-2}.

An isomer of α- and *β-chloropropylene,* which have been referred to above, is called *allyl chloride.* The halogen atom in this compound takes part in double decompositions as easily as that in an alkyl chloride. Allyl chloride is obtained by the action of phosphorus pentachloride upon allyl alcohol, which can be prepared by a method to be described later (**158**). This alcohol yields *n*-propyl alcohol by addition of hydrogen, and its hydroxyl-group must therefore be at the end of the carbon chain. Hence, the halogen atom in allyl chloride must also be attached to the end of the chain, since it takes the place of the hydroxyl-group. Given the constitutions of α- and β-propylene chloride, which are deduced from that of propionaldehyde and acetone, the allyl halides can only have the constitutional formula

$$CH_2=CH\cdot CH_2X.$$

Here the halogen atom is attached to a singly-linked carbon atom, and retains its normal character in spite of the presence of a double bond in the molecule.

This dependence of the character of a halogen atom on its position in the molecule of an unsaturated compound affords a means of determining whether it is attached to a singly-linked or doubly-linked carbon atom, by ascertaining whether it does or does not possess the power to take part in double decompositions.

The following are examples of individual members of the series.

Vinyl chloride $CH_2:CHCl$ is a gas, *vinyl bromide* $CH_2:CHBr$ a liquid of ethereal odour. Both these compounds polymerize readily.

Allyl chloride, *allyl bromide*, and *allyl iodide*, boil respectively at 46°, 70°, and 103°. They are often used in syntheses for the introduction of an unsaturated group into a compound. They have a characteristic odour resembling that of mustard.

The *propargyl compounds*, $CH \equiv C \cdot CH_2X$, may be mentioned as a type of the series $C_nH_{2n-3}X$. Their constitution is inferred from the fact that they yield metallic derivatives, showing that they contain the group $C \equiv H$, and also because their halogen atom is capable of taking part in double decompositions, and is therefore attached to a singly-linked carbon atom. They are obtained from propargyl alcohol (**138**) by the action of phosphorus pentahalide, and are liquids possessing a pungent smell.

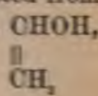
The compound $CHBr:C$, *bromoacetylidene*, which is assumed by NEF to contain a divalent carbon atom, can be obtained from acetylene bromide, $CHBr:CHBr$, by treatment with alcoholic potash. It is a gas, taking fire spontaneously in the air: its solution in alcohol is phosphorescent, owing to slow oxidation, and the gas itself has an odour very similar to that of phosphorus.

II. UNSATURATED ALCOHOLS.

136. The hydroxyl-group of the unsaturated alcohols may be attached to a singly-linked or doubly-linked carbon atom:

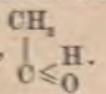
$$\underset{\text{Allyl alcohol}}{CH_2:CH \cdot CH_2OH,} \qquad \underset{\text{Vinyl alcohol}}{CH_2:CH \cdot OH.}$$

Very few compounds of the type of vinyl alcohol are known. In the majority of cases in which their formation might be expected, their isomers are obtained. Thus, when water is abstracted from glycol, $CH_2OH \cdot CH_2OH$, there results, not *vinyl alcohol*,



$$\begin{matrix} CHOH, \\ \| \\ CH_2 \end{matrix}$$

but an isomer, acetaldehyde,



$$\begin{matrix} CH_3 \\ | \\ C{<}^{H}_{O} \end{matrix}.$$

When β-bromopropylene, $CH_3 \cdot CBr:CH_2$, is heated with water, there is formed not β-hydroxypropylene, $CH_3 \cdot C(OH):CH_2$, but the isomeric acetone, $CH_3 \cdot CO \cdot CH_3$. It has been generally observed that in cases in which a grouping of the atoms in the form $—CH:C(OH)—$ would be naturally expected, a transformation into $—CH_2·CO—$ occurs. Substances containing hydroxyl attached to a doubly-linked carbon atom are therefore *unstable,* that is, they have a tendency to become transformed into isomers. It will be seen later, however, that compounds do exist in which the group $—CH:C(OH)—$ is *stable* (**240**).

The following compounds either contain hydroxyl attached to a doubly-linked carbon atom, or are related to substances of this type.

Vinyl alcohol, $CH_2:CHOH$, so called because it contains the *vinyl*-group, $CH_2:CH—$, probably occurs in ordinary ethyl ether which has stood for some time, and thereby undergone partial oxidation. When such ether is shaken up with an alkaline solution of a mercury salt, a precipitate of the composition $Hg_3Cl_2O_2C_2H_2$ is formed, which on treatment with a haloid acid yields vinyl-compounds.

A vinyl-derivative of great physiological importance, called *neurine,* is formed in the decay of flesh, and in other fermentation-processes. Its constitution is $(CH_3)_3N<\begin{matrix}CH:CH_2\\OH\end{matrix}$, as indicated by the following synthesis. When trimethylamine reacts with ethylene bromide, a substituted ammonium bromide is obtained with the formula $(CH_3)_3N<\begin{matrix}CH_2·CH_2Br\\Br\end{matrix}$. HBr is abstracted from the group $—CH_2·CH_2Br$ by the action of moist silver oxide, the bromine atom attached to nitrogen being replaced by hydroxyl at the same time. A substance of the constitution indicated above is obtained from it, and is in all respects identical with neurine.

found in ptomaine

Allyl Alcohol, $CH_2:CH·CH_2OH$.

137. Many unsaturated alcohols containing hydroxyl attached to a singly-linked carbon atom are known. The most important of these is *allyl alcohol,* obtained by a method to be described later (**158**). Its constitution follows from that of the chlorine derivative formed by the action of phosphorus pentachloride (**135**), as well as from that of the products obtained by oxidation, by which allyl alcohol is converted first into an aldehyde, *acroleïn,* and then into *acrylic acid:*

$$\underset{\text{Allyl alcohol}}{CH_2:CH·CH_2OH} \rightarrow \underset{\text{Acroleïn}}{CH_2:CH·C\leqslant^{H}_{O}} \rightarrow \underset{\text{Acrylic acid}}{CH_2:CH·COOH}.$$

Allyl alcohol must therefore contain the group $—CH_2OH$, which is characteristic of primary alcohols.

Allyl alcohol is a liquid with an irritating odour, solidifying at $-50°$, and boiling at $96·5°$, and is miscible with water in all proportions. Its specific gravity at 0° is 0·872. It forms addition-products with the halogens and with [illegible]drogen, yielding with the latter *n*-propyl alcohol.

Many other compounds containing the allyl-grou[illegible] $CH_2:CH·CH_2—$, are known. Of these *allyl sulphide* $(CH_2:CH·CH_2)_2S$, the principal constituent of oil of garlic, may be mentioned. It is synthetically obtained by the action of potassium sulphide, K_2S, on allyl iodide.

We have seen that the influence of the double bond in the unsaturated halogen compounds and alcohols is very pronounced when it is situated in the immediate neighbourhood of halogen or hydroxyl, but that otherwise it is much less marked. The rule is that *when two groups are situated in immediate proximity to one another in the same molecule, each group exercises a strong influence upon the properties of the other.*

Propargyl Alcohol, $CH{\equiv}C·CH_2OH$.

138. *Propargyl alcohol* contains a triple bond, and is prepared in the following way. $CH_2Br·CHBr·CH_2Br$, tribromhydrin (**153**), is converted by treatment with caustic potash into $CH_2:CBr·CH_2Br$. When treated with potassium acetate and then saponified, this yields $CH_2:CBr·CH_2OH$, since only the terminal Br-atom is capable of taking part in a double decomposition (**135**). When this alcohol is again brought into contact with caustic potash, HBr is split off, with formation of propargyl alcohol, the constitution of which is indicated by this method of formation, and also by its properties. The presence of the group $\equiv CH$ is shown by the formation of metallic derivatives, and that it is a primary alcohol is proved by the fact that on oxidation it yields *propiolic acid*, $CH{\equiv}C·COOH$, an acid containing the same number of carbon atoms.

Propargyl alcohol is a liquid of agreeable odour, soluble in water, and boiling at 114°–115°; its specific gravity at 21° is 0·963. Its metallic derivatives are explosive.

MONOBASIC UNSATURATED ACIDS.

I. ACIDS OF THE OLEÏC SERIES, $C_nH_{2n-2}O_2$.

139. The acids of the oleïc series may be obtained from the saturated acids $C_nH_{2n}O_2$ by the general methods for converting saturated into unsaturated compounds.

1. Substitution of one hydrogen atom in the alkyl-group of a saturated acid by a halogen atom, and subsequent abstraction of haloid acid by heating with alcoholic potash.
2. Removal of the elements of water from the monohydroxy-acids:

$$\underset{\beta\text{-Hydroxybutyric acid}}{CH_3\cdot CHOH\cdot CH_2\cdot COOH} - H_2O = \underset{\text{Crotonic acid}}{CH_3\cdot CH:CH\cdot COOH}.$$

The acids of this series can also be prepared from unsaturated compounds by

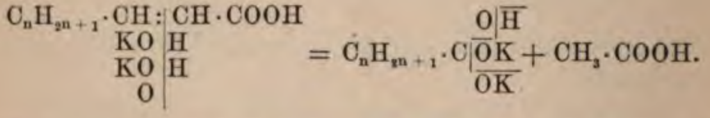
3. Oxidation of the unsaturated alcohols and aldehydes.
4. The action of potassium cyanide on unsaturated halogen compounds, such as allyl iodide, and hydrolysis of the resulting nitrile.

Nomenclature.

140. The majority of the acids of the oleïc series are named after the substances from which they were first obtained, but a few of the middle members have names indicating the number of carbon atoms in the molecule. The first member, $CH_2:CH\cdot COOH$, is called *acrylic acid;* others are $C_4H_6O_2$ *crotonic acid*, $C_5H_8O_2$ *angelic and tiglic acids*, $C_{11}H_{20}O_2$ *undecylenic acid*, $C_{18}H_{34}O_2$ *oleïc acid*, $C_{22}H_{42}O_2$ *erucic acid*, etc.

General Properties.

141. Like all compounds containing a double bond, the acids of this series possess the power of forming addition-products. They are "stronger" acids than the corresponding fatty acids containing the same number of carbon atoms in the molecule; thus, the value of the constant K (**93**) for propionic acid $C_3H_6O_2$ is 0·00134, for acrylic acid $C_3H_4O_2$ 0·0056, for butyric acid $C_4H_8O_2$ 0·00149, for crotonic acid $C_4H_6O_2$ 0·00204, etc. The double bond causes the acids of the oleïc series to be much more readily attacked by oxidizing-agents than those of the fatty series (**129**). The former are converted by energetic oxidation into two saturated acids, but when the reaction is restrained by using a dilute solution of potassium permanganate, a dihydroxy-acid containing the group —CHOH·CHOH— is formed as an intermediate product, and on further oxidation is split up at the bond between these two carbon atoms (**129**). This affords a means of determining the position of the double bond in the molecule. A breaking-up of the molecule with formation of saturated fatty acids also takes place when an unsaturated acid is fused with caustic potash with access of air:



$$\begin{array}{r|l} C_nH_{2n+1}\cdot CH: & CH\cdot COOH \\ KO & H \\ KO & H \\ O & \end{array} = C_nH_{2n+1}\cdot C\begin{array}{l} O|\overline{H} \\ |\overline{OK} \\ \overline{OK} \end{array} + CH_3\cdot COOH.$$

This reaction was at one time often employed to determine the position of the double bond, under the impression that the decomposition of the molecule was effected at the point where this bond was situated in the first instance. It is now known that under the influence of fused caustic potash, or even by boiling with a solution of caustic soda, the position of the double bond becomes shifted nearer to that of the carboxyl-group. Fusion with caustic potash is therefore not applicable to the determination of the position of double bonds.

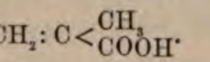
Acrylic Acid, $CH_2:CH\cdot COOH$.

142. Acrylic acid is obtained by removal of HI from β-iodopropionic acid, $CH_2I\cdot CH_2\cdot COOH$. It is a liquid with a pungent odour, boiling at 140°, and is reduced by nascent hydrogen to propionic acid.

Acids with the formula $C_4H_6O_2$.

143. Several acids with the formula $C_4H_6O_2$ are known. In accordance with the theory of constitution, the following are possible:

$$1.\ CH_2{:}CH{\cdot}CH_2{\cdot}COOH; \quad 2.\ CH_3{\cdot}CH{:}CH{\cdot}COOH;$$

3. 

$$CH_2{:}C{<}\begin{matrix}CH_3\\COOH\end{matrix}.$$

Four isomeric acids with the formula $C_4H_6O_2$ are actually known.

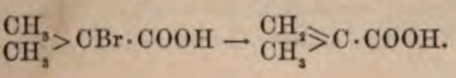
An acid of the constitution indicated in formula 1, *vinylacetic acid*, may be obtained synthetically (**239**). Its formation by the action of potassium cyanide on allyl iodide, and saponification of the nitrile thus formed, might be expected:

$$\underset{\text{Allyl iodide}}{CH_2{:}CH{\cdot}CH_2I} \rightarrow CH_2{:}CH{\cdot}CH_2CN \rightarrow CH_2{:}CH{\cdot}CH_2{\cdot}COOH.$$

Actually, however, an acid having the formula 2 is obtained, *solid* crotonic acid, which melts at 71° and boils at 180°; for it is converted by careful oxidation with permanganate into oxalic acid, HOOC—COOH.

Isocrotonic acid, a liquid boiling at 172°, has also the constitution 2, because, on the one hand, like solid crotonic acid it can be reduced to *n*-butyric acid, showing that it too contains a normal carbon chain; on the other, it is converted by careful oxidation into oxalic acid. Ordinary constitutional formulæ are incapable, therefore, of accounting for the isomerism of these acids. We shall see later (**170**) how it is explained.

An acid with the formula 3 is obtained by the abstraction of HBr from bromo-isobutyric acid, and is called *methacrylic acid:*



$$\begin{matrix}CH_3\\CH_3\end{matrix}{>}CBr{\cdot}COOH \rightarrow \begin{matrix}CH_2\\CH_3\end{matrix}{\gg}C{\cdot}COOH.$$

Oleïc Acid, $C_{18}H_{34}O_2$.

144. Oleïc acid is obtained by the saponification of oils and soft fats (**91**). In order to separate it from the saturated fatty acids, stearic and palmitic acids, which are set free at the same time, use is made of its lead salt, which is readily soluble in ether, in contradistinction to those of the saturated fatty acids. The oleïc acid is liberated from the lead oleate by treatment with acids.

At ordinary temperatures, oleïc acid is a liquid melting at 14°, without odour and of an oily nature. It oxidizes readily in the air, and cannot be distilled without decomposition under ordinary pressures.

Oleïc acid contains a normal carbon chain, since it is converted by reduction into stearic acid.

Krafft has proved the normal structure of stearic acid by converting it step by step into acids containing a smaller number of carbon atoms. His method is as follows. When submitted to dry distillation in a vacuum, barium stearate and barium acetate yield a ketone, $C_{17}H_{35}\cdot CO\cdot CH_3$:

$$\underset{\text{Barium stearate}}{C_{17}H_{35}\cdot \boxed{COOba^{*} +} }\underset{\text{Barium acetate}}{\boxed{baO\cdot} OC\cdot CH_3} \rightarrow \underset{\text{Margarylmethylketone}}{C_{17}H_{35}\cdot CO\cdot CH_3.}$$

On oxidation, this ketone yields acetic acid and an acid of the formula $C_{17}H_{34}O_2$. This shows that in the ketone there must be a CH_2-group next to the carbonyl-group, so that it has the formula $C_{16}H_{33}\cdot CH_2\cdot CO\cdot CH_3$, since only in this case could oxidation produce an acid with seventeen carbon atoms. This acid, $C_{17}H_{34}O_2$, (*margaric acid*,) is converted in the same way into a ketone, $C_{16}H_{33}\cdot CO\cdot CH_3$, which on oxidation yields an acid $C_{16}H_{32}O_2$. The formula of margaric acid must therefore be $C_{15}H_{31}\cdot CH_2\cdot COOH$, and that of stearic acid, $C_{15}H_{31}\cdot CH_2\cdot CH_2\cdot COOH$. The acid $C_{16}H_{32}O_2$, *palmitic acid*, is in its turn converted into a ketone, etc., and the process continued until an acid is obtained, *capric acid*, $C_{10}H_{20}O_2$, which has been proved by synthesis (**235**. 1) to contain a normal carbon chain.

The presence of a double bond in oleïc acid is proved by its forming an addition-product with bromine, and by its power of reducing an alkaline permanganate solution (**123**). The double bond is situated at the middle of the molecule, the constitution of oleïc acid being

$$CH_3\cdot (CH_2)_7\cdot CH : CH\cdot (CH_2)_7\cdot COOH.$$

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* $ba = \frac{1}{2}Ba$

This constitution is inferred from the products of careful oxidation, which yields *pelargonic acid*, $C_8H_{17}\cdot COOH$, and *azelaïc acid*, $HOOC\cdot(CH_2)_7\cdot COOH$.

Oleïc acid reacts in a very remarkable manner with nitrous acid, even when it is brought in contact with a mere trace of this substance. The reaction is best carried out by passing the red gas, which is a mixture of NO_2 and NO, obtained by heating arsenic trioxide with nitric acid, into oleïc acid, the same effect being produced by the addition of nitric acid of specific gravity 1·25. The oleïc acid becomes solid after a time, being converted into an isomer, *elaïdic acid*. This reaction is called the "elaïdic transformation." It is also undergone by other acids of this series; thus, *erucic acid*, $C_{22}H_{42}O_2$, is converted by a trace of nitrous acid into *brassidic acid*.

Elaïdic acid has the same structural formula as oleïc acid, the double bond occupying an identical position in the molecule of each, since each acid readily forms a bromine addition-product, which, by removal of 2HBr, yields the same acid in both cases, $C_{18}H_{32}O_2$, *stearolic acid:*

$$\underset{\text{Oleïc and elaïdic acids}}{C_{18}H_{34}O_2} \rightarrow \underset{\text{Bromine addition-product}}{C_{18}H_{34}Br_2O_2} \rightarrow \underset{\text{Stearolic acid}}{C_{18}H_{32}O_2}.$$

These two acids yield the same ketostearic acid by the addition of one molecule of water, which is effected by the action of concentrated sulphuric acid. The isomerism of oleïc acid and elaïdic acid is therefore, like that of erucic acid and brassidic acid, analogous to the isomerism of the two crotonic acids (**143**).

II. ACIDS OF THE PROPIOLIC SERIES, $C_nH_{2n-4}O_2$.

145. The acids of the propiolic series have one triple bond, or two double bonds, in the molecule. The first-named are formed by the action of carbon dioxide upon the sodium compounds of the acetylene hydrocarbons:

$$CH{\equiv}CNa + CO_2 = \underset{\text{Sodium propiolate}}{CH{\equiv}C\cdot COONa}.$$

The acids thus formed have a triple bond attached to the α-carbon atom. Acids of this nature are very easily split up into an acetylene hydrocarbon and CO_2, especially on heating their silver salts.

A general method for the preparation of acids with triple bonds consists in the addition of two bromine atoms to acids containing a double bond, and subsequent abstraction of 2HBr:

$$\underset{\text{Crotonic acid}}{CH_3\cdot CH:CH\cdot COOH} \rightarrow \underset{\text{Dibromobutyric acid}}{CH_3\cdot CHBr\cdot CHBr\cdot COOH} \rightarrow$$
$$\rightarrow \underset{\text{Tetrolic acid}}{CH_3\cdot C \vdots C\cdot COOH.}$$

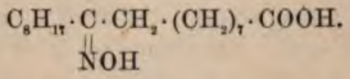
Substances containing a triple bond possess the property of adding on water under the influence of concentrated sulphuric acid, with formation of ketones:

$$—C\equiv C— \rightarrow —CH_2\cdot CO—.$$

Thus, stearolic acid, mentioned above, is converted into a keto-stearic acid of the formula

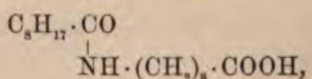
$$C_8H_{17}\cdot CO\cdot CH_2\cdot (CH_2)_7\cdot COOH,$$

which is transformed into the corresponding oxime by treatment with hydroxylamine:



$$\underset{\overset{\|}{NOH}}{C_8H_{17}\cdot C}\cdot CH_2\cdot (CH_2)_7\cdot COOH.$$

Under the influence of concentrated sulphuric acid, this oxime undergoes the **Beckmann** transformation (**112**), among the products being the substituted acid amide

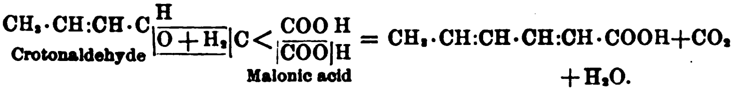


$$\begin{array}{l} C_8H_{17}\cdot CO \\ \qquad\quad | \\ \qquad\quad NH\cdot (CH_2)_8\cdot COOH, \end{array}$$

which is proved to have this formula by its decomposition into pelargonic acid, $C_8H_{17}\cdot COOH$, and the 9-aminononoïc acid, $NH_2\cdot (CH_2)_8\cdot COOH$, when acted upon by fuming hydrochloric acid. This is a confirmation of the constitution above indicated for oleïc acid and elaïdic acid, since they can be converted into stearolic acid in the way already described.

Acids with Two Double Bonds, $C_nH_{2n-4}O_2$.

146. Very few of these are known. Among them may be mentioned *sorbic acid*, $C_6H_8O_2$, which is crystalline, and melts at 134·5°. It occurs in the unripe berries of the mountain-ash, and has the constitution $CH_3\cdot CH{:}CH\cdot CH{:}CH\cdot COOH$, as is proved by its synthesis, the condensation of malonic acid with crotonaldehyde under the influence of pyridine as a condensing-agent:



$$\underset{\text{Crotonaldehyde}}{CH_3\cdot CH{:}CH\cdot C^{H}}\boxed{O+H_2}C<\underset{\text{Malonic acid}}{\begin{matrix}COO\,H\\ \boxed{COO}H\end{matrix}} = CH_3\cdot CH{:}CH\cdot CH{:}CH\cdot COOH+CO_2 + H_2O.$$

Isomeric with stearolic acid is *linoleic acid*, $C_{18}H_{32}O_2$, obtained by the saponification of linseed oil. When carefully oxidized with potassium permanganate it is converted into a tetrahydroxystearic acid, $C_{18}H_{32}O_2(OH)_4$, which proves that it contains two double bonds in the molecule.

UNSATURATED ALDEHYDES AND KETONES.

I. UNSATURATED ALDEHYDES.

147. The first member of the unsaturated aldehydes is *acroleïn*, $CH_2{:}CH{\cdot}CHO$. It is obtained by removal of water from glycerol, a process best effected by heating with potassium anhydrosulphate, $K_2S_2O_7$, or with boric acid. It is a colourless liquid, boiling at 52·4°, and has an extremely powerful, penetrating odour, to which it owes its name (*acer*, sharp, and *oleum*, oil). The disagreeable, pungent smell produced when a tallow candle or an oil-lamp is extinguished is due to the formation of acroleïn. On reduction, it yields allyl alcohol, from which it is regenerated by oxidation. It is converted into acrylic acid by further oxidation.

It has the properties peculiar to aldehydes—the susceptibility to reduction and oxidation, resinification in presence of alkalis, and the power of forming polymerization-products. It possesses this last property in such a marked degree that it usually becomes wholly converted into a polymer in the course of a few days or even hours, probably under the catalytic influence of traces of impurities. The presence of the double bond in acroleïn modifies to some extent its aldehydic properties. This is exhibited in its behaviour towards ammonia, with which it does not combine in the same way as acetaldehyde (**113**), but in accordance with the following equation:

$$2C_3H_4O + NH_3 = C_6H_9NO + H_2O.$$

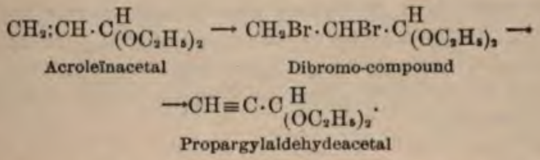
Acroleïn-ammonia is an amorphous, basic substance, is soluble in water, and in its appearance and behaviour towards water bears a close resemblance to glue.

Acroleïn does not unite with one molecule of an acid sulphite, but with two, yielding a compound from which acroleïn itself cannot again be obtained by the action of acids, which only split off one molecule of the acid sulphite. It must therefore be supposed that the other molecule of acid sulphite has attached itself at the double bond.

Crotonaldehyde, $CH_3 \cdot CH : CH \cdot CHO$.

148. *Crotonaldehyde* results on the splitting off of water from aldol, $CH_3 \cdot CH\underbrace{\boxed{OH} \cdot \underline{CH}\boxed{H}} \cdot C^{H}_{O}$ **(115)**, when it is heated to 140°. It is a liquid boiling at 104°-105°, and is converted by oxidation with silver oxide into solid crotonic acid, a reaction which proves it to have the constitution indicated by the above formula.

Propargylaldehyde, $CH \equiv C \cdot C {<}^{H}_{O}$, can be obtained from acroleïn-acetal by the addition of two bromine atoms, and subsequent removal of 2HBr, by means of caustic potash, from the addition-product thus formed :



$$CH_2{:}CH \cdot C^{H}_{(OC_2H_5)_2} \rightarrow CH_2Br \cdot CHBr \cdot C^{H}_{(OC_2H_5)_2} \rightarrow$$

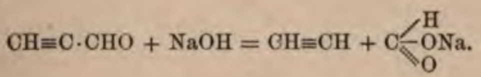
Acroleïnacetal Dibromo-compound

$$\rightarrow CH \equiv C \cdot C^{H}_{(OC_2H_5)_2}.$$

Propargylaldehydeacetal

The latter acetal is converted by warming with dilute sulphuric acid into the corresponding aldehyde, which has the same irritating action on the mucous membrane as acroleïn.

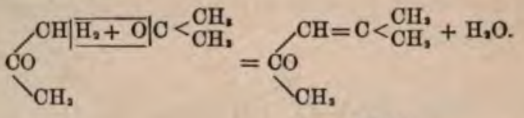
The behaviour of propargylaldehyde with alkalis is remarkable. It is split up into acetylene and formic acid:



$$CH \equiv C \cdot CHO + NaOH = CH \equiv CH + C{\begin{smallmatrix} \diagup H \\ - ONa \\ \diagdown\!\!\diagdown O \end{smallmatrix}}.$$

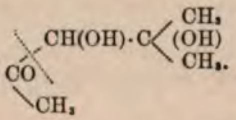
II. UNSATURATED KETONES.

149. Among these may be mentioned *mesityl oxide*, $C_6H_{10}O$, and *phorone*, $C_9H_{14}O$. Both are obtained by the condensation of acetone, with elimination of water. Mesityl oxide is a colourless liquid, B.P. 130° and sp. gr. 0·848 at 23°, is insoluble in water, and possesses a strong peppermint-like odour. It is recognized as an unsaturated ketone on account of its yielding an oxime, and being capable of forming addition-products. Its ketonic character is further manifested by its failing to yield an acid containing the same number of carbon atoms on oxidation. The formation of mesityl oxide is represented by the following equation:

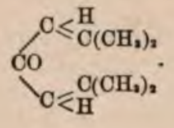


Mesityl oxide

This constitutional formula for mesityl oxide is further supported by the result of its oxidation with permanganate. The products of this treatment are α-hydroxyisobutyric acid, $(CH_3)_2C(OH)\cdot COOH$, and acetic acid. Remembering that the addition of 2OH at the position of the double bond precedes the splitting up of the molecule, it is easy to understand how the acids named can be produced by its oxidation:



Phorone is a crystalline, greenish-yellow substance, and melts at 28°. Its forming an oxime is a proof that it contains a carbonyl-group, and it can also add on four bromine atoms; hence it is assumed to have the following structural formula, which gives expression to these properties:



FIN.

COMPOUNDS CONTAINING MORE THAN ONE SUBSTITUTING-GROUP.

I. HALOGEN DERIVATIVES OF METHANE.

150. It is possible to replace all four hydrogen atoms in methane, in successive stages, by the direct action of chlorine or bromine in presence of sunlight. Iodine does not react with methane, or with its homologues, while the action of fluorine is very energetic, effecting complete substitution.

In practice, however, this is not the method adopted for the preparation of the compounds CH_2X_2, CHX_3, or CX_4. They are obtained from the trihalogen derivatives, readily prepared by another method, which yield tetrachloromethane or tetrabromomethane without any difficulty, on chlorination or bromination, and are converted on reduction into dihalogen methane. On account of their important therapeutical properties, the compounds CHX_3 are prepared on the large scale.

Chloroform, $CHCl_3$.

151. Chloroform is obtained by distilling alcohol with bleaching-powder. In this reaction, in which oxidation and chlorination go on together, it is supposed that aldehyde is first produced by oxidation of the alcohol, and is then converted into *trichloroaldehyde*, or *chloral*, $CCl_3 \cdot CHO$. This substance is converted by bases, in this case by the slaked lime present in the bleaching-powder, into chloroform and formic acid (**204**).

Chloroform is a liquid boiling at 61°, and solidifying at $-70°$. Its specific gravity at 15° is 1·498; it is only very slightly soluble in water, and possesses a characteristic ethereal odour and sweet taste. Its prolonged inhalation produces unconsciousness, whence it derives its value as an anæsthetic in surgical operations.

Its use for this purpose is not wholly unattended with danger. Notwithstanding the great fund of experience resulting from the frequency of its application, it occasionally happens that the use of chloroform is attended by fatal results. Ordinary ether is less dangerous, does not produce such disagreeable after-effects, and hence has in later years been preferred as an anæsthetic (**63**).

Chloroform is a somewhat unstable substance, and decomposes under the influence of light and air, yielding chlorine, hydrochloric acid, and carbon oxychloride, $COCl_2$. This decomposition can be prevented to a great extent by the addition of 1% of alcohol, and keeping the chloroform in bottles of non-actinic glass. The preservative action of alcohol probably depends upon its combination with the decomposition-products of the chloroform, thus preventing their exercising a catalytic accelerating influence on the decomposition. The halogen atoms of chloroform take part in double decompositions; thus, sodium ethoxide yields the ethyl ester of orthoformic acid:

$$CH\boxed{Cl_3 + 3Na}\cdot OC_2H_5 = CH(OC_2H_5)_3 + 3NaCl.$$

Formic acid can be obtained from chloroform by warming it with dilute alkalis, orthoformic acid being probably formed as an intermediate product, although the latter has not been isolated. When chloroform is treated with an aqueous solution of caustic potash (40%), carbon monoxide is evolved; it is assumed that chloromethylene, CCl_2, is formed as an intermediate product in this reaction.

When chloroform is warmed with alcoholic ammonia and caustic potash, its three chlorine atoms are replaced by nitrogen, with production of potassium cyanide. The formation of isonitriles from chloroform, alcoholic potash, and primary amines, has been already mentioned (**84**).

Chloropicrin, CCl_3NO_2, is obtained from chloroform by replacement of the hydrogen atom by a nitro-group by treatment with concentrated nitric acid. The constitution of chloropicrin is indicated by its yielding methylamine on reduction. It is a liquid with an extremely pungent odour, and is usually obtained by the distillation of picric acid with bleaching-powder, to which mode of preparation it owes its name.

Methylene chloride, CH_2Cl_2, is obtained from chloroform by reduction with zinc and hydrochloric acid in alcoholic solution. It is a liquid, boiling at 40°, and having a specific gravity of 1·337.

Tetrachloromethane, or *carbon tetrachloride*, CCl_4, produced by the action of chlorine on chloroform or carbon disulphide, is also a liquid, and boils at 76°. When heated with excess of water at 250° it yields HCl and CO_2. Its specific gravity is 1·593 at 20°. It will be noticed that these higher chlorine substitution-products have high specific gravities. The bromine and iodine compounds have considerably higher densities than the corresponding chlorine compounds.

Bromoform, $CHBr_3$, is obtained analogously to chloroform. It melts at 7·8°, boils at 151°, and has a specific gravity of 2·904 at 15°. It finds therapeutic application.

Iodoform, CHI_3.

152. Iodoform is a substance of great importance, and is obtained from alcohol by the action of potassium carbonate and iodine. The intermediate product, $CI_3 \cdot CHO$, analogous to chloral, has not been isolated.

Iodoform can also be prepared by the electrolysis of a solution containing 60 g. of potassium iodide, 20 g. of sodium carbonate, and 80 cc. of alcohol, in each 400 cc., the temperature being kept at 60° to 65°. Iodine is set free at the anode, so that the alcohol, K_2CO_3, and I, necessary to the formation of iodoform, are all present in the mixture. About 80% of the potassium iodide is by this method converted into iodoform, while the remainder of the iodine is finally obtained as potassium iodate. The formation of iodate can be avoided to a great extent by surrounding the cathode, at which caustic potash is formed, with parchment, which prevents the potash from coming in contact with the iodine set free at the anode.

Iodoform is a solid, and crystallizes in yellow hexagonal plates. It has a peculiar saffron-like odour, sublimes very readily, and melts at 119°.

These characteristic properties of iodoform make its formation an important test for alcohol, although it must be remembered that aldehyde, acetone, and several other substances similarly yield iodoform. Substances containing the group $CH_3 \cdot C$ linked to oxygen answer to the *iodoform test*. It is carried out by adding iodine to the liquid to be tested, and then caustic potash, drop by drop, until the colour of the iodine vanishes. If a large quantity of alcohol is present, a yellow precipitate is at once formed; if only traces, some time has to elapse before this takes place. The reaction is sufficiently delicate to show traces of alcohol in well-water and rain-water, after it has been concentrated as much as possible by repeated distillation, the first fraction in each case being collected.

Iodoform is used in surgery as an antiseptic. It is worthy of notice that it does not directly kill the bacteria, but that its action on the micro-organisms depends upon a previous decomposition brought about, under the influence of the heat of the body, by a fermentative action of the matter separated from the wound.

Methylene iodide, CH_2I_2, is obtained by the reduction of iodoform with hydriodic acid, phosphorus being added to regenerate HI (**29**). It is a liquid of remarkably high specific gravity, 3·292 at 18°.

II. HALOGEN DERIVATIVES OF THE HOMOLOGUES OF METHANE.

153. It is evident that among these derivatives numerous isomers are possible. For example, replacement by chlorine of three hydrogen atoms in normal pentane may take place in a number of different ways; a methyl-group may be converted into CCl_3, two chlorine atoms may replace the hydrogen of one methylene-group, while the third replaces another hydrogen atom in the molecule, or all three chlorine atoms may attach themselves to different carbon atoms; and so on.

The methods for the preparation of many of the halogen compounds included under this heading have already been mentioned, the compounds $C_pH_{2n+1} \cdot CHX_2$ and $C_nH_{2p+1} \cdot CX_2 \cdot C_qH_{2q+1}$ being obtained by the action of phosphorus pentahalide on aldehydes and ketones respectively (**106**). Compounds containing two halogen atoms attached to two adjoining carbon atoms are obtained by the addition of halogens to the hydrocarbons C_nH_2 ; those with four halogen atoms, two of which are directly attached to each of two adjoining carbon atoms, are produced by the addition of halogen to hydrocarbons containing a triple bond; while compounds of the type $C_pH_{2p+1} \cdot CHX \cdot CHX \cdot C_rH_{2r} \cdot CHX \cdot CHX \cdot C_mH_{2m+1}$ are obtained by addition of halogen to the hydrocarbons C_nH_{2n-4}, containing two double bonds; etc.

A general method for the preparation of compounds rich in halogen from the saturated hydrocarbons is the exchange of one hydrogen atom for halogen, removal of haloid acid by means of alcoholic potash, halogenation of the hydrocarbon C_nH_{2n} thus obtained, removal of HX, renewed halogenation of the product, and so on.

$$\underset{\text{Ethane}}{CH_3\cdot CH_3} \rightarrow \underset{\text{Ethyl chloride}}{CH_3\cdot CH_2Cl} - HCl \rightarrow \underset{\text{Ethylene}}{CH_2:CH_2} + 2Cl \rightarrow$$

$$\rightarrow \underset{\text{Ethylene chloride}}{CH_2Cl\cdot CH_2Cl} - 2HCl \rightarrow \underset{\text{Acetylene}}{CH\equiv CH} + 4Cl \rightarrow$$

$$\rightarrow \underset{\text{Ethylene tetrachloride}}{CHCl_2\cdot CHCl_2\cdot} - HCl \rightarrow \underset{\text{Trichloroethylene}}{CHCl:CCl_2} + 2Cl \rightarrow$$

$$\rightarrow \underset{\text{Pentachloroethane}}{CHCl_2\cdot CCl_3} - HCl \rightarrow \underset{\text{Tetrachloroethylene}}{CCl_2:CCl_2} + 2Cl \rightarrow \underset{\text{Hexachloroethane}}{CCl_3\cdot CCl_3}.$$

A general method for the preparation of compounds rich in bromine was discovered by VICTOR MEYER, and consists in the direct action of bromine on the hydrocarbons of the series C_nH_{2n+2} in presence of a small quantity of anhydrous iron bromide, or more simply, of iron-wire. Under these conditions, the substitution takes place very readily, and it has been shown that each carbon atom of a normal chain only takes up one bromine atom. Thus, propane yields tribromhydrin, $CH_2Br\cdot CHBr\cdot CH_2Br$, since the product is identical with the addition-product obtained by the action of bromine on allyl bromide, $CH_2:CH\cdot CH_2Br$.

When many of the hydrogen atoms of a hydrocarbon C_nH_{2n+2} have already been replaced by chlorine or bromine, it is no longer possible to substitute hydrogen by the direct action of a halogen. Chlorine has no action on pentachloroethane, for example. MOUNEYRAT has, however, shown that substitution readily takes place in presence of a small quantity of aluminium chloride, which first splits off haloid acid. In this way, pentachloroethane with aluminium chloride yields tetrachloroethylene, and the addition of halogen takes place at the double bond thus formed, the product being in this instance hexachloroethane.

Nomenclature, and Individual Members.

154. Compounds containing a halogen attached to a terminal carbon atom are denoted by the prefix ω, if to other carbon atoms, by α, β, etc. $CH_2Br\cdot CH_2\cdot CH_2Br$ is $\omega\omega'$-dibromopropane; $CH_2Br\cdot CHBr\cdot CH_3$ is $\omega\alpha$-dibromopropane.

Only a few of the numerous compounds of this group will be described.

Ethylene bromide is employed for syntheses, and as a solvent. It is prepared by leading ethylene into bromine covered with a layer of water to prevent evaporation, the addition taking place very readily. Ethylene bromide is a colourless liquid of agreeable odour, solidifies at 8°, boils at 131°, and has a specific gravity of 2·189 at 15°.

Ethylene chloride, $CH_2Cl \cdot CH_2Cl$, is called "Dutch Liquid," or the "Oil of the Dutch Chemists," owing to the fact that it was first prepared at the end of the eighteenth century by four Dutch chemists, DEIMAN, BONDT, PAETS VAN TROOSTWYK, and LAUWERENBURGH, by the action of chlorine upon ethylene. It is a liquid boiling at 84·9°, and has a specific gravity of 1·28 at 0°.

Trimethylene bromide, $CH_2Br \cdot CH_2 \cdot CH_2Br$, ωω′-dibromopropane, also plays an important part in syntheses, and is obtained by addition of HBr to allyl bromide, $CH_2 : CH \cdot CH_2Br$, produced from allyl alcohol. This method of formation suggests its having the constitution $CH_3 \cdot CHBr \cdot CH_2Br$, when it would be identical with the addition-product obtained by the action of bromine upon propylene, $CH_3 \cdot CH : CH_2$. Since this is not the case, the first constitutional formula given above is of necessity assigned to it. Trimethylene bromide is a liquid, B.P. 165°, sp. gr. 1·974 at 17°.

III. POLYHYDRIC ALCOHOLS

155. When more than one hydrogen atom of a saturated hydrocarbon is replaced by hydroxyl, it is theoretically possible to have more than one hydroxyl-group in union with a single carbon atom, or to have each attached to a different one. It should be possible to obtain compounds of the first class by replacement of halogen by hydroxyl in the halogen compounds $R \cdot CHX_2$, $R \cdot CX_3$, and $R \cdot CX_2 \cdot R'$. When this is attempted, for instance by bringing halogen compounds of this type into contact with silver acetate, with the intention of subsequently saponifying the compound thus obtained, stable acetates, such as $CH_2 < \begin{matrix} OC_2H_3O \\ OC_2H_3O \end{matrix}$, are indeed readily formed. But on saponification, a dihydric alcohol $CH_2(OH)_2$ is not obtained from them, aldehyde resulting instead by the elimination of one molecule of water. When compounds of the type $RCCl_3$ are treated with sodium ethoxide, substances with the general formula $R \cdot C(OC_2H_5)_3$, called *ortho-esters*, are obtained. On saponification, however, $R \cdot C(OH)_3$ does not result, the corresponding acid being formed instead, through loss of water. Ethers of dihydric alcohols, such as $CH_3 \cdot CH < {OC_2H_5 \atop OC_2H_5}$ are known, and are called *acetals* (**113**, 2). The decomposition of these substances yields, not $R \cdot CH(OH)_2$, but an aldehyde. It follows from these considerations that *compounds with more than one hydroxyl-group attached to the same carbon atom are unstable.* We shall see later that it is possible to obtain such compounds in certain cases (**204**, **233**, **237**, and **266**).

Many compounds are known containing several hydroxyl-groups, of which not more than one is attached to each carbon atom. Some of these are described below.

1. Glycols or Dihydric Alcohols.

156. The glycols are obtained from the corresponding halogen compounds analogously to the monohydric alcohols (**43**):

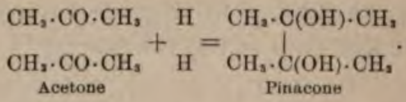
$$\underset{\text{Trimethylene bromide}}{CH_2Br \cdot CH_2 \cdot CH_2Br} + 2H_2O = \underset{\text{Trimethyleneglycol}}{CH_2OH \cdot CH_2 \cdot CH_2OH} + 2HBr.$$

The exchange of halogen for hydroxyl can be brought about by treatment with acetate of silver or of an alkali-metal, and saponification of the diacetate thus obtained. It can also be effected by boiling with sodium carbonate solution, or water and lead oxide.

Glycols of the type $R \cdot CHOH \cdot CHOH \cdot R$, in which the carbon atoms attached to hydroxyl are in direct union with one another, are formed from olefines either through the medium of their bromine addition-products, or by the direct addition of two OH-groups by means of careful oxidation with potassium permanganate. In this way ethylene yields the simplest dihydric alcohol, called *glycol*:

$$CH_2:CH_2 + H_2O + O = CH_2OH \cdot CH_2OH.$$

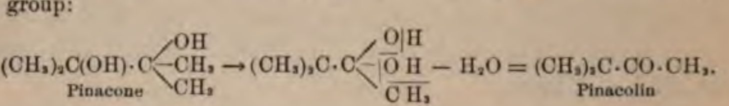
Another method for the formation of glycols of this type consists in the reduction of ketones. This may be either carried out with sodium in aqueous solution, or better, by electrolysis. For this purpose, the ketone is dissolved in dilute sulphuric acid; on passing a current through this solution, the reduction takes place at the cathode. Thus, acetone yields *pinacone*, in addition to isopropyl alcohol. All the glycols obtained by this method are distinguished by the name pinacones. The constitution of pinacone is indicated by this synthesis:



$$\begin{matrix} CH_3\cdot CO\cdot CH_3 \\ CH_3\cdot CO\cdot CH_3 \end{matrix} + \begin{matrix} H \\ H \end{matrix} = \begin{matrix} CH_3\cdot C(OH)\cdot CH_3 \\ | \\ CH_3\cdot C(OH)\cdot CH_3 \end{matrix}.$$

Acetone Pinacone

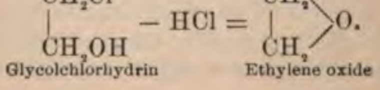
When distilled with dilute sulphuric acid, pinacone undergoes a remarkable intramolecular transformation which may be explained by assuming that a hydroxyl-group changes place with a methyl-group:



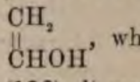
Pinacone Pinacolin

The constitution of *pinacolin* may be deduced from its synthesis by the action of zinc-methyl on the chloride of trimethylacetic acid, $(CH_3)_3C\cdot COCl$, and in other ways.

The majority of the glycols are colourless, viscous liquids of sweet taste, whence the series derives its name. Their boiling-points and specific gravities are considerably higher than those of the monohydric alcohols containing the same number of carbon atoms. Thus, glycol boils at 197·5°, and ethyl alcohol at 78°; at 0° the specific gravity of glycol is 1·128, and of ethyl alcohol 0·806. The behaviour of the hydroxyl-group in glycol and in the monohydric alcohols is perfectly analogous; exchange of OH for halogen, the formation of ethers, esters, and alkoxides, and, in the case of primary glycols, the formation of aldehydes and acids, may take place in connection with one or both of the hydroxyl-groups. For instance, the compounds $CH_2OH\cdot CH_2Cl$, *glycolchlorhydrin*, $CH_2OC_2H_5\cdot CH_2OH$, *glycol monoethylether*, $CH_2OC_2H_5\cdot CH_2OC_2H_5$, *glycol diethylether*, etc., are known. The glycols possess, however, one property due to the presence of two hydroxyl-groups, the power of forming anhydrides. The first member of the series, glycol, $CH_2OH\cdot CH_2OH$, does not yield an anhydride by the direct elimination of water, but a compound of the formula C_2H_4O is obtained by first replacing one hydroxyl-group by Cl and then splitting off HCl:



Glycolchlorhydrin Ethylene oxide

This compound, *ethylene oxide*, boils at 14°, and is therefore gaseous at ordinary temperatures: it readily takes up water, forming glycol; or hydrochloric acid, forming glycolchlorhydrin. To ethylene oxide is assigned the constitutional formula given above, because it yields ethylene chloride when treated with phosphorus pentachloride, the oxygen atom being replaced by two chlorine atoms. If the compound had the constitution  $\begin{matrix} CH_2 \\ \| \\ CHOH \end{matrix}$, which seems also possible, but is, however, less probable (**136**), it would not yield ethylene chloride when thus treated.

Some of the higher homologues of glycol, between the hydroxyl-groups of which four or five carbon atoms intervene, yield anhydrides with a constitution analogous to that of ethylene oxide. They show a marked diminution in the power of forming addition-products with water; or, in other words, the *closed chain* of carbon atoms and one oxygen atom is not so easily broken as in ethylene oxide itself.

2. Trihydric Alcohols.

157. The principal representative of the group of trihydric alcohols is *glycerol*, or *glycerine*, $C_3H_5(OH)_3$. In accordance with the rule given above, that two hydroxyl-groups cannot attach themselves to the same carbon atom, glycerol can only have the structure

$$CH_2OH \cdot CHOH \cdot CH_2OH.$$

This structure finds support in the following proofs.

1. On careful oxidation of allyl alcohol by means of potassium permanganate, two OH-groups are added at the position of the double bond:

$$CH_2{:}CH \cdot CH_2OH \rightarrow CH_2OH \cdot CHOH \cdot CH_2OH.$$

2. When glycerol, $C_3H_8O_3$, is carefully oxidized, *glyceric acid*, $C_3H_6O_4$, is first formed, corresponding to the formation of acetic acid, $C_2H_4O_2$, from ethyl alcohol, C_2H_6O, by exchange of two hydrogen atoms for one oxygen atom, which makes it evident that glycerol contains one —CH_2OH-group. Further oxidation converts glyceric acid into *tartronic acid*, $C_3H_4O_5$, two hydrogen atoms being replaced by one oxygen atom, with formation of a new

carboxyl-group. Hence, glycerol contains two —CH_2OH-groups in the molecule, so that its constitution is $CH_2OH \cdot CH_2O \cdot CH_2OH$. Since tartronic acid, $COOH \cdot CH_2O \cdot COOH$, still possesses alcoholic properties, the group CH_2O must have the constitution $>CHOH$, and since it must have the same constitution in the molecule of glycerol, the structure of the latter is proved to be $CH_2OH \cdot CHOH \cdot CH_2OH$.

3. A further proof of the constitution given above is the formation of glycerol from tribromhydrin (**153**).

Glycerol is a colourless, oily liquid of sweet taste, is very hygroscopic, and miscible in all proportions with water and alcohol, but insoluble in ether. It solidifies only after standing for some time at a low temperature, but the crystals thus formed do not melt below 17°. B.P. 290°, sp. gr. 1·265 at 15°. Its chemical behaviour is completely in accordance with the constitution of a trihydric alcohol. Thus, it yields three esters, by replacement of one, two, or three hydroxyl-groups.

Since glycerol is a substance which plays a very important part in the economy of nature as a constituent of the fats (**159**), its synthesis from its elements is of great interest. This was effected by FRIEDEL and SILVA. The starting-point was acetic acid. This can be synthesized from its elements in several ways, for example by the oxidation of acetaldehyde obtained by the action of water on acetylene (**132**). The dry distillation of calcium acetate gave acetone, which was reduced to isopropyl alcohol. On elimination of water from the latter, propylene was formed, which, on addition of chlorine, was converted into propylene dichloride, from which trichlorhydrin was obtained by treatment with iodine chloride. Trichlorhydrin was converted into glycerol by heating with water at 170°:

$$\underset{\text{Acetic acid}}{CH_3 \cdot COOH} \rightarrow \underset{\text{Acetone}}{CH_3 \cdot CO \cdot CH_3} \rightarrow \underset{\text{Isopropyl alcohol}}{CH_3 \cdot CHOH \cdot CH_3} \rightarrow \underset{\text{Propylene}}{CH_3 \cdot CH{:}CH_2} \rightarrow$$

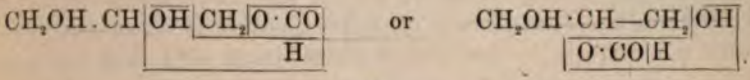
$$\rightarrow \underset{\text{Propylene dichloride}}{CH_3 \cdot CHCl \cdot CH_2Cl} \rightarrow \underset{\text{Trichlorhydrin}}{CH_2Cl \cdot CHCl \cdot CH_2Cl} \rightarrow \underset{\text{Glycerol}}{CH_2OH \cdot CHOH \cdot CH_2OH}.$$

158. Several compounds, difficult to prepare from any other substance, may be obtained from glycerol. Among them may be mentioned allyl alcohol, allyl iodide, acrolein, and isopropyl iodide.

Allyl alcohol, $CH_2{:}CH \cdot CH_2OH$, can be obtained from glycerol by heating it with oxalic acid, $COOH \cdot COOH$. The monoformic acid ester of glycerol, *monoformin*,

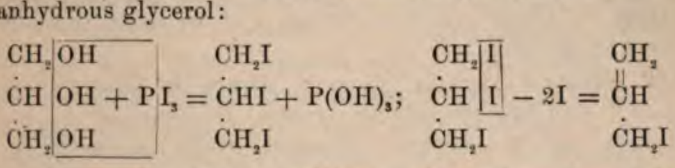
$$CH_2OH \cdot CHOH \cdot CH_2 \cdot O\underset{\dot{H}}{C}O \quad \text{or} \quad CH_2OH \cdot \underset{OC_O^H}{\underset{|}{CH}} \cdot CH_2OH,$$

is first formed, as under these conditions oxalic acid loses one molecule of CO_2, yielding formic acid, $\overline{COO}|H—COOH$, which combines with the glycerol to produce monoformin. When heated more strongly, this decomposes into allyl alcohol, water, and carbon dioxide:



$$CH_2OH.CH\boxed{OH}\,\underset{H}{\underline{CH_2\boxed{O\cdot CO}}}\qquad\text{or}\qquad CH_2OH\cdot CH{-}\underset{\boxed{O\cdot CO|H}}{CH_2}\boxed{OH}.$$

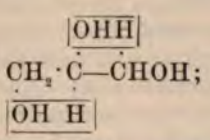
Allyl iodide is obtained by the action of phosphorus and iodine on anhydrous glycerol:



$$\begin{array}{lllll} CH_2|OH & & CH_2I & CH_2|I| & CH_2 \\ \dot{C}H|OH & +\ PI_3 = & \dot{C}HI + P(OH)_3; & \dot{C}H|I| - 2I = & \overset{\|}{C}H \\ \dot{C}H_2|OH & & \dot{C}H_2I & \dot{C}H_2I & \dot{C}H_2I \end{array}$$

The tri-iodhydrin, $C_3H_5I_3$, which is probably formed as an intermediate product in this reaction, is unstable, and at once loses two atoms of iodine, yielding allyl iodide.

Acrolein (**147**) is formed by the elimination of water from glycerol:



$$\begin{array}{c}\boxed{OHH}\\ CH_2\cdot\dot{C}{-}\dot{C}HOH;\\ \boxed{OH\ H}\end{array}$$

whereby $CH_2{:}C{:}CHOH$ should result, but immediately changes into acrolein, $CH_2{:}CH\cdot C^{H}_{O}$ (**136**).

Isopropyl iodide is formed by the addition of water to a mixture of glycerol with iodine and phosphorus. In this reaction, propylene, $CH_3\cdot CH{:}CH_2$, is formed as an intermediate product, and is evolved in the free state when care is not taken to have sufficient hydriodic acid present. By the addition of HI, produced by the interaction of iodine, phosphorus, and water, isopropyl iodide is formed from the propylene thus generated:

$$\underset{\text{Propylene}}{CH_3\cdot CH{:}CH_2} + HI = \underset{\text{Isopropyl iodide}}{CH_3\cdot CHI\cdot CH_3}.$$

Formic acid (**88**) is usually prepared by the action of glycerol on oxalic acid. As mentioned above, when these substances are heated together, carbon dioxide is evolved, and the glyceryl ester of formic acid produced. Formic acid is obtained from the latter by saponification, the glycerol being regenerated at the same time. This is best carried out by the addition of a fresh quantity of oxalic acid, $C_2H_2O_4$, 2aq, whose water of crystallization effects the saponification of the ester, the formic acid distilling over. The glycerol thus regenerated is again converted into monoformin by the freshly-added oxalic acid, and the ester once more decomposed by the addition of a further quantity of oxalic acid, etc. It is in this way possible to convert unlimited quantities of oxalic acid into formic acid by means of a given quantity of glycerol.

159. Glycerol exists in nature in large quantities in the form of esters. The fats and oils are glyceryl tri-esters of the higher fatty acids, and of oleïc acid; glycerol and the fatty acids are obtained from them by saponification (**91** and **101**).

The saponification of the tri-esters of glycerol with caustic soda or lime takes place in stages, the di-esters and mono-esters being formed as intermediate products; this may be proved as follows. On complete saponification, pure tristearin, or glyceryl tristearate, yields only stearic acid and glycerol, so that if no intermediate products are formed, a partially-saponified portion, in which the soap produced has been decomposed by hydrochloric acid, and the glycerol removed by washing with water, should contain only unchanged tristearin and stearic acid. Neither tristearin nor stearic acid can yield acetyl-derivatives with acetic anhydride. If the saponification take place in stages, monostearin and distearin would be formed, and the free hydroxyl-groups of the glyceryl-residue in these compounds would react with acetic anhydride to form acetyl-compounds. On treatment with this anhydride, and subsequent complete saponification, acetic acid would be among the products; it has been shown by experiment that this actually does occur.

Inversely, the fats can be synthesized from glycerol and the fatty acids; for instance, *tristearin* is obtained by heating glycerol with excess of stearic acid under reduced pressure at 200° until separation of water ceases.

When kept for some time, many fats become *rancid*, and develop a disagreeable smell and taste. This is due to atmospheric oxidation, which is facilitated by the influence of light. The unsaturated fatty acids become converted into others containing a smaller number of carbon atoms, and with a characteristic odour and taste.

Glycerol

ether

$H_2O - C_2H_5OH$

160. Glycerol is extensively employed in the arts and in medicine. One of its most important uses is for the preparation of the so-called "nitroglycerine." This explosive has a misleading name, since it is glyceryl trinitrate,

$$\begin{array}{l} CH_2O\cdot NO_2 \\ \dot{C}HO\cdot NO_2, \\ \dot{C}H_2O\cdot NO_2 \end{array}$$

and not a nitro-compound (**75**); for on saponification with alkalis it yields glycerol, and the nitrate of the corresponding alkali-metal.

Nitroglycerine is prepared by bringing glycerol into contact with a mixture of concentrated sulphuric and nitric acids, care being taken to avoid a rise in temperature. After a time, the reaction-mixture is poured into water, whereupon the nitrate separates in the form of an oily liquid of faint, headache-producing odour, and can be purified by washing with water. When perfectly pure, it does not explode spontaneously.

Nitroglycerine is a liquid, and as its use in this form for technical purposes would be attended with difficulties, it is mixed with infusorial earth (kieselguhr), which absorbs it, forming a soft, plastic mass, *dynamite*, containing usually 75% of nitroglycerine, and 25% of the earth. Nitroglycerine can also be obtained in the solid form by dissolving in it a small amount of guncotton (**231**), which converts it into an elastic solid resembling jujubes in consistence, called "blasting gelatine." This substance has the advantage over dynamite of not leaving any solid residue after explosion. Dynamite cannot be used as ammunition, its velocity of explosion being so great as to produce an impulse too violent for a gun to resist without bursting; that is, it exerts a *brisant* effect.

FIN. 54

3. Tetrahydric and Polyhydric Alcohols.

161. Among the tetrahydric alcohols may be mentioned *erythritol*, $CH_2OH\cdot CHOH\cdot CHOH\cdot CH_2OH$, which is a natural product. That it contains a normal carbon chain is proved by its conversion into *n*-secondary butyl iodide, $CH_3\cdot CHI\cdot CH_2\cdot CH_3$, on reduction with hydriodic acid.

Examples of pentahydric alcohols are *arabitol and xylitol*, $C_5H_{12}O_5$, which are stereoisomers, as are also the hexahydric alcohols *dulcitol and mannitol*, $C_6H_{14}O_6$, both of which are found in nature. These all have normal carbon chains, since, like erythritol, they yield *n*-secondary iodides on reduction with hydriodic acid; for example, mannitol is converted into

$$\mathrm{CH_3 \cdot CH_2 \cdot CHI \cdot CH_2 \cdot CH_2 \cdot CH_3}.$$

They can be obtained artificially by the reduction of the corresponding aldehydes or ketones. The reason for assuming their stereoisomerism will appear later (**212**). It is sufficient to remark here that the polyhydric alcohols contain asymmetric carbon atoms, indicated in the following formulæ by asterisks:

$$\mathrm{CH_2OH \cdot \overset{*}{C}HOH \cdot CHOH \cdot \overset{*}{C}HOH \cdot CH_2OH};$$

Arabitol and Xylitol

$$\mathrm{CH_2OH \cdot \overset{*}{C}HOH \cdot \overset{*}{C}HOH \cdot \overset{*}{C}HOH \cdot \overset{*}{C}HOH \cdot CH_2OH}.$$

Dulcitol and Mannitol

The presence of polyhydric alcohols prevents the precipitation of the salts of copper, iron, and other metals by means of alkalis; thus, a solution of copper sulphate to which glycerol has been added does not yield a precipitate of copper hydroxide with caustic potash. This is due to the formation of soluble metallic compounds of the polyhydric alcohols, whose hydroxyl-hydrogen is replaced by the metal. This property is not only possessed by the polyhydric alcohols, but also by many other compounds containing several hydroxyl-groups (**192**).

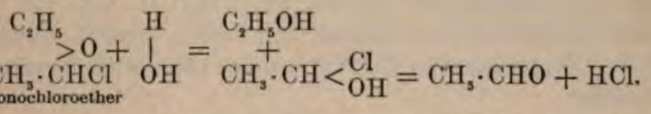
IV. DERIVATIVES CONTAINING HALOGEN ATOMS, HYDROXYL-GROUPS, NITRO-GROUPS, OR AMIDO-GROUPS.

162. We shall only consider a few of the numerous compounds belonging to this class, of which it may be said in general that the chemical properties of its members are determined by the substituents.

No compounds containing halogen and hydroxyl attached to the same carbon atom are known; when their formation might be expected, halogen acid is split off, with production of aldehydes or ketones. It has more than once been mentioned that stable alkyl-derivatives of compounds themselves unstable or unknown, such as the ortho-esters, exist (**155**). This is true in this instance, for while compounds of the type $\mathrm{R \cdot CH} <\!\begin{smallmatrix}\mathrm{Cl}\\ \mathrm{OH}\end{smallmatrix}$ are unknown, derivatives of the formula $\mathrm{R \cdot CH} <\!\begin{smallmatrix}\mathrm{Cl}\\ \mathrm{O \cdot C_nH_{2n+1}}\end{smallmatrix}$ are known. These substances are called *chloroethers*. When chlorine is passed into ethyl ether, which is kept cool and away from the action of light, to avoid explosion, the hydrogen atoms are replaced by chlorine; the monosubstituted product has the constitution

$$\underset{\text{Monochloroether}}{CH_3\cdot CH_2\cdot O\cdot CHCl\cdot CH_3},$$

as is proved by the action of sulphuric acid, under whose influence it takes up one molecule of water, forming ethyl alcohol, acetaldehyde, and hydrochloric acid:



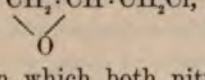
$$\underset{\text{Monochloroether}}{\begin{matrix}C_2H_5\\ CH_3\cdot CHCl\end{matrix}\!>O} + \begin{matrix}H\\ |\\ OH\end{matrix} = \begin{matrix}C_2H_5OH\\ +\\ CH_3\cdot CH<^{Cl}_{OH}\end{matrix} = CH_3\cdot CHO + HCl.$$

Compounds containing halogen and hydroxyl attached to different carbon atoms are obtained from the polyhydric alcohols by partial exchange of hydroxyl for halogen, and have the general name *halogen-hydrins*. The *dichlorhydrin* of glycerol, $C_3H_5(OH)Cl_2$, is formed when a solution of glycerol in glacial acetic acid is saturated with hydrochloric-acid gas. It has the symmetrical formula

$$CH_2Cl\cdot CHOH\cdot CH_2Cl,$$

since it differs from the dichlorhydrin obtained by addition of chlorine to allyl alcohol, this having the constitution

$$CH_2OH\cdot CHCl\cdot CH_2Cl.$$

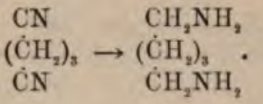
On treatment of the unsymmetrical dichlorhydrin with caustic potash, *epichlorhydrin*,  is obtained.

Dinitro-compounds in which both nitro-groups are linked to the same carbon atom, are obtained from primary bromo-nitro-compounds by the action of potassium nitrite:

$$CH_3\cdot CHBrNO_2 + KNO_2 = CH_3\cdot CH(NO_2)_2 + KBr.$$

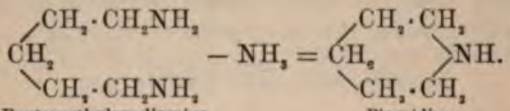
The hydrogen atom in union with the carbon atom carrying the nitro-groups, can be readily replaced by metals, so that these primary dinitro-compounds have an acidic character (**281**).

Diamines in which the two amido-groups are attached to the same carbon atom, are not numerous; most of them have their amido-groups attached to different carbon atoms. Some of these compounds are formed by the putrefaction of animal matter, such as flesh, and are classed, with other basic substances formed in the same way, as *ptomaïnes*. Among them may be mentioned *cadaverine* (*pentamethylenediamine*), $NH_2 \cdot CH_2 \cdot (CH_2)_3 \cdot CH_2 \cdot NH_2$, and *putrescine* (*tetramethylenediamine*), $NH_2 \cdot CH_2 \cdot (CH_2)_2 \cdot CH_2 \cdot NH_2$. The constitution of these substances has been proved by synthesis, pentamethylenediamine being thus obtained: trimethylene bromide, $Br \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot Br$, is converted by treatment with potassium cyanide into trimethylene cyanide, $CN \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CN$. This substance is reduced with sodium and boiling alcohol, which converts the CN-groups into CH_2NH_2-groups (**85**), with formation of the diamine:



$$\begin{matrix} CN \\ (\dot{C}H_2)_3 \\ \dot{C}N \end{matrix} \rightarrow \begin{matrix} CH_2NH_2 \\ (\dot{C}H_2)_3 \\ \dot{C}H_2NH_2 \end{matrix}.$$

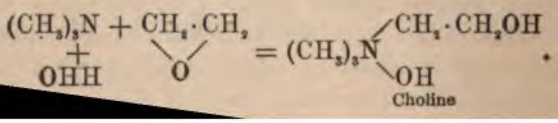
When pentamethylenediamine hydrochloride is heated, it loses one molecule of ammonia, and is converted into *piperidine*, which has the character of a saturated secondary amine. For this and other reasons (**387**), it is assigned the ring-formula given in the following equation:



Pentamethylenediamine Piperidine

When heated, tetramethylenediamine and trimethylenediamine yield analogous closed-chain compounds, but less readily, whereas ethylenediamine is incapable of doing so.

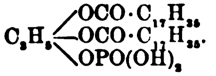
A substance, partly amine and partly alcohol, should be referred to here, on account of its physiological importance; it is *choline*, $C_5H_{15}NO_2$, which is widely distributed in the vegetable kingdom. Its constitution is inferred from its synthesis by the interaction of trimethylamine and ethylene oxide in aqueous solution:



Choline

Ethylene oxide can also combine with substances like ethylamine, with formation of amino-alcohols.

Choline is a constituent of a very complicated substance called *lecithin*, which is present in brain-matter, and also in yolk of egg. On treatment with dilute acids, lecithin is converted into choline, and a tri-ester of glycerol, *glycerophosphoric acid distearate*,



$$C_3H_5\begin{cases}OCO\cdot C_{17}H_{35}\\OCO\cdot C_{17}H_{35}.\\OPO(OH)_2\end{cases}$$

Lecithin is, therefore, the choline salt of this compound.

FINISH

POLYBASIC ACIDS.

I. SATURATED DIBASIC ACIDS, $C_nH_{2n-2}O_4$.

163. Many isomers of the acids $C_nH_{2n}(COOH)_2$ are theoretically possible, and differ from one another in the positions at which the carboxyl-groups are linked to the carbon chain. For many reasons, the most important are those whose carboxyl-groups are in union with the terminal carbon atom of the normal chain, the $\omega\omega'$-acids (**154**). On this account, these will be described here.

The general methods for the preparation of the dibasic and the monobasic acids are analogous. The former are produced by the oxidation of the corresponding glycols and aldehydes, and by the hydrolysis of the dinitriles, although many of them are prepared by special methods.

Physical and Chemical Properties.

164. These acids are well-defined crystalline substances; those containing more than three carbon atoms can be distilled *in vacuo* without decomposition. Many of them split off water when distilled under ordinary pressure.

The melting-points of these acids exhibit the same peculiarity as those of the fatty acids (**87**); the members containing an even number of carbon atoms have higher melting-points than those immediately succeeding them, with an uneven number of carbon atoms. This is seen from the table on p. 189.

This relation is graphically represented in Fig. 31, from which it is seen that the melting-points of the even and uneven series approximate more and more closely as the number of the carbon atoms increases.

A similar peculiarity is displayed in the solubility of these acids in water, given in the last column of the table. The solubility of the acids with an uneven number of carbon atoms is much greater four [illegible] acids

Name.	Formula.	Melting-point.	Parts by Weight Soluble in 100 Parts of Water.
Oxalic acid..........	$COOH \cdot COOH$	189° *	10·2 at 20°
Malonic acid........	$COOH \cdot CH_2 \cdot COOH$	132°	139·37 ,, 15°
Succinic acid........	$COOH \cdot (CH_2)_2 \cdot COOH$	182°	5·14 ,, 14·5°
Glutaric acid........	$COOH \cdot (CH_2)_3 \cdot COOH$	97·5°	80·3 ,, 14°
Adipic acid..........	$COOH \cdot (CH_2)_4 \cdot COOH$	149°	1·44 ,, 15°
Pimelic acid........	$COOH \cdot (CH_2)_5 \cdot COOH$	103°	4·1 ,, 20°
Suberic acid........	$COOH \cdot (CH_2)_6 \cdot COOH$	141°	0·142 ,, 15·5°
Azelaïc acid.........	$COOH \cdot (CH_2)_7 \cdot COOH$	108°	
Sebacic acid........	$COOH \cdot (CH_2)_8 \cdot COOH$	133°	0·1 ,, 17°
Decamethylene-dicarboxylic acid..	$COOH \cdot (CH_2)_{10} \cdot COOH$	125°	
Brassylic acid.......	$COOH \cdot (CH_2)_{11} \cdot COOH$	112°	
Dodecamethylene-dicarboxylic acid..	$COOH \cdot (CH_2)_{12} \cdot COOH$	123°	

* Anhydrous oxalic acid.

than the solubility of those with an even number, and it diminishes in both cases as the number of carbon atoms increases.

Oxalic acid is a very much stronger acid than its higher homologues, as is shown by the dissociation constants. For oxalic acid *K* is about 10·0, for malonic acid, 0·163, and for succinic acid, 0·0065; for the remaining acids it has values which diminish with increase in the number of carbon atoms, but are of the same order as the last number. The further the carboxyl-groups are removed from each other, the weaker is the acid.

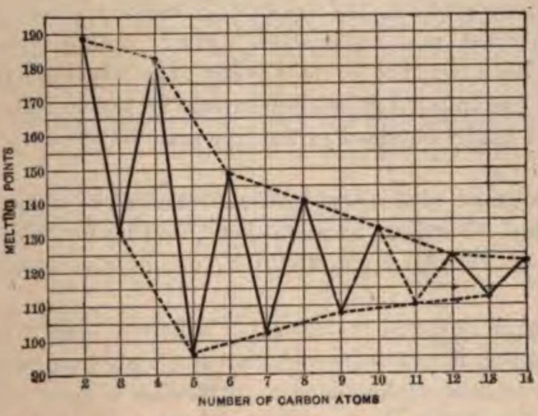


FIG. 31.—GRAPHIC REPRESENTATION OF THE MELTING-POINTS OF THE ACIDS $C_nH_{2n-2}O_4$.

Oxalic Acid, $C_2H_2O_4 + 2H_2O$.

165. Between oxalic acid and formic acid there exists a genetic interdependence; it is possible to prepare formic acid from oxalic, or conversely, oxalic from formic acid. On rapidly heating potassium or sodium formate, hydrogen is evolved from the fusing mass, and potassium or sodium oxalate is formed:

$$\begin{array}{l|l|} \text{KOOC} & \text{H} \\ \text{KOOC} & \text{H} \end{array} = \begin{array}{r} \text{KOOC} \\ | \\ \text{KOOC} \end{array} + H_2.$$

The reverse transformation of oxalic into formic acid has already been described (**158**), and constitutes the ordinary method for the preparation of formic acid.

Oxalic acid is frequently produced by the oxidation of organic substances with nitric acid; thus, it is formed by the action of this acid on sugar. It is prepared on the manufacturing scale by heating a mixture of caustic potash and caustic soda to the point of fusion along with sawdust. A formate is produced as an intermediate product, and, on further heating, loses hydrogen, and is converted into an oxalate. After cooling, the mass is lixiviated with water, the oxalate going into solution; the oxalic acid is then precipitated as calcium oxalate by the addition of milk of lime, and finally obtained in the free state by the action of sulphuric acid.

The production of this acid by the interaction of carbon dioxide and potassium or sodium at about 360°, and its formation by the hydrolysis of cyanogen gas, CN·CN, are of theoretical importance.

Oxalic acid is found in nature in different plants, chiefly in species of *oxalis*, in the form of potassium hydrogen, or calcium, salt. It is sometimes found as a crystalline deposit of calcium oxalate in plant-cells. It crystallizes with two molecules of water of crystallization, which it begins to lose at 30°. The anhydrous acid can be sublimed by careful heating, but when strongly heated, either alone or with concentrated sulphuric acid, decomposes into CO_2, CO, and H_2O. The same decomposition takes place when a solution of uranium oxalate is exposed to sunlight, CO and CO_2 being energetically evolved. Oxalic acid is very easily oxidized; a

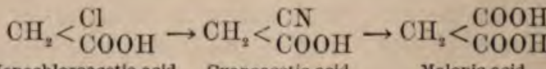
The following derivatives of oxalic acid are worthy of mention. The *dimethyl ester* is solid, M.P. 54°, and is used in the preparation of pure methyl alcohol; the *diethyl ester* is a liquid. Both are prepared by distilling a solution of anhydrous oxalic acid in the absolute alcohol. The amide, *oxamide*, $CONH_2 \cdot CONH_2$, is a white solid, nearly insoluble in water, alcohol, and ether, and is obtained as a crystalline precipitate by the addition of ammonia to a solution of a dialkyl oxalate.

The monoamides of the dibasic acids are called *amic acids*, that of oxalic acid being *oxamic acid*, $CONH_2 \cdot COOH$. It is a crystalline compound, readily soluble in ~~c~~old water, and insoluble in alcohol.

made by heating $\begin{array}{l}COOH\\COONH_4\end{array}$

Malonic Acid, $COOH \cdot CH_2 \cdot COOH$.

166. The constitution of *malonic acid* is proved by its synthesis from monochloroacetic acid. When an aqueous solution of potassium monochloroacetate is boiled with potassium cyanide, cyanoacetic acid is formed, and can be converted into malonic acid by hydrolysis of the nitrile-group:



$$CH_2<\begin{array}{l}Cl\\COOH\end{array} \rightarrow CH_2<\begin{array}{l}CN\\COOH\end{array} \rightarrow CH_2<\begin{array}{l}COOH\\COOH\end{array}.$$

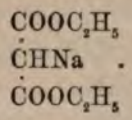
Monochloroacetic acid Cyanoacetic acid Malonic acid

Malonic acid is a crystalline substance; its physical properties will be found in the table on page 189. When heated a little above its melting-point, it loses one molecule of carbon monoxide, being converted into acetic acid:

$$COOH \cdot CH_2 \cdot \boxed{COO}H = CO_2 + COOH \cdot CH_3.$$

Experience shows that *when compounds in which two carboxyl-groups are in union with one carbon atom, are heated above their melting-points, each molecule loses one molecule of carbon dioxide.*

The most important compound of malonic acid is its *diethyl ester*, on account of the many important syntheses which can be accomplished by its aid. It is a liquid of faint odour, boiling at 198°, and having a specific gravity of 1·061 at 15°. On treatment with sodium, in the proportion of one atom to each molecule of ester, hydrogen is evolved, and the malonic ester converted into a solid mass. In this reaction, hydrogen is replaced by sodium, yielding ***sodiomalonic ester***, a compound of the structure



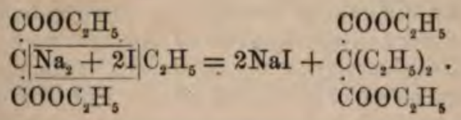
$$\begin{array}{l} COOC_2H_5 \\ CHNa \\ COOC_2H_5 \end{array} .$$

This is proved by treating it with an alkyl halide (iodide), by which sodium halide and an ester are obtained:

$$C_2H_5\boxed{I + Na}CH(COOC_2H_5)_2 = C_2H_5\cdot CH(COOC_2H_5)_2 + NaI.$$

On saponification, this ester yields a homologue of malonic acid.

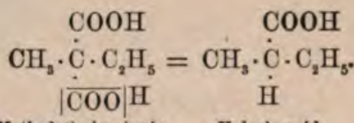
If two atoms of sodium, instead of one, react with one molecule of malonic ester, two hydrogen atoms are replaced. Both of these hydrogen atoms are in the methylene-group, because, on treatment of the disodio-compound with two molecules of an alkyl iodide, the two sodium atoms are replaced by alkyl, with production of a substance which on saponification is converted into a homologue of malonic acid:



$$\begin{array}{l} COOC_2H_5 \\ C\boxed{Na_2 + 2I}C_2H_5 \\ COOC_2H_5 \end{array} = 2NaI + \begin{array}{l} COOC_2H_5 \\ C(C_2H_5)_2 \\ COOC_2H_5 \end{array} .$$

It is also possible to introduce two different alkyl-groups into malonic ester. Thus, when monosodiomalonic ester is treated with *methyl* iodide, the ester of methylmalonic acid is formed, which on treatment with sodium again yields a sodio-compound; this is converted by *ethyl* iodide into the ester of ethylmethylmalonic acid.

It is evident from the examples which have been given, that, with malonic ester as a starting-point, it is possible to synthesize a great number of dibasic acids. Moreover, since all these acids contain two carboxyl-groups linked to the same carbon atom, and have in common with malonic acid the property of losing CO_2 when heated above their melting-points, it is evident that the malonic ester synthesis is also available for the preparation of the monobasic fatty acids. For example, methylethylmalonic acid loses CO_2 on heating, yielding methylethylacetic acid, identical in constitution with active valeric acid **(51)**. It can be resolved into its two active components:



$$\begin{array}{c}\text{COOH}\\ \text{CH}_3\cdot\dot{\text{C}}\cdot\text{C}_2\text{H}_5\\ |\overline{\text{COO}}|\text{H}\end{array} = \begin{array}{c}\text{COOH}\\ \text{CH}_3\cdot\dot{\text{C}}\cdot\text{C}_2\text{H}_5.\\ \text{H}\end{array}$$

Methylethylmalonic acid **Valeric acid**

The malonic ester synthesis is one of the most generally applicable methods for the preparation of acids, and it will be frequently necessary to refer to it later.

Method of carrying out the malonic ester synthesis.—This is always effected in the following way. One gramme-molecule of malonic ester is mixed with a ten per cent. solution of sodium ethoxide (1 equivalent) in absolute alcohol, obtained by the action of sodium on alcohol. To this mixture is added one gramme-molecule of an alkyl iodide, and the reaction-mixture heated on a water-bath under a reflux-condenser until the liquid is no longer alkaline. After the alcohol has been distilled off, the residue is treated with water to dissolve the sodium iodide formed, and the alkyl-malonic ester extracted with ether. The ethereal solution is dried over calcium chloride, the ether distilled off, and the residue purified by fractionation.

If it is desired to introduce two alkyl-groups or other groups, this is accomplished by employing two equivalents of sodium ethoxide, and two gramme-molecules of an alkyl iodide. When two different groups are to be substituted, one of them is first introduced into the molecule, and on subsequent treatment with a second gramme-molecule of sodium ethoxide and of alkyl iodide, the dialkyl-malonic ester is produced. In both these cases, the remainder of the process is identical with that described above.

END

Succinic Acid, $\text{COOH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$.

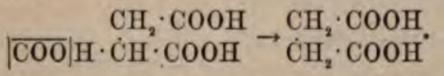
167. *Succinic acid* is a crystalline substance, melting at 182°, and dissolving with difficulty in cold water. It is present in amber, in fossilized wood, and in many plants, and can be synthetically prepared by the following methods.

1. From ethylene bromide by treatment with potassium cyanide, which converts it into ethylene cyanide, $\text{CN}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CN}$; on ponification, this yields succinic acid.

2. From malonic acid by treating monosodiomalonic ester with monochloroacetic ester:

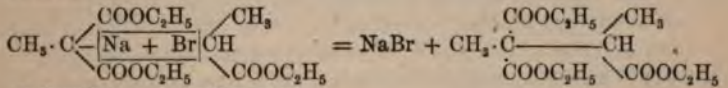
$$(COOC_2H_5)_2CH\boxed{Na + Cl}H_2C\cdot COOC_2H_5 =$$
$$= NaCl + (COOC_2H_5)_2CH\cdot CH_2\cdot COOC_2H_5.$$

In this reaction an ester of *ethanetricarboxylic acid* is formed; when heated above its melting-point, the acid corresponding to this loses CO_2, yielding succinic acid:

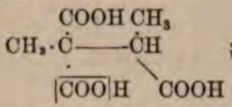
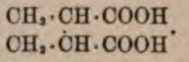


$$\begin{array}{r} CH_2\cdot COOH \\ \boxed{COO}H\cdot \dot{C}H\cdot COOH \end{array} \rightarrow \begin{array}{l} CH_2\cdot COOH \\ \dot{C}H_2\cdot COOH \end{array}.$$

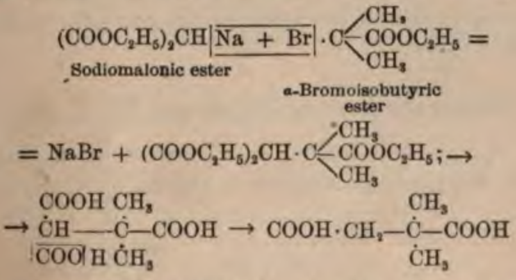
Substituted succinic acids can be obtained in the same way. On the one hand, starting not from malonic ester itself, but from a monoalkylmalonic ester, and on the other, from an α-halogen-substituted ester, $C_nH_{2n+1}\cdot CHCl\cdot COOC_2H_5$, symmetrical dialkyl-succinic acids are obtained:



Sodiomethyl-malonic ester α-Bromopropionic ester

Saponification yields  ; and finally, splitting off CO_2 gives symmetrical dimethylsuccinic acid,  $\begin{array}{l} CH_3\cdot CH\cdot COOH \\ CH_3\cdot \dot{C}H\cdot COOH \end{array}$.

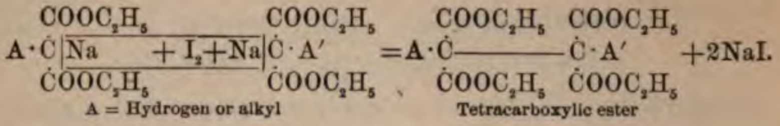
Unsymmetrical substituted succinic acids, in which the hydrogen atoms of only one methylene-group have been replaced, can be obtained in an analogous manner. The following equations indicate the method for the preparation of unsymmetrical dimethylsuccinic acid:



Sodiomalonic ester

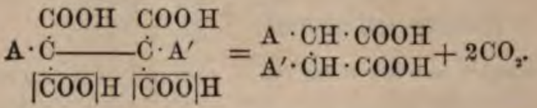
α-Bromoisobutyric ester

Succinic acid, and symmetrical substituted succinic acids, can also be obtained by the action of an ethereal solution of iodine or bromine upon monosodiomalonic ester, or its monoalkyl-derivatives:



$$\begin{array}{llll} COOC_2H_5 & COOC_2H_5 & COOC_2H_5 & COOC_2H_5 \\ A\cdot\dot{C}\boxed{Na \quad + I_2 + Na}\dot{C}\cdot A' & = A\cdot\dot{C}\text{———}\dot{C}\cdot A' + 2NaI. \\ \dot{C}OOC_2H_5 & \dot{C}OOC_2H_5 , & \dot{C}OOC_2H_5 & \dot{C}OOC_2H_5 \\ A = \text{Hydrogen or alkyl} & & \text{Tetracarboxylic ester} & \end{array}$$

By saponification, and elimination of CO_2, the ester formed is converted into the desired compound:

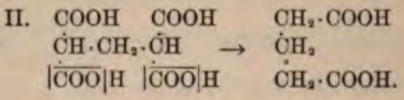


$$\begin{array}{ll} COOH \quad COO\,H & \\ A\cdot\dot{C}\text{———}\dot{C}\cdot A' & = \dfrac{A\ \cdot CH\cdot COOH}{A'\cdot\dot{C}H\cdot COOH} + 2CO_2. \\ |\dot{\overline{COO}}|H \ |\dot{\overline{COO}}|H & \end{array}$$

Glutaric Acid, $COOH\cdot CH_2\cdot CH_2\cdot CH_2\cdot COOH$.

168. Glutaric acid can be synthesized by a method which furnishes an example of another type of malonic ester synthesis. It is obtained by the action of two molecules of monosodiomalonic ester on one molecule of methylene iodide, saponification of the product, and splitting off $2CO_2$:

$$\text{I.}\quad (COOC_2H_5)_2CH\boxed{Na + I}\cdot CH_2\cdot\boxed{I + Na}\,CH(COOC_2H_5)_2 =$$
$$= (COOC_2H_5)_2CH\cdot CH_2\cdot CH(COOC_2H_5)_2.$$

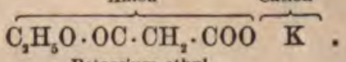


$$\text{II.}\quad \begin{array}{lcl} COOH \quad COOH & & CH_2\cdot COOH \\ \dot{C}H\cdot CH_2\cdot\dot{C}H & \rightarrow & \dot{C}H_2 \\ |\dot{\overline{COO}}|H \ |\dot{\overline{COO}}|H & & \dot{C}H_2\cdot COOH. \end{array}$$

By using ethylene bromide, or trimethylene bromide, instead of methylene iodide, the two malonic-acid residues can be joined together in an analogous manner through a chain of two or three methylene-groups, and the higher $\omega\omega'$-dicarboxylic acids obtained by splitting off $2CO_2$.

Electro-synthesis of Dibasic and Other Acids.

When the aqueous solution of an ester-salt of a dibasic acid is electrolyzed, the metallic ion goes to the cathode, the anion to the anode:



$$\overbrace{C_2H_5O\cdot OC\cdot CH_2\cdot COO}^{\text{Anion}}\ \overbrace{K}^{\text{Cation}}\ .$$

Potassium ethyl-malonate

This anion, however, is not stable; after being discharged at the anode, it decomposes into carbon dioxide and $C_2H_5OOC\cdot CH_2-$, and two of these residues unite to form succinic ester:

$$C_2H_5OOC\cdot CH_2-CH_2\cdot COOC_2H_5.$$

By this method, it is possible to synthesize the higher dibasic acids from the lower.

Hofer has devised a very suitable apparatus (Fig. 32) for this *electro-synthesis*. It consists of two glass vessels, which can be joined at *CD*, their contents being separated at this point by a sheet of parchment-paper. *B* is partially filled with a concentrated solution of the ester-salt, and *A* with a solution of potassium carbonate, since it is only at the anode that the desired action takes place. The gases evolved can escape through *E* and *F*, which serve at the same time for the introduction of the electrodes. The tap-funnel *G* contains more of the solution of the ester-salt.

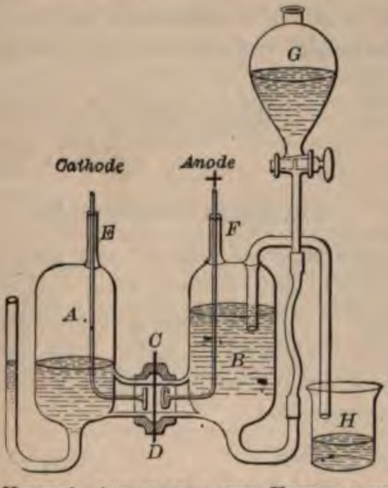


Fig. 32.—Hofer's Apparatus for Electro-synthesis.

During the electrolysis the tap is opened, which causes the solution to circulate slowly through the apparatus, local secondary actions at the anode being thus avoided. When *H* is full, its contents are poured back into the tap-funnel. To prevent rise of temperature in the solution, due to the action of the electric current, the whole apparatus is placed in water. It will be observed from the figure that the anode is very small. This is to obtain at it a high *density of the electric current;* that is, the quantity of electricity (ampères) which leaves the electrode per unit of surface. As the quantity of anions discharged at the anode is proportional to the number of ampères of the current, it is clear that a high density of current causes a great many discharged anions to be present at the anode, this being most favourable for their interaction.

This synthesis of dibasic acids is an extension of an electrosynthesis carried out long ago by Kolbe. He showed that, on electrolysis, a solution of potassium acetate yields ethane:

$$\begin{array}{llcl} CH_3\cdot|\overline{COO} & K & & CH_3 \\ CH_3\cdot|\underline{COO} & K & \rightarrow & CH_3. \\ \quad\text{Anion} & \text{Cation} & & \end{array}$$

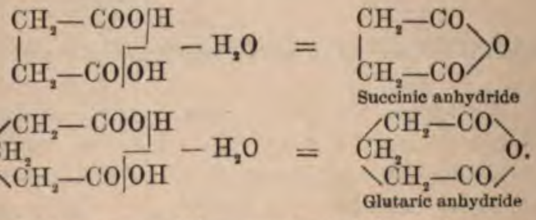
Besides this extension, many others are known, of which one may be mentioned here.

A mixture of a salt of a monobasic fatty acid and of an estersalt gives, at the anode, the ester of a monobasic acid:

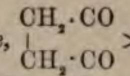
$$\underbrace{CH_3\cdot|COO|\overline{K}}_{\text{Potassium acetate}} + \underbrace{\overline{K}|OOC\cdot|CH_2\cdot CH_2\cdot CCOO_2H_5}_{\text{Potassium ethyl succinate}} \rightarrow$$
$$\rightarrow \underbrace{CH_3\cdot CH_2\cdot CH_2\cdot COOC_2H_5}_{\text{Ethyl butyrate}}.$$

Formation of Anhydrides.

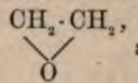
169. Oxalic and malonic acids do not yield anhydrides, while succinic acid, $C_4H_6O_4$, and glutaric acid, $C_5H_8O_4$, can be made to do so very readily. The formation of anhydride is due to the splitting-off of one molecule of water from one molecule of the dibasic acid, this being proved by a determination of the molecular weights of the anhydrides:



These anhydrides are rapidly reconverted into the corresponding dibasic acids by dissolving them in water.

A derivative of succinic acid, *succinimide*,  $\begin{matrix} CH_2\cdot CO \\ | \\ CH_2\cdot CO \end{matrix}>NH$, contains a closed chain with four carbon atoms and one nitrogen atom; it is formed by the rapid distillation of ammonium succinate. The atoms situated at the extremities of a carbon chain containing four or five C-atoms react very readily with one another; those in shorter chains only react with difficulty, or not at all. Analogous phenomena were alluded to in connection with the splitting-off of one molecule of water from the $\omega\omega'$-glycols (**156**), and the elimination of ammonia from $\omega\omega'$-diamines (**162**). In both these instances the splitting-off is very easily effected from a carbon chain of four or five C-atoms, but is not possible, or leads to the formation of very unstable compounds, when the chain is shorter. It will be necessary later to refer to other examples of the same phenomenon, of which a satisfactory explanation may be arrived at by a consideration of the direction of the bonds in space. It was assumed (**53**) that the four affinities of the carbon atom are so directed that they may be regarded as lying towards the angles of a regular tetrahedron, of which the carbon atom is the centre. In the case of a single bond between two carbon atoms, it is assumed that one affinity of each of these atoms is linked to one affinity of the other (Fig. 33, p. 200). The position in space of the C-atoms in a chain of three or more members, and the direction of their affinities, are represented in the figure.

It will be seen from this that in a normal chain of four C-atoms, the affinities situated at the extremities approach one another closely, and in a chain of five C-atoms they approach still more closely, so that they are able to enter into reaction with one another.

A few instances of compounds with a closed chain containing only two C-atoms, such as ethylene oxide,  $\begin{matrix} CH_2\cdot CH_2 \\ \diagdown\diagup \\ O \end{matrix}$, are known. The figure shows that the direction of the affinities must undergo a considerable change to render possible the closing of the chain. Experience shows that compounds of this kind are unstable, the closed chain being very easily converted into an open one, as is indicated by the "tension theory" of Baeyer (**129**).

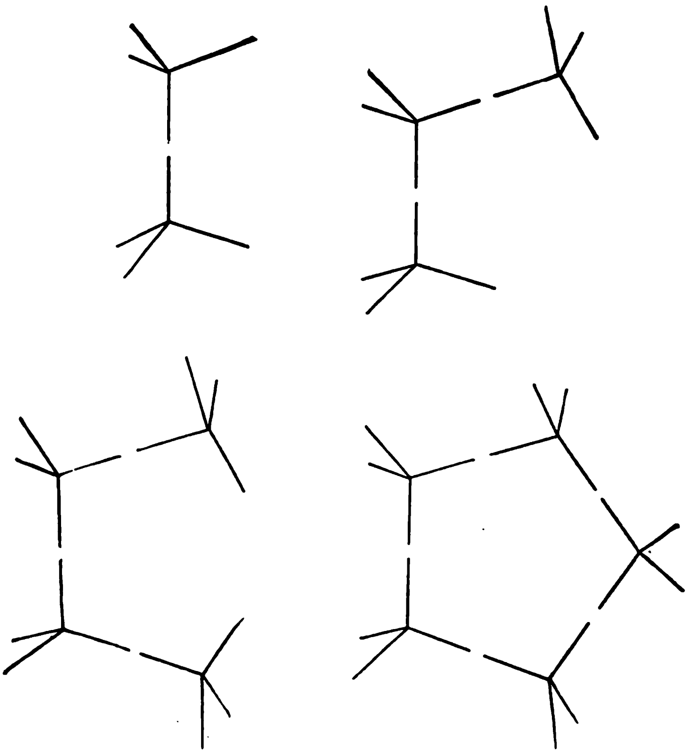
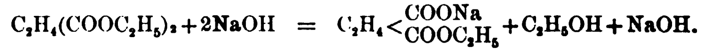


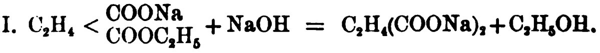
FIG. 33.—SPACIAL REPRESENTATION OF THE BONDS BETWEEN 2–5 C-ATOMS.

Saponification of the Esters of the Dibasic Acids.

It was stated (159) that the esters of a polyhydric alcohol are saponified in stages, tristearin, for instance, yielding first distearin and then monostearin. The saponification of the esters of the polybasic acids takes place similarly; thus, ethyl succinate decomposes as follows:

I. 

$$C_2H_4(COOC_2H_5)_2 + 2NaOH = C_2H_4<\begin{matrix}COONa\\COOC_2H_5\end{matrix} + C_2H_5OH + NaOH.$$

II. 

$$C_2H_4 < \begin{matrix}COONa\\COOC_2H_5\end{matrix} + NaOH = C_2H_4(COONa)_2 + C_2H_5OH.$$

In this reaction the acid ester-salt is first formed, and is afterwards converted into succinic acid. REICHER has shown that the velocity constant (101) for the saponification of ethyl succinate by caustic soda has a different value at different stages of the reaction, being less at the end than at the beginning. The reaction at first takes place chiefly according to the first equation, and finally according to the second; this affords a satisfactory explanation of the varying value of the velocity constant.

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II. UNSATURATED DIBASIC ACIDS.

Fumaric and Maleïc Acids, $C_4H_4O_4$.

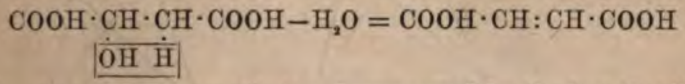
170. The most important members of the group of unsaturated dibasic acids are *fumaric acid* and *maleïc acid*, both of which have the formula $C_4H_4O_4$. They have been made the subject of numerous investigations, a complete explanation of their isomerism having been finally arrived at by an application of the principles of stereoisomerism.

Fumaric acid is somewhat widely distributed in the vegetable kingdom. It does not melt at the ordinary pressure, but sublimes at about 200°; it dissolves with difficulty in water. Maleïc acid is not found in nature; it melts at 130°, and is very readily soluble in water.

Both acids can be obtained by heating malic acid,

$$COOH\cdot CHOH\cdot CH_2\cdot COOH,$$

the particular one formed being dependent on the way in which the heating is effected. Fumaric acid is the principal product when the temperature is maintained at 140°–150° for a long time, but when a higher temperature is employed, and the heating is quickly carried out, the anhydride of maleïc acid distils over along with water. This anhydride easily takes up water, regenerating the acid. This is the ordinary method for the preparation of these acids, and it indicates that both have the same structural formula:



$$COOH\cdot\underset{\boxed{OH\ \ H}}{\dot{C}H\cdot\dot{C}H}\cdot COOH-H_2O=COOH\cdot CH:CH\cdot COOH$$

This view of their constitution is supported by the fact that both acids yield succinic acid on treatment with sodium amalgam and water, monobromosuccinic acid by addition of HBr, and malic acid by heating with water at a high temperature. Both acids have therefore the same constitutional formula,

$$COOH\cdot CH:CH\cdot COOH.$$

Similar isomerism of the crotonic acids (**143**) has been mentioned. We shall now consider how this isomerism can be explained by the aid of stereochemistry.

It was stated in **169** that a single bond between two carbon atoms may be represented as in Fig. 34. If the tetrahedra are drawn in full, then the single bond will be as represented in Fig. 35. Supposing the tetrahedra are free to rotate round their common axis, isomerism cannot be expected for compounds *Cabc-Cdef*, nor has it ever been observed.

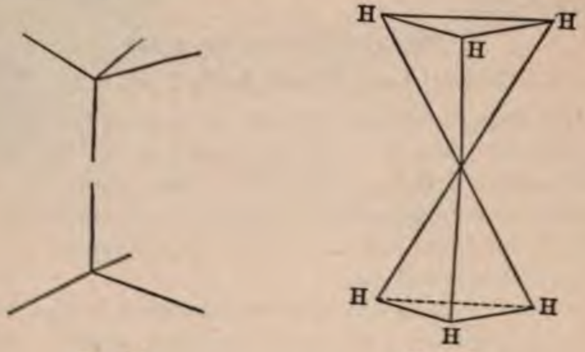


Fig. 34. Fig. 35.

Single Bond between two Carbon Atoms.

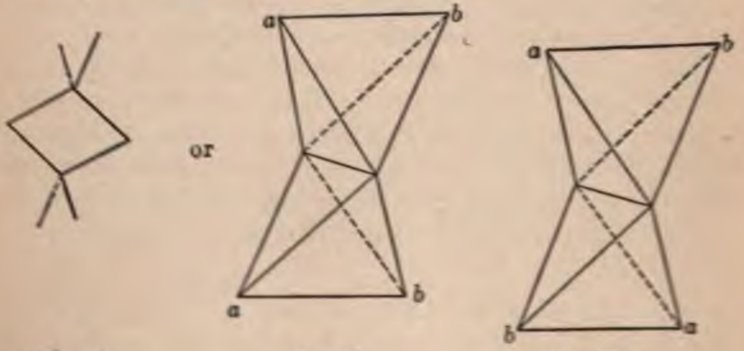
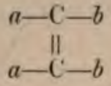


Fig. 36. Fig. 37. Fig. 38.

Graphic Spacial Representation of the Double Bond Between two Carbon Atoms.

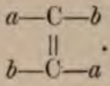
When a double bond is present, then two affinities of each carbon atom come into play, as graphically represented in Figs. 36, 37, and 38. Free rotation of the tetrahedra in relation to one another is then no longer possible.

It is seen from the foregoing figures that difference of grouping depends on the position of the groups a and b of one tetrahedron with reference to the similar groups a and b of the other. In one case, a may be over a, and b over b, which is the grouping in Fig. 37; and in the other, a may be over b, and b over a, as in Fig. 38. This can be represented by the formulæ



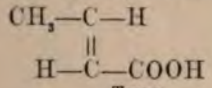
$$\begin{array}{c} a-\mathrm{C}-b \\ \| \\ a-\mathrm{C}-b \end{array}$$

and



$$\begin{array}{c} a-\mathrm{C}-b \\ \| \\ b-\mathrm{C}-a \end{array}.$$

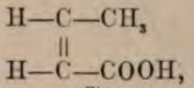
Thus, the two crotonic acids would be



$$\begin{array}{l} \mathrm{CH_3-C-H} \\ \qquad\;\; \| \\ \quad \mathrm{H-C-COOH} \end{array}$$

Trans

and



$$\begin{array}{l} \mathrm{H-C-CH_3} \\ \quad\;\; \| \\ \mathrm{H-C-COOH}, \end{array}$$

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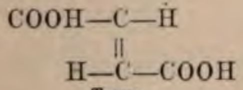
and fumaric and maleïc acids would have the formulæ

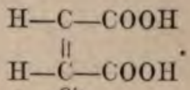
I.



$$\begin{array}{l} \mathrm{COOH-C-H} \\ \qquad\qquad\;\; \| \\ \qquad\;\; \mathrm{H-C-COOH} \end{array}$$

Trans

and II.

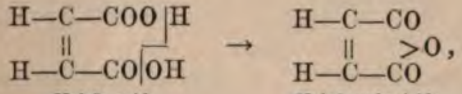


$$\begin{array}{l} \mathrm{H-C-COOH} \\ \quad\;\; \| \\ \mathrm{H-C-COOH} \end{array}.$$

Cis

It must now be proved which of these two formulæ belongs to fumaric acid, and which to maleïc acid.

Maleïc acid yields an anhydride, while fumaric acid does not do so. It will be noticed that in formula II the carboxyl-groups are in juxtaposition to one another, but in formula I they are as far removed from each other as possible. Only in the acid having the *cis*-formula are the carboxyl-groups represented in a position to react readily with one another:



$$\begin{array}{l} \mathrm{H-C-COO|H} \\ \quad\;\; \| \\ \mathrm{H-C-CO|OH} \end{array} \rightarrow \begin{array}{l} \mathrm{H-C-CO} \\ \quad\;\; \| \quad >\mathrm{O}, \\ \mathrm{H-C-CO} \end{array}$$

Maleïc acid — Maleïc anhydride

from which it is assumed that *fumaric acid has the constitution indicated in formula* I, *and maleïc acid that in formula* II.

Further consideration will show that this also accounts for the other known properties of these acids. It should be observed that neither formula contains an asymmetric C-atom, so that neither optical activity nor the great resemblance in such properties as specific gravity, melting-point, solubility, etc., due to the similarity in internal structure characteristic of the isomerism occasioned by an asymmetric carbon atom, is to be expected. Fumaric and maleïc acids do, in fact, display great differences in these physical properties.

Both fumaric acid and maleïc acid combine with bromine, but the dibromo-addition-products thus obtained are different. Fumaric acid yields *dibromosuccinic acid*, soluble with difficulty in water; and maleïc acid *isodibromosuccinic acid*, much more readily soluble in water. A consideration of Figs. 39 to 42 will show that different acids must result from this reaction. Figs. 40 and 42, representing dibromosuccinic acid and isodibromosuccinic acid respectively, cannot be made to coincide by rotation; this is seen more clearly from a comparison of Figs. 42 and 43. The latter may be obtained

+ 2Br =

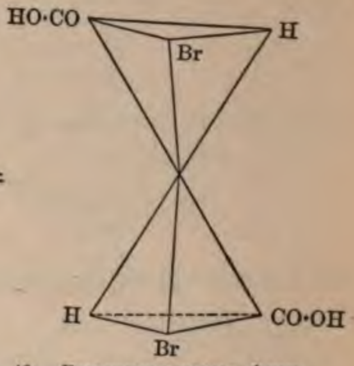
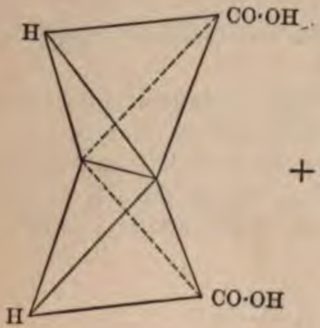


FIG. 39.—FUMARIC ACID.

FIG. 40.—DIBROMOSUCCINIC ACID.



+ 2Br =

FIG. 41.—MALEÏC ACID.

FIG. 42.—ISODIBROMOSUCCINIC ACID.

from Fig. 40 by rotation of the upper tetrahedron round the vertical axis, the position of the lower tetrahedron remaining unaltered. It will be observed from the figures that the order of the groups linked to both carbon atoms of the iso-acids is H, Br, COOH from left to right, and also for the lower carbon atom, of the other acid (Fig. 40), but for the upper carbon atom it is from right to left.

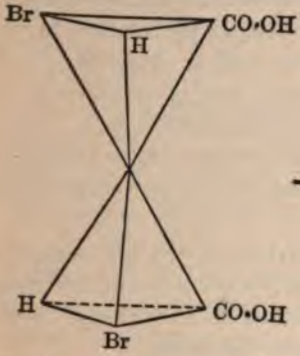


Fig. 43.—Dibromosuccinic Acid.

—HBr =

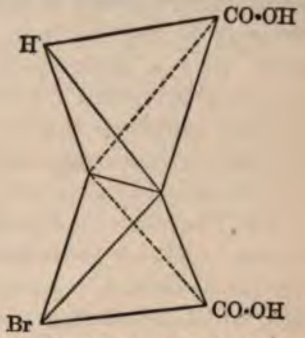


Fig. 44.—Bromomaleïc Acid.

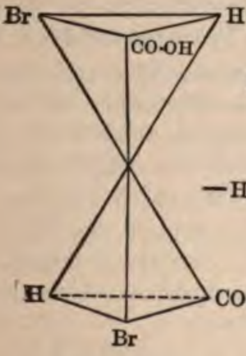


Fig. 45.—Isodibromosuccinic Acid.

—HBr =

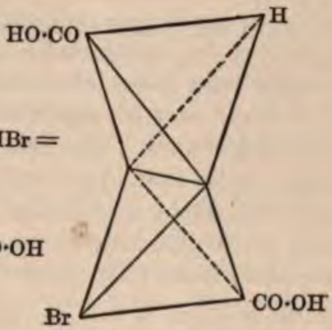


Fig. 46.—Bromofumaric Acid.

When HBr is removed from dibromosuccinic acid (Fig. 43), the H-atom linked to one carbon atom, and the Br-atom linked to the other, are eliminated, yielding an acid COOH·CH:CBr·COOH. This removal of HBr could not be effected if the tetrahedra were in the position shown in Fig. 40; rotation round the vertical axis must first take place, so as to bring H and Br into "corresponding" positions, as in Fig. 43, when splitting off HBr produces the acid represented in Fig. 44. This acid easily yields an anhydride, since the COOH-groups are in the corresponding positions; it is therefore *bromomaleïc acid.*

When HBr is split off from isodibromosuccinic acid, represented in Fig. 45 (which may be obtained from Fig. 42 by rotation in the same way as Fig. 43 from Fig. 40), an acid is obtained which cannot yield a corresponding anhydride, but is converted by removal of water into the anhydride of bromomaleïc acid. This behaviour resembles that of fumaric acid, which, under the same conditions, yields maleïc anhydride. This acid must therefore be *bromofumaric acid* (Fig. 46).

It will be seen from the foregoing that the constitution assumed for these acids on stereochemical grounds does account for their chemical properties. Another example will be mentioned later (**195**), which also supports the explanation just given.

Maleïc acid can be converted into fumaric acid in several ways: by keeping it for some time at a temperature above its melting-point; by bringing it into contact with hydrogen halides at ordinary temperatures; by exposing a concentrated solution of maleïc acid in presence of a trace of bromine to the action of sunlight, a reaction which takes place only slowly in absence of light; by treating the ethyl ester of maleïc acid with small quantities of iodine; or in other ways. The ease with which all these decompositions take place shows that maleïc acid is the unstable, and fumaric acid the stable, modification. Inversely, fumaric acid is converted by distillation into maleïc anhydride. The mechanism of these reactions is not fully understood.

The last reaction, as well as that by which maleïc acid is converted into fumaric acid by the action of heat alone, may be explained by the assumption that an exchange of hydrogen and carboxyl takes place at one of the doubly-linked C-atoms:

$$\begin{array}{r} \mathrm{H{-}C{-}COOH} \\ \| \quad\quad\;\; \\ \mathrm{H{-}C{-}COOH} \end{array} \quad \rightarrow \quad \begin{array}{c} \mathrm{H{-}C{-}COOH} \\ \| \\ \mathrm{HOOC{-}C{-}H} \end{array}$$

Acetylenedicarboxylic Acid, $COOH \cdot C{\equiv}C \cdot COOH$.

171. *Acetylenedicarboxylic acid*, the simplest type of dibasic acids containing a triple bond in the molecule, is prepared by the action of alcoholic potash on dibromosuccinic acid, COOH·CHBr·CHBr·COOH, a method of formation indicating its constitution. The silver salt of acetylenedicarboxylic acid readily splits off two molecules of carbon dioxide, with production of silver acetylene:

$$\boxed{\mathrm{CO_2}}\mathrm{Ag{\cdot}C{\equiv}C{\cdot}}\boxed{\mathrm{CO_2}}\mathrm{Ag} = 2\mathrm{CO_2} + \mathrm{AgC{\equiv}CAg}.$$

Acetylenedicarboxylic acid melts at 175°, and yields a beautiful, crystalline acid potassium salt, which is soluble with difficulty in water.

Affinity Constants of the Unsaturated Acids.

172. Like the monobasic unsaturated acids (**141**), the dibasic unsaturated acids have greater affinity constants than the corresponding saturated acids. For succinic acid, $K = 0{\cdot}00665$, and for fumaric acid, $K = 0{\cdot}093$. The strength of acetylenedicarboxylic acid is about equal to that of sulphuric acid. Thus, the presence of a double bond, and even more of a triple bond, intensifies the acidic character. For maleïc acid $K = 1{\cdot}17$, or about twelve times as much as for fumaric acid. This shows the great influence which the distance between the carboxyl-groups in the molecule exercises upon the strength of these acids.

173. Baeyer has prepared dibasic acids containing more than one triple bond in the molecule from acetylenedicarboxylic acid. When heated with water, its acid potassium salt is converted into the potassium salt of propiolic acid (**145**), with loss of CO_2:

$$\mathrm{KOOC{\cdot}C{\equiv}C{\cdot}}\boxed{\mathrm{CO_2}}\mathrm{H} = \mathrm{CO_2} + \mathrm{KOOC{\cdot}C{\equiv}CH}.$$

When the copper derivative of this salt, KOOC·C≡Ccu, is treated with potassium ferricyanide in alkaline solution, CuO is formed, while the two acid-residues unite at the same time, with production of the potassium salt of *diacetylenedicarboxylic acid*, KOOC·C≡C—C≡C·COOK. The acid potassium salt of this acid also loses CO_2 easily, and the copper derivative of the monobasic acid thus formed is converted by similar oxidation into CuO and the potassium salt of *tetra-acetylenedicarboxylic acid:*

$$2\mathrm{KOOC{\cdot}C{\equiv}C{\cdot}C{\equiv}Ccu} \rightarrow \mathrm{KOOC{\cdot}C{\equiv}C{\cdot}C{\equiv}C{\cdot}C{\equiv}C{\cdot}C{\equiv}C{\cdot}COOK}.$$

These compounds are very unstable, being decomposed by the action of light, and in other ways.

III. POLYBASIC ACIDS.

174. Acids containing three carboxyl-groups in union with one carbon atom are not known, except in the form of esters. The triethyl ester of *methanetricarboxylic acid* is obtained by the action of chlorocarbonic ester (**249**) on sodiomalonic ester:

$$\underset{\text{Chlorocarbonic ester}}{C_2H_5OOC}|\boxed{Cl + Na}|CH(COOC_2H_5)_2 = C_2H_5OOC\cdot CH(COOC_2H_5)_2.$$

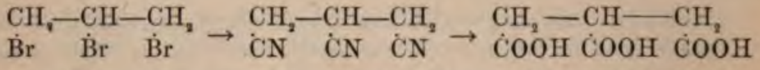
When this ester is saponified, CO_2 is split off at the same time, malonic acid being formed instead of the corresponding tribasic acid. This is another instance of the phenomenon that *several negative groups do not remain in union with one carbon atom*, two being the maximum number in the case of carboxyl.

A description of the syntheses of a few of the polybasic acids will afford examples of the methods adopted for the preparation of compounds of this class.

Tribasic Acids.

175. A type of the tribasic acids is *ωαω′-propanetricarboxylic acid*, or tricarballylic acid, which can be obtained in several ways.

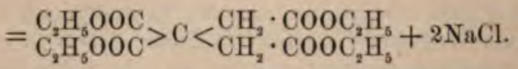
1. From tribromhydrin by treatment with potassium cyanide, and saponification of the tricyanhydrin thus formed:



$$\underset{Br}{CH_2}-\underset{Br}{CH}-\underset{Br}{CH_2} \rightarrow \underset{CN}{CH_2}-\underset{CN}{CH}-\underset{CN}{CH_2} \rightarrow \underset{COOH}{CH_2}-\underset{COOH}{CH}-\underset{COOH}{CH_2}$$

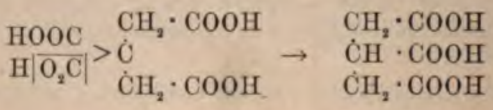
2. From malonic ester and monochloroacetic ester:

$$(C_2H_5OOC)_2C|\boxed{Na_2 + 2Cl}|CH_2\cdot COOC_2H_5 =$$



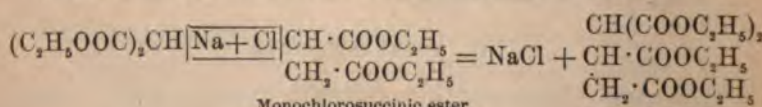
$$= \begin{matrix}C_2H_5OOC\\ C_2H_5OOC\end{matrix}>C<\begin{matrix}CH_2\cdot COOC_2H_5\\ CH_2\cdot COOC_2H_5\end{matrix} + 2NaCl.$$

On saponification of this ester, an acid is obtained which on being heated loses CO_2, with formation of tricarballylic acid:



$$\begin{matrix}HOOC\\ H|\boxed{O_2C}|\end{matrix}>\overset{CH_2\cdot COOH}{\underset{CH_2\cdot COOH}{C}} \rightarrow \begin{matrix}CH_2\cdot COOH\\ CH\cdot COOH\\ CH_2\cdot COOH\end{matrix}$$

3. From monochlorosuccinic ester and malonic ester:

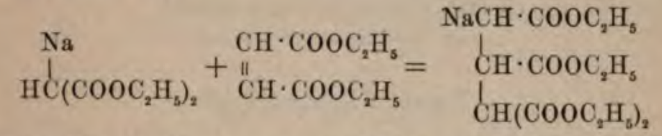


$$(C_2H_5OOC)_2CH|\boxed{Na + Cl}|\begin{matrix}CH\cdot COOC_2H_5\\ CH_2\cdot COOC_2H_5\end{matrix} = NaCl + \begin{matrix}CH(COOC_2H_5)_2\\ CH\cdot COOC_2H_5\\ CH_2\cdot COOC_2H_5\end{matrix}$$

Monochlorosuccinic ester

When the ester thus obtained is saponified, CO_2 is split off, with formation of tricarballylic acid.

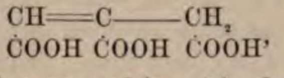
4. A synthesis peculiar to the polybasic acids consists in the *addition* of sodiomalonic ester to the esters of unsaturated acids, such as fumaric acid:



$$\begin{array}{c}Na\\|\\HC(COOC_2H_5)_2\end{array} + \begin{array}{c}CH\cdot COOC_2H_5\\\|\\CH\cdot COOC_2H_5\end{array} = \begin{array}{l}NaCH\cdot COOC_2H_5\\|\\CH\cdot COOC_2H_5\\|\\CH(COOC_2H_5)_2\end{array}$$

Saponification, with subsequent splitting off of CO_2, yields tricarballylic acid. It melts at 166°, and is easily soluble in water.

Aconitic acid, M.P. 191°, is a type of an *unsaturated tribasic acid*. It is obtained from citric acid (**198**) by the elimination of water by heating. The constitution of aconitic acid is



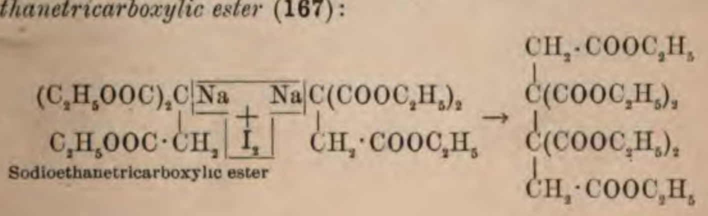
$$\begin{array}{ccc}CH & = C & — CH_2\\COOH & COOH & COOH\end{array}$$

since on reduction it is converted into tricarballylic acid.

Tetrabasic Acids.

176. Some examples of the synthetic methods employed in the preparation of the tetrabasic acids have been already mentioned in connection with the syntheses of dibasic and tribasic acids by means of malonic ester. In these reactions the tetrabasic acids are often formed as intermediate products, being converted by splitting off one or two molecules of carbon dioxide into tribasic and dibasic acids respectively. This reaction, however, always yields acids containing two carboxyl-groups in union with one carbon atom. *ωαβω'-Butanetetracarboxylic acid*, in which only one carboxyl-group is linked to each carbon atom, can be obtained by splitting off $2CO_2$ from a hexabasic acid, *ωα₂β₂ω'-butanehexacarboxylic acid*, which is itself obtained by the action of iodine on *sodioethanetricarboxylic ester* (**167**):

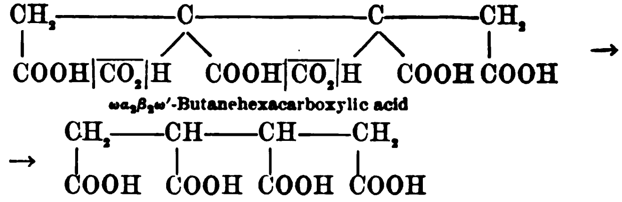
I.



$$\begin{array}{l}(C_2H_5OOC)_2C\boxed{Na}\\ \quad\quad |\\ C_2H_5OOC\cdot CH_2\end{array} + \begin{array}{c}\boxed{Na}\\ \boxed{I_2}\end{array} \begin{array}{l}C(COOC_2H_5)_2\\|\\CH_2\cdot COOC_2H_5\end{array} \rightarrow \begin{array}{l}CH_2\cdot COOC_2H_5\\|\\C(COOC_2H_5)_2\\|\\C(COOC_2H_5)_2\\|\\CH_2\cdot COOC_2H_5\end{array}$$

Sodioethanetricarboxylic ester

II.



$\omega\alpha_2\beta_2\omega'$-Butanehexacarboxylic acid

$\omega\alpha\beta\omega'$-Butanetetracarboxylic acid

Higher Polybasic Acids.

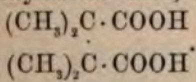
177. The last example shows how it is possible to obtain higher members of the series of polybasic acids. In general, the hydrogen atom in the esters of acids containing a carbon atom in union with two carboxyl-groups and one hydrogen atom, is replaceable by sodium. When a sodium compound of this kind is treated with a halogen derivative of a polybasic acid, a higher polybasic acid is formed, the same effect being produced by means of iodine, which causes the union of two molecules. These reactions afford a means of synthesizing numerous polybasic acids, the ester of even a 14-basic acid having been thus obtained.

FINISH

SUBSTITUTED ACIDS.

I. HALOGEN-SUBSTITUTED ACIDS.

178. The halogen-substituted acids can be obtained by the direct action of chlorine or of bromine upon the saturated fatty acids, but this process is not very satisfactory. The monochloro-acids and monobromo-acids can be better prepared by the action of chlorine or bromine, not upon the acid, but upon its chloride or bromide. The process is carried out by treating the acid with phosphorus and a halogen, the phosphorus halide produced reacting with the acid to form an acid chloride or bromide, $R\cdot COX$, which is then attacked by the excess of halogen present.

Some acids cannot be brominated in this way: for example, trimethylacetic acid, $(CH_3)_3C\cdot COOH$, and tetramethylsuccinic acid,  $\begin{array}{l}(CH_3)_2C\cdot COOH \\ \quad\quad\;\;\, | \\ (CH_3)_2C\cdot COOH\end{array}$. In these acids there is no hydrogen in union with the α-carbon atom, which is directly linked to carboxyl. As a general rule, it is only possible to brominate acids of which the α-carbon atom is linked to hydrogen, the acids formed being called α-bromo-acids. The constitution of these is proved by converting them into hydroxy-acids (**182**), which are shown to be α-compounds through their synthesis by another method.

Halogen-substituted acids can also be prepared by addition of hydrogen halide or halogen to the unsaturated acids, or by the action of phosphorus halides on the hydroxy-acids. The iodinated acids can sometimes be advantageously obtained from the corresponding chlorinated derivatives by heating them with potassium iodide.

The introduction of halogen into the molecule causes a marked increase in the strength of an acid, as will be seen from the table on next page of dissociation constants, *K*.

Name.	Formula.	K.
Acetic Acid	$CH_3\cdot CO_2H$	0·0018
Monochloroacetic Acid	$CH_2Cl\cdot CO_2H$	0·155
Monobromoacetic Acid	$CH_2Br\cdot CO_2H$	0·138
Monoiodoacetic Acid	$CH_2I\cdot CO_2H$	0·075
Dichloroacetic Acid	$CHCl_2.CO_2H$	5·14
Trichloroacetic Acid	$CCl_3\cdot CO_2H$	121
Propionic Acid	$CH_3\cdot CH_2\cdot CO_2H$	0·00134
β-Iodopropionic Acid	$CH_2I\cdot CH_2\cdot CO_2H$	0·0090

This table shows that the strength of an acid is increased to a greater extent by chlorine than by bromine, and by bromine than by iodine, and that the introduction of more than one chlorine atom occasions a marked increase in the strength of the acid. The position of the halogen atom also exerts an influence; for iodoacetic acid, in which the I-atom occupies the α-position, the value of the constant is 32 times as great as that for acetic acid, while for β-iodopropionic acid K is only 7 times as great as for propionic acid.

The influence of the carboxyl-groups upon the halogen atoms is such that *the properties of the monohalogen-substituted acids depend chiefly upon the relative position of the halogen atom and the carboxyl-group.*

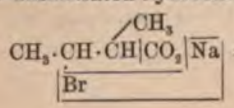
On boiling with alkalis, the α-halogen-substituted acids are easily converted into the α-hydroxy-acids by exchange of halogen for hydroxyl:

$$\underset{\text{Monochloroacetic acid}}{CH_2Cl\cdot COOH} + KOH = KCl + \underset{\text{Potassium glycollate}}{CH_2OH\cdot COOK.}$$

Under the same treatment, the β-halogen-substituted acids split off hydrogen halide, with formation of unsaturated acids:

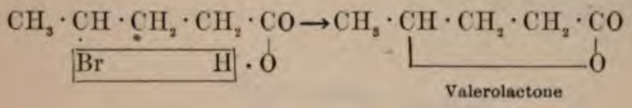
$$\underset{\beta\text{-Chlorobutyric acid}}{CH_3\cdot CHCl\cdot CH_2\cdot COOH} = \underset{\text{Crotonic acid}}{CH_3\cdot CH:CH\cdot COOH} + HCl.$$

The behaviour of the β-halogen-substituted acids when treated with sodium carbonate is very characteristic; when they are warmed with an aqueous solution of it, not only is hydrogen halide eliminated from the molecule, but CO_2 is split off at the same time, with formation of an unsaturated hydrocarbon:



$$CH_3\cdot CH\cdot \overset{CH_3}{\underset{Br}{CH}}|CO_2|Na = \underset{\text{Butylene}}{CH_3\cdot CH:CH\cdot CH_3} + NaBr + CO_2.$$

On boiling with water or with an alkali-carbonate, the γ-halogen-substituted acids readily split off HX, forming a peculiar class of compounds known as *lactones* (**183** and **188**):



$$CH_3\cdot \underset{\boxed{Br}}{CH}\cdot CH_2\cdot CH_2\cdot \underset{\boxed{H}\cdot O}{CO} \rightarrow CH_3\cdot \underset{|}{CH}\cdot CH_2\cdot CH_2\cdot \underset{O}{CO}$$

Valerolactone

Chloroacetic Acids.

179. *Monochloroacetic acid,* $CH_2Cl\cdot COOH$, is obtained by the action of chlorine upon acetic acid, in presence of sulphur as a chlorine-carrier. It is a crystalline solid, melting at 63°. *Dichloroacetic acid,* $CHCl_2\cdot COOH$, and *trichloroaçetic acid,* $CCl_3\cdot COOH$, are best prepared from chloral (**204**). Trichloroacetic acid is unstable, and is decomposed on boiling with water into carbon dioxide and chloroform:

$$CCl_3\cdot\boxed{CO_2}H = CCl_3H + CO_2.$$

This is another example of the fact that "loading" a carbon atom with negative elements and groups makes the compound in which it is contained unstable.

β-Iodopropionic Acid, $CH_2I\cdot CH_2\cdot COOH$.

180. *β-Iodopropionic acid* is sometimes used in syntheses, and is therefore of some importance. It forms well-defined crystals, slightly soluble in cold water, and melting at 82°. It is obtained by addition of hydriodic acid to acrylic acid:

$$CH_2:CH\cdot COOH + IH = CH_2I\cdot CH_2\cdot COOH.$$

As a general rule, addition of hydrogen halide to acids containing a double bond between the α- and β-carbon atoms, denoted by $\Delta^{\alpha\beta}$, results in the union of halogen with the β-carbon atom. The constitution of β-iodopropionic acid is deduced from its transformation into succinic acid in the following way:

$$CN\boxed{K + I}CH_2\cdot CH_2\cdot COOH \rightarrow CN\cdot CH_2\cdot CH_2\cdot COOH \rightarrow$$

$$\rightarrow \underset{\text{Succinic acid}}{COOH\cdot CH_2\cdot CH_2\cdot COOH.}$$

Acids containing more than one Halogen Atom in the Molecule.

181. Isomerism in this type of compounds may be occasioned by a difference in position of the halogen atoms in the molecule. Addition of halogen to an unsaturated acid results in the formation of a compound in which the halogen atoms are linked to neighbouring carbon atoms.

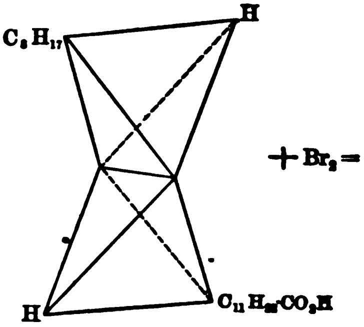


FIG. 47.—ERUCIC ACID.
Trans-formula.

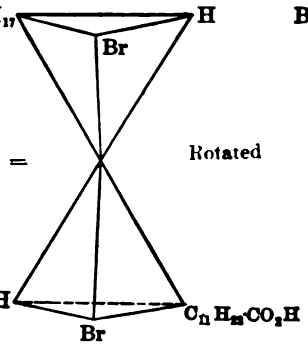


FIG. 48.—DIBROMOERUCIC ACID.

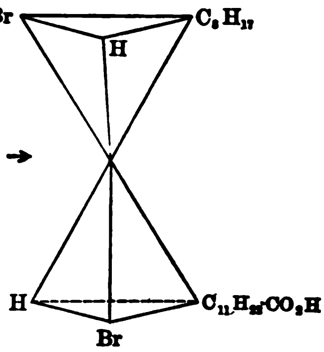


FIG. 49.—DIBROMOERUCIC ACID.
Each H-atom in corresponding position to a Br-atom.

The splitting off of hydrogen halide from acids of this class affords a striking example of the value of stereochemistry in explaining phenomena for which the ordinary constitutional formulæ are unable to account. It was mentioned in connection with the stereoisomerism of the unsaturated acids that the dibromide of one modification splits off 2HBr very readily, yielding an acid with a triple bond, while with the dibromide of the other modification, this either does not take

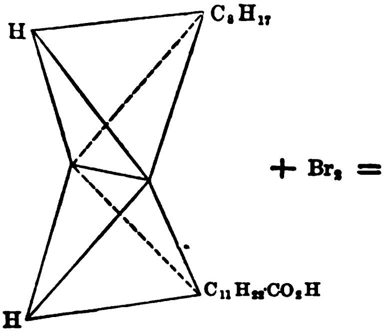


FIG. 50.—BRASSIDIC ACID.
Cis-formula.

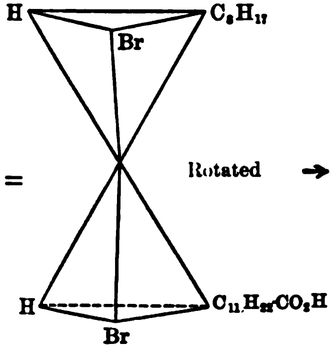


FIG. 51. DIBROMOBRASSIDIC ACID.

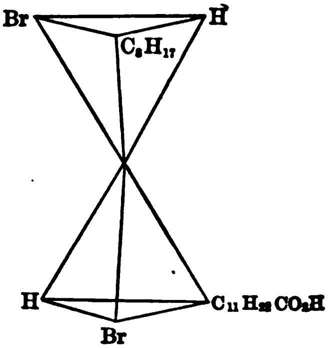


FIG. 52.—DIBROMOBRASSIDIC ACID.
One H-atom in corresponding position
to one Br-atom.

place at all, or only with great difficulty. An example of this is afforded by erucic and brassidic acids, which have been proved, by the method indicated in **145**, to have the constitution

$$C_8H_{17}\cdot CH : CH\cdot C_{11}H_{22}\cdot COOH.$$

On addition of bromine, and subsequent heating with alcoholic potash at 150°-170°, dibromoerucic acid easily loses 2HBr, yielding *behenolic acid*, $C_8H_{17}\cdot C{\equiv}C\cdot C_{11}H_{22}\cdot COOH$; while under the same treatment, dibromobrassidic acid splits off one molecule of hydrobromic acid, with production of a monobromoerucic acid. This difference is accounted for by assigning the *trans*-formula to erucic, and the *cis*-formula to brassidic, acid, as indicated in Figs. 47 to 52.

In the formula for dibromoerucic acid, the tetrahedra may be rotated so as to bring each Br-atom above a H-atom (**170**), making the elimination of 2HBr possible (Figs. 48 and 49); while in that for dibromobrassidic acid, only one Br-atom and one H-atom can be brought into the "corresponding positions" to one another (Figs. 51 and 52).

II. MONOBASIC HYDROXY-ACIDS.

182. The hydroxy-acids are substances containing one or more hydroxyl-groups and carboxyl-groups in the molecule. The general methods for their formation depend upon the introduction of hydroxyl-groups and carboxyl-groups. They are produced in the following reactions.

1. By the careful oxidation of polyhydric alcohols:

$$\underset{\text{Propyleneglycol}}{CH_3\cdot CHOH\cdot CH_2OH} \rightarrow \underset{\text{Lactic acid}}{CH_3\cdot CHOH\cdot COOH.}$$

2. By replacement of the halogen in halogen-substituted acids by hydroxyl, as already described (**156**).

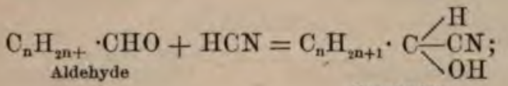
3. By reduction of the aldehydic acids and ketonic acids, which contain both a carboxyl-group and a carbonyl-group:

$$\underset{\text{Pyroracemic acid}}{CH_3\cdot CO\cdot COOH} + 2H = \underset{\text{Lactic acid}}{CH_3\cdot CHOH\cdot COOH.}$$

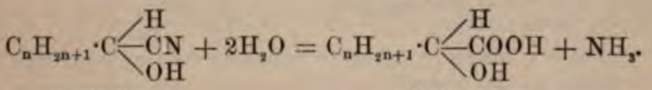
4. By the action of nitrous acid upon acids containing an amido-group in the alkyl-residue:

$$\underset{\text{Glycocoll}}{NH_2\cdot CH_2\cdot COOH} + HNO_2 = \underset{\text{Glycollic acid}}{CH_2OH\cdot COOH} + N_2 + H_2O.$$

5. By addition of hydrocyanic acid to aldehydes or ketones, and hydrolysis of the nitrile thus obtained (**110**, 3); this method yields only *α*-hydroxy-acids:



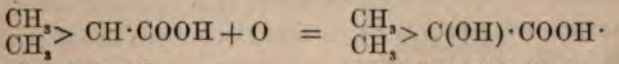
$$\underset{\text{Aldehyde}}{C_nH_{2n+}\cdot CHO} + HCN = \underset{\text{Cyanhydrin}}{C_nH_{2n+1}\cdot C\begin{cases}H\\ CN;\\ OH\end{cases}}$$



$$\underset{\text{Cyanhydrin}}{C_nH_{2n+1}\cdot C\begin{cases}H\\ CN\\ OH\end{cases}} + 2H_2O = \underset{\text{α-Hydroxy-acid}}{C_nH_{2n+1}\cdot C\begin{cases}H\\ COOH\\ OH\end{cases}} + NH_3.$$

By exchange of Br for OH, acids which have been brominated by the method described in **178** yield hydroxy-acids identical with those obtained by this *cyanhydrin synthesis*. It follows that in these acids the bromine is in union with the *α*-carbon atom.

6. Oxidation with potassium permanganate effects the direct replacement of hydrogen by hydroxyl in acids containing a hydrogen atom linked to a tertiary carbon atom:



$$\underset{\text{Isobutyric acid}}{\substack{CH_3\\ CH_3}> CH\cdot COOH} + O \;=\; \underset{\text{α-Hydroxyisobutyric acid}}{\substack{CH_3\\ CH_3}> C(OH)\cdot COOH\cdot}$$

Properties.

183. Different compounds are obtained from the hydroxy-acids by substitution in the hydroxyl-group and carboxyl-group. When the H-atom of the hydroxyl-group is replaced by alkyl, an *acid ether* is obtained:

$$\underset{\text{Glycollic acid}}{CH_2OH\cdot COOH} \rightarrow \underset{\text{Ethylglycollic acid}}{CH_2OC_2H_5\cdot COOH}.$$

Like an ordinary ether, $C_nH_{2n+1}\cdot O\cdot C_mH_{2m+1}$, ethylglycollic acid cannot be saponified. When, on the other hand, the H-atom of the carboxyl-group is exchanged for alkyl, an ester is produced:

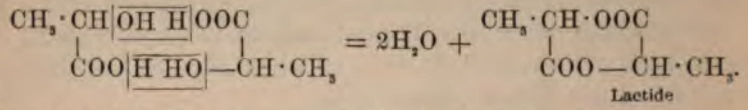
$$CH_2OH\cdot COOH \rightarrow \underset{\text{Ethyl glycollate}}{CH_2OH\cdot COOC_2H_5}.$$

Like other esters, these compounds can be saponified.

The introduction of hydroxyl strengthens the fatty acids to an extent dependent on its position relative to the carboxyl-group, an effect analogous to that produced by the halogens (**178**). This is seen from the following table, containing the values of the dissociation constant, K, for several acids:

Name.	Formula.	K.
Acetic Acid	$CH_3\cdot COOH$	0·00180
Glycollic Acid (Hydroxyacetic Acid)	$CH_2OH\cdot COOH$	0·0152
Propionic Acid	$CH_3\cdot CH_2\cdot COOH$	0·00134
Lactic Acid (α-Hydroxypropionic Acid)	$CH_3\cdot CHOH\cdot COOH$	0·0138
β-Hydroxypropionic Acid	$CH_2OH\cdot CH_2\cdot COOH$	0·00311

On heating, the *α-hydroxy-acids* easily lose water, two molecules of the latter being simultaneously split off from two molecules of acid; this reaction takes place between the hydroxyl-group of one molecule and the carboxyl-group of the other. In this way, lactic acid yields *lactide:*

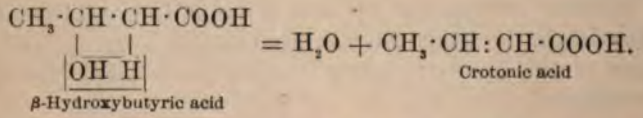


$$\begin{array}{l} CH_3\cdot CH\boxed{OH\ H}OOC \\ \ \ | \qquad\qquad\qquad | \\ COO\boxed{H\ HO}-CH\cdot CH_3 \end{array} = 2H_2O + \begin{array}{l} CH_3\cdot CH\cdot OOC \\ \ \ | \qquad\quad | \\ COO-CH\cdot CH_3. \end{array}$$

Lactide

The formula of this compound shows that it is a double ester, its constitution being proved by its behaviour when boiled with water or dilute acids; like the esters, it is saponified, yielding lactic acid.

β-Hydroxy-acids readily split off water, with formation of unsaturated acids:



$$\begin{array}{l} CH_3\cdot CH\cdot CH\cdot COOH \\ \quad\ |\quad\ \ | \\ \quad \boxed{OH\ H} \end{array} = H_2O + CH_3\cdot CH:CH\cdot COOH.$$

β-Hydroxybutyric acid

Crotonic acid

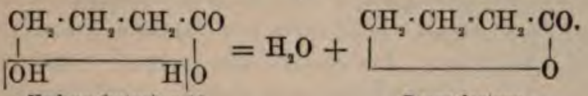
When a β-hydroxy-acid is boiled with excess of a 10 per cent. solution of caustic soda, it is partly converted into an $\alpha\beta$-, and partly into a $\beta\gamma$-unsaturated acid, while a portion remains unacted upon. An equilibrium is thus reached:

$$R\cdot CH:CH\cdot CH_2\cdot COOH \rightleftarrows R\cdot CH_2\cdot CHOH\cdot CH_2\cdot COOH \rightleftarrows$$

$$\rightleftarrows R\cdot CH_2\cdot CH:CH\cdot COOH.$$

If this reaction is really a reversible one, the same point of equilibrium should be reached by starting from the hydroxy-acid, or from either of the two unsaturated acids. FITTIG proved that this is actually the case.

γ- and δ-hydroxy-acids lose water, with formation of inner anhydrides, called *lactones* (**178** and **188**):



$$\begin{array}{l}CH_2\cdot CH_2\cdot CH_2\cdot CO\\ |\qquad\qquad\qquad\quad |\\ \boxed{OH\qquad\quad H}\,O\end{array} = H_2O + \begin{array}{l}CH_2\cdot CH_2\cdot CH_2\cdot CO.\\ |\qquad\qquad\qquad\quad |\\ \underline{\qquad\qquad\qquad\quad}O\end{array}$$

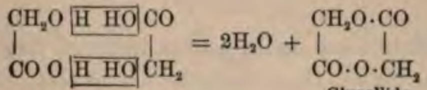
γ-Hydroxybutyric acid Butyrolactone

Glycollic Acid, $C_2H_4O_3$,

184. *Glycollic acid* is present in unripe grapes. It is usually prepared by treating monochloroacetic acid with caustic potash:

$$COOH\cdot CH_2\boxed{Cl + K}OH = COOH\cdot CH_2OH + KCl.$$

Glycollic acid is a crystalline solid, melting at 80°; it is very readily soluble in water, alcohol, and ether; the calcium salt dissolves with difficulty in water. When distilled *in vacuo*, glycollic acid splits off water, with formation of glycollide:



$$\begin{array}{l}CH_2O\,\boxed{H\ HO}\,CO\\ |\qquad\qquad\qquad |\\ CO\ O\,\boxed{H\ HO}\,CH_2\end{array} = 2H_2O + \begin{array}{l}CH_2O\cdot CO\\ |\qquad\quad\ \ |\\ CO\cdot O\cdot CH_2\end{array}$$

Glycollide

Lactic Acids, $C_3H_6O_3$.

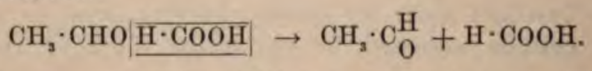
185. Two *lactic acids* are known, differing from one another in the position occupied by the hydroxyl-group; they are α-hydroxypropionic acid, $CH_3\cdot CHOH\cdot COOH$, and β-hydroxypropionic acid, $CH_2OH\cdot CH_2\cdot COOH$. The first of these is ordinary lactic acid.

α-Hydroxypropionic acid can be obtained synthetically by the methods described in **182**, although it is usually prepared by other means. In presence of an organized ferment, called the "lactic acid bacillus," certain sugars, such as milk-sugar, cane-sugar, and grape-sugar, undergo "lactic fermentation," the principal product being lactic acid. These bacilli occur, for example, in decaying cheese, and cannot live in a solution of lactic acid of more than a certain concentration; in order to make fermentation go on, chalk is added, which neutralizes the lactic acid formed. Lactic acid can also be prepared by heating glucose or invert-sugar with caustic soda.

Lactic acid derives its name from its presence in sour milk, as a result of the fermentation of the milk-sugar present. The faint acid odour possessed by sour milk is due, not to lactic acid, but to traces of volatile fatty acids simultaneously formed; lactic acid itself is odourless. Lactic acid also occurs in other fermented substances, such as *Sauerkraut*, and in large quantities in ensilage, used for feeding cattle, which is prepared by submitting piles of grass, clover, etc., to pressure.

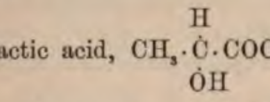
Lactic acid is purified by distilling the aqueous acid at very low pressures (1 mm.), when it is obtained as a crystalline solid melting at 18°. It is more usually met with in the form of a colourless, syrupy liquid of strongly acid taste, and containing water. When heated under ordinary pressure, with the object of removing water, it is partially converted into the anhydride (**183**) even before complete dehydration has taken place; this can be detected by the diminution of the acid-equivalent on titration. Its zinc salt forms well-defined crystals with three molecules of water.

The constitution of lactic acid is deduced from its formation from acetaldehyde by the cyanhydrin synthesis (**182**, 5), and by the oxidation of propyleneglycol. When lactic acid is heated alone, or with dilute sulphuric acid, it splits up into acetaldehyde and formic acid:



$$CH_3\cdot CHO\boxed{H\cdot COOH} \rightarrow CH_3\cdot C\overset{H}{\underset{O}{}} + H\cdot COOH.$$

This decomposition may be looked upon as a reversal of the cyanhydrin synthesis, and is characteristic of many α-hydroxy-acids.



Lactic acid, $CH_3\cdot\overset{H}{\underset{OH}{C}}\cdot COOH$, contains one asymmetric carbon atom. In accordance with the principles laid down in **53**, it ought to exist in three isomeric modifications; all of these are known. Ordinary lactic acid, obtained by synthesis or fermentation, is *racemic;* that is to say, it consists of equal quantities of the dextro-acid and lævo-acid, and is therefore optically inactive. The dextro-lactic and lævo-lactic acids can be obtained from the inactive modification by methods described in **196**. The dextro-rotatory variety is a constituent of meat-juices, and is therefore sometimes called *sarcolactic acid.*

186. It has just been stated that synthesis yields inactive lactic acid. It is usually not possible to prepare optically active products from inactive substances by wholly chemical means. Since the inactive modification consists of equal parts of dextro-rotatory and lævo-rotatory substance, both of these must be formed in equal quantities in the synthesis. The question arises, why this is so, and an insight into the phenomenon is afforded by a consideration of the following examples.

The nitrile of lactic acid is obtained by the addition of hydrocyanic acid to acetaldehyde (**182,** 5), the structural formula of which is represented in Fig. 53:

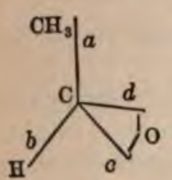


Fig. 53.
Acetaldehyde.

→

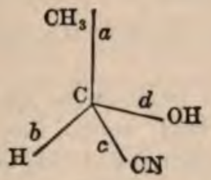


Fig. 54.
Lactonitrile.

or

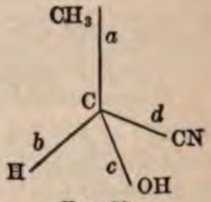


Fig. 55.
Lactonitrile.

The addition of H · CN can take place in two ways; the oxygen, which is doubly linked to the central carbon atom of the figure, becomes severed either from the bond *c*, or *d*. In the first case, the group CN becomes linked to *c* (Fig. 54), and a hydroxyl-group is formed at *d*; in the second case this is reversed (Fig. 55). The configurations thus obtained are mirror-images of each other, and cannot be made to coincide; they represent asymmetric C-atoms.

The possibility of the formation of both active components is thus evident, and that these must be formed in equal amounts is seen by a consideration of the *probability* of their formation. This is alike for both, since *d* and *c* occupy similar positions with respect to *a* and *b*, and there is therefore no tendency for the oxygen to remain linked to the one more than to the other.

In the example just given, an asymmetric carbon atom has resulted from an *addition*-reaction. The following is an example of the formation, by *substitution*, of a compound containing such an atom. α-bromopropionic acid, $\begin{matrix}\mathrm{Br}\\ \mathrm{H}\end{matrix}>\mathrm{C}<\begin{matrix}\mathrm{CH_3}\\ \mathrm{COOH}\end{matrix}$, can be obtained from propionic acid, $\begin{matrix}c\mathrm{H}\\ d\mathrm{H}\end{matrix}>\mathrm{C}<\begin{matrix}\mathrm{CH_3}\\ \mathrm{COOH}\end{matrix}$. By replacement of H*c* and H*d* respectively, two acids of opposite rotation are produced, the probability of the formation of one being equal to that of the formation of the other.

Compounds containing an asymmetric carbon atom can also result from the splitting-off of a group, as in the formation of methylethylacetic acid, $\begin{matrix}\mathrm{CH_3}\\ \mathrm{C_2H_5}\end{matrix}>\mathrm{C}<\begin{matrix}\mathrm{H}\\ \mathrm{COOH}\end{matrix}$, from methylethylmalonic acid, $\begin{matrix}\mathrm{CH_3}\\ \mathrm{C_2H_5}\end{matrix}>\mathrm{C}<\begin{matrix}\overset{c}{\mathrm{COOH}}\\ \underset{d}{\mathrm{COOH}}\end{matrix}$, by loss of CO_2. The probability that this will take place at *c* and at *d* is equal, so that an inactive mixture is produced.

When optically active lactic acids, and optically active substances in general, are strongly heated, they are converted into the optically inactive modification, containing equal proportions of the dextro-modification and lævo-modification. This necessitates the conversion of one-half of the optically active substance into its optical isomer, it being sufficient that two of the groups or atoms linked to the asymmetric C-atom should change places. In order to convert Fig. 56 into its mirror-image, Fig. 57, it is only essential, for example, for B and D to exchange positions. This can only happen through a breaking of the bonds between B and D and the carbon atom, for a period however brief, followed by a reunion, either, as at first, B to *b* and D to *d*, or in the reverse order, D to *b* and B to *d*. In consequence of the similarity of the positions occupied by *b* and *d* with respect to *a* and *c*, the probability

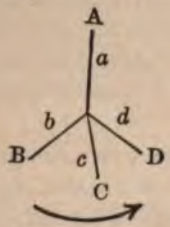


Fig. 56.

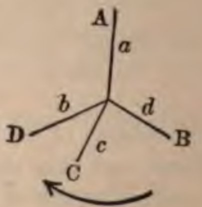


Fig. 57.

of the union of B with *b* and D with *d* is equal to that of the union of D with *b* and B with *d*. As a result of this, dextro-rotatory and lævo-rotatory molecules are formed in equal numbers, so that after heating, the substance is optically inactive.

Optical inactivity is sometimes developed without the aid of heat. WALDEN found that the dextro-rotatory isobutyl ester of bromopropionic acid, $CH_3 \cdot CHBr \cdot COOC_4H_9$, and some other compounds containing a Br-atom in union with an asymmetric C-atom, became optically inactive through being kept for three or four years at the ordinary temperature. The velocity of transformation at ordinary temperatures, for most substances too small to be appreciable after the lapse of even long periods—and only measurable at higher temperatures, which have an accelerating effect upon most reactions—has in these cases a measurable value.

187. *β-Hydroxypropionic acid*, or *hydracrylic acid*, has the formula $CH_2OH \cdot CH_2 \cdot COOH$, and is a type of the β-hydroxy-acids. It can be synthesized from ethylene by the addition of hypochlorous acid, HOCl, treatment of the addition-product with potassium cyanide, and hydrolysis of the resulting nitrile:

$$\underset{\text{Ethylene}}{CH_2{:}CH_2} \rightarrow \underset{\text{Glycolchlorhydrin}}{CH_2OH \cdot CH_2Cl} \rightarrow \underset{\text{Glycolcyanhydrin}}{CH_2OH \cdot CH_2 \cdot CN} \rightarrow \underset{\text{β-Hydroxypropionic acid}}{CH_2OH \cdot CH_2 \cdot COOH.}$$

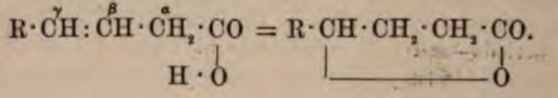
This compound can also be obtained from β-iodopropionic acid. It has a syrupy consistency, and chiefly differs from α-hydroxypropionic acid in being decomposed on heating, with loss of water and formation of acrylic acid (**183**).

Aldol (**115**) is converted by oxidation into *β-hydroxybutyric acid*, $CH_3 \cdot CHOH \cdot CH_2 \cdot COOH$, which easily loses water, forming crotonic acid. The constitution of β-hydroxybutyric acid follows from its formation by the reduction of the corresponding ketonic acid, acetoacetic acid (**235**).

Lactones.

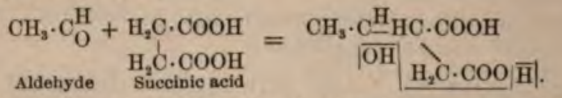
188. It was mentioned (**178** and **183**) that the γ-hydroxy-acids lose water very readily, with formation of lactones. So great is this tendency that some γ-hydroxy-acids, when set free from their salts, at once split off one molecule of water, yielding a lactone. This phenomenon is another example of the readiness with which ring-compounds containing four carbon atoms are formed (**169**). In many cases the γ-hydroxy-acids are not known in the free state, but only in the form of esters, salts, or amides. The lactones are stable towards an aqueous solution of sodium carbonate, but are converted by the hydroxides of the alkali-metals into salts of γ-hydroxy-acids; this reaction proves their constitution. They may be looked upon as the inner esters of the hydroxy-acids.

The lactones can be prepared by several methods. Thus, acids containing a double bond at the $\beta\gamma$- or $\gamma\delta$-position are readily converted into lactones by warming with dilute sulphuric acid. The formation of lactones in this way may be looked upon as an addition of the carboxyl-group at the double bond:



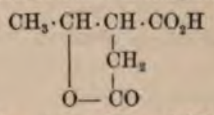
$$\mathrm{R\cdot\overset{\gamma}{C}H:\overset{\beta}{C}H\cdot\overset{\alpha}{C}H_2\cdot \underset{H\cdot O}{\underset{|}{CO}} = R\cdot \underset{|\_\_\_\_\_\_\_\_\_\_\_\_}{CH}\cdot CH_2\cdot CH_2\cdot \underset{O}{\underset{|}{CO}}.}$$

Unsaturated acids $\Delta^{\beta\gamma}$ (**180**) can be obtained by several methods, one being the action of aldehydes upon sodium succinate in presence of acetic anhydride:



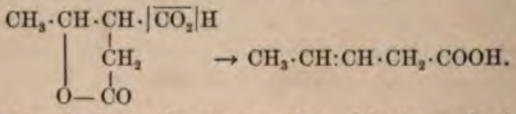
$$\underset{\text{Aldehyde}}{\mathrm{CH_3\cdot C{}^{H}_{O}}} + \underset{\text{Succinic acid}}{\begin{array}{l}\mathrm{H_2C\cdot COOH}\\ \mathrm{H_2\overset{|}{C}\cdot COOH}\end{array}} = \begin{array}{l}\mathrm{CH_3\cdot C\overset{H}{-}HC\cdot COOH}\\ \boxed{\mathrm{OH}}\;\;\underline{\mathrm{H_2\overset{\diagdown}{C}\cdot COO}\boxed{\mathrm{H}}}.\end{array}$$

By elimination of one molecule of water, there results a lactone-acid,



$$\begin{array}{l}\mathrm{CH_3\cdot CH\cdot CH\cdot CO_2H}\\ \qquad\;|\qquad\;\mathrm{\overset{|}{C}H_2}\\ \qquad\;\mathrm{O - \overset{|}{C}O}\end{array}$$

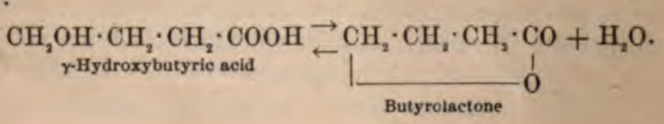
which, on dry distillation, loses CO_2, yielding the unsaturated acid:



$$\begin{array}{l}\mathrm{CH_3\cdot CH\cdot CH\cdot}\boxed{\mathrm{CO_2}}\mathrm{H}\\ \qquad|\qquad\mathrm{\overset{|}{C}H_2}\\ \qquad\mathrm{O - \overset{|}{C}O}\end{array} \rightarrow \mathrm{CH_3\cdot CH:CH\cdot CH_2\cdot COOH.}$$

Another method for the preparation of lactones is the reduction of γ-ketonic acids, the synthesis of which will be described later. δ- and ϵ-lactones are also known.

On boiling with water, the lactones are partly converted into the corresponding hydroxy-acids; the quantity of acid formed is in part dependent upon the amount of water present. A state of equilibrium is arrived at between the acid, and the lactone + water:



$$\underset{\gamma\text{-Hydroxybutyric acid}}{\mathrm{CH_2OH\cdot CH_2\cdot CH_2\cdot COOH}} \rightleftarrows \underset{\text{Butyrolactone}}{\mathrm{\underset{|\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_O}{CH_2\cdot CH_2\cdot CH_2\cdot CO}}} + \mathrm{H_2O}.$$

If the molecular concentration per litre of the γ-hydroxybutyric acid is A, and if, after the lapse of a time t, x molecules have been converted into lactone, the velocity of lactone-formation at that instant, s, is given by the following equation, in which k is the reaction constant:

$$s = k(A - x).$$

But the reverse also takes place, the acid being regenerated from the lactone and water. If the lactone is dissolved in a large excess of water, no appreciable error is introduced by assuming the quantity of the latter to be constant. The velocity s' of this reverse reaction is then represented by the equation

$$s' = k'x,$$

in which k' is again the reaction constant. The total velocity of the lactone-formation for each instant is, therefore, equal to the difference between these velocities:

$$s - s' = \frac{dx}{dt} = k(A - x) - k'x \quad . \quad . \quad . \quad . \quad (1)$$

When equilibrium is reached, $s = s'$; and if the value of x at this point has become equal to x_1, then

$$k(A - x_1) - k'x_1 = 0, \quad \text{or} \quad \frac{k}{k'} = \frac{x_1}{A - x_1} \quad . \quad . \quad (2)$$

Equations 1 and 2 can be solved for k and k'. The same method of calculation may be applied to ester-formation from acid and alcohol, by which the reaction constant of the ester-formation, and of the ester-decomposition, can be computed.

The lactones form addition-products with hydrobromic acid as well as with water, yielding γ-bromo-acids, the constitution of which follows from their reconversion into lactone (**178**). The lactones also form addition-products with ammonia, yielding the amides of the γ-hydroxy-acids.

III. DIBASIC HYDROXY-ACIDS.

189. The simplest member of this series is *tartronic acid*, COOH·CHOH·COOH. It can be obtained by the action of moist oxide of silver upon bromomalonic acid, and is a crystalline solid, melting at 187° with evolution of CO_2. The glycollic acid, $CH_2OH \cdot COOH$, thus formed, at once loses water, yielding a polymer of glycollide (**184**).

190. A substance of greater importance is *malic acid*, $C_4H_6O_5$, which is present in various unripe fruits, and is best prepared from unripe mountain-ash berries. It is a crystalline solid, melting at 100°, and is readily soluble in water and in alcohol. Natural malic acid is optically active.

It is possible to prove in several ways that malic acid is hydroxysuccinic acid, $COOH \cdot CHOH \cdot CH_2 \cdot COOH$. Among these are its reduction to succinic acid by heating with hydriodic acid, and its conversion into monochlorosuccinic acid by the action of phosphorus pentachloride, etc. Its alcoholic character is indicated by the formation of an acetate when its diethyl ester is treated with acetyl chloride.

The formation of fumaric and maleïc acids from malic acid under the influence of heat has been already mentioned (**170**). In addition to the natural lævo-rotatory acid, both a dextro-rotatory and an inactive modification are known. The latter can be split up, by fractional crystallization of its cinchonine salt, into its two optically active components. As seen from its structural formula, malic acid contains an asymmetric C-atom.

Tartaric Acids, $C_4H_6O_6$.

191. Four acids of this composition are known; all have the constitutional formula

$$COOH \cdot CHOH \cdot CHOH \cdot COOH.$$

They are called *dextro-rotatory tartaric acid, lævo-rotatory tartaric acid, racemic acid,* and *mesotartaric acid;* the last two are optically inactive. Their constitution is proved by their formation from the dibromosuccinic acids—obtained from fumaric or maleïc acids by the action of bromine—by boiling their silver salts with water, as well as by their production from glyoxal by the cyanhydrin synthesis. The inactive modifications are produced by these reactions (**186**).

In accordance with the constitutional formula given above, the tartaric acids contain two asymmetric C-atoms in the molecule, and it is necessary to consider how many stereoisomers are theoretically possible.

The formula of a substance of this kind may be represented by $C(abc)—C(def)$. The groups linked to the asymmetric C-atoms are in this general formula dissimilar; the two asymmetric C-atoms are assumed to be unlike. Since the mode of arrangement of the groups relative to each of these C-atoms results in dextro-rotation and lævo-rotation respectively, the following combinations are possible in the molecule of a substance containing two asymmetric C-atoms:

	1	2	3	4
C(*abc*)	Dextro	Dextro	Lævo	Lævo
C(*def*)	Dextro	Lævo	Lævo	Dextro

There are, therefore, four isomers possible, apart from the optically inactive modifications containing equal quantities of two of these (1 and 3, 2 and 4).

Since tartaric acid, however, contains two similar asymmetric C-atoms, that is to say, asymmetric C-atoms in union with similar groups, 2 and 4 become identical, leaving so far three isomers possible. 1 and 3 being able to unite, to form a racemic compound, the total number of possible isomers is raised to four:

	1	2	3	4
CH(OH)(COOH)	Dextro	Dextro	Lævo	Inactive combination of 1 and 3
CH(OH)(COOH)	Dextro	Lævo	Lævo	

The four acids, $C_4H_6O_6$, mentioned above, correspond in their properties to the four theoretically possible isomers. Dextro-tartaric and lævo-tartaric acids must be represented respectively by 1 and 3, since in these both C-atoms rotate the plane of polarization in the same direction, and should, therefore, reinforce one another's influence. The optically inactive mesotartaric acid, whose two oppositely rotatory C-atoms neutralize each other, is represented by 2. Finally, the isomer 4 is racemic acid.

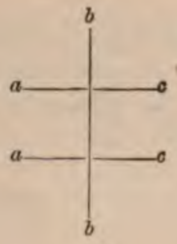
An important difference exists between the two optically inactive isomers, racemic and mesotartaric acid. The former, obtained by mixing equal quantities of the dextro-acid and lævo-acid, can be split up into its components; the latter, consisting only of one kind of molecules, cannot be split up. The rotation caused by the dextro-acid is equal in amount but opposite in sign to that caused by the lævo-acid.

Emil Fischer has introduced a simple mode of writing the spacial formulæ of optically active compounds, of which frequent use will be made later. His representation in space of two C-atoms in union, in a compound $\begin{array}{c}\mathrm{C}abc\\|\\\mathrm{C}abc\end{array}$, is shown in Fig 58 (**169**).

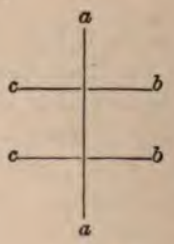
Fig. 58.

Fig. 59.

If the two bonds uniting the two carbon atoms are supposed to lie in the plane of the paper, then the positions of *a* and *c* are to the back, and of *b* to the front. If *a*, *b*, and *c* are imagined to be projected upon the plane of the paper, and *a* and *c* simultaneously so altered in position that they lie in the same straight line at right angles to the vertical axis, and *b* lies in this axis produced, then projection-figure I is obtained:



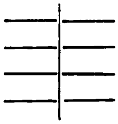
I.



II.

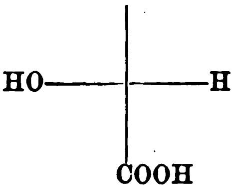
If Fig. 58 is rotated round its vertical axis, so that *a*, for example, lies in front of the plane of the paper, Fig. 59 is obtained, the projection of which is represented by II. These apparently different configurations are identical.

For a chain of several carbon atoms, e.g., four, there is obtained in an analogous way the projection-figure



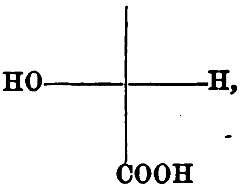
This will be understood if it is imagined that the figures on p. 200 (Fig. 33) are so placed that the plane in which the carbon bonds lie is at right angles to that of the paper, and the figures in this position are projected in the manner just described.

The projection-formulæ for the four isomeric tartaric acids are obtained in the following way. If the projection-figure for two asymmetric C-atoms is divided in the middle of the vertical line, and the upper half of the figure rotated through 180° in the plane of the paper, the similar grouping of HO, H, and COOH about the asymmetric C-atoms in both halves,



$$\begin{array}{ccc} & | & \\ \mathrm{HO} & - & \mathrm{H} \\ & | & \\ & \mathrm{COOH} & \end{array}$$

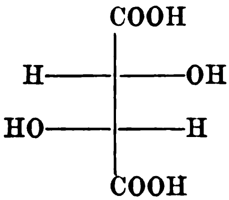
and



$$\begin{array}{ccc} & | & \\ \mathrm{HO} & - & \mathrm{H,} \\ & | & \\ & \mathrm{COOH} & \end{array}$$

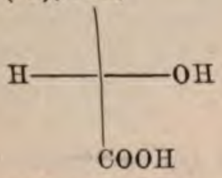
indicates that both C-atoms rotate the plane of polarization in the same direction. We shall arbitrarily assume that this grouping occasions dextro-rotation.

When the two carbon atoms again become united with one another, by transposing one of the halves in the plane of the paper, the following figure results, and is therefore the projection-formula for the dextro-rotatory acid:

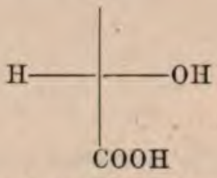


$$\begin{array}{ccc} & \mathrm{COOH} & \\ \mathrm{H} & - & \mathrm{OH} \\ \mathrm{HO} & - & \mathrm{H} \\ & \mathrm{COOH} & \end{array}$$

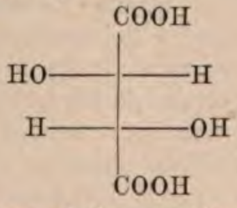
The grouping with respect to the two C-atoms in the lævo-rotatory acid must be the mirror-image of that in the dextro-rotatory (**53**); thus,



and

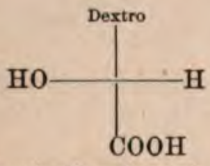


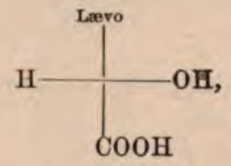
The combination of these two gives the following projection-formula for the lævo-rotatory acid:



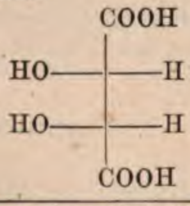
These representations of the constitutions of dextro-tartaric and lævo-tartaric acid cannot be made to coincide by altering their position in the plane of the paper,* and are therefore different.

When the acid contains a dextro-rotatory and a lævo-rotatory C-atom, as in mesotartaric acid, the arrangement of the groups will be





and their projection-formula



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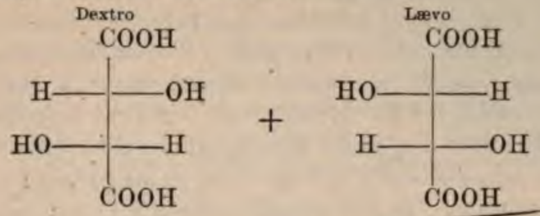
* These projection-formulæ can be made to coincide by rotating one of them through 180° about the line HO—H. It will be seen from a model, however, that the *spacial* formulæ cannot be made to coincide by this treatment. To determine whether this is possible for spacial formulæ by means of projection-formulæ, it is only admissible to transpose the latter in the plane of the paper.

The projection-formula for racemic acid is



FIN.

Dextro-tartaric Acid.

192. The *acid potassium salt*, $C_4H_5O_6K$, is present in the juice of grapes, and during alcoholic fermentation is deposited on the bottom of the casks, being even more sparingly soluble in dilute alcohol than in water. The crude product is called "argol"; when purified, it is known as "cream of tartar." To obtain dextro-tartaric acid, the crude argol is boiled with hydrochloric acid, and the acid precipitated as calcium tartrate, $CaC_4H_4O_6$, with milk of lime. After washing, the calcium salt is treated with an equivalent quantity of sulphuric acid, which precipitates calcium sulphate, and sets free the tartaric acid; this can be obtained by evaporation in the form of large, transparent crystals, free from water of crystallization, and having the composition $C_4H_6O_6$.

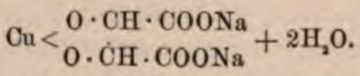
Dextro-tartaric acid melts at 170°, is very readily soluble in water, to a less extent in alcohol, and is insoluble in ether. When heated above its melting-point under atmospheric pressure, it loses water and yields various anhydrides, according to the intensity and duration of the heating. On heating further, it turns brown, with production of a caramel-like odour, and at a still higher temperature, chars, with formation of pyroracemic and pyrotartaric acids. It can be converted into succinic acid by the action of certain bacteria.

In addition to the acid potassium salt may be mentioned the *neutral potassium salt*, $C_4H_4O_6K_2$, which is readily soluble in water, and *potassium antimonyl tartrate*,

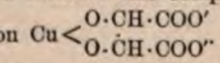
$$2[\mathrm{COOK \cdot CHOH \cdot CHOH \cdot COO(SbO)}] + H_2O,$$

On account of its medicinal properties, the latter is known as "tartar emetic." It is obtained by boiling acid potassium tartrate with antimony oxide and water, and is readily soluble in water.

The precipitation of hydroxides from metallic salts—copper hydroxide from copper sulphate, for example—is often prevented (**161**) by the presence of tartaric acid. The liquid obtained by dissolving copper sulphate, tartaric acid, and excess of caustic potash in water, is called "Fehling's solution." It is an important means of testing the reducing power of compounds, since reducing-agents precipitate yellowish-red cuprous oxide, or its hydroxide, from the dark-blue solution. In this alkaline copper solution the hydroxyl-groups of the central C-atoms have reacted with the copper hydroxide, since one gramme-molecule of neutral alkali tartrate can dissolve one gramme-molecule of copper hydroxide. These copper alkali tartrates have also been obtained in a crystalline form; for example, the compound $C_4H_2O_6Na_2Cu + 2H_2O$ is known, and to it must therefore be assigned the constitutional formula



$$\mathrm{Cu}<\begin{matrix}\mathrm{O\cdot CH\cdot COONa}\\ \mathrm{O\cdot \dot{C}H\cdot COONa}\end{matrix} + 2H_2O.$$

In aqueous solution this compound is ionized into $Na^{\cdot}$, and the complex anion  $\mathrm{Cu}<\begin{matrix}\mathrm{O\cdot CH\cdot COO'}\\ \mathrm{O\cdot \dot{C}H\cdot COO'}\end{matrix}$. This is shown by the following facts. First, the solution no longer gives the ordinary reactions for copper ions; although the liquid is alkaline, copper hydroxide is not precipitated. Second, when the solution is electrolyzed, the copper goes towards the anode. This has been proved by **Küster** by the aid of the apparatus shown in Fig. 60. One U-tube contains copper sulphate solution at *b*; the other, Fehling's solution at *d*; into both limbs of each is then carefully poured a solution of sodium sulphate, *a* and *c*. The common surfaces of the sodium sulphate and copper sulphate solutions in the two U-tubes lie in the same horizontal plane. When an electric current is passed through the tubes, preferably arranged in parallel, and not in series, a different effect is produced on the posi-

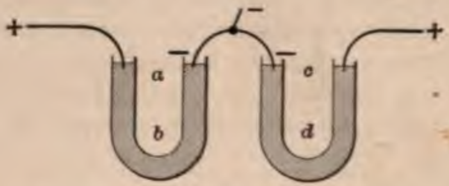


Fig. 60.—Electrolysis of an Alkaline Copper Solution.

tion of the surfaces of the copper solutions in each tube. In the copper sulphate solution, a rise in level takes place at the cathode, since the Cu-ions are cations, and tend towards the cathode. The reverse effect is observed in the Fehling's solution, showing that here the copper forms part of the anion.

Moreover, the colour of Fehling's solution is a much more intense blue than that of a copper sulphate solution of equivalent concentration, which is evidence of the presence in Fehling's solution of a complex ion containing copper.

Fehling's solution decomposes on standing, so that it is best prepared as required. Ost has discovered a much more stable alkaline copper solution, which can be used for the same purposes as that of Fehling. It is a mixture of copper sulphate with acid and neutral carbonates of potassium, and contains a soluble double carbonate of copper and potassium.

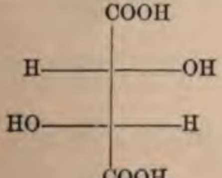
Lævo-tartaric Acid.

Lævo-tartaric acid is obtained from racemic acid. With the exception of their causing opposite rotation, and the fact that the salts formed by the lævo-acid with the optically active alkaloids differ in solubility from those derived from the dextro-acid (**196**), the properties of the lævo-acid and its salts are identical with those of the dextro-modification and its salts.

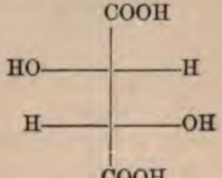
Racemic Acid.

193. It has been already stated (**186**) that optically active substances can be converted by the action of heat into optically inactive compounds; that is, changed into a mixture of the dextro-modification and lævo-modification in equal proportions. This change is often facilitated by the presence of certain substances; thus, dextro-tartaric acid is easily converted into racemic acid when boiled with excess of a concentrated solution of caustic soda. Mesotartaric acid is formed at the same time (**194**).

The optical inactivity is occasioned by conversion of one half of the dextro-acid into the lævo-modification. If formula I represents



I.



II.

the dextro-acid, then formula II will correspond with the lævo-acid, and the formulæ show that the exchange of groups, by which an active compound is converted into its optical isomer (**186**), must in this instance take place at both asymmetric C-atoms, in order that the dextro-acid may yield its lævo-isomer.

Racemic acid is not so soluble in water as the two optically active acids, and differs in crystalline form from them; the crystals have the composition $2C_4H_6O_6 + 2H_2O$. Many of its salts contain amounts of water of crystallization differing from those in the salts of the corresponding optically active isomers. Racemic acid is proved to consist of two components by its synthesis from solutions of the dextro-acid and the lævo-acid. If the solutions are concentrated, heat is developed on mixing, and the less soluble racemic acid crystallizes out. Racemic acid can also be split up into the two optically active modifications.

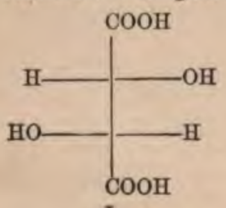
Although racemic acid in the solid state differs from both dextro-tartaric acid and lævo-tartaric acid, yet in solution, or as ester in the state of vapour, it seems only to be a mixture of them; at least, the lowering of the freezing-point produced by it in dilute solution corresponds to the molecular formula $C_4H_6O_6$, and the vapour density of its ester to single, instead of to double, molecules.

The term "racemic" is applied to substances whose optical inactivity is occasioned by their consisting of isomers of equal and opposite rotatory power in equimolecular proportions. This phenomenon was first observed by PASTEUR in his researches on racemic acid (**196**).

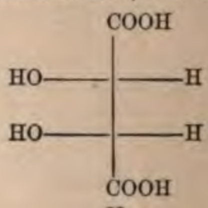
Mesotartaric Acid.

194. *Mesotartaric acid*, like racemic acid, is optically inactive, but cannot be split up into optically active components. It is formed when dextro-tartaric acid is boiled for several hours under a reflux-condenser with a large excess of caustic soda (**193**).

If formula I is assigned to dextro-tartaric acid, it is evident that



I.



II.

to convert it into mesotartaric acid, formula II, it is only necessary for two groups in union with a single asymmetric C-atom to change places, while racemic acid can only result through exchange of the groups linked to both C-atoms. This affords an explanation of the fact that when dextro-tartaric acid is heated with dilute hydrochloric acid, or boiled with dilute caustic soda, mesotartaric acid is first formed, and racemic acid only after prolonged heating.

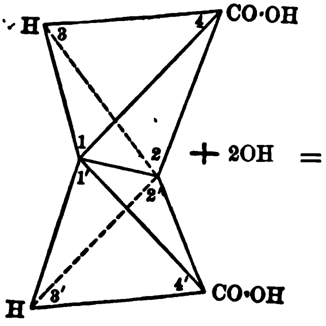
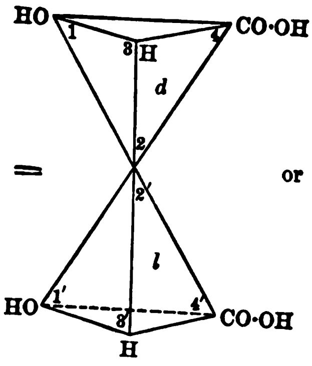


Fig. 61.—Maleïc Acid.



or

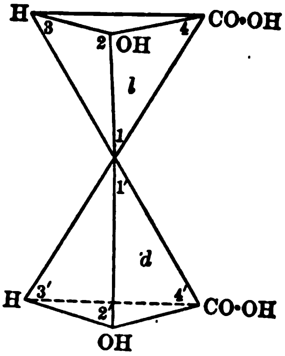


Fig. 62.—Mesotartaric Acid. Fig. 63.—Mesotartaric Acid.

The *acid potassium salt* of mesotartaric acid is readily soluble in cold water, differing in this way from the corresponding salts of the other tartaric acids.

196. This view of the structure of the tartaric acids is in complete accord with their relation to fumaric and maleïc acid (170), which, on treatment with a dilute aqueous solution of potassium permanganate, yield respectively racemic and mesotartaric acid by addition of two hydroxyl-groups. Addition of 2OH to maleïc acid may result from the breaking of the bond 1, 1′ or 2, 2′ in Fig. 61, with production of the configurations represented in Figs. 62 and 63. The projection-formulæ corrresponding to Figs. 62 and 63 are:

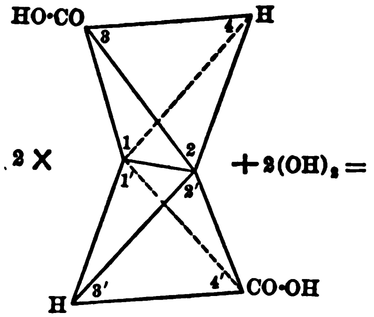


Fig. 64.—Fumaric Acid.

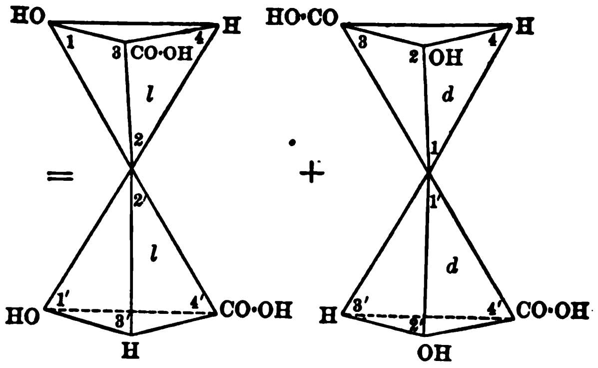
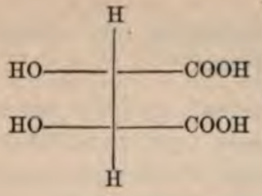
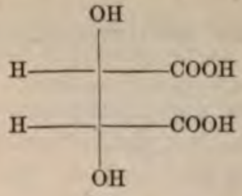


Fig. 65.—Racemic Acid.



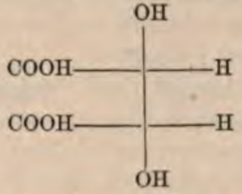
I.

and



II.

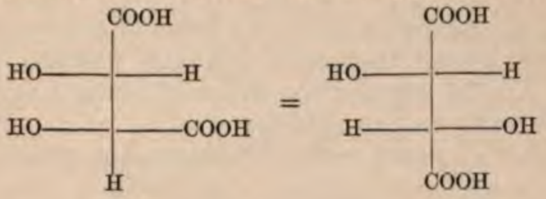
These apparently different configurations are identical, as may be easily seen by writing the first in another way (p. 228):

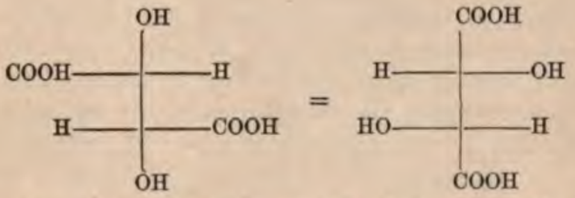


If the last projection-formula is rotated in the plane of the paper through 180°, it will coincide with II. A comparison of this scheme with that in **194** shows it to be the configuration representing mesotartaric acid. It follows that addition of two hydroxyl-groups to maleïc acid produces only mesotartaric acid.

A different result is obtained by addition of two OH-groups to fumaric acid, as will be seen from Figs. 64 and 65.

By the breaking of the bonds 1, 1′, or 2, 2′ by addition, two configurations are obtained which cannot be made to coincide by rotation. This will be better understood from the following projection-formulæ:





A comparison of these with those on p. 231 shows that the former represent dextro-tartaric and lævo-tartaric acids.

Racemic Substances, and their Separation into Optically Active Constituents.

196. Experience has shown that optically active isomers, rotating the plane of polarization in opposite directions, display no difference in their other physical or in their chemical properties. They have the same solubility, boiling-point, and melting-point; their salts crystallize with the same number of molecules of water of crystallization, etc. It follows that the separation of an optically inactive substance into its optically active components cannot be effected by the ordinary methods, since these are based on differences in physical properties.

Pasteur has put forward three methods for effecting this separation. The first of these depends upon the fact that the salts of racemic acids sometimes crystallize from solution in two forms, one corresponding to the dextro-salt, and one to the lævo-salt; these may subsequently be mechanically separated. Pasteur showed this for sodium ammonium racemate, $C_8H_8O_{12}Na_2(NH_4)_2 + 2H_2O$. Van 't Hoff proved later that crystals of the dextro-tartrate and lævo-tartrate are only obtained from this solution at temperatures below 28°, this being the transition-point for these salts ("Inorganic Chemistry," **70**):

$$\underset{\text{Dextro- + lævo- Na-NH}_4\text{-tartrate}}{2Na\cdot NH_4C_4H_4O_6\cdot 4H_2O} \rightleftarrows \underset{\text{Na-NH}_4\text{-racemate}}{C_8H_8O_{12}Na_2(NH_4)_2\cdot 2H_2O} + 6H_2O.$$

Fig. 66 represents the crystal-forms of the two tartrates, the difference between them being due to the positions of the planes *a* and *b*. The crystal-forms are mirror-images of one another, and cannot be made to coincide.

Pasteur's second method of separation depends upon a difference in solubility of the salts of the optically active acids, when they contain an optically active base. So long as the base with which a dextro-acid or a lævo-acid is united is optically inactive, as in the metallic salts, the internal structure of the molecule remains unchanged; the constitution of the salt-molecules, like that of the free acids, may be represented by configurations which are the mirror-images of one another. But this is not so when the dextro-acid and the lævo-acid have united with an optically active (for example, a dextro-rotatory) base; the configurations of the salt-molecules are then no longer mirror-images of one another, and identity of physical properties must of necessity cease.

Racemic acid can in this way be separated by means of its cinchonine salt, since cinchonine lævo-tartrate is less soluble than the dextro-tartrate, and crystallizes out from solution first. Strychnine may be advantageously used in the separation of lactic acid into its components, and other examples of the same kind might be cited.

The conversion of optically active substances into others whose configurations are no longer mirror-images of one another, can be effected in other ways; thus, in the case of acids, by the formation of an ester with an optically active alcohol. The velocity of ester-formation with an optically inactive alcohol must be the same for both isomers, on account of the perfectly symmetrical structure of the esters formed; but with an optically active alcohol the two isomers are not esterified at the same rate, since the compounds formed are no longer mirror-images of one another. **Marckwald** has shown that when racemic mandelic acid (**347**, 3) is heated for one hour at 155° with menthol (**363**), an active alcohol, the non-esterified acid is lævo-rotatory.

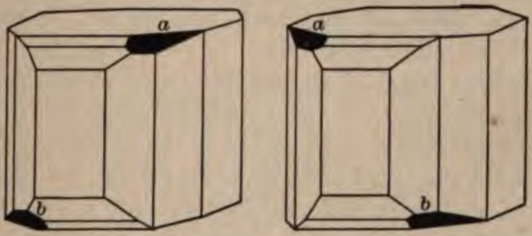


Fig. 66.—Crystal-forms of the Sodium Ammonium Tartrates.

Whilst the solubility of optical isomers in an optically inactive solvent is the same, it must be different in an optically active solvent. For, it is evident that the solubility of a compound depends on the configuration of its molecules as well as on those of the solvent, since, on the one hand, the solubility of isomers is in general dissimilar, and, on the other, the same substance dissolves in different solvents in wholly different proportions. It is true that optically active isomers have a perfectly similar structure, but in relation to an optically active solvent their configurations are different; so that they behave towards it like ordinary isomers, and must, therefore, have different solubilities. **Kipping** and **Pope** have proved this for sodium ammonium racemate by fractional crystallization from a solution of dextrose, which is dextro-rotatory; in the first fractions they found a marked preponderance in the amount of the dextro-rotatory salt.

The third method of separation devised by **Pasteur** depends on the action of mould-fungi (*Penicillium glaucum*), or of bacteria. Thus, when racemic lactic acid in very dilute solution is treated with the *Bacillus acidi lævolactici*, after addition of the necessary nutriment for the bacteria, the optically inactive solution becomes lævo-rotatory, since only the dextro-rotatory acid is converted by the bacilli into other substances. A dilute solution of racemic acid, into which traces of the mould-fungus *Penicillium glaucum* have been introduced, becomes lævo-rotatory, since the fungus propagates itself with decomposition of the dextro-rotatory acid.

The second and third methods of separation are alike in principle. During their growth, the bacteria and fungi develop substances called enzymes, which decompose compounds in a way hitherto unexplained. These enzymes are optically active; hence, a difference in their action on the optical isomers, analogous to that described above, is to be expected.

197. When a racemic substance is liquid or gaseous, it consists only of a mixture of the two isomers; an example of this was cited in connection with racemic acid in solution, and in the form of esters (**193**). If the substance is crystalline, there are three possibilities.

First, the individual crystals may be dextro-rotatory or lævo-rotatory, so that the two modifications can be mechanically separated. This is expressed by the statement that the racemic substance is a *conglomerate* of the isomers.

Second, it may be a true compound of the dextro-modification and lævo-modification, a *racemic* compound, the formation of which may be compared to that of a double salt, when a solution containing two salts is allowed to crystallize under certain conditions.

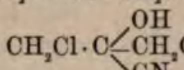
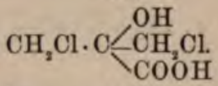
The third possibility is also analogous to the crystallization of salt-solutions, whereby crystals are sometimes obtained containing both salts, but in proportions varying in different crystals. It sometimes happens that the salts crystallize together in all proportions, but usually these can vary only between certain limits. The simultaneous crystallization of salts in this way gives rise to the so-called *mixed crystals*. When this occurs with optical isomers, *pseudoracemic* mixed crystals result.

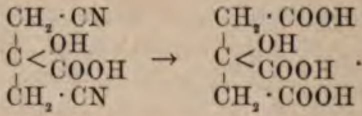
Which of these three kinds of crystals crystallize from a given solution or fused mass of a racemic substance—a conglomerate, a racemic compound, or pseudoracemic mixed crystals—depends upon the temperature at which the crystallization takes place, and upon other conditions. An example of this has been already mentioned, sodium ammonium racemate; when concentrated above 28° the racemate crystallizes from the solution of this salt; below this temperature a mixture of the individual tartrates—the conglomerate—is obtained.

Bakhuis Roozeboom has indicated a general method of distinguishing between these three classes of compounds. For a conglomerate, this is simple. A saturated solution is made; it will be of necessity optically inactive, and saturated alike for the dextro-rotatory and for the lævo-rotatory body. If now the solid dextro-compound or lævo-compound is added, and the mixture shaken up, nothing further will dissolve, since the liquid is already saturated with the two isomers; the amount of dissolved substance is still the same, and the solution remains optically inactive. On the other hand, if a racemic compound was present, although the solution was saturated in the first instance with respect to this, it is unsaturated with respect to the two optically active modifications; addition of the solid dextro-rotatory or lævo-rotatory substance would cause a change in the total quantity of solid dissolved, and the liquid would become optically active. The methods employed to detect pseudoracemic mixed crystals are sometimes less simple.

IV. POLYBASIC HYDROXY-ACIDS.

198. Of these acids it will be sufficient to describe the tribasic *citric acid*, $C_6H_8O_7$, which is widely distributed in the vegetable kingdom, and is also found in cows' milk. It is prepared from the juice of unripe lemons, in which it is present to the extent of 6–7%. The tricalcium salt of citric acid is easily soluble in cold water, but very slightly in boiling water; this property is made use of for its separation from lemon juice, the acid being obtained in the free state by the subsequent addition of sulphuric acid. Another technical method for its preparation depends upon the fact that certain mould-fungi (*Citromyces pfefferianus* and *C. glaber*) produce considerable quantities of citric acid from glucose or sugar.

Citric acid can be obtained synthetically by a method which proves its constitution. On oxidation, symmetrical dichlorhydrin, $CH_2Cl\cdot CHOH\cdot CH_2Cl$ (**162**), is converted into symmetrical dichloroacetone, $CH_2Cl\cdot CO\cdot CH_2Cl$. The cyanhydrin synthesis converts this into  $CH_2Cl\cdot C\!\begin{array}{l}\diagup OH\\ -CH_2Cl\\ \diagdown CN\end{array}$, which, on hydrolysis, yields the hydroxy-acid,  $CH_2Cl\cdot C\!\begin{array}{l}\diagup OH\\ -CH_2Cl\\ \diagdown COOH\end{array}$. On treatment of this compound with potassium cyanide, a dicyanide is formed, which is converted by hydrolysis into citric acid:



$$\begin{array}{l}CH_2\cdot CN\\ \mid\\ C{<}\begin{array}{l}OH\\ COOH\end{array}\\ \mid\\ CH_2\cdot CN\end{array} \rightarrow \begin{array}{l}CH_2\cdot COOH\\ \mid\\ C{<}\begin{array}{l}OH\\ COOH\end{array}\\ \mid\\ CH_2\cdot COOH\end{array}.$$

The alcoholic character of citric acid is indicated by the reaction of its triethyl ester with acetyl chloride, an acetyl-compound being formed.

Citric acid forms well-defined crystals containing one molecule of water of crystallization, and is readily soluble in water and alcohol. It loses its water of crystallization at 130°, and melts at 153°. It is used in the manufacture of lemonade, and in calico-printing.

FINISH

V. AMINO-ACIDS.

199. The amino-acids contain one or more amido-groups in direct union with carbon. They are of physiological importance, since many of them result from the decomposition of albumins, and some of them also occur in nature. They can be obtained synthetically by the following methods.

1. By the action of the halogen-substituted fatty acids on ammonia, a method analogous to the formation of amines:

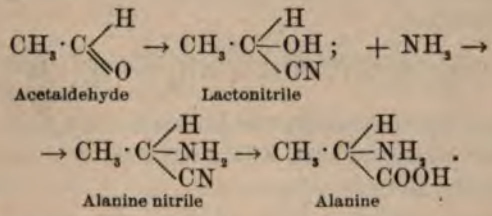
$$H_2N\boxed{H + Cl}H_2C\cdot COOH = H_2N\cdot CH_2\cdot COOH + HCl.$$

2. By reduction of oximes with sodium amalgam:

$$R\cdot C(NOH)\cdot COOH + 4H = R\cdot CHNH_2\cdot COOH + H_2O.$$

This is, therefore, a method for converting ketonic acids into amino-acids.

3. α-Amino-acids are formed by the action of ammonia upon the cyanhydrins of aldehydes or ketones, and subsequent hydrolysis of the nitrile-group:



$$CH_3\cdot C\begin{smallmatrix}H\\O\end{smallmatrix} \rightarrow CH_3\cdot C\begin{smallmatrix}H\\OH\\CN\end{smallmatrix}; \quad + NH_3 \rightarrow$$

Acetaldehyde   Lactonitrile

$$\rightarrow CH_3\cdot C\begin{smallmatrix}H\\NH_2\\CN\end{smallmatrix} \rightarrow CH_3\cdot C\begin{smallmatrix}H\\NH_2\\COOH\end{smallmatrix}.$$

Alanine nitrile   Alanine

The amino-acids possess two opposite characters; they form salts with both acids and bases, and are therefore both basic and acidic at the same time.

Replacement of the hydrogen of the amido-group by radicles yields amino-acids of a more complicated character. Thus, like ammonia, with acid chlorides they yield an acid amide, in which one hydrogen atom of the amido-group has been replaced:

$$R\cdot CO\boxed{Cl + H}HN\cdot CH_2\cdot COOH = R\cdot CO\cdot NH\cdot CH_2\cdot COOH + HCl.$$

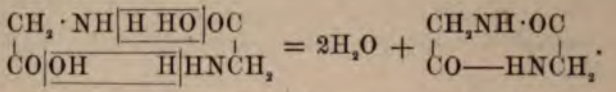
Compounds of this kind are therefore both amino-acids and acid amides.

Amino-acids in which the hydrogen of the amido-group is replaced by alkyl are also known. They are obtained by the action of amines, instead of ammonia, on the halogen-substituted acids:

$$(CH_3)_2N\boxed{H + Cl}H_2C\cdot COOH = (CH_3)_2N\cdot CH_2\cdot COOH + HCl.$$

The amino-acids undergo most of the decompositions characteristic of amines; thus, with nitrous acid they yield hydroxy-acids, just as the amines yield alcohols.

The same remarkable difference of properties, occasioned by the position of the amido-groups relative to the carboxyl-groups, is displayed by the amino-acids, as has been described in **178** and **183** in connection with the halogen-substituted acids and hydroxy-acids. The α-amino-acids readily yield anhydrides (acid amides) by the elimination of two molecules of water from two molecules of acid:

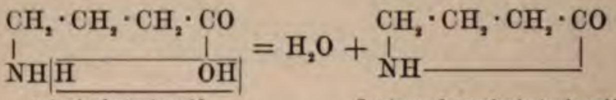


$$\begin{array}{l}CH_2\cdot NH\boxed{H\ HO}OC\\ CO\boxed{OH\qquad H}HNCH_2\end{array} = 2H_2O + \begin{array}{l}CH_2NH\cdot OC\\ CO—HNCH_2\end{array}.$$

The β-amino-acids easily split off ammonia, with formation of unsaturated acids. In this way, β-aminopropionic acid, obtained from β-iodopropionic acid, is converted on heating into acrylic acid and ammonia:

$$\boxed{NH_2}\cdot \underline{CH_2\cdot CH}\boxed{H}\cdot COOH = NH_3 + CH_2{:}CH\cdot COOH.$$

Like the γ-hydroxy-acids, the γ-amino-acids yield inner anhydrides; these substances are called *lactams* on account of their similarity to the lactones:



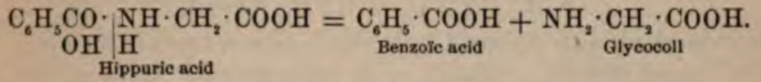
$$\begin{array}{l}CH_2\cdot CH_2\cdot CH_2\cdot CO\\ NH\boxed{H\qquad\qquad OH}\end{array} = H_2O + \begin{array}{l}CH_2\cdot CH_2\cdot CH_2\cdot CO\\ NH—————\end{array}$$

γ-Aminobutyric acid — Lactam of γ-aminobutyric acid

The *esters of amino-acids* can be obtained in the usual way, by dissolving the acids in absolute alcohol and treating this solution with hydrochloric-acid gas (**97**). The salts of hydrochloric acid are the primary products (e.g., $HCl\cdot NH_2\cdot CH_2\cdot CO_2C_2H_5$, the hydrochloride of glycocoll ester), because the amido-group in these esters has its usual basic properties. The esters themselves are prepared from these salts by treating them in aqueous solution with a concentrated solution of potassium hydroxide at a low temperature, and immediately extracting the liquid with ether. EMIL FISCHER has proved that these esters are very useful for the purification and separation of amino-acids. This is of great importance in the chemistry of proteïds, which are split up into a series of these acids by the action of acids or of bases.

Individual Members.

200. *Glycocoll*, or aminoacetic acid, $NH_2\cdot CH_2\cdot COOH$, can be obtained by boiling glue with dilute sulphuric acid or with barium hydroxide; it owes its name to this method of formation, and to its sweet taste (γλυκύς, sweet; κόλλα, glue). It is also prepared from *hippuric acid,* which is present in the urine of horses, and may be looked upon as glycocoll in which one of the hydrogen atoms of the amido-group has been replaced by benzoyl, C_6H_5CO; hippuric acid has therefore the formula $C_6H_5\cdot CO\cdot NH\cdot CH_2\cdot COOH$, and, like all acid amides, when boiled with dilute acids, splits up with addition of the elements of water:

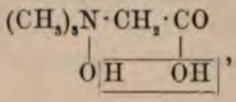


$$\underset{\text{Hippuric acid}}{C_6H_5\underset{\text{OH}}{CO}\cdot\Big|\underset{\text{H}}{NH}\cdot CH_2\cdot COOH} = \underset{\text{Benzoïc acid}}{C_6H_5\cdot COOH} + \underset{\text{Glycocoll}}{NH_2\cdot CH_2\cdot COOH}.$$

Glycocoll can be synthetically prepared by the action of ammonia on monochloroacetic acid.

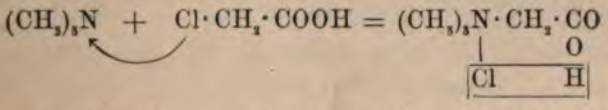
Glycocoll is a crystalline solid, and melts at 232° with decomposition; it is very readily soluble in water, and insoluble in absolute alcohol. Like many amino-acids, it forms a well-crystallized, blue copper salt, soluble with difficulty in water, and obtained by boiling copper carbonate with a solution of glycocoll. It crystallizes with one molecule of water of crystallization, and has the formula $(NH_2\cdot CH_2\cdot COO)_2Cu + H_2O$.

Betaïne, $C_5H_{11}NO_2$, is a derivative of trimethylglycocoll; it is found in the juice of the sugar-beet, and accumulates in the molasses during the manufacture of sugar. It must be looked upon as an inner ammonium salt,



$$\begin{array}{l}(CH_3)_3N\cdot CH_2\cdot CO\\ \qquad\quad\ |\qquad\quad\ \ |\\ \qquad\ \ O\,\boxed{H\qquad OH}\end{array},$$

since it is synthetically obtained from trimethylamine by the action of monochloroacetic acid, with elimination of HCl:



$$(CH_3)_3N + Cl\cdot CH_2\cdot COOH = \begin{array}{l}(CH_3)_3N\cdot CH_2\cdot CO\\ \qquad\quad\ \ |\qquad\qquad O\\ \qquad\ \ \boxed{Cl\qquad\quad H}\end{array}$$

This reaction is analogous to the interaction of alkyl halides and tertiary amines, yielding the salts of the ammonium base.

Betaïne forms large crystals with one molecule of water, which it loses at 100°, or when allowed to stand over sulphuric acid. On heating, it decomposes, with formation of trimethylamine.

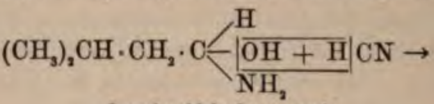
Many tertiary amines can be converted into substances with a constitution analogous to that of betaine; that is, inner salts of ammonium bases. These compounds have the general name betaïnes.

Alanine, or α-aminopropionic acid, $CH_3\cdot CH(NH_2)\cdot COOH$, is synthetically prepared by the action of ammonia on α-chloropropionic acid.

Leucine, or α-aminoisobutylacetic acid,

$$(CH_3)_2CH\cdot CH_2\cdot CH(NH_2)\cdot COOH,$$

results along with glycocoll from the decomposition of albumins by the action of acids or alkalis, or by putrefaction. It is synthetically obtained from isovaleraldehyde-ammonia by the action of hydrocyanic acid, and hydrolysis of the resulting nitrile:



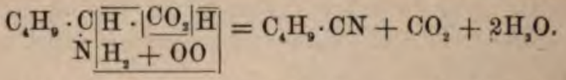
$$(CH_3)_2CH\cdot CH_2\cdot C\overset{H}{\underset{NH_2}{\boxed{OH + H}}}CN \rightarrow$$

Isovaleraldehyde-ammonia

$$\rightarrow (CH_3)_2CH\cdot CH_2\cdot CH(NH_2)\cdot CO_2H.$$

Leucine

Oxidation with manganese dioxide and dilute sulphuric acid converts leucine into carbon dioxide, water, and valeronitrile:



$$C_4H_9\cdot \underset{N}{C}\boxed{\begin{matrix}H\cdot|CO_2|H\\ H_2 + OO\end{matrix}} = C_4H_9\cdot CN + CO_2 + 2H_2O.$$

It is remarkable that in this oxidation a substance is obtained which does not contain oxygen. The leucine obtained from albumins is optically active; its formula contains an asymmetric carbon atom.

Asparagine is often present in sprouting seeds; to the extent of 20–30% in dried *lupine* seeds. It may be looked upon as the amic acid (**165**) of aminosuccinic acid, $C_2H_3(NH_2)<^{CONH_2}_{COOH}$, since on hydrolysis it is converted into aminosuccinic acid (*aspartic acid*), $COOH\cdot CH(NH_2)\cdot CH_2\cdot COOH$, whose structure is inferred from its conversion into malic acid by treatment with nitrous acid. Asparagine prepared from seeds is sometimes dextro-rotatory, but generally lævo-rotatory. The former is sweet, the latter tasteless.

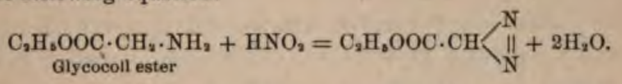
Homologous with asparagine is *glutamine*, which is also present in the seeds of sprouting plants. It is the amic acid of α-aminoglutaric acid, $COOH\cdot CH(NH_2)\cdot CH_2\cdot CH_2\cdot COOH$.

Diamino-acids are also obtained by the splitting up of proteïds; thus, *lysine*, $C_6H_{14}N_2O_2$ is produced by the action of acids on albumins. Putrefaction-bacilli decompose it with formation of pentamethylenediamine (**162**), and, as it is an acid, it is probable that it has the formula $NH_2\cdot CH_2\cdot (CH_2)_3\cdot CH < \begin{smallmatrix}NH_2\\ COOH\end{smallmatrix}$, and is an $\alpha\epsilon$-diaminocaproïc acid.

Ornithine is the next lower homologue of lysine; it has the formula $C_5H_{12}N_2O_2$ or $NH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(NH_2)\cdot COOH$; by the action of bacteria it yields putrescine or tetramethylenediamine (**162**). Its structure is proved by EMIL FISCHER'S synthesis (**328**).

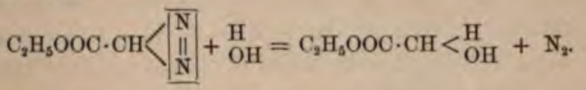
Diazoacetic Ester.

201. CURTIUS has obtained a yellow oil of characteristic odour by the action of nitrous acid on the ethyl ester of glycocoll; this substance explodes on heating, and has the formula $C_4H_6N_2O_2$. The method of its formation, and its constitutional formula, are indicated in the following equation:



$$\underset{\text{Glycocoll ester}}{C_2H_5OOC\cdot CH_2\cdot NH_2} + HNO_2 = C_2H_5OOC\cdot CH\left\langle\begin{matrix}N\\ \|\\ N\end{matrix}\right. + 2H_2O.$$

It is called *diazoacetic ester;* its constitution is inferred from the fact that its two nitrogen atoms are replaceable by two monovalent groups or elements; thus, on heating with water, it is converted into the ethyl ester of glycollic acid:



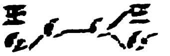
$$C_2H_5OOC\cdot CH\left\langle\boxed{\begin{matrix}N\\ \|\\ N\end{matrix}}\right. + \begin{matrix}H\\ OH\end{matrix} = C_2H_5OOC\cdot CH < \begin{matrix}H\\ OH\end{matrix} + N_2.$$

In this way it yields monochloroacetic ester with hydrochloric acid and di-iodoacetic ester with iodine. The hydrogen atom of the CHN_2-group is replaceable by metals, sodium dissolving in diazoacetic ester with evolution of hydrogen.

DIALDEHYDES AND DIKETONES. HALOGEN-SUBSTITUTED ALDEHYDES AND KETONES

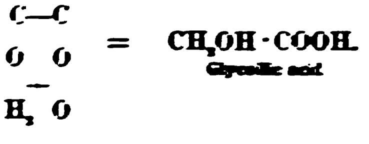
Dialdehydes

[illegible]. Only the simplest member of the series of dialdehydes, glyoxal, is known. It is a combination of two aldehyde-groups



It is usually prepared by carefully floating a layer of water on the surface of strong nitric acid contained in a tall glass cylinder, and pouring ethyl alcohol on the surface of the water, care being taken that the layers do not mix. The nitric acid and alcohol diffuse into the water; the alcohol is slowly oxidized, with formation of glyoxal, glycollic and oxalic acids, and other substances.

Glyoxal is a colourless, amorphous substance; when moist, it dissolves readily in water, but very slowly after complete drying at [illegible]°. Its combining with two molecules of sodium hydrogen sulphite, and its yielding a dioxime, prove it to be a double aldehyde. It also undergoes the other reactions peculiar to the aldehydes, such as the formation of a silver mirror. On oxidation it takes up two atoms of oxygen, yielding oxalic acid, of which it is the dialdehyde. On treatment with caustic potash, glyoxal is converted into glycollic acid, one aldehyde-group being reduced and the other oxidized. This reaction may be explained by the assumption that an addition-product with water is formed, in accordance with the scheme:



$$\begin{matrix} H & H \\ C & \!\!-\!\! C \\ O & O \\ H_2 & O \end{matrix} = CH_2OH \cdot COOH$$

Glycollic acid

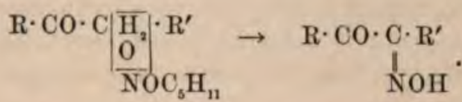
Diketones.

203. The diketones contain two carbonyl-groups, whose relative positions determine the methods of preparation of these compounds, and their properties. 1:2-Diketones are known containing the group $—\overset{1}{C}O \cdot \overset{2}{C}O—$; 1:3-diketones with $—\overset{1}{C}O \cdot \overset{2}{C}H_2 \cdot \overset{3}{C}O—$; 1:4-diketones with $—\overset{1}{C}O \cdot \overset{2}{C}H_2 \cdot \overset{3}{C}H_2 \cdot \overset{4}{C}O—$; and so on.

1:2-*Diketones* cannot be obtained by the elimination of chlorine from the acid chlorides by the action of a metal,

$$R \cdot CO\boxed{Cl + Na_2 + Cl}OC \cdot R,$$

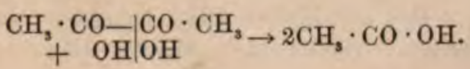
a method which naturally suggests itself. Their preparation has to be effected by the action of amyl nitrite and a little hydrochloric acid on a ketone, whereby one of the CH_2-groups is converted into $C{=}NOH$.



$$\begin{array}{l} R \cdot CO \cdot C\boxed{\begin{array}{c}H_2\\O\end{array}} \cdot R' \\ \quad\quad\quad\; NOC_5H_{11} \end{array} \rightarrow \begin{array}{c} R \cdot CO \cdot C \cdot R' \\ | \\ NOH \end{array}.$$

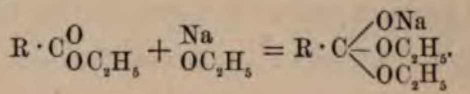
These compounds are called *isonitrosoketones*. When boiled with dilute sulphuric acid, the oxime-group is split off as hydroxylamine, with formation of the diketone. The *ketoaldehydes*, which are both ketones and aldehydes, and contain the group $—CO \cdot C\begin{smallmatrix}\diagup H\\ \diagdown O\end{smallmatrix}$, can also be obtained by this method.

Diacetyl, $CH_3 \cdot CO \cdot CO \cdot CH_3$, can be prepared from methylethylketone in the way described above. It is a yellow liquid with a pungent, sweetish odour, and is soluble in water; its vapour has the same colour as chlorine. Diacetyl boils at 88°, and has a specific gravity of 0·973 at 20°. Its behaviour is that of a substance containing two carbonyl-groups; it adds on 2HCN, yields a mono-oxime and a di-oxime, etc. The two carbonyl-groups are shown to be next to each other by the action of hydrogen peroxide, which converts it quantitatively into acetic acid:



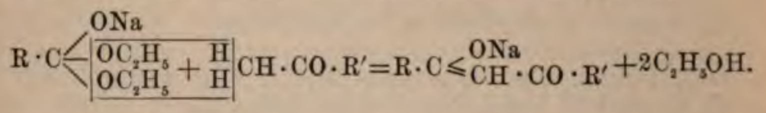
$$\begin{array}{l|l} CH_3 \cdot CO— & CO \cdot CH_3 \\ \quad + \; OH & OH \end{array} \rightarrow 2CH_3 \cdot CO \cdot OH.$$

1:3-*Diketones* can be prepared by a condensation-method discovered by CLAISEN, which is of general application. He employs sodium ethoxide as the condensing-agent, an addition-product being formed when this substance is brought into contact with an ester:



$$R\cdot C\begin{matrix}O\\OC_2H_5\end{matrix} + \begin{matrix}Na\\OC_2H_5\end{matrix} = R\cdot C\left\langle\begin{matrix}ONa\\OC_2H_5\\OC_2H_5\end{matrix}\right.$$

This addition-product is then treated with a ketone $R'\cdot CO\cdot CH_3$, whose methyl-group reacts in such a way as to eliminate two molecules of alcohol, with formation of a condensation-product:



$$R\cdot C\left\langle\begin{matrix}ONa\\ \boxed{\begin{matrix}OC_2H_5+H\\OC_2H_5+H\end{matrix}}\end{matrix}\right. CH\cdot CO\cdot R' = R\cdot C\leqslant\begin{matrix}ONa\\CH\cdot CO\cdot R'\end{matrix} + 2C_2H_5OH.$$

On treatment of this compound with a dilute acid, the sodium atom is replaced by hydrogen. This might be expected to produce a compound containing a hydroxyl-group in union with a doubly-linked carbon atom; it has been already mentioned (**136**) that compounds of this type are as a rule unstable, the group $-\overset{OH}{C}=CH-$ passing into $-CO-CH_2-$. This rule holds good in the present instance, $R\cdot C=\overset{OH}{C}H\cdot CO\cdot R'$ yielding a 1:3-diketone, $R\cdot CO-CH_2-CO\cdot R'$.

Another method for the preparation of 1:3-diketones is the action of acid chlorides on the sodium compounds of acetylene homologues:

$$\underset{\text{Sodio-}n\text{-amylacetylene}}{CH_3\cdot(CH_2)_4\cdot C\equiv C}\boxed{Na + Cl}\underset{\text{Acetyl chloride}}{OC\cdot CH_3} \rightarrow CH_3\cdot(CH_2)_4\cdot C\equiv C\cdot CO\cdot CH_3.$$

By treating this ketone with concentrated sulphuric acid, water is added on, and the desired diketone obtained:

$$\begin{matrix}CH_3\cdot(CH_2)_4\cdot C\equiv C\cdot CO\cdot CH_3\\ +\ \ O\ \ H_2\end{matrix} = CH_3\cdot(CH_2)_4\cdot CO\cdot CH_2\cdot CO\cdot CH_3.$$

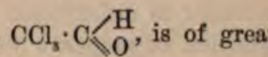
These diketones have a weak acidic character, their dissociation constants, which have been determined for some, including *acetylacetone*, $CH_3\cdot CO\cdot CH_2\cdot CO\cdot CH_3$, being very small. They contain two H-atoms replaceable by metals—those of the methylene-group between two negative carbonyl-groups; for if it were the other hydrogen atoms which could be thus exchanged for metals, there is no reason, since they are of equal value, why two, and only two, should be replaceable.

Acetylacetone is obtained by the condensation of ethyl acetate and acetone in the manner described above. It is a colourless liquid of agreeable odour; B.P. 137°, sp. gr. 0·979 at 15°. When boiled with water, it splits up into acetone and acetic acid, this reaction affording another example of the instability of compounds containing a carbon atom loaded with negative groups.

Among the salts of acetylacetone may be mentioned the copper salt, $(C_5H_7O_2)_2Cu$, which is sparingly soluble in water; and the volatile aluminium salt, $(C_5H_7O_2)_3Al$. By a determination of the vapour density of this compound, COMBES has shown that the aluminium atom is trivalent. Many of these salts are insoluble in water, but soluble in benzene, chloroform, or other organic solvents; this makes it doubtful whether they are true salts.

As a type of the 1:4-*diketones* may be cited *acetonylacetone*, $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO \cdot CH_3$, the preparation of which will be described later (**235**). It is a colourless liquid of agreeable odour; B.P. 193°, sp. gr. 0·970 at 21°. Acetonylacetone and other 1:4-diketones yield a variety of compounds containing a closed chain, which will be treated of in **391–393**.

Halogen-substituted Aldehydes.

204. *Chloral* or trichloroacetaldehyde,  $CCl_3 \cdot C\langle{}^{H}_{O}$, is of great importance from a medical standpoint. With one molecule of water it forms a crystalline compound, which is used as a soporific under the name *chloral hydrate*, and is technically prepared by saturating ethyl alcohol with chlorine. The alcohol must be as free from water as possible, and the chlorine must be carefully dried. At first the reaction-mixture is artificially cooled, but after a few days the process becomes less energetic, and the temperature is slowly raised to 60°, and finally to 100°.

This reaction may be explained by assuming that the alcohol is first converted into aldehyde, which is then transformed into acetal, dichloroacetal, and trichloroacetal; the last compound is

[illegible]

$$[illegible]$$

[illegible]

[illegible]

$$[illegible]$$

On account of its purity, chloroform prepared in this manner is preferred for pharmaceutical use.

The formation of chloroform from chloral by the action of alkaline liquids suggested the use of chloral as a soporific, it being expected that the alkaline constituents of the blood would decompose it with the formation of chloroform, thus generating the latter in the body itself. **Liebreich** showed that chloral has in fact a soporific action, but more recent investigation has proved this to be independent of the formation of chloroform, since the chloral is eliminated from the system as a complicated derivative, urochloralic acid.

Halogen-substituted Ketones.

205. An example of this class of compounds, dichloroacetone, $CH_2Cl \cdot CO \cdot CH_2Cl$, was mentioned in **198**. Variously substituted ketones, some of which have a powerful odour, are obtained from acetone by direct chlorination.

FINISH

ALDEHYDE AND KETONE ALCOHOLS OR SUGARS.

206. The term "sugars" formerly included compounds containing six, or a multiple of six, carbon atoms, and hydrogen and oxygen in the proportions to form water. To this they owed the name *carbohydrates*. When boiled with dilute acids, the sugars containing a multiple of six carbon atoms decompose, taking up the elements of water, with formation of carbohydrates containing six carbon atoms:

$$\underset{\text{Cane-sugar}}{C_{12}H_{22}O_{11}} + H_2O = 2C_6H_{12}O_6.$$

The latter had the general name *monosaccharides*, while those containing $n \times 6$ carbon atoms were called *polysaccharides*. Among the monosaccharides were grape-sugar, or glucose, and fruit-sugar, or fructose, both with the formula $C_6H_{12}O_6$; the polysaccharides included cane-sugar and milk-sugar, with the formula $C_{12}H_{22}O_{11}$, and starch and cellulose, $(C_6H_{10}O_5)_x$, of unknown molecular weight.

Many monosaccharides containing six carbon atoms have been prepared since 1887, chiefly through the researches of EMIL FISCHER, and several new saccharides containing more or less than six carbon atoms have also been discovered. The constitution of most of these compounds has been determined with great certainty, so that a new light has been thrown upon the chemistry of the sugars, and the definition of these substances from a chemical standpoint has, therefore, undergone considerable modification.

The monosaccharides are aldehyde alcohols or ketone alcohols containing one or more hydroxyl-groups, one of which is directly linked to a carbon atom in union with carbonyl. The characteristic group of these compounds is therefore —CHOH—CO—.

Nomenclature and General Properties of the Monoses and their Derivatives.

207. The monosaccharides have now the general name *monoses:* when they are aldehydes they are called *aldoses,* and when ketones, *ketoses.* The number of carbon atoms in the molecule is indicated by their names: thus, *pentose, hexose, heptose,* etc. To denote whether a compound is an aldehyde or a ketone, the prefixes "aldo-" and "keto-" respectively are used; as *aldohexose, ketohexose,* and so on.

The polysaccharides are now called *polyoses.* When they may be regarded as derived from two monose molecules by the elimination of one molecule of water, they are called *bioses;* thus, *hexobioses* when they are formed from two molecules of hexose. The polysaccharides derived from three monose molecules by the elimination of two molecules of water are called *trioses;* as *hexotriose,* etc.

Like aldehydes, the aldoses are converted by oxidation into monobasic acids containing the same number of carbon atoms, the pentoses yielding the monobasic *pentonic acids,* and the hexoses yielding the *hexonic acids,* etc. The oxidation can be carried further; for the general formula of an aldose is $CH_2OH \cdot (CHOH)_n \cdot C{<}^{H}_{\leqslant O}$ (**209**), and the group CH_2OH can be oxidized to carboxyl, yielding a dibasic acid containing the same number of carbon atoms as the aldose from which it is derived. On oxidation, the ketoses yield acids containing a smaller number of carbon atoms.

On reduction, the aldoses and ketoses take up two hydrogen atoms, with formation of the corresponding alcohols; thus, hexose yields a *hexahydric alcohol,* and pentose a *pentahydric alcohol* (**209** and **211**).

208. Four reactions are known which are characteristic of all monoses; two of these they possess in common with the aldehydes (**116**).

1. They reduce an ammoniacal silver solution on warming, forming a metallic mirror.

2. When warmed with alkalis, they give a yellow, and then a brown, colouration, and ultimately resinify.

3. When an alkaline copper solution (Fehling or Ost, **192**) is heated with a solution of a monose, reduction takes place, with formation of yellow-red suboxide of copper.

4. When a monose is heated with excess of phenylhydrazine, $C_6H_5 \cdot NH \cdot NH_2$, in dilute acetic-acid solution, a yellow compound, crystallizing in fine needles, is formed; substances of this type

are insoluble in water, and are called *osazones*. Their formation may be explained in the following way.

It was mentioned in **206** that the sugars are characterized by their containing the group —CHOH—CO—. The action of phenylhydrazine on a carbonyl-group has been already explained (**112**); water is eliminated, and a hydrazone is formed:

$$\overset{|}{\underset{|}{C}}\boxed{O + H_2}N\cdot NHC_6H_5 = \overset{|}{\underset{|}{C}}:N\cdot NHC_6H_5 + H_2O.$$

A second molecule of phenylhydrazine then reacts with the group —CHOH—, from which two hydrogen atoms are eliminated, the molecule of phenylhydrazine being split up into ammonia and aniline:

$$\begin{array}{l} \underset{\text{Phenylhydrazine}}{C_6H_5\cdot NH\cdot NH_2} \\ \quad + \quad H \;\; H \end{array} = \underset{\text{Aniline}}{C_6H_5\cdot NH_2} + NH_3.$$

The removal of two hydrogen atoms from the group —CHOH— converts it into a carbonyl-group, —CO—, with which a third molecule of phenylhydrazine reacts, forming a hydrazone, so that the group $\begin{array}{l} | \\ CHOH \\ | \\ CO \\ | \end{array}$ is converted into $\begin{array}{l} | \\ C{=}N\cdot NHC_6H_5 \\ | \\ C{=}N\cdot NHC_6H_5 \\ | \end{array}$; *this group is characteristic of the osazones.*

The osazones dissolve in water with difficulty, and this property makes them of great service in the separation of the monoses, since these substances are very soluble in water, and crystallize with great difficulty, especially in presence of salts; so that their purification by this method is often impracticable. By means of the sparingly soluble osazones, however, they can be separated; these are readily obtained in the pure state by crystallization from a dilute solution of pyridine (**386**). Moreover, the identity of the monose can be established by a determination of the melting-point of the osazone thus obtained.

Constitution of the Monoses.

209. It will be shown later that the constitution of all the monoses follows from that of the aldohexoses, whose structure may be deduced in the following way.

1. The aldohexoses have the molecular formula $C_6H_{12}O_6$.

2. The aldohexoses are aldehydes, and, therefore, contain a carbonyl-group in the molecule. This follows from the fact that they show the reactions peculiar to aldehydes; that they are converted by oxidation into acids containing the same number of C-atoms, and by reduction into an alcohol; and that they have the power of forming addition-products with hydrocyanic acid.

3. All known hexoses contain a normal chain of six carbon atoms, since they can be reduced to a hexahydric alcohol, which, on further reduction at a high temperature with hydriodic acid, yields *n*-secondary hexyl iodide, $CH_3 \cdot CH_2 \cdot CHI \cdot CH_2 \cdot CH_2 \cdot CH_3$.

The constitution of this iodide is inferred from the fact that it can be converted into an alcohol, which on oxidation yields

$$CH_3 \cdot CH_2 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH_3;$$

for on further oxidation this is converted into *n*-butyric and acetic acids.

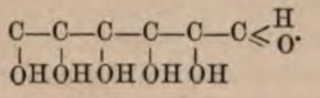
4. The hexoses have five hydroxyl-groups, since, when heated with acetic anhydride and a small quantity of sodium acetate or zinc chloride, they yield penta-acetyl-derivatives.

These facts indicate the existence, in an aldohexose, of

a normal carbon chain, $C—C—C—C—C—C$;

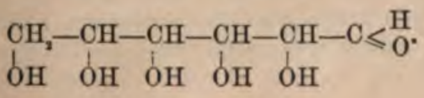
an aldehyde-group, $C—C—C—C—C—C\lt{}^{H}_{O}$; and

five hydroxyl-groups,



$$\underset{OH}{C}—\underset{OH}{C}—\underset{OH}{C}—\underset{OH}{C}—\underset{OH}{C}—C\lt{}^{H}_{O}.$$

There are six other hydrogen atoms in the formula $C_6H_{12}O_6$, and these will fit in with the last scheme, if the C-atoms of the chain are singly linked to each other; the formula of an aldohexose will then be

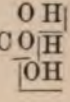


$$\underset{OH}{CH_2}—\underset{OH}{CH}—\underset{OH}{CH}—\underset{OH}{CH}—\underset{OH}{CH}—C\lt{}^{H}_{O}.$$

In these formulæ a somewhat arbitrary assumption has been made as to the distribution of the hydroxyl-groups and hydrogen atoms relative to the carbon atoms; it is, however, in accordance with the rule (**155**) that a carbon atom cannot usually be linked to more than one hydroxyl-group. A more convincing proof of the fact that the monoses do not contain two hydroxyl-groups in union with the same carbon atom, may be deduced from the following considerations.

When a hexose, $C_6H_{12}O_6$, is reduced to a hexahydric alcohol, $C_6H_{14}O_6$, only two hydrogen atoms are added on, and this addition must take place at the doubly-linked oxygen atom, since the carbon chain remains unbroken. If the hexose contains two hydroxyl-groups in union with one carbon atom, the same must, therefore, hold good for the hexahydric alcohol derived from it. Compounds containing a C-atom in union with two OH-groups readily split off water, with formation of aldehydes or ketones; they also possess most of the properties characteristic of these substances (**204**). The hexahydric alcohols, however, have an exclusively alcoholic character, and do not exhibit any of the reactions peculiar to the aldehydes and ketones. It follows that the hexahydric alcohols, and hence the hexoses, cannot contain two hydroxyl-groups linked to a single carbon atom.

The possibility of three hydroxyl-groups being in union with one carbon atom is also excluded, since, when the production of a compound with such a grouping might be expected, water is always split off, with formation of an acid (**86**):



$$\begin{array}{rl} & \mathrm{O\,H} \\ -\mathrm{C} & \mathrm{O\,H} \\ & \mathrm{OH} \end{array}$$

The monoses have none of the properties which distinguish acids: when in aqueous solution, they do not conduct the electric current; whereas the dissociation constant for an acid containing so many OH-groups should be considerably higher than for a saturated fatty acid, such as acetic acid (**183**).

With calcium and strontium hydroxides, and other bases, the carbohydrates form compounds called *saccharates*, which are, therefore, to be looked upon as alcoholates. They are decomposed by carbonic acid.

From what has been said, it will be seen that the constitution of the aldohexoses cannot be other than that given above, and, since the same method of proof is applicable to each member, they must all have the same constitutional formula, and are therefore stereoisomers. This is due to the presence in the molecule of asymmetric carbon atoms; an aldohexose has four such atoms, indicated by asterisks in the formula

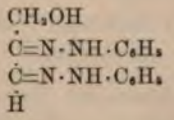
$$CH_2OH \cdot \overset{*}{C}HOH \cdot \overset{*}{C}HOH \cdot \overset{*}{C}HOH \cdot \overset{*}{C}HOH \cdot C\genfrac{}{}{0pt}{}{H}{O}.$$

Methods of Formation of the Monoses.

210. 1. From the polyoses, by hydrolysis; that is, decomposition with addition of water (**206**).

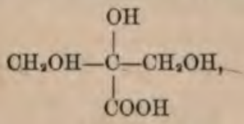
2. From the corresponding alcohols, by the action of oxidizing-agents, such as nitric acid. In this way arabitol, $C_5H_{12}O_5$, yields arabinose, $C_5H_{10}O_5$; xylitol yields xylose; mannitol yields mannose, etc.

When glycerol is carefully oxidized with nitric acid, or with bromine and caustic soda, a syrupy liquid is obtained, which shows the four reactions given on p. 255 for the monoses; it is called *glycerose*. Its osazone, *glycerosazone*,



$$\begin{array}{l} CH_2OH \\ \dot{C}{=}N \cdot NH \cdot C_6H_5 \\ \dot{C}{=}N \cdot NH \cdot C_6H_5 \\ \dot{H} \end{array}$$

crystallizes in yellow leaves, melting at 131°. Glycerose is *dihydroxyacetone*, $CH_2OH \cdot CO \cdot CH_2OH$, as is proved by the cyanhydrin synthesis (**182**, 5), by means of which trihydroxyisobutyric acid,



$$\begin{array}{c} OH \\ | \\ CH_2OH{-}C{-}CH_2OH, \\ | \\ COOH \end{array}$$

is obtained. The structure of this acid follows from its reduction to isobutyric acid. In accordance with the nomenclature already indicated, glycerose is a *triose*.

When lead glycerate is oxidized with bromine, the product, besides dihydroxyacetone, contains glyceraldehyde; the presence of this substance is proved by its forming a crystallized condensation-product with phloroglucinol (**314**):

$$C_3H_6O_3 + 2C_6H_6O_3 = C_{15}H_{16}O_8 + H_2O.$$

Glycer-aldehyde Phloro-glucinol

Dihydroxyacetone does not yield a similar oxidation-product.

Glyceraldehyde can be obtained in the pure state by treating the acetal of acroleïn with a dilute solution of potassium permanganate (**157**, 1), and removing the two $-OC_2H_5$-groups of the acetal by means of dilute sulphuric acid (**113**, 2).

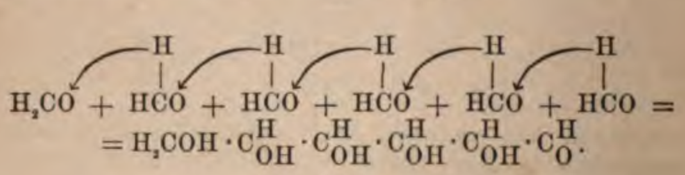
When sorbose-bacteria are cultivated in a solution of glycerol, the final product obtained by the action of the atmospheric oxygen is dihydroxyacetone. These bacteria can oxidize other monoses to ketoses.

3. From bromo-compounds of aldehydes, by exchange of bromine for hydroxyl, which can be effected by cold baryta-water.

In this manner the simplest member of the sugars, *glycollaldehyde* $CH_2OH \cdot C^{H}_{O}$, is obtained from monobromoaldehyde, $CH_2Br \cdot C^{H}_{O}$; it shows all the reactions of the monoses.

The addition of bromine to acroleïn (**147**) yields $CH_2Br \cdot CHBr \cdot C^{H}_{O}$, which is converted by the action of baryta-water into glyceraldehyde.

4. From formaldehyde, by the action of lime-water (aldol condensation). The crude condensation-product, called formose, is a sweet, syrupy substance; it consists of a mixture of compounds of the formula $C_6H_{12}O_6$. In this reaction, six molecules of formaldehyde undergo the aldol condensation (**115**):



$$H_2CO + \overset{H}{\overset{|}{HCO}} + \overset{H}{\overset{|}{HCO}} + \overset{H}{\overset{|}{HCO}} + \overset{H}{\overset{|}{HCO}} + \overset{H}{\overset{|}{HCO}} =$$
$$= H_2COH \cdot C^{H}_{OH} \cdot C^{H}_{OH} \cdot C^{H}_{OH} \cdot C^{H}_{OH} \cdot C^{H}_{O}.$$

By the aid of sunlight and moisture, plants are able to convert the carbon dioxide of the atmosphere into starch, a polyose of the formula $(C_6H_{10}O_5)_x$. The reaction may be represented empirically, thus:

$$6CO_2 + 5H_2O = C_6H_{10}O_5 + 6O_2.$$

Baeyer has suggested that the CO_2 is first reduced to formaldehyde, CH_2O, which condenses to a monose, the latter being then converted into the polyose, starch.

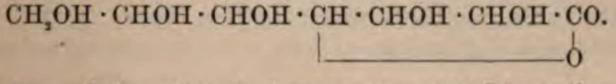
Berthelot has obtained substances of the nature of carbohydrates by the action of a silent electric discharge on a mixture of carbon dioxide, carbon monoxide, and hydrogen.

A hexose can also be obtained from glyceraldehyde, two molecules of which yield, by the aldol condensation, one molecule of the hexose. This hexose is called *acrose*, on account of its relation to acroleïn, from which glyceraldehyde can be obtained by method 3. Acrose is a constituent of formose, and, like all compounds prepared by purely chemical synthesis, is optically inactive.

5. A very important general method for the conversion of an aldose into another containing one more carbon atom in the molecule is the formation of an addition-product with hydrocyanic acid. An aldohexose yields a cyanhydrin which is converted on hydrolysis into a monobasic acid containing seven C-atoms,

$$\underset{1}{\mathrm{CH_2OH}}\cdot\underset{2}{\mathrm{CHOH}}\cdot\underset{3}{\mathrm{CHOH}}\cdot\underset{4}{\overset{\gamma}{\mathrm{C}}\mathrm{HOH}}\cdot\underset{5}{\overset{\beta}{\mathrm{C}}\mathrm{HOH}}\cdot\underset{6}{\overset{\alpha}{\mathrm{C}}\mathrm{HOH}}\cdot\underset{7}{\mathrm{COOH}}.$$

The γ-hydroxyl-group easily reacts with the carboxyl-group, forming a lactone,



$$\mathrm{CH_2OH\cdot CHOH\cdot CHOH\cdot CH\cdot CHOH\cdot CHOH\cdot CO.}$$

In aqueous solution, these lactones can be reduced by sodium amalgam to the corresponding aldehydes, the aldoses.

The great importance of this synthesis consists in the theoretical possibility of obtaining from the lower members, step by step, aldoses with any desired number of C-atoms in the molecule, by repeated application of the cyanhydrin synthesis, and reduction of the lactone thus obtained. In this manner, it has been possible to prepare *nonoses*, with nine C-atoms, by conversion of an aldohexose into a *heptonic acid*, whose lactone can then be reduced to a *heptose*. This compound can be converted into an *octose*, and the latter into a nonose, by the same process.

FINISH

I. MONOSES.

Pentoses.

211. A reference has already been made to the bioses and trioses (**207**). Tetroses can be obtained by the oxidation of pentonic acid, in the form of its calcium salt, by means of hydrogen peroxide, a small quantity of ferric acetate being used as a catalytic agent:

$$\underset{\text{Pentonic acid}}{CH_2OH \cdot CHOH \cdot CHOH \cdot CHOH \cdot COOH} + O =$$

$$= \underset{\text{Tetrose}}{CH_2OH \cdot CHOH \cdot CHOH \cdot C^{H}_{O}} + CO_2 + H_2O.$$

Also pentoses can be obtained from hexoses by this method.

A number of different pentoses have been identified; of these, *arabinose* and *xylose*, both of which are present in many plants as polyoses, called *pentosans*, may be considered.

Arabinose can be prepared by boiling gum-arabic or cherry-gum with dilute acids. *Xylose*, or *wood-sugar*, can be got in the same way from bran, wood, straw, and other substances, especially the shells of apricot-stones. Arabinose and xylose can be prepared from any plant-cells which have been converted into wood, and which possess the reactions of lignin (**230**). The racemic modification of arabinose is present in the urine of patients suffering from the disease known as *pentosuria*.

Arabinose forms well-defined crystals, melts at 160°, and has a sweet taste. Its osazone melts at 157°. Xylose also crystallizes well, and yields an osazone which melts at 160°.

Arabinose and xylose are aldoses, and have the same formula,

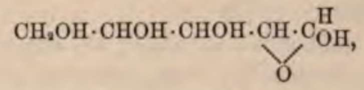
$$CH_2OH \cdot CHOH \cdot CHOH \cdot CHOH \cdot C^{H}_{O}.$$

This constitution is proved by their conversion, on gentle oxidation with bromine-water, into *arabonic acid* and *xylonic acid* respectively, both of which have the formula $CH_2OH \cdot (CHOH)_3 \cdot COOH$, and are therefore stereoisomers. On stronger oxidation, both arabinose and xylose yield *trihydroxyglutaric acid*, $COOH \cdot (CHOH)_3 \cdot COOH$, the constitution of which follows from its reduction to glutaric acid. The acid obtained from arabinose is optically active, and that from xylose is inactive, so that they, too, are stereoisomers. On reduction, these two pentoses yield respectively *arabitol* and *xylitol*, which are stereoisomeric pentahydric alcohols. Arabinose and xylose can be converted into hexoses by the cyanhydrin synthesis, a proof that neither contains a C-atom in union with more than one OH-group (**209**):

$$\underset{\text{Pentose}}{CH_2OH\cdot(CHOH)_3\cdot C{}^{H}_{O}} \rightarrow CH_2OH\cdot(CHOH)_3\cdot C<^{OH}_{CN} \rightarrow$$
$$\rightarrow \underset{\text{Hexonic acid}}{CH_2OH\cdot(CHOH)_3\cdot CHOH\cdot COOH.}$$

This hexonic acid yields a lactone which, on reduction, gives the hexose. Arabinose and xylose contain three asymmetric C-atoms, and are optically active. Their aqueous solutions, in common with those of several other optically active substances, exhibit a phenomenon called *multi-rotation*, fresh solutions rotating the plane of polarization much more than those which have stood for some time. For xylose, five minutes after it has been dissolved, the value of $[\alpha]$ is 75°–80°; this gradually diminishes to 19°, after which it remains constant.

This phenomenon is probably due to the conversion of the substance into another modification, analogous to that of lactones into acids. Thus, a fresh solution of xylose would contain



$$CH_2OH\cdot CHOH\cdot CHOH\cdot \underbrace{CH\cdot C}_{O}{}^{H}_{OH},$$

while later $CH_2OH\cdot(CHOH)_2\cdot CHOH\cdot C{}^{H}_{O}$ is formed. This view is supported by the fact that the rotatory power of a lactone is diminished by opening its ring; an example of this is furnished by galactonic acid, only that in it the change of rotatory power takes place more quickly than among sugars.

The probability of the correctness of this interpretation is strengthened by the fact that the change of rotatory power has the character of a unimolecular reaction.

The pentoses have one property in common, by which they may be recognized and distinguished from hexoses. When boiled with dilute sulphuric acid, or hydrochloric acid of sp. gr. 1·06, the pentoses and their polyoses form a volatile compound, *furfuraldehyde*, $C_5H_4O_2$ (**391**), which, on treatment with aniline and hydrochloric acid, yields an intense red dye.

The presence of the polyose of xylose may be detected in such a substance as straw, by distillation with hydrochloric acid of sp. gr. 1·06. With aniline and hydrochloric acid, the distillate gives an intense red colouration, and with phenylhydrazine yields a phenylhydrazone very sparingly soluble in water. Both these reactions indicate the presence of furfuraldehyde.

Hexoses.

212. The *hexoses* are colourless compounds of sweet taste, which crystallize with difficulty, and cannot be distilled without decomposition. They dissolve readily in water, with difficulty in absolute alcohol, and are insoluble in ether. Since all the aldohexoses are stereoisomers (**209**), their oxidation-products, the monobasic and dibasic acids, are also stereoisomers.

1. *Glucose*, or grape-sugar, is present in many plants, notably in the juice of grapes, and in other sweet fruits; it is found in the urine of diabetic patients, and in small quantities in normal urine. It can be obtained from many polyoses; cane-sugar is converted by hydrolysis—*inversion*, (**217**)—into a mixture of glucose and fructose, called *invert-sugar*. By the same treatment, starch yields glucose, which is technically prepared from it by boiling with dilute acids.

Glucose crystallizes from water, or alcohol, with some difficulty; the crystals obtained from methyl alcohol contain no water of crystallization, and melt at 146°. It has been already mentioned (**47**) that glucose can be readily fermented, producing chiefly alcohol and carbon dioxide. It is dextro-rotatory, and exhibits multi-rotation; a lævo-rotatory and an optically inactive modification have been artificially prepared. The dextro-rotatory, lævo-rotatory, and optically inactive isomers are respectively distinguished by the prefixes *d* (*dexter*), *l* (*lævus*), and *i* (*inactive*); thus, *d*-glucose, *l*-glucose, *i*-glucose.

By convention, all other monoses derived from a *d*-, *l*-, or *i*-hexose are also distinguished by the letters *d*, *l*, or *i*, even when they possess a rotatory power opposite in sign to that indicated by these letters. In this way, ordinary fructose, which can be obtained from *d*-glucose, and is lævo-rotatory, is called *d*-fructose on account of its genetic relation to *d*-glucose. The same method of classification is adopted for the hexahydric alcohols, the hexonic acids, and in general for all derivatives of the hexoses.

d-Glucose is an aldose, as is proved by its oxidation to a hexonic acid, d-*gluconic acid*, $CH_2OH \cdot (CHOH)_4 \cdot COOH$; further oxidation produces the dibasic *d*-saccharic acid, $COOH \cdot (CHOH)_4 \cdot COOH$.

Saccharic acid forms a characteristic acid potassium salt of slight solubility, which serves as a test for *d*-glucose. The substance suspected to contain glucose is oxidized with nitric acid; saccharic acid is produced from this hexose, if present, and can be precipitated in the form of the acid potassium salt by addition of a concentrated solution of potassium acetate.

On reduction, *d*-glucose yields a hexahydric alcohol, d-*sorbitol;* it also gives an osazone, d-*glucosazone*, which is soluble with difficulty in water, and crystallizes in yellow needles which melt at 204°-205°.

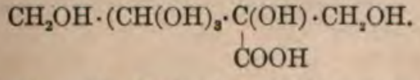
d-Glucose is employed as a substitute for cane-sugar, and applied to many other purposes, on account of its sweet taste, which is however less pronounced than that of cane-sugar. With a small quantity of water, it yields a colourless syrup, used in the preparation of liqueurs and of confectionery.

2. d-*Fructose* is present along with *d*-glucose in most sweet fruits. It is a constituent of invert-sugar (**217**), and of honey, which is chiefly a natural invert-sugar. *Inulin* is a polyose contained in dahlia-tubers, and when hydrolyzed, yields only *d*-fructose, just as starch yields *d*-glucose. *d*-Fructose crystallizes with difficulty, being readily soluble in water, although less so than grape-sugar. It is lævo-rotatory, and can be fermented.

d-Fructose is a type of the ketoses, few of which are known. Its formula, $CH_2OH \cdot (CHOH)_3 \cdot CO \cdot CH_2OH$, is deducible from the following considerations. First, when oxidized with mercuric oxide in presence of baryta-water, it is converted into glycollic acid, $CH_2OH \cdot COOH$, and trihydroxyglutaric acid, ?

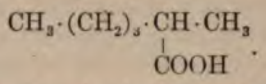
$$COOH \cdot (CHOH)_3 \cdot COOH.$$

Since oxidation takes place in the carbonyl-group, the production of these acids necessitates the adoption of this constitutional formula. Second, application of the cyanhydrin synthesis to a compound of this constitution would yield a heptonic acid with the formula



$$CH_2OH \cdot (CH(OH))_3 \cdot \underset{\displaystyle COOH}{\underset{|}{C}}(OH) \cdot CH_2OH.$$

That the heptonic acid obtained from *d*-fructose has this constitution, is proved by heating it at a high temperature with hydriodic acid, whereby all the hydroxyl-groups are replaced by hydrogen, and a heptylic acid is formed. This is found to be identical with the synthetically-prepared *methyl-*n*-butylacetic acid* (**235**, 2), whose constitutional formula is



$$CH_3\cdot(CH_2)_3\cdot\underset{\mid \atop COOH}{CH}\cdot CH_3 .$$

The osazone of *d*-fructose is identical with that of *d*-glucose. A comparison of the formula of *d*-glucose,

$$CH_2OH\cdot(CHOH)_3\cdot\overset{\alpha}{C}HOH\cdot C{}^{H}_{O},$$

with that of *d*-fructose, $CH_2OH\cdot(CHOH)_3\cdot CO\cdot CH_2OH$, shows that the two osazones can only be identical if the α-C-atom of the *d*-glucose, and the terminal C-atom of the *d*-fructose, unite, after formation of the hydrazone, with the second phenylhydrazine-residue; that is, when in both cases this reaction takes place at a C-atom directly linked to a carbonyl-group. For this reason, it is assumed that the formation of an osazone always results in the union of two phenylhydrazine-residues with neighbouring C-atoms. The glucosazone, or fructosazone, has the constitution

$$\begin{array}{l} CH_2OH \\ \dot{} \\ (CHOH)_3 \\ \dot{} \\ C{=}N\cdot NH\cdot C_6H_5 \\ \dot{} \\ C{=}N\cdot NH\cdot C_6H_5 \\ \dot{} \\ H \end{array}$$

It is a somewhat remarkable fact that methylphenylhydrazine, $C_6H_5\cdot N(CH_3)\cdot NH_2$, yields osazones only with ketoses, and not with aldoses. The latter form colourless hydrazones with this compound, and these can easily be separated from the intensely yellow osazones. Methylphenylhydrazine therefore affords a valuable means of detecting ketoses.

When the osazones are carefully warmed with hydrochloric acid, two molecules of phenylhydrazine are split off, with formation of compounds, *osones*, containing two carbonyl-groups. In this way, glucosazone yields *glucosone*,

$$CH_2OH\cdot(CHOH)_3\cdot CO\cdot C{}^{H}_{O}.$$

The osones can be reduced by treatment with zinc-dust and acetic acid, and experience has shown that addition of hydrogen always takes place at the terminal C-atom. Glucosone yields fructose, $CH_2OH\cdot(CHOH)_3\cdot CO\cdot CH_2OH$. This reaction affords a means of converting aldoses into ketoses:

Aldose → Osazone → Osone → Ketose.

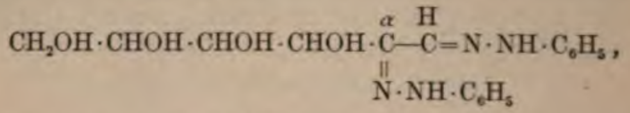
Inversely, an aldose can be obtained from a ketose. On reduction, the latter yields a hexahydric alcohol, which is converted by oxidation into a monobasic hexonic acid. This substance splits off water, yielding the corresponding lactone, which on reduction gives the aldose:

Ketose → Hexahydric Alcohol → Hexonic Acid → Lactone → Aldose.

3. d-*Mannose* is an aldose, and is present as a polyose in the vegetable-ivory nut; it is also obtained by the careful oxidation of the hexahydric alcohol *mannitol*, found in several plants. *d*-Mannose, a hard, amorphous, hygroscopic substance, can be readily fermented, and is very soluble in water. It forms a characteristic hydrazone which melts at 195°-200°, and, unlike the hydrazones of the other monoses, dissolves with difficulty in water. On oxidation, *d*-mannose is first converted into the monobasic d-*mannonic acid*, $CH_2OH\cdot(CHOH)_4\cdot COOH$, and then into the dibasic d-*mannosaccharic acid*, $COOH\cdot(CHOH)_4\cdot COOH$. It yields *d*-glucose by a method generally applicable to the conversion of aldoses into their stereoisomers. For this purpose, it is first converted into *d*-mannonic acid; this is heated, preferably by boiling its solution in quinoline, which converts it partly into the stereoisomeric *d*-gluconic acid, whose lactone can be reduced to *d*-glucose. Inversely, *d*-gluconic acid is partly changed into *d*-mannonic acid, by boiling its quinoline solution, so that *d*-glucose can be converted into *d*-mannose.

Mannonic acid is one of the intermediate products in **Emil Fischer**'s synthesis of *d*-glucose. He converted glyceraldehyde into acrose (**210**, 4), and this into *i*-mannitol, by reduction with sodium amalgam. On oxidation, *i*-mannitol yields first *i*-mannose, and then *i*-mannonic acid, which can be split up, by means of its strychnine salt, into its optically active modifications. When the *d*-mannonic acid thus obtained is heated with pyridine, it is converted into *d*-gluconic acid, the lactone of which, on reduction with sodium amalgam, yields *d*-glucose.

The stereoisomerism of *d*-mannose and *d*-glucose, as well as of *d*-mannonic acid and *d*-gluconic acid, is occasioned only by different grouping round the α-C-atom, since the osazone of *d*-mannose is identical with that of *d*-glucose. As this has the constitution



$$CH_2OH\cdot CHOH\cdot CHOH\cdot CHOH\cdot \underset{\overset{\|}{N\cdot NH\cdot C_6H_5}}{\overset{\alpha}{C}}-\overset{H}{C}=N\cdot NH\cdot C_6H_5,$$

these osazones can only be identical when the residue

$$CH_2OH\cdot (CHOH)_2\cdot CHOH-$$

in *d*-mannose and *d*-glucose is also identical; their stereoisomerism can then only result from a difference in the arrangement of the groups linked to the α-C-atom.

So far as the transformations of the monobasic hexonic acids when boiled with quinoline or pyridine, have been studied, it has always been found that an alteration takes place, as in the above instance, at only one C-atom, the one adjoining the aldehyde-group, the α-C-atom.

Very remarkable is the conversion into each other, discovered by LOBRY DE BRUYN, of glucose, fructose, and mannose, under the influence of very dilute alkalis. Their rotatory power is considerably reduced thereby; each of these hexoses forms both the others, and the one originally present is not completely converted. An equilibrium is thus established which may be represented by the scheme

$$\text{Glucose} \rightleftarrows \text{Fructose} \rightleftarrows \text{Mannose.}$$

That fructose is actually an intermediate product of this transformation, is shown by the behaviour of the dextro-rotatory solution of mannose, which, owing to the formation of fructose, first develops lævo-rotation, this gradually decreasing as the dextro-rotatory glucose is produced.

4 and 5. l-*Glucose* and l-*mannose* are important on account of their method of formation. They result simultaneously from *l*-arabinose by application of the cyanhydrin synthesis, and reduction of the lactone of the acid thus formed. It was mentioned (**186**) why the application of this synthesis to aldehydes always leads to the production of two stereoisomers; an asymmetric C-atom results, and one optically active isomer is as likely to be formed as the other. In the case of *l*-arabinose, there are asymmetric C-atoms already present in the molecule, and an additional one is produced by this synthesis; the isomers display dissimilar rotatory power, but this is no longer equal and opposite in sign, since the original rotation is increased in one

isomer by the new asymmetric C-atom to the same extent as it is diminished in the other. The rotation of the isomers is equal and of opposite sign only when the original molecule was optically inactive.

6. d-*Galactose* can be obtained by the hydrolysis of lactose, or by the oxidation of the hexahydric alcohol *dulcitol*, which occurs in certain plants. *d*-Galactose is crystalline, melting at 168°; it is strongly dextro-rotatory, is capable of undergoing fermentation, and exhibits multi-rotation. Galactose is proved to be an aldose by its conversion, on oxidation, into the monobasic d-*galactonic acid*, $C_6H_{12}O_7$. Further oxidation yields the sparingly soluble dibasic *mucic acid*, $COOH \cdot (CHOH)_4 \cdot COOH$, which is optically inactive, and cannot be split up into optically active components; its formation serves as a test for *d*-galactose. In practice this is carried out by oxidizing the hexose under examination with nitric acid.

Their conversion into *lævulinic acid* (**236**), on treatment with hydrochloric acid, constitutes a general reaction for the hexoses. Brown, amorphous masses, known as "humus substances," are produced at the same time. Lævulinic acid can be identified by means of its silver salt, which dissolves with difficulty, and yields crystals of characteristic appearance.

FINISH

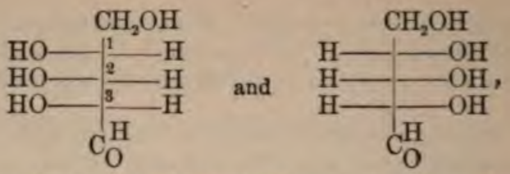
Heptoses, Octoses, and Nonoses.

213. These substances are not natural products, but can be built up from the hexoses by the cyanhydrin synthesis; mannose, for example, yields *mannoheptose*, *manno-octose*, and *mannononose*.

Stereochemistry of the Monoses.

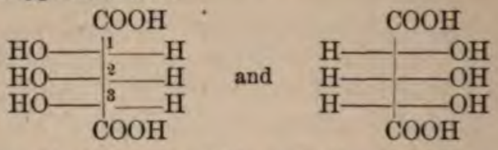
214. It was stated (**209**) that all the aldohexoses and aldopentoses have the same structure, so that their isomerism must be stereoisomerism. Although it would be beyond the scope of this book to deduce the configuration corresponding to the pentoses and hexoses mentioned in it, it is desirable to indicate how this is determined for compounds of this kind; that is, for those containing several asymmetric carbon atoms in the molecule.

It was mentioned (**191**) that the presence of two dissimilar asymmetric C-atoms in a molecule causes the existence of a greater number of stereoisomers than that of two similar asymmetric C-atoms. It can be readily seen from a projection-formula that the same holds good for a greater number of asymmetric C-atoms in the molecule. The projection-formulæ for two aldopentoses,



$$\begin{array}{rcl} & \mathrm{CH_2OH} & \\ \mathrm{HO}- & |^{1} & -\mathrm{H} \\ \mathrm{HO}- & |^{2} & -\mathrm{H} \\ \mathrm{HO}- & |^{3} & -\mathrm{H} \\ & \mathrm{C}^{\mathrm{H}}_{\mathrm{O}} & \end{array} \quad \text{and} \quad \begin{array}{rcl} & \mathrm{CH_2OH} & \\ \mathrm{H}- & | & -\mathrm{OH} \\ \mathrm{H}- & | & -\mathrm{OH}, \\ \mathrm{H}- & | & -\mathrm{OH} \\ & \mathrm{C}^{\mathrm{H}}_{\mathrm{O}} & \end{array}$$

cannot be made to coincide by rotation in the plane of the paper (**191**); the aldopentoses, therefore, are not identical. The corresponding trihydroxyglutaric acids



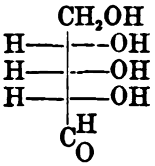
$$\begin{array}{rcl} & \mathrm{COOH} & \\ \mathrm{HO}- & |^{1} & -\mathrm{H} \\ \mathrm{HO}- & |^{2} & -\mathrm{H} \\ \mathrm{HO}- & |^{3} & -\mathrm{H} \\ & \mathrm{COOH} & \end{array} \quad \text{and} \quad \begin{array}{rcl} & \mathrm{COOH} & \\ \mathrm{H}- & | & -\mathrm{OH} \\ \mathrm{H}- & | & -\mathrm{OH} \\ \mathrm{H}- & | & -\mathrm{OH} \\ & \mathrm{COOH} & \end{array}$$

are, however, identical, since their projection-formulæ can be made to coincide. In these compounds, the asymmetric C-atoms 1 and 3 are similar, while in the pentoses they are dissimilar.

Assuming that the determination of the configuration of trihydroxyglutaric acid is possible, and that in a given instance it leads to the projection-formula given above, it follows that the pentose from which it is obtained by oxidation must have one of the above configurations, and that all others are excluded. It thus only remains to distinguish between these two configurations.

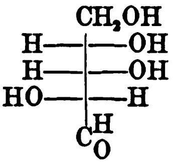
In order to determine the stereochemical structure of a pentose, it is, therefore, first necessary to determine that of the corresponding trihydroxyglutaric acid. The optical behaviour of these acids affords a ready means of effecting this. Xylose, which is optically active, is converted by oxidation into an optically inactive trihydroxyglutaric acid which melts at 152°. Since an optically inactive substance is here obtained from an optically active one, not from a racemic compound, this must be occasioned by intramolecular compensation, which must find expression in the configuration allotted to this particular trihydroxyglutaric acid. Projection-formulæ of compounds which are optically inactive on account of intramolecular compensation must fulfil this condition: each and its mirror-image must be capable of being made to coincide by rotation in the plane of the paper; that is, they must be identical. For, if this were not the case, two enantiomorphous configurations—the formula and its mirror-image—would be possible, while for intramolecular compensation only one configuration is possible.

The above reasoning may be applied to the determination of the stereochemical structure of arabinose. Eight stereoisomeric formulæ are possible for a pentose, but, by arranging these in pairs of mirror-images, and taking one of each pair, four different types are obtained:



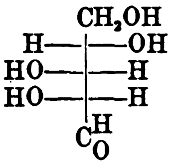
$$\begin{array}{rcl} & \mathrm{CH_2OH} & \\ \mathrm{H} & | & \mathrm{OH} \\ \mathrm{H} & | & \mathrm{OH} \\ \mathrm{H} & | & \mathrm{OH} \\ & \mathrm{C}^{\mathrm{H}}_{\mathrm{O}} & \end{array}$$

I



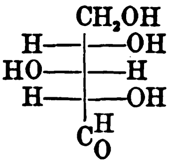
$$\begin{array}{rcl} & \mathrm{CH_2OH} & \\ \mathrm{H} & | & \mathrm{OH} \\ \mathrm{H} & | & \mathrm{OH} \\ \mathrm{HO} & | & \mathrm{H} \\ & \mathrm{C}^{\mathrm{H}}_{\mathrm{O}} & \end{array}$$

II



$$\begin{array}{rcl} & \mathrm{CH_2OH} & \\ \mathrm{H} & | & \mathrm{OH} \\ \mathrm{HO} & | & \mathrm{H} \\ \mathrm{HO} & | & \mathrm{H} \\ & \mathrm{C}^{\mathrm{H}}_{\mathrm{O}} & \end{array}$$

III



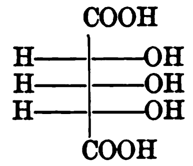
$$\begin{array}{rcl} & \mathrm{CH_2OH} & \\ \mathrm{H} & | & \mathrm{OH} \\ \mathrm{HO} & | & \mathrm{H} \\ \mathrm{H} & | & \mathrm{OH} \\ & \mathrm{C}^{\mathrm{H}}_{\mathrm{O}} & \end{array}$$

IV

The mirror-image of I is represented on p. 270.

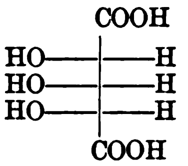
Arabinose is converted by oxidation into an optically active trihydroxyglutaric acid. This excludes the trihydroxyglutaric acids which could be obtained from types I and IV, since each of these could be made to coincide with its mirror-image, and thus would be optically inactive :

I.



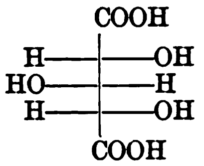
$$\begin{array}{rcl} & \mathrm{COOH} & \\ \mathrm{H} & | & \mathrm{OH} \\ \mathrm{H} & | & \mathrm{OH} \\ \mathrm{H} & | & \mathrm{OH} \\ & \mathrm{COOH} & \end{array}$$

identical with its mirror-image,



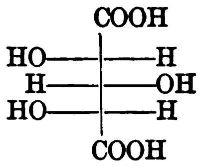
$$\begin{array}{rcl} & \mathrm{COOH} & \\ \mathrm{HO} & | & \mathrm{H} \\ \mathrm{HO} & | & \mathrm{H} \\ \mathrm{HO} & | & \mathrm{H} \\ & \mathrm{COOH} & \end{array}$$

IV.



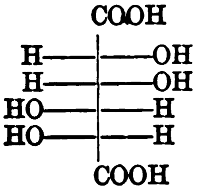
$$\begin{array}{rcl} & \mathrm{COOH} & \\ \mathrm{H} & | & \mathrm{OH} \\ \mathrm{HO} & | & \mathrm{H} \\ \mathrm{H} & | & \mathrm{OH} \\ & \mathrm{COOH} & \end{array}$$

identical with its mirror-image,



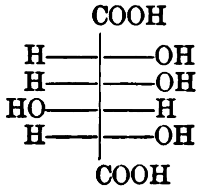
$$\begin{array}{rcl} & \mathrm{COOH} & \\ \mathrm{HO} & | & \mathrm{H} \\ \mathrm{H} & | & \mathrm{OH} \\ \mathrm{HO} & | & \mathrm{H} \\ & \mathrm{COOH} & \end{array}$$

The fact that by the aid of the cyanhydrin synthesis arabinose can be converted into a mixture of glucose and mannose, which on oxidation yields the optically active saccharic and mannosaccharic acids, enables a choice between types II and III to be made. Since in the cyanhydrin synthesis only the group C^{H}_{O} in $CHOH\cdot C^{H}_{O}$ is altered, the configuration of the rest of the C-atoms remaining unchanged, saccharic acid and mannosaccharic acid must have the stereochemical structure



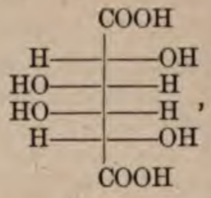
$$\begin{array}{rcl} & \mathrm{COOH} & \\ \mathrm{H} & | & \mathrm{OH} \\ \mathrm{H} & | & \mathrm{OH} \\ \mathrm{HO} & | & \mathrm{H} \\ \mathrm{HO} & | & \mathrm{H} \\ & \mathrm{COOH} & \end{array}$$

or



$$\begin{array}{rcl} & \mathrm{COOH} & \\ \mathrm{H} & | & \mathrm{OH} \\ \mathrm{H} & | & \mathrm{OH} \\ \mathrm{HO} & | & \mathrm{H} \\ \mathrm{H} & | & \mathrm{OH} \\ & \mathrm{COOH} & \end{array}$$

if arabinose is represented by formula II. Neither of these can be made to coincide with its mirror-image, so that formula II is assumed to represent arabinose. Formula III is excluded, since its assumption would necessitate that one of the acids mentioned above should have the stereochemical constitution



$$\begin{array}{rcl} & COOH & \\ H- & | & -OH \\ HO- & | & -H \\ HO- & | & -H \\ H- & | & -OH \\ & COOH & \end{array},$$

which is identical with its mirror-image: one of the acids would then be optically inactive, which is not the case.

Arabinose has, therefore, a formula of the type II, but it is still uncertain whether it should be represented by the formula given above, or by its mirror-image.

II. DIOSES.

215. Numerous *dioses* (or *bioses*) are known, which are almost exclusively derived from hexoses, and therefore have the formula

$$C_{12}H_{22}O_{11} = 2C_6H_{12}O_6 - H_2O.$$

No dioses are known which can be decomposed into a pentose and a hexose; on hydrolysis, some of the hexodioses yield two different monoses, and some only one.

The hydrolysis can be effected not only by boiling with dilute acids, but also by the action of enzymes (**222**). On account of the readiness with which decomposition with water takes place, it is assumed that the monoses from which a diose is formed are not linked together through the carbon atoms, but through one or more oxygen atoms.

Up to the present, success in the attempt to synthesize dioses from monoses has been confined to the case of maltose; Croft Hill found that maltose is produced by the action of an enzyme called *maltase* (**222**) on a concentrated solution of glucose. As this enzyme is also able to split up maltose into glucose, it is evident that an equilibrium must be reached:

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \rightleftarrows \underset{\text{Glucose}}{2C_6H_{12}O_6}.$$

The best-known dioses, such as *sucrose* or cane-sugar, and *lactose* or milk-sugar, have not yet been prepared synthetically.

Maltose.

Maltose in the crystallized state has the formula $C_{12}H_{22}O_{11} + H_2O$, and can be prepared from starch by the action of diastase (**47**); it is an important intermediate product in the industrial production of alcohol.

Maltose crystallizes in small, white needles, and is strongly dextro-rotatory. When boiled with dilute mineral acids, it yields only d-*glucose*. It exhibits all the characteristics of the monoses: thus, it reduces an alkaline copper solution; yields an osazone, *maltosazone*, $(C_{12}H_{22}O_{11} - 2H_2O - 2H + 2C_6H_5NH \cdot NH_2)$; and it can be oxidized to the monobasic *maltobionic acid*, $C_{12}H_{22}O_{12}$, which, on hydrolysis, splits up into *d*-glucose and *d*-gluconic acid, $CH_2OH \cdot (CHOH)_4 \cdot COOH$.

These properties show that maltose contains only one of the two carbonyl-groups present in two molecules of *d*-glucose; thus, it yields an osazone with two, instead of four, molecules of phenylhydrazine, and a monobasic instead of a dibasic acid. The linking of the two molecules of *d*-glucose must, therefore, take place in such a way that the carbonyl-oxygen of only one molecule enters into the reaction. A union of this kind between two monose molecules is called the *monocarbonyl-bond*. If this is denoted by the sign <, and a free carbonyl-group in a molecule by <, then maltose can be represented by

$$\underset{\text{Glucose}}{C_6H_{11}O_5} < O \cdot \underset{\text{Glucose}}{C_6H_{11}O_5} <.$$

Lactose or Milk-sugar.

216. *Lactose* is present in milk, and is prepared from it.

Whey is usually employed for this purpose; it is the liquid which remains after the cream has been separated and the skimmed milk has been used for making cheese. In these processes the milk is deprived of most of its fats and albuminous substances; the whey contains nearly all the lactose, and a large proportion of the mineral constituents of the milk. The lactose is obtained by evaporation, and purified by recrystallization.

Lactose crystallizes in well-defined, large, hard crystals. It has not such a sweet taste as sucrose, and in the mouth resembles sand, on account of the hardness of its crystals, so that it is sometimes called *sand*-sugar.

On hydrolysis, lactose splits up into *d*-galactose and *d*-glucose. It shows the reactions of the monoses, and can be proved, by a method analogous to that employed for maltose, to contain one free carbonyl-group in the molecule, so that it is a combination of *d*-glucose and *d*-galactose, linked by a monocarbonyl-bond. The free carbonyl-group belongs to the *d*-glucose molecule, since lactose is converted by oxidation with bromine-water into *lactobionic acid*, which is split up by hydrolysis into *d*-galactose and *d*-gluconic acid. Lactose is, therefore, represented by

$$\underset{d\text{-Galactose}}{C_6H_{11}O_5} < O\cdot\underset{d\text{-Glucose}}{C_6H_{11}O_5} <$$

Sucrose or Cane-sugar.

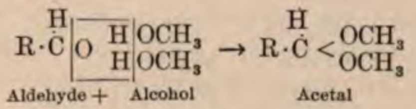
217. *Sucrose* (saccharose) is present in many plants, and is prepared from sugar-beet and sugar-cane. It crystallizes well, and is very readily soluble in water. It melts at 160°, and solidifies on cooling to an amorphous, glass-like mass, which after a considerable time becomes crystalline. When strongly heated it turns brown, being converted into a substance called *caramel*. On hydrolysis, sucrose yields *d*-glucose and *d*-fructose in equal proportions. This mixture is called *invert-sugar*, and is lævo-rotatory, since *d*-fructose rotates the plane of polarization more to the left (**212**) than *d*-glucose does to the right. Sucrose itself is strongly dextro-rotatory, so that the rotation has been reversed by hydrolysis. This is called *inversion*, a term also applied to the hydrolysis of other dioses and of polyoses. Sucrose does not show the reactions characteristic of the monoses; thus, it does not reduce an alkaline copper solution, is not turned brown by caustic potash, and does not yield an osazone. Hence, it is evident that there are no free carbonyl-groups in its molecule; it may, therefore, be concluded that both of these have entered into reaction in the union of the two monoses. Such a linking between two monoses is called a *dicarbonyl-bond*, and is represented by the sign $<O>$; so that sucrose is

$$\underset{d\text{-Glucose}}{C_6H_{11}O_5} <O> \underset{d\text{-Fructose}}{C_6H_{11}O_5}.$$

218. The discovery that alcohols are able, under the influence of hydrochloric acid, to unite with monoses with elimination of water, affords an insight into the nature of the monocarbonyl-bond and the dicarbonyl-bond. The substances thus formed are called *glucosides*, since they are in many ways analogous to the natural glucosides, substances which are split up into a sugar, and one or more compounds of various kinds, on boiling with dilute acids. The artificial glucosides are obtained by the action of one molecule of an alcohol upon a monose:

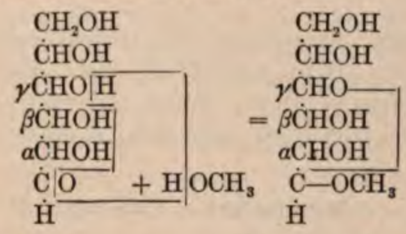
$$C_6H_{12}O_6 + CH_3OH = \underset{\text{Methyl glucoside}}{C_6H_{11}O_6 \cdot CH_3} + H_2O.$$

These compounds were discovered by EMIL FISCHER, who has assigned to them a constitution analogous in some respects to that of the acetals (**113**, 2):



$$\underset{\text{Aldehyde} + \text{Alcohol}}{R\cdot\overset{H}{C}\,O \begin{array}{l} H\,OCH_3 \\ H\,OCH_3 \end{array}} \rightarrow \underset{\text{Acetal}}{R\cdot\overset{H}{C} < \begin{array}{l} OCH_3 \\ OCH_3 \end{array}}$$

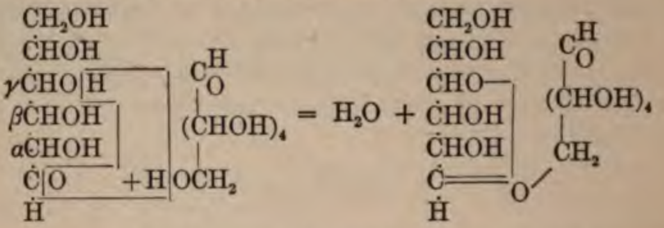
In the formation of glucoside, only one molecule of alcohol acts upon the aldose, so that one of the hydroxyl-groups of the latter plays the part of a second alcohol molecule:



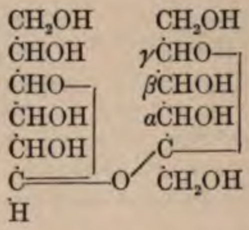
$$\begin{array}{lll} CH_2OH & & CH_2OH \\ \dot{C}HOH & & \dot{C}HOH \\ \gamma\dot{C}HO\,H & & \gamma\dot{C}HO- \\ \beta\dot{C}HOH & = & \beta\dot{C}HOH \\ \alpha\dot{C}HOH & & \alpha\dot{C}HOH \\ \dot{C}\,O \quad + H\,OCH_3 & & \dot{C}-OCH_3 \\ \dot{H} & & \dot{H} \end{array}$$

The grounds for the assumption of this constitution are: first, these glucosides are readily split up into their components, which argues against the existence of a carbon bond between them; second, the hydroxyl of the γ-C-atom is assumed to be the one which reacts, since other compounds containing the group —CHOH·CO— do not yield glucosides; the α-hydroxyl-group, therefore, does not react. The γ-hydroxyl is, moreover, the most likely to enter into reaction, since a number of instances of similar behaviour are known, such as that of the lactones.

The combination of two monoses with elimination of one molecule of water may be represented in a way analogous to the formation of a glucoside from an alcohol and a monose. Maltose and lactose, which are united by a monocarbonyl-bond, and contain one free carbonyl-group, are combined thus:



The constitution of sucrose, in which fructose and glucose are united by a dicarbonyl-bond, may be shown in an analogous way to be



Sucrose forms compounds with bases, called **saccharates**; among them are $C_{12}H_{22}O_{11} \cdot CaO \cdot 2H_2O$, and $C_{12}H_{22}O_{11} \cdot 2CaO$, which are readily soluble in water. When this solution is boiled, the nearly insoluble tricalcium saccharate $C_{12}H_{22}O_{11} \cdot 3CaO \cdot 3H_2O$ is precipitated.

Manufacture of Cane-sugar.

219. Sucrose is present in solution in the cell-fluid of the sugar-beet and sugar-cane. The cell-walls are lined with a thin, continuous layer of protoplasm, constituting a semi-permeable membrane (**13**), which prevents the diffusion of the sugar from the cells at ordinary temperatures. When placed in water at 80°–90°, the protoplasm is killed, coagulates, and develops minute ruptures, through which the cell-fluid can diffuse. The process is facilitated by cutting up the cane or beet into pieces 2 to 3 mm. in thickness. In order to make the diffusion-process as complete as possible with a minimum amount of water, the slices are placed in vats through which water circulates in such a way that the nearly exhausted material is acted on by fresh water, while that which is only partly exhausted comes into contact with the solution already obtained, so that the material richest in sugar is treated with the strongest extract, and *vice versa* (principle of the counter-current). In this way, a 12–15 per cent. sugar-solution is obtained, which is about the proportion of sugar contained in the beet itself.

Slaked lime is added to this solution, whereby a double object is attained. First, the free acids in the sap, such as oxalic and citric acids, are precipitated, along with the phosphates; the removal of these is necessary, since they would cause inversion on concentrating the solution. Second, albuminous and colouring matters are precipitated from the solution. For both these purposes, it is necessary to add an excess of lime, part of which goes into solution as saccharate, which has to be decomposed by a current of carbon dioxide, care being taken to leave the liquid faintly alkaline. The precipitate is separated by a filter-press, and the filtrate concentrated. In order to obtain the maximum yield of sugar, it is necessary that this concentration should take place at a low temperature. This is attained by the use of vacuum-pans, in which the sugar-solution boils under diminished pressure. The first product of the concentration is a thick syrup, more strongly alkaline than the original solution. Calcium carbonate is precipitated by repeated treatment with carbon dioxide until the thick syrup is almost neutral after which it is filtered, and concentrated until crystals of sugar begin to separate. The solution is then allowed to cool, when more crystals are obtained, mixed with a syrupy liquid, which is removed in a centrifugal machine. This syrup is further crystallized by slow agitation with a stirring-apparatus, and the crystals are again separated by means of the centrifugal machine. The syrup thus obtained (molasses) is worked up for the preparation of alcohol.

The cane-sugar thus prepared is not pure; it is brown, and contains a certain amount of syrup. The crude product is purified by dissolving it, decolourizing with animal charcoal, and concentrating in vacuum-pans.

Quantitative Estimation of Cane-sugar.

220. The great practical importance of cane-sugar makes it desirable to have a quick and accurate method of estimating it quantitatively. This is almost exclusively done by examining its aqueous solution with the polarimeter (**27**, 2). Since sucrose is strongly dextro-rotatory ($[\alpha]_D = + 66 \cdot 5°$), a small quantity produces an appreciable amount of rotation. This is almost independent of the temperature, and for practical purposes may be considered as strictly proportional to the concentration. It is obvious that this method will only yield accurate results when no other optically active substances are present in the solution. If such substances are present, either they must be removed, or their effect taken into account. The former method is adopted in the determination of the amount of sugar in beet. The sample is grated with a fine rasp, to destroy the cell walls, and a weighed quantity of the product is made up to a certain volume with cold water, which dissolves not only the sucrose, but also optically active albuminous substances. The latter are precipitated with lead acetate, filtered off, and the amount of rotation observed.

When another sugar is present in the solution along with the sucrose, it is necessary to proceed by the second method. Supposing glucose is also present, the rotatory power of the solution, which will be dextro-rotatory, is determined. If it be now inverted, the solution will either diminish in dextro-rotation, or will become lævo-rotatory, since invert-sugar is lævo-rotatory. The rotatory power of an invert-sugar solution obtained from a sucrose solution of given strength being known, these two observations furnish the data by which the percentage of glucose in cane-sugar can be easily calculated.

Velocity of Inversion of Sucrose.

221. The equation for unimolecular reactions (**101**) may be applied to the inversion of a dilute solution of sucrose. If the original amount of the latter present was p, and after a certain time the quantity x has been inverted, then the velocity s in the fraction of time immediately following, can be expressed by the equation

$$s = \frac{dx}{dt} = k(p - x),$$

in which k is a constant. The inversion can be effected by means of different acids, upon the nature of which the velocity of the reaction is dependent, so that different values are obtained for the velocity constant k. When the values of this constant, and of the election is inseparable from the presence and propagation of yeast-cells. If it were found possible to bring about fermentation without their presence, this theory would fall to the ground. **Eduard Buchner** has recently effected this. He triturated fresh yeast with sand, whereby the cell-walls were destroyed. The dough-like mass was submitted to great pressure, which expressed a liquid (German, *Pressaft*); this was separated by filtration from the cells still floating in it. **Buchner** proved in various ways that this "press-fluid" contains neither living cells nor living protoplasm: for instance, the yeast may be first killed by bringing it into a mixture of alcohol and ether; the press-fluid from this can nevertheless set up active fermentation in a solution of sugar quite as well as when it was obtained from living yeast. The fermentation is caused by a dissolved substance, which, on account of its properties, such as coagulation on warming, must be classed with albuminous bodies; it is a kind of enzyme, to which **Buchner** has given the name *zymase*. The yeast-cells only have the function of producing zymase.

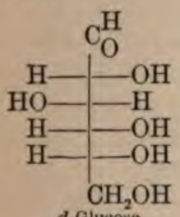
The chemical structure of the enzymes is still wholly unknown. Most of them have not been obtained in the pure state. Their power of splitting up and decomposing compounds is also not understood. Hitherto, only small insight has been obtained into the conditions upon which their action depends.

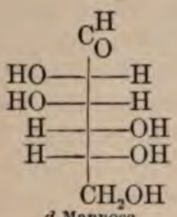
First, the enzymes only act at the ordinary, or at a slightly elevated, temperature; below the freezing-point their activity is suspended, but returns at the ordinary temperature; on heating, they are decomposed. Second, they are sometimes rendered inactive ("poisoned") by the presence of small quantities of certain substances, such as hydrocyanic acid. Third, it is very remarkable that a given enzyme can only produce changes in a few substances, and has no action on other similar compounds. Thus, of the different monoses containing two to nine C-atoms, only the trioses, hexoses, and nonoses undergo the alcoholic fermentation; in fact, these are the only ones which, according to their formula, can be readily converted into CO_2 and C_2H_5OH; for instance

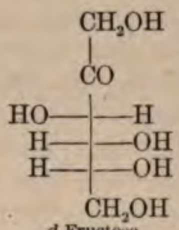
$$C_3H_6O_3 = C_2H_5OH + CO_2.$$

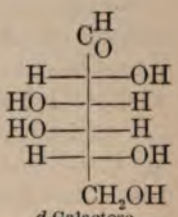
Only the monoses are capable of being fermented by enzymes; dioses must first be converted into monoses. Yeast contains an enzyme, *invertase*, which first splits up sucrose into fructose and glucose. This is proved by the fact that certain varieties of yeast, which do not contain invertase, are incapable of fermenting sucrose; thus, BEYERINCK discovered *Schizosaccharomyces octosporus*, which can ferment maltose, but not sucrose. This variety of yeast contains no invertase, but maltase, which is the enzyme by which maltose is hydrolyzed.

The property of being split up by enzymes, possessed by the monoses, has been proved by EMIL FISCHER to be intimately connected with their stereochemical configuration. The three naturally occurring sugars, *d*-glucose, *d*-mannose, and *d*-fructose, are capable of undergoing fermentation, and there is a great similarity in their configurations, since they differ only in the grouping round two C-atoms:


d-Glucose


d-Mannose


d-Fructose


d-Galactose

d-Galactose, which is also a natural product, has a somewhat different configuration. and is either more slowly fermented by certain varieties of yeast, or not at all. The mirror-images of these compounds, *l*-glucose, etc., are not capable of undergoing fermentation.

The cause of these phenomena is probably the asymmetric structure of the enzyme molecule. Although these substances have not been obtained in the pure state, their great resemblance to the albumins, and the probability of their formation from them, render their optical activity undoubted; that is, they are to be looked upon as built up of asymmetric molecules. This has led to the hypothesis that there must be a resemblance in molecular configuration between the enzymes and the substances which they decompose; and that when this resemblance is wanting, no reaction can take place. EMIL FISCHER appropriately compares this resemblance in structure to that necessary between a lock and a key, in order that the latter may pass the lock.

The application of these views to the chemical processes which go on in the more highly developed organisms, leads to the conception that generally in reactions in which proteïd bodies act, as is undoubtedly the case in the protoplasm, the configuration of the molecule has the same importance as its structure. Various phenomena may be thus explained: the sweet taste possessed by one of the optically active asparagines, and the absence of taste in the other; the different amount to which the three stereoisomeric tartaric acids are oxidized in the body of a dog fed with them; the fact that, on subcutaneous injection of a rabbit with *l*- or *d*-arabinose, of the first only 7 per cent., of the latter 36 per cent., is excreted from the body unchanged in the urine; and so on.

223. Investigation of the stereoisomerism of the monoses has contributed towards explaining why optically active bodies are formed in plants, whilst laboratory syntheses usually produce the racemic forms. It has been shown that this is not the case in artificial syntheses effected with compounds already having an asymmetric structure. Mannose, for example, yields mannoheptonic acid by the cyanhydrin synthesis, and it would be expected, from analogy with other cyanhydrin syntheses, that equal quantities of two stereoisomeric mannoheptonic acids would be formed. This is, however, not so; only one acid is obtained. This shows that the building up of a molecule from one which is asymmetric can continue in an asymmetric sense. Suppose that mannose is converted into *mannononose* by three repetitions of the cyanhydrin synthesis, this always going on in only one direction. This nonose might be capable of being split up into the original hexose and a product containing three carbon atoms; the latter should then be optically active, and *one optically active molecule would have occasioned the formation of another*.

The formation of sugar in the plant has been proved by vegetable physiologists to take place in the chlorophyll-grains, which are composed of optically active substances. It may be assumed that the production of sugar results from a combination of carbon dioxide or formaldehyde with these substances, whose asymmetry has the effect of making the sugar formed by condensation also asymmetric. As the other substances which occur in plants are probably formed from sugar, their optical activity is easily understood, since they are formed from optically active material.

This by no means solves the problems of how the first optically active compound arose, and of why nature has not pro-

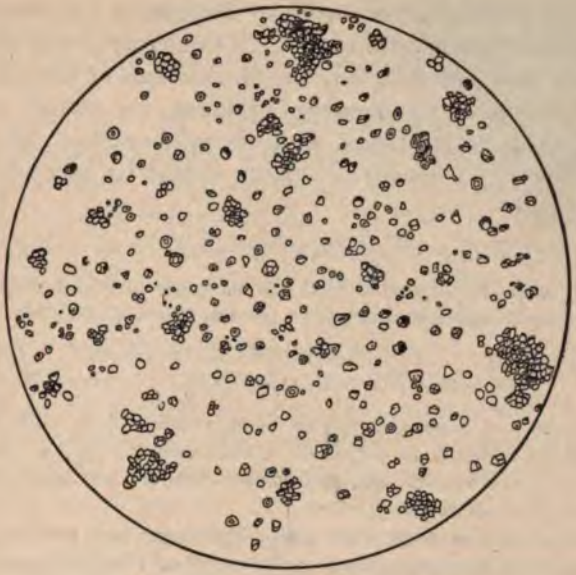


Fig. 68.—Rice-starch. × 320.

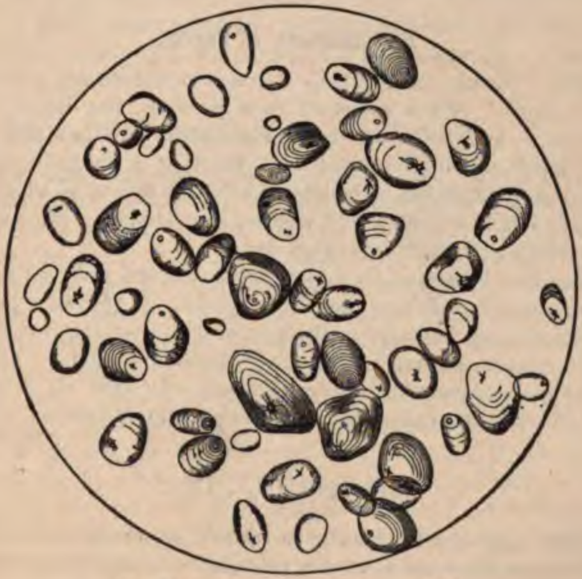


Fig. 69.—Potato-starch. × 250.

which is the formula deduced from the results of analysis. On hydrolysis, nearly all the polyoses yield monoses with the same number of C-atoms, but a polyose which can be split up into pentose and hexose seems to be present in the gums of plants.

Starch.

226. *Starch* is the first observable assimilation-product of plants. It occurs in large quantities in the tubers, roots, and seeds of many plants, in which it is present in the form of granules differing in form and size in different plants. These are represented in Figs. 67, 68, and 69.

FIG. 67.—RYE-STARCH. × 320.

Starch is insoluble in cold water; in hot water it swells up without dissolving. It yields an intense blue colouration with a dilute solution of iodine, for which this reaction serves as a test. When boiled with dilute acids, starch is wholly split up, yielding only *d*-glucose. When starch-paste is treated with diastase, it first dissolves, then the molecule splits up, with ultimate formation of maltose and isomaltose, $C_{12}H_{22}O_{11}$. Both these methods of treatment yield intermediate products, however; these are gum-like substances, polyoses containing a smaller number of atoms in the mole-

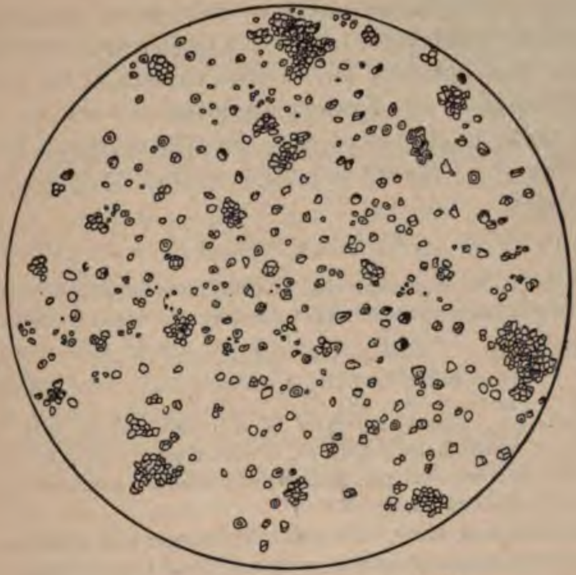


FIG. 68.—RICE-STARCH. × 320.

FIG. 69.—POTATO-STARCH. × 250.

cule than starch, called *dextrins*. Dextrin is also obtained by heating starch alone, or to 110° with a small quantity of nitric acid.

Starch does not show any of the reactions of the monoses; it does not reduce an alkaline copper solution, nor resinify with alkalis, and yields no compound with phenylhydrazine. This proves the absence of a free carbonyl-group, so that its molecule must be represented by

$$C_6H_{10}O_5{<}O \;.\;.\;.\;.\; C_6H_{10}O_4{<}O{>}C_6H_{10}O_4 \;.\;.\;.\;.\; O{>}C_6H_{10}O_5.$$

It might be suggested that the molecule of starch contains more than one dicarbonyl-bond, when the formula would be, for example,

$$C_6H_{10}O_5{<}O \;.\;.\;.\;.\; C_6H_{10}O_4{<}O{>}C_6H_{10}O_4{\cdot}O{>}C_6H_{10}O_5 \;.\;.\;.\;.\; O{>}C_6H_{10}O_4{<}$$
$${<}O{>}C_6H_{10}O_4{\cdot}O{>}C_6H_{10}O_5{\cdot}O{>}C_6H_{10}O_5 \;.\;.\;.\; O{>}C_6H_{10}O_5.$$

It does not, since hydrolysis of a compound of this type must yield, in addition to *d*-glucose, a substance $>C_6H_{12}O_6<$, containing two free carbonyl-groups, and no such product has been obtained by the hydrolysis of starch.

Dextrin can unite with phenylhydrazine, and exhibits the reactions of the monoses, such as reduction of an alkaline copper solution, and the formation of a yellow colouration with alkalis. It must, therefore, be assumed to contain a free carbonyl-group.

Manufacture of Starch.

227. The process by which starch is manufactured is theoretically very simple. When prepared from potatoes, the latter are finely ground, so as to destroy the cell-tissue and lay bare the starch-granules. The latter are then treated with water in a specially constructed apparatus, somewhat resembling a sieve, by means of which they are washed out of the cell-tissue, and settle on standing, after which they are carefully washed, and dried slowly.

Starch is employed for many purposes in the arts; as an adhesive paste, and for stiffening linen in laundries. In the latter process, the starch-paste is converted by the heat of the smoothing-iron into a stiff, shining layer of dextrin, coating the fibres of the linen. Starch is of great importance as a large constituent of foods. It is more fully treated of in this connection in physiological text-books.

Glycogen, $(C_6H_{10}O_5)_x$.

228. *Glycogen* is a substance resembling starch, and is present in the animal organism, the other polyoses being vegetable products. It is usually prepared from liver, and is a white, amorphous powder, dissolving in water with formation of an opalescent solution. On hydrolysis, it yields only *d*-glucose. Apparently there are different kinds of glycogen, varying with the animal from which it is isolated.

Cellulose, $(C_6H_{10}O_5)_x$.

229. Cellulose is a polyose of very high molecular weight. The cell-walls of plants consist principally of this substance, together with *lignin*, which is probably not a polyose. Cellulose is very stable towards dilute acids and alkalis. This property is made use of in the technical preparation of cellulose, in order to free it from the substances present along with it in the plant-material. *Linen*, *cotton*, and *paper* consist almost exclusively of cellulose; pure filter-paper is nearly chemically pure cellulose. When it is dissolved in strong sulphuric acid, and the solution boiled, after dilution with water, it is completely hydrolyzed. Cellulose from cotton-wool, paper, etc., yields exclusively *d*-glucose; from coffee-beans, cocoa-nibs, etc., *d*-mannose. Cellulose is converted by treatment with sulphuric acid containing half its volume of water into a colloidal modification, *amyloid*, which gives a blue colouration with iodine; this reaction furnishes a test for cellulose. The latter is soluble in an ammoniacal solution of copper oxide (SCHWEITZER's reagent); from this solution it is precipitated chemically unchanged by acids and salts, and forms an amorphous powder when dried.

Technical Applications of Cellulose.

230. *Linen* is obtained from the stalk of the flax-plant. The linen fibres can be obtained from the flax in several ways, since cellulose is very stable towards chemical reagents: this can be effected by immersion of the flax in water for a period of ten days to a fortnight, which causes the decay of the external fibre, giving rise to a very unpleasant smell. The process is known as "steeping." The flax is spread out to dry, and is then passed through corrugated "rollers" to loosen the external woody fibre; the latter is stripped off by revolving wooden arms called "wipers," this being called "scutching." The linen fibres can also be obtained from the flax by the action of a very dilute solution of alkali; they have a gray colour, and are bleached by either being spread out in the open, or by means of bleaching-powder.

Paper was formerly prepared almost exclusively from linen rags, but is now largely manufactured from wood and straw, which must be divided into fibres, and these separated as much as possible from the other, so-called incrusting, substances present. This is effected by the *sulphite method*, in which the wood is heated under pressure with a solution of acid sulphite of calcium. When straw is used, it is heated with caustic soda under pressure. By this process most of the incrusting substances are dissolved, the wood or straw being bleached at the same time; the cellulose which remains can be readily separated into fine fibres, which is necessary to the manufacture of paper-pulp. It is not, however, possible to remove all the lignin by this process, with the result that wood-paper and straw-paper answer to the tests for lignin, and can be easily recognized by means of these. Lignin gives a yellow colouration with salts of aniline, and a red colouration with a solution of phloroglucinol in concentrated hydrochloric acid.

Parchment-paper is prepared by converting the outer surface of paper into amyloid (**229**), a process which imparts toughness to the paper.

Nitrates of Cellulose.

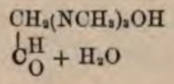
231. These compounds are of great technical importance. When cotton-wool is treated with a mixture of nitric and sulphuric acids, dinitrates to hexanitrates are obtained, this being dependent upon the concentration of the acids, and the duration of the process. Cellulose is arbitrarily assumed to have the formula $C_{12}H_{20}O_{10}$, so that to the dinitrate is assigned the formula $C_{12}H_{18}O_8(ONO_2)_2$, and to the hexanitrate $C_{12}H_{14}O_4(ONO_2)_6$. The solution in a mixture of alcohol and ether of the dinitrate, trinitrate, and tetranitrate is known as *collodion*, which on evaporation leaves an elastic skin, and is employed in photography. The hexanitrate is *guncotton*, which looks like cotton-wool, but feels somewhat rough to the touch, and is extensively employed as an explosive. It burns quietly when a loose tuft of it is ignited, but can be made to explode by the detonation of a small amount of mercury fulminate, and yields only gaseous products, nitrogen, hydrogen, water-vapour, carbon monoxide, and carbon dioxide. It exerts a *brisant* action (**160**), and without modification is, therefore, unsuitable for use in artillery.

When guncotton is dissolved in acetone or ethyl acetate, a gelatinous mass is obtained; after removal of the solvent, an amorphous, transparent substance is left, having the same chemical composition as guncotton, but burning and exploding more slowly. By this means the velocity of explosion can be so regulated as to make guncotton available for use in artillery, and it is employed in this form under the name "smokeless powder."

The hexanitrate of cellulose is also used in the manufacture of *artificial silk*. In de Chardonnet's method, the nitrate is dissolved in a mixture of alcohol and ether, and the solution pressed through fine glass tubes under a pressure of forty to fifty atmospheres. The filaments are received in water, which takes up the solvent, leaving a very fine thread; when ten to twenty of these are spun together, a thread capable of being woven is obtained. When the fabric thus prepared is treated with a solution of calcium sulphide, obtained from the tank-waste in the manufacture of sodium carbonate by the LE BLANC process ("Inorganic Chemistry," **226**), the NO_2-groups of the nitrate are eliminated, with production of nearly pure cellulose in a form exactly resembling silk.

AMINO-DERIVATIVES OF ALDEHYDES AND KETONES.

232. Very few examples of this class of compounds are known. *Aminoacetaldehyde*, $CH_2NH_2 \cdot C_{O}^{H}$, a very unstable compound, can be obtained from *aminoacetal*, $CH_2NH_2 \cdot C_{(OC_2H_5)_2}^{H}$, which can be prepared from monochloroacetal, $CH_2Cl \cdot CH(OC_2H_5)_2$. ***Muscarine*** is possibly the corresponding trimethylammonium base:



$$\begin{array}{l} CH_2(NCH_3)_3OH \\ | \\ C_{O}^{H} + H_2O \end{array}$$

It is a crystalline, excessively poisonous substance, and is present in certain plants—for example, toad-stool (*Agaricus muscarius*).

Chitine is one of the principal constituents of the shells of the crustacea, such as the crab and lobster; when heated with hydrochloric acid, it yields *chitosamine hydrochloride*, from which the free base *chitosamine*, $C_6H_{13}NO_5$, can be obtained by the action of sodium methoxide dissolved in methyl alcohol. Chitosamine undergoes a change when its solution in methyl alcohol is boiled, since, on cooling, there gradually separates from the liquid a crystalline substance, identical with *fructosamine*, which is slowly developed in a solution of fructose in methyl alcohol containing ammonia.

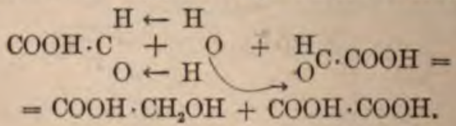
FINISH

ALDEHYDIC AND KETONIC ACIDS.

Glyoxylic Acid, $COOH\cdot C\overset{H}{\underset{O}{}} + H_2O$.

233. *Glyoxylic acid* is the first member of the series of aldehydic acids. It is present in unripe fruits, and can be prepared by heating dibromoacetic acid, $CHBr_2\cdot COOH$, with water. It also results in the oxidation of alcohol with nitric acid, by the method described under glyoxal (**202**).

As seen from the formula given above, glyoxylic acid contains one molecule of water, which cannot be separated from the acid or its salts without their undergoing decomposition. For this reason, the water is often assumed to be in chemical combination (**155**), $CH(OH)_2\cdot COOH$, as it is in chloral hydrate (**204**). In both these substances the aldehyde-group, $—C\overset{H}{\underset{O}{}}$, is under the influence of a strongly negative group, $—CCl_3$ in chloral, and $—COOH$ in glyoxylic acid. The latter, moreover, possesses all the properties characteristic of aldehydes; it reduces an ammoniacal silver solution, forms an addition-product with sodium hydrogen sulphite, yields an oxime, etc. When boiled with caustic potash, it is converted into glycollic and oxalic acids, the formation of which may be explained by the assumption that one molecule of the acid takes up the two hydrogen atoms, and another the oxygen atom, from one molecule of water:



$$COOH\cdot C\overset{H \leftarrow H}{\underset{O \leftarrow H}{}} + O + \overset{H}{\underset{O}{}}C\cdot COOH =$$
$$= COOH\cdot CH_2OH + COOH\cdot COOH.$$

Pyroracemic Acid, $CH_3\cdot CO\cdot COOH$.

234. *Pyroracemic acid*, the first member of the series of ketonic acids, owes its name to its formation by the distillation of either tartaric or racemic acid with potassium hydrogen sulphate. It is probable that carbon dioxide is first split off from tartaric acid, $\boxed{COO}H\cdot CHOH\cdot CHOH\cdot COOH$, with formation of glyceric acid,

$CH_2|\overline{O}|\underline{H\cdot C}|\overline{H}|\underline{O}|\overline{H}|\cdot COOH$, which gives pyroracemic acid by loss of one molecule of water; for glyceric acid itself is converted into pyroracemic acid by heating with potassium hydrogen sulphate. Pyroracemic acid can be obtained synthetically by hydrolysis of the nitrile formed by the action of potassium cyanide on acetyl chloride:

$$CH_3\cdot COCl \rightarrow CH_3\cdot CO\cdot CN \rightarrow CH_3\cdot CO\cdot CO_2H.$$

This is a general method for the preparation of a-ketonic acids.

When heated to 150° with dilute sulphuric acid, pyroracemic acid splits up into carbon dioxide and acetaldehyde:

$$CH_3\cdot CO\cdot|\overline{CO_2}|H = CH_3\cdot C_{O}^{H} + CO_2.$$

Pyroracemic acid is liquid at ordinary, but solid at low, temperatures; it melts at 9°, boils at 165°, and is miscible with water in all proportions; its specific gravity is 1·27 at 20°, and it has an odour resembling that of acetic acid. It is a stronger acid than propionic acid, for which K is 0·00134; for pyroracemic acid K is 0·56, which must be explained by assuming the presence of a negative carbonyl-group in juxtaposition to the carboxyl-group.

Pyroracemic acid has all the properties characteristic of ketones; it yields an oxime, a hydrazone, an addition-product with hydrocyanic acid, etc.

The electrolysis of a very concentrated solution of potassium pyroracemate yields acetic acid and diacetyl. The formation of acetic acid must be looked upon as due to the interaction of the anion of the acid and the hydroxyl-ion, after being discharged at the anode:

$$CH_3\cdot CO\cdot COO' + OH' = CH_3\cdot COOH + CO_2;$$

and that of diacetyl as resulting from the union of two acid anions, with elimination of CO_2:

$$\begin{matrix} CH_3\cdot CO\cdot COO' \\ CH_3\cdot CO\cdot COO' \end{matrix} = CH_3\cdot CO\cdot CO\cdot CH_3 + 2CO_2.$$

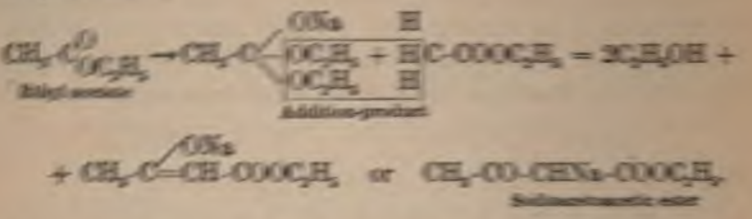
The potassium salts of other ketonic acids are decomposed by electrolysis in an analogous manner.

Acetoacetic Acid, $CH_3\cdot CO\cdot CH_2\cdot COOH$.

235. *Acetoacetic acid* is a β-ketonic acid. It is not of much importance, but its ethyl ester, *acetoacetic ester*, is a very interesting compound.

Acetoacetic ester is obtained by CLAISEN's condensation-method

(293) through the action of sodium on ethyl acetate in presence of ethyl alcohol:



$$CH_3\cdot C\begin{matrix}O\\OC_2H_5\end{matrix} \rightarrow CH_3\cdot C\begin{matrix}ONa & & H\\ \boxed{OC_2H_5 + H} & & \\ OC_2H_5 & & H\end{matrix}C\cdot COOC_2H_5 = 2C_2H_5OH +$$

$$+ CH_3\cdot C\overset{ONa}{=}CH\cdot COOC_2H_5 \quad \text{or} \quad \underbrace{CH_3\cdot CO\cdot CHNa\cdot COOC_2H_5}_{\text{Sodioacetoacetic ester}}.$$

This explanation of the condensation was proved to be correct in this instance by CLAISEN, who found that acetoacetic ester cannot be prepared by the action of sodium on ethyl acetate which has been carefully purified from alcohol. The free ester, $CH_3\cdot CO\cdot CH_2\cdot COOC_2H_5$, can be obtained by treatment of the sodium compound with acetic acid.

Acetoacetic ester is a colourless liquid, slightly soluble in water, and characterized by an agreeable odour; it boils at 181°, and has a specific gravity of 1·030 at 15°. It can be split up in two ways, respectively known as the *ketone decomposition* and the *acid decomposition*, on account of the nature of the products.

The ketone decomposition is effected by heating acetoacetic ester with dilute sulphuric acid, or with a dilute aqueous solution of alkali, the products being acetone, carbon dioxide, and alcohol:

$$\begin{array}{l|l|l}CH_3\cdot CO\cdot CH_2\cdot & CO_2 & C_2H_5\\ \quad\;\; + H & & OH\end{array} = CH_3\cdot CO\cdot CH_3 + CO_2 + C_2H_5OH.$$

The acid decomposition takes place when acetoacetic ester is heated with a very concentrated solution of alcoholic potash or soda:

$$\begin{array}{l|l|l}CH_3\cdot CO\cdot & CH_2\cdot COO & C_2H_5\\ \quad + OH & H + H & OH\end{array} = CH_3\cdot COOH + CH_3\cdot COOH + C_2H_5OH.$$

The great importance of acetoacetic ester for syntheses arises from its capability of undergoing these two decompositions, together with the fact that the Na-atom in sodioacetoacetic ester can be substituted by a great variety of groups. If it is replaced by a group R, there is obtained the compound

$$CH_3\cdot CO\cdot CHR\cdot COOC_2H_5,$$

which, by the ketone decomposition, yields a ketone $CH_3 \cdot CO \cdot CH_2R$, this reaction affording a general method of synthesizing methylketones (**110**).

The compound $CH_3 \cdot CO \cdot CHR \cdot COOC_2H_5$ can be converted by the acid decomposition into acetic acid, and an acid of the formula $RH_2C \cdot COOH$, so that this is a general method of preparing monobasic acids synthetically.

Sodium can again react with the compound

$$CH_3 \cdot CO \cdot C\overset{*}{H}R \cdot COOC_2H_5,$$

with replacement of the hydrogen atom $\overset{*}{H}$, and production of a compound whose Na-atom can also be exchanged for the most varied groups, yielding substances of the type

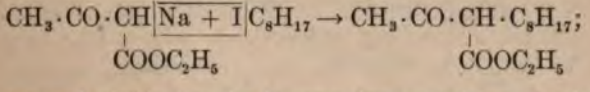
$$CH_3 \cdot CO \cdot CRR' \cdot COOC_2H_5.$$

These are converted by the ketone or acid decomposition into

$$CH_3 \cdot CO \cdot CHRR' \quad \text{or} \quad CHRR' \cdot COOH.$$

On account of this property, the number of compounds which can be synthesized by the aid of acetoacetic ester is very great. The process, called the *acetoacetic ester synthesis*, is carried out in the way already described for the malonic ester synthesis (**166**). A few examples of this synthetical method may be mentioned.

1. *Methylnonyl ketone*, the principal constituent of oil of rue (from *Ruta graveolens*), can be obtained by the action of *n*-octyl iodide upon sodioacetoacetic ester:



$$\underset{\displaystyle COOC_2H_5}{CH_3 \cdot CO \cdot CH}\boxed{Na + I}C_8H_{17} \rightarrow \underset{\displaystyle COOC_2H_5}{CH_3 \cdot CO \cdot CH} \cdot C_8H_{17};$$

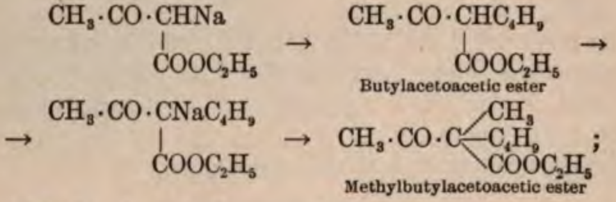
this compound yields, by the ketone decomposition, methylnonylketone,

$$CH_3 \cdot CO \cdot CH_2 \cdot C_8H_{17}.$$

n-Octylacetoacetic ester yields, by the acid decomposition, capric acid, $C_{10}H_{20}O_2$, whose carbon chain must therefore be a normal one (**144**).

2. Heptylic acid, which is obtainable from *d*-fructose by the cyanhydrin synthesis (**212**, 2), can be synthetically built up from acetoacetic ester by the successive introduction of a *n*-butyl-

group and a methyl-group; this proves it to be *n*-butylmethylacetic acid:

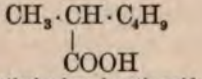


$$\begin{array}{llll}
CH_3\cdot CO\cdot \begin{array}[t]{l}CHNa\\ |\\ COOC_2H_5\end{array} & \rightarrow & CH_3\cdot CO\cdot \begin{array}[t]{l}CHC_4H_9\\ |\\ COOC_2H_5\end{array} & \rightarrow\\
\rightarrow CH_3\cdot CO\cdot \begin{array}[t]{l}CNaC_4H_9\\ |\\ COOC_2H_5\end{array} & \rightarrow & CH_3\cdot CO\cdot C\begin{array}{l}\diagup CH_3\\ -C_4H_9\\ \diagdown COOC_2H_5\end{array}; &
\end{array}$$

Butylacetoacetic ester

Methylbutylacetoacetic ester

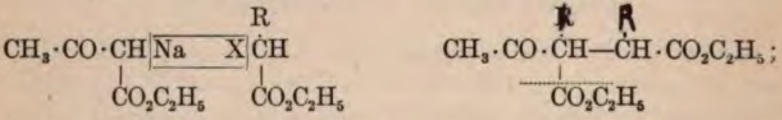
this yields, by the acid decomposition,



$$\begin{array}{l}CH_3\cdot CH\cdot C_4H_9\\ \qquad\;\; |\\ \qquad COOH\end{array}$$

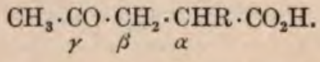
Methyl-*n*-butylacetic acid

3. γ-Ketonic acids are obtained by the action of acetoacetic ester upon the esters of the α-halogen-substituted fatty acids, followed by the ketone decomposition:



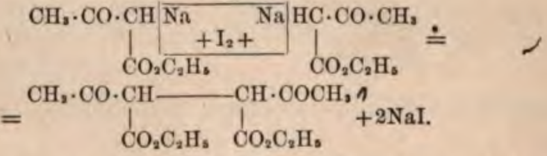
$$CH_3\cdot CO\cdot\begin{array}[t]{c}CH\\|\\CO_2C_2H_5\end{array}\boxed{Na\quad X}\begin{array}[t]{c}R\\ \dot{C}H\\|\\CO_2C_2H_5\end{array}\qquad CH_3\cdot CO\cdot\begin{array}[t]{c}R\\ \dot{C}H\\|\\CO_2C_2H_5\end{array}\!\!-\!\!\begin{array}[t]{c}R\\ \dot{C}H\end{array}\cdot CO_2C_2H_5;$$

This yields, by the ketone decomposition,



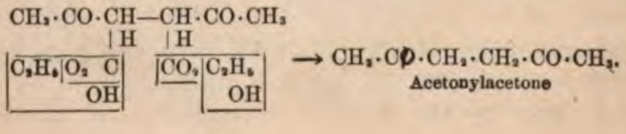
$$\underset{\gamma}{CH_3\cdot CO}\cdot\underset{\beta}{CH_2}\cdot\underset{\alpha}{CHR}\cdot CO_2H.$$

4. When iodine acts upon sodioacetoacetic ester, the sodium is removed, and the two residues unite thus:



$$\begin{array}{l}
CH_3\cdot CO\cdot\begin{array}[t]{c}CH\\|\\CO_2C_2H_5\end{array}\boxed{\begin{array}{c}Na\qquad Na\\ +I_2+\end{array}}\begin{array}[t]{c}HC\cdot CO\cdot CH_3\\|\\CO_2C_2H_5\end{array}\doteq\\
=\;CH_3\cdot CO\cdot\begin{array}[t]{c}CH\\|\\CO_2C_2H_5\end{array}\!\!-\!\!\!-\!\!\!-\!\!\begin{array}[t]{c}CH\cdot COCH_3,\\|\\CO_2C_2H_5\end{array}+2NaI.
\end{array}$$

Diacetylsuccinic ester is formed, and, when boiled with a 20 per cent. solution of potassium carbonate, readily splits off carbon dioxide and alcohol, with formation of *acetonylacetone* (**203**):



$$\begin{array}{l}CH_3\cdot CO\cdot CH-CH\cdot CO\cdot CH_3\\ \qquad\qquad\;\; |H\quad |H\\ \boxed{C_2H_5|\overline{O_2\;C}\atop \quad OH}\quad\boxed{\overline{CO_2}|C_2H_5\atop \quad OH}\end{array}\longrightarrow CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3.$$

Acetonylacetone

Lævulinic Acid, $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot COOH$.

236. *Lævulinic acid* is the simplest γ-ketonic acid; it can be obtained by the synthetical method described in **235**, 3—from acetoacetic ester by the action of monochloroacetic ester; in this instance, in the formula given R = H. It was mentioned (**212**, 6) that lævulinic acid is produced when hexoses are boiled with concentrated hydrochloric acid, and it is usually prepared by this method, which has not yet been fully explained.

Lævulinic acid is crystalline; it melts at 33·5°, and boils with slight decomposition at 250°. It yields an oxime and a hydrazone, and an addition-product with hydrocyanic acid; in short, it exhibits all the reactions characteristic of ketones.

Mesoxalic Acid, $C_3H_2O_5 + H_2O$.

237. *Mesoxalic acid* is a type of the *dibasic ketonic acids.* Its constitution is proved by the formation of *ethyl mesoxalate* when dibromomalonic ester, $Br_2C(COOC_2H_5)_2$, is boiled with baryta-water:

$$(C_2H_5OOC)_2C\boxed{Br_2 + Ba}(OH)_2 = (C_2H_5OOC)_2C(OH)_2 + BaBr_2.$$

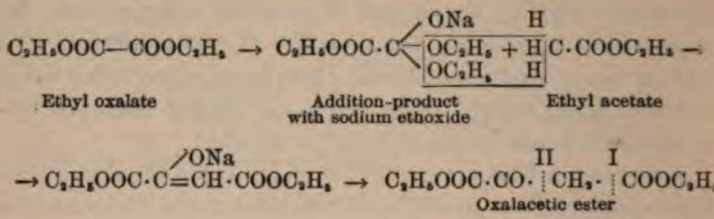
Mesoxalic acid, like glyoxylic acid (**233**), can only be obtained with one molecule of water. An ester of the anhydrous acid is, however, known; it very readily adds on water. The constitution $(COOH)_2C(OH)_2$ must therefore be assigned to the free acid (**155**), which has most of the properties of ketones, in the same way as chloral hydrate (**204**) and glyoxylic acid show most of the reactions of aldehydes. When boiled with water, mesoxalic acid loses carbon dioxide, forming glyoxylic acid:

$$\boxed{CO_2}H \cdot C(OH)_2 \cdot COOH.$$

It is not surprising that a compound containing a carbon atom loaded with four negative groups should split up in this way; the decomposition takes place more readily than that of malonic acid, which does not lose carbon dioxide till heated above its melting-point, to 140°–150°.

Oxalacetic Ester, $C_2H_5OOC\cdot CO\cdot CH_2\cdot COOC_2H_5$.

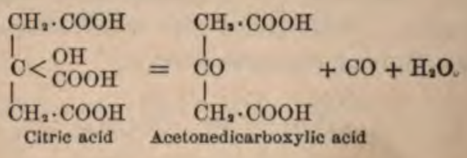
238. *Oxalacetic ester* can be obtained, in accordance with CLAISEN'S method (**203**), by the condensation of ethyl oxalate with ethyl acetate:



Oxalacetic ester, like acetoacetic ester, can be split up with addition of one molecule of water; the two points at which decomposition can occur are indicated in the formula by the dotted lines I and II. Dilute sulphuric acid causes decomposition at I, with formation of pyroracemic acid (**234**), carbon dioxide, and alcohol. Decomposition at II results from the action of alkalis, and yields oxalic and acetic acids. The ketonic nature of oxalacetic ester is shown by the formation of an oxime and by other reactions. Free oxalacetic acid is not obtained by saponification of the ester, since decomposition occurs. It can, however, be obtained otherwise; its melts with decomposition at 172°. Reduction with sodium amalgam yields malic acid, and this reaction, together with the synthesis given above and the formation of an oxime, establishes the constitution of oxalacetic ester.

Acetonedicarboxylic Acid, $COOH\cdot CH_2\cdot CO\cdot CH_2\cdot COOH$.

239. Acetonedicarboxylic acid is formed by the action of concentrated sulphuric acid on citric acid, water-vapour and carbon monoxide being evolved:



$$\begin{array}{l} CH_2\cdot COOH \\ | \\ C<^{OH}_{COOH} \\ | \\ CH_2\cdot COOH \end{array} = \begin{array}{l} CH_2\cdot COOH \\ | \\ CO \\ | \\ CH_2\cdot COOH \end{array} + CO + H_2O.$$

Citric acid Acetonedicarboxylic acid

This decomposition is analogous to that undergone by other α-hydroxy-acids into aldehyde, and formic acid or $CO + H_2O$ (**185**).

The constitution of acetonedicarboxylic acid is inferred from its forming with hydrocyanic acid an addition-product which is the mononitrile of citric acid. Four H-atoms of acetonedicarboxylic

CO- / COOH : oxal. radical

CO- / CO- = oxalyl radical

acid can be successively replaced by sodium; this is explained by the presence in the molecule of two methylene-groups in union with negative groups. It is thus possible to introduce in succession four different radicles, which makes the formation of numerous derivatives feasible.

Acetonedicarboxylic acid is crystalline, and melts at 135°, with loss of two molecules of carbon dioxide, and formation of acetone.

Vinylacetic acid (**143**) can be obtained by the aid of acetonedicarboxylic acid. It is first reduced to β-hydroxyglutaric acid, whose OH is then substituted by bromine by treatment with concentrated hydrobromic acid:

$$\underset{\text{Acetonedicarboxylic acid}}{\mathrm{COOH\cdot CH_2\cdot CO\cdot CH_2\cdot COOH}} \rightarrow \underset{\beta\text{-Hydroxyglutaric acid}}{\mathrm{COOH\cdot CH_2\cdot CHOH\cdot CH_2\cdot COOH}} \rightarrow$$
$$\rightarrow \mathrm{COOH\cdot CH_2\cdot CHBr\cdot CH_2\cdot COOH.}$$

The sodium salt of the latter displays the property common to β-halogen-substituted acids (**178**), of splitting off NaBr and CO_2; it thus yields the desired vinylacetic acid:

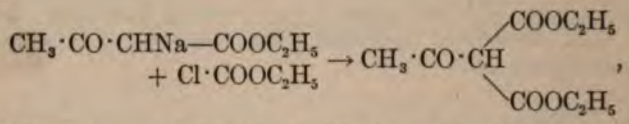
$$\mathrm{COO}\boxed{\mathrm{Na}}\underline{\mathrm{\cdot CH_2\cdot CH}}\boxed{\mathrm{Br}}\mathrm{\cdot CH_2COONa} =$$
$$= \mathrm{NaBr} + \mathrm{CO_2} + \underset{\text{Sodium vinylacetate}}{\mathrm{CH_2:CH\cdot CH_2\cdot COONa}}.$$

TAUTOMERISM.

240. Acetoacetic ester, and in general such substances as 1:3-diketones, which contain the group —CO—CH_2—CO—, afford instances of a remarkable kind of isomerism called *tautomerism*. Compounds of this kind behave as though they contained sometimes the group named, sometimes the group —C(OH):CH—CO—; a few examples will serve to make this clearer.

When alkyl-groups are introduced into acetoacetic ester (**235**), they become united to a carbon atom: thus, methylacetoacetic ester must have the constitution $CH_3\cdot CO\cdot CH(CH_3)\cdot COOC_2H_5$, since by the ketone decomposition it yields methylethylketone, and by the acid decomposition methylacetic acid, or propionic acid. Since it has this constitution, the formation of methylacetoacetic acid is best explained by supposing that sodioacetoacetic ester, $CH_3\cdot CO\cdot CHNa\cdot COOC_2H_5$, is first formed, the Na-atom being then exchanged for a methyl-group by the action of methyl iodide. The majority of substitutions in acetoacetic ester are to be looked upon as taking place in this way, with formation of *C-derivatives* of the ester.

A different effect is produced by the interaction of sodioacetoacetic ester and chlorocarbonic ester, $Cl\cdot COOC_2H_5$ (**249**), which results in the formation of two substances in different quantities. The one formed in smaller quantity results by the reaction indicated above:

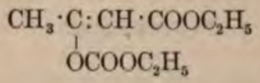


since this substance is identical with the product obtained by the action of acetyl chloride on sodiomalonic ester:

$$CH_3\cdot COCl + NaCH(COOC_2H_5)_2 \rightarrow CH_3CO\cdot CH(COOC_2H_5)_2.$$

Its constitution also follows from its solubility in alkalis, indicating that it contains an H-atom replaceable by metals. This must be in the CH-group.

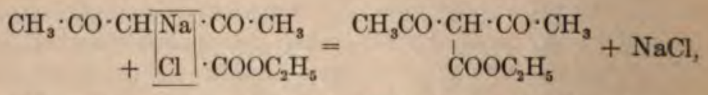
The main product of this reaction is an isomeric compound, which is assumed to have the constitution



$$CH_3\cdot\underset{\displaystyle OCOOC_2H_5}{\underset{|}{C}}:CH\cdot COOC_2H_5$$

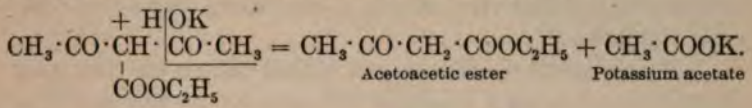
on account of its method of formation and its insolubility in alkalis; the latter proves that it does not contain a CH-group between two carboxyethyl-groups. The formation of a compound of this type is best explained by the assumption that sodioacetoacetic ester has the constitution $CH_3\cdot C(ONa):CH\cdot COOC_2H_5$, as replacement of the Na-atom in this by the group $—COOC_2H_5$ would lead to the formation of a substance of the above constitution.

An analogous reaction takes place between chlorocarbonic ester and sodioacetylacetone; the process is to a small extent in accordance with the equation



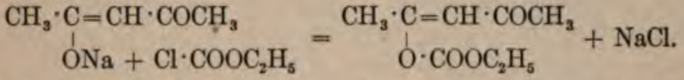
$$\begin{array}{l} CH_3\cdot CO\cdot CH\boxed{Na}\cdot CO\cdot CH_3 \\ \qquad\qquad + \boxed{Cl}\cdot COOC_2H_5 \end{array} = CH_3CO\cdot\underset{\displaystyle COOC_2H_5}{\underset{|}{CH}}\cdot CO\cdot CH_3 + NaCl,$$

since the compound formed is soluble in alkalis, and therefore contains a CH-group in union with three negative groups; when warmed with an equivalent quantity of caustic potash it readily splits up into potassium acetate and acetoacetic ester:



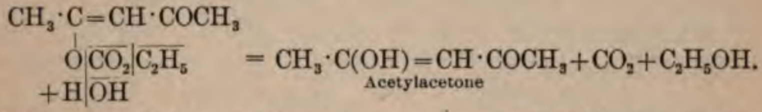
$$\begin{matrix} & +\;H\,| OK \\ CH_3\cdot CO\cdot CH\cdot & |\underline{CO\cdot CH_3} \\ | & \\ COOC_2H_5 & \end{matrix} = \underset{\text{Acetoacetic ester}}{CH_3\cdot CO\cdot CH_2\cdot COOC_2H_5} + \underset{\text{Potassium acetate}}{CH_3\cdot COOK}.$$

The main reaction, however, takes place thus:



$$\begin{matrix} CH_3\cdot C{=}CH\cdot COCH_3 \\ | \\ ONa + Cl\cdot COOC_2H_5 \end{matrix} = \begin{matrix} CH_3\cdot C{=}CH\cdot COCH_3 \\ | \\ O\cdot COOC_2H_5 \end{matrix} + NaCl.$$

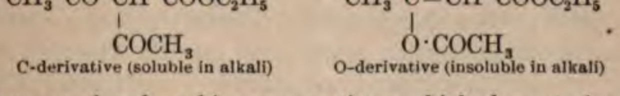
This is proved by the insolubility of the compound in dilute alkalis, which split it up, even at ordinary temperatures, into acetylacetone, alcohol, and carbon dioxide:



$$\begin{matrix} CH_3\cdot C{=}CH\cdot COCH_3 \\ | \\ O|\overline{CO_2}|\overline{C_2H_5} \\ +H|\overline{OH} \end{matrix} = \underset{\text{Acetylacetone}}{CH_3\cdot C(OH){=}CH\cdot COCH_3} + CO_2 + C_2H_5OH.$$

This makes it improbable that the group $—COOC_2H_5$ is in union with a carbon atom.

When acid chlorides react with acetoacetic ester, it is possible at will to obtain a C-derivative or an O-derivative, that is, a compound in which the acid group is linked to the rest of the molecule either through carbon or through oxygen. A C-derivative is obtained by the usual method—the treatment of sodioacetoacetic ester with the acid chloride. When, however, acetoacetic ester is mixed with pyridine (**386**), and the acid chloride allowed to flow slowly into the mixture, an O-derivative only is formed:



$$\underset{\text{C-derivative (soluble in alkali)}}{\begin{matrix} CH_3\cdot CO\cdot CH\cdot COOC_2H_5 \\ | \\ COCH_3 \end{matrix}} \qquad \underset{\text{O-derivative (insoluble in alkali)}}{\begin{matrix} CH_3\cdot C{=}CH\cdot COOC_2H_5 \\ | \\ O\cdot COCH_3 \end{matrix}}$$

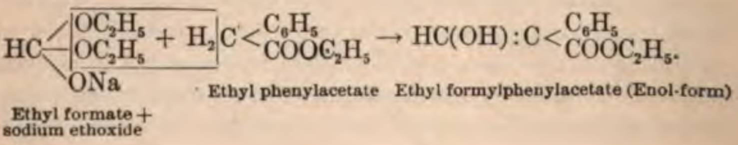
By means of such ambiguous reactions, which characterize many other substances, it is not possible to determine whether a body is a *keto-compound*, containing the group $—CO\cdot CH_2\cdot CO—$, or an *enol-compound*, with the group $—C(OH){:}CH\cdot CO—$. It was formerly usual to assign one of the two formulæ to substances which exhibited tautomerism, and to explain reactions not in accordance with this formula by assuming that transformation had occurred. It is now known that *a tautomeric substance, in the liquid state or in* *solution, consists of a mixture of the keto-compound and the enol-compound,* the proportion of each present being dependent on certain conditions, and this view affords a satisfactory explanation of the observed facts.

The fundamental phenomenon is that tautomers can react as though they consisted wholly of the keto-compound, or wholly of the enol-compound. This is explained as follows. If, from a mixture of two isomers capable of changing into one another with such readiness that the balance between them is rapidly restored, an attempt is made to remove one of the components by chemical methods, the second component should become transformed into the first, on account of the disturbance of the equilibrium; the mixture should then react as though it consisted wholly of the first component. If a chemical reagent which only reacts with the second component is used, the mixture should behave, for the same reason, as though the latter were the only substance present.

It is, however, possible to effect the separation of tautomers by chemical means—first, when the disturbed balance is only slowly restored; second, by reactions with nearly the same velocity for both forms, resulting in different products.

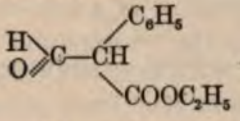
> These conditions are to a certain extent attained in the reactions described on pp. 298 and 299 for chlorocarbonic ester. SCHIFF cites another example, the addition of benzalaniline, $C_6H_5 \cdot N:CH \cdot C_6H_5$, to acetoacetic ester, which also yields two isomeric substances. It is by no means certain whether the proportion of the isomers formed is the same as that of the tautomeric forms present in the acetoacetic ester, because it is unknown how far the above conditions are fulfilled.

Experience has shown that the enol-form gives an intense colour-reaction with ferric chloride, which is not obtained with the keto-form. This gives a ready means of identifying a tautomer, and of recognizing the conversion of one form into the other; it has been applied in various instances, such as the investigation of formylphenylacetic ester. This substance results, by CLAISEN's condensation-method (**203**), from the action of the ester of phenylacetic acid upon that of formic acid:



$$\mathrm{HC}\begin{array}{l}\diagup\\ -\\ \diagdown \mathrm{ONa}\end{array}\!\!\boxed{\begin{array}{l}\mathrm{OC_2H_5}\\ \mathrm{OC_2H_5} + \mathrm{H_2}\end{array}}\mathrm{C}<\begin{array}{l}\mathrm{C_6H_5}\\ \mathrm{COOC_2H_5}\end{array} \rightarrow \mathrm{HC(OH)}:\mathrm{C}<\begin{array}{l}\mathrm{C_6H_5}\\ \mathrm{COOC_2H_5}.\end{array}$$

The keto-form, or, in this instance, more correctly, the "aldo-form," of this substance has the formula



.

The enol-compound is solid, and melts gradually between 60° and 70°; the aldo-compound is a liquid. In dilute alcoholic solution the former gives a deep violet-blue colouration with ferric chloride; the latter does not give any colour. If, however, equally concentrated solutions of the enol-form and the aldo-form are made, and equal quantities of ferric chloride added to each, after some days the solutions are alike, the tint of the enol-compound having become lighter, and the aldo-compound having developed a blue colour. This proves that after standing for an interval both solutions contain the aldo-form and the enol-form and, since the tint is the same in each solution, in equal amounts. It follows that an equilibrium between the opposite transformations exists.

Other methods are known by which this transformation of tautomers can be recognized, of which two may be mentioned. Bruhl has shown that rays of light are much more strongly dispersed and refracted by substances containing a double bond than by their isomers which do not contain such a bond. Since a double bond results from the *enolization* of a keto-form, it is possible, by a determination of the dispersive and refractive powers, to prove that in alcoholic solution enol-compounds are transformed into keto-compounds, and *vice versa.*

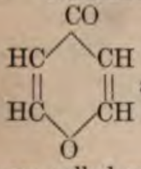
W. H. Perkin, Sen.. has discovered another aid to the investigation of these transformations in the electromagnetic rotation of the plane of polarization. The plane of a plane-polarized ray, passed through a tube containing an optically inactive substance, is rotated when an electric current is passed through a wire wound round the tube, enclosing the column of liquid. The value of this rotation of the plane of polarization is characteristic for chemical compounds, supposing that the current, and the length and temperature of the column, are kept constant; and Perkin found that substances containing a double bond in the molecule occasion a much greater magnetic rotation than their isomers, from which such a bond is absent.

The investigations which have been carried out have given an insight into the conditions upon which the *ketization* of an enol-compound, and the *enolization* of a keto-compound, respectively depend; among them is the temperature. CLAISEN found that acetyldibenzoylmethane, $CH_3CO \cdot CH(COC_6H_5)_2$ (benzoyl$=C_6H_5CO$, *cf.* **296**), has the keto-form at ordinary temperatures. It is then insoluble in alkalis, and in aqueous solution gives no colouration with ferric chloride. When heated to 110°, and quickly cooled to prevent immediate re-transformation, it is found to be converted into the enol-form, since it answers to the colour-test with ferric chloride, and is readily soluble in alkalis.

It has further been shown that the nature of the solvent has a great influence upon the transformation. In solution in chloroform, an enol-form will remain unchanged for months, while in alcoholic solution it becomes partly or wholly transformed into the keto-form in the course of a few days.

PYRONE DERIVATIVES.

A number of compounds which are assumed to contain the group

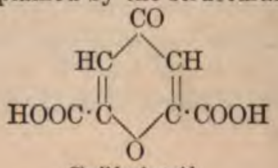


are known; some of these are natural products. They are called *pyrone derivatives*. Some of them will be dealt with here.

Chelidonic acid, $C_7H_4O_6$, so-called because it is found in *Chelidonium majus* (greater celandine), forms colourless salts, $C_7H_2O_6M_2$; it also yields yellow salts, $C_7H_2O_7M_4$, which are derived from an acid $C_7H_6O_7$, *xanthochelidonic acid;* this acid, however, when set free from its salts, readily loses one molecule of water, being reconverted into chelidonic acid. By boiling with alkalis, the latter is split up almost quantitatively into two molecules of oxalic acid and one molecule of acetone:

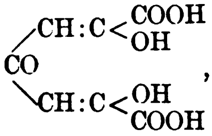
$$C_7H_4O_6 + 3H_2O = \underset{\text{Oxalic acid}}{2C_2H_2O_4} + \underset{\text{Acetone}}{C_3H_6O}.$$

These facts are explained by the structural formula

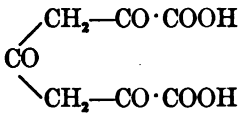


Chelidonic acid

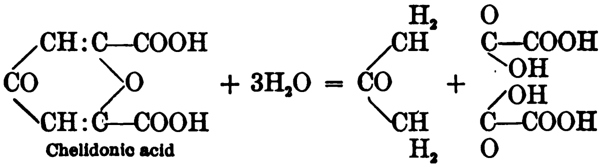
in accordance with which the acid can be called *pyronedicarooxylic acid*. Xanthochelidonic acid must then have the structural formula



, in which the two hydroxyl-hydrogen atoms are also replaceable by metals; or, in its tautomeric form,

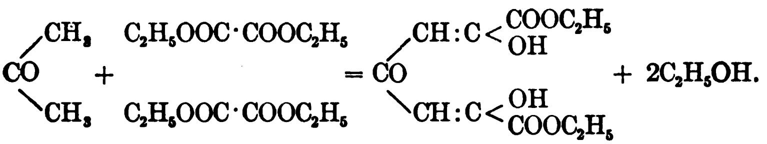


The manner in which $3H_2O$ causes the above-mentioned splitting-up is evident from the equation



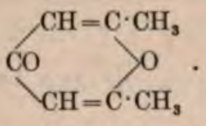
Chelidonic acid

Moreover, a synthesis of chelidonic acid corroborates this formula. The starting-point of this is acetone, which by Claisen's method (**203** and **235**) can be condensed with two molecules of oxalic ester:

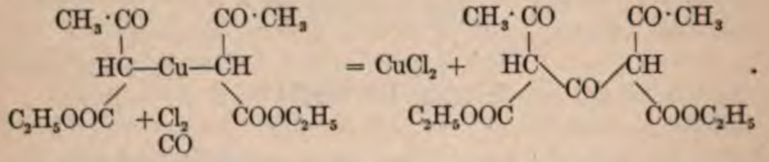


The product is seen to be an ester of xanthochelidonic acid. When this is heated with concentrated hydrochloric acid, two objects are simultaneously attained—the ester is saponified, and one molecule of water split off. These reactions yield a compound with the structural formula given above for chelidonic acid, and identical with it.

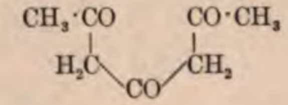
A pyrone derivative which has recently attracted attention is *dimethylpyrone* :



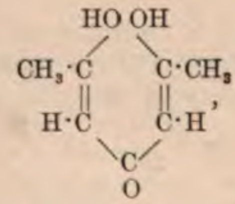
It can be synthesized from copper acetoacetic ester and carbonyl chloride (**249**):



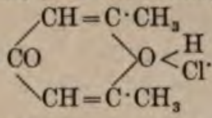
On saponification with dilute sulphuric acid, two molecules of carbon dioxide are simultaneously eliminated from the molecule, so that



should result. Its tautomeric form,



however, loses one molecule of water, yielding dimethylpyrone.

Dimethylpyrone is characterized by the formation of addition-products with acids, which must be looked upon as salts. These "salts" are formed by dissolving dimethylpyrone in an aqueous solution of hydrochloric acid, oxalic acid, etc.; they are obtained crystalline by the spontaneous evaporation of these solutions. By dissolving them in a large quantity of water, they are completely hydrolyzed, so that it is improbable that the acid in them is linked to the carbonyl-group. COLLIE and TICKLE, the discoverers of these compounds, accordingly assume the *tetravalency of the oxygen* *atom* closing the carbon chain, thus attributing to dimethylpyr hydrochloride the structure  They have nam these compounds *oxonium* salts, on account of their analogy t the ammonium salts.

These compounds can be proved to be true salts—electrolytes— by various methods. It must be remembered that an aqueous solution of dimethylpyrone has a neutral reaction with litmus, and that its electric conductivity is very small. Thus, the oxonium base is only feebly basic; its salts—if they really deserve this name—must, therefore, have the properties characteristic of the salts of a weak base. These properties can be summed up in the statement that in aqueous solution such salts are hydrolyzed to a high degree, or, in other words, are to a large extent split up into free acid and free base ("Inorganic Chemistry," **239**). The aqueous solution of a dimethylpyronium salt actually has all the properties which would be anticipated for the solution of a highly hydrolyzed salt. In the first place, its solution has a strongly acid reaction; the oxonium salt, however, is partly present as such in the solution, as Walden has demonstrated for the picrate of dimethylpyrone. He compared the quantity of picric acid extracted from its aqueous solution by benzene with the quantity extracted after addition of dimethylpyrone to the aqueous solution. The latter proved to be less in amount; this must be explained by assuming the partial formation of a salt, whereby the quantity of free picric acid in the solution is diminished (**24**).

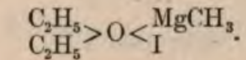
Hydrolysis can also be detected by observing the depression of the freezing-point. When this is determined for solutions of pure hydrochloric acid of different concentrations, and subsequently after addition of dimethylpyrone to the acid solution, the depression of the freezing-point in the latter case is less than the sum of the depressions caused by the hydrochloric acid and by the dimethylpyrone in their pure solutions; further, the difference between the value thus calculated and the value observed is the smaller the more the solutions are diluted, as the following example shows. The addition of 3 c.c. of normal hydrochloric acid to 10 c.c. of water caused a depression of 0·846°; the addition of 0·1262 gramme of dimethylpyrone to the mixture caused a depression of 0·936°; the same quantity of dimethylpyrone dissolved in 13 c.c. of water lowered the freezing-point 0·142°. The sum of the depressions was thus $0{\cdot}846° + 0{\cdot}142° = 0{\cdot}988°$; the difference between this and the observed depression, 0·936°, was therefore 0·052°. When 1 c.c. of hydrochloric acid and the same quantity (0·1262 gramme) of dimethylpyrone were added to 10 c.c. of water, the difference was only 0·030°, which is in complete agreement with the theory of hydrolytic dissociation. The latter increases with the dilution; in fact, a very dilute solution of dimethylpyrone + hydrochloric acid must behave as though the two substances were not in combination at all. Partial combination takes place, however, when the solution is more concentrated, and this causes a depression of the freezing-point smaller than the sum of the depressions observed separately for each substance.

Among the other ways in which the salts of dimethylpyrone can be proved to behave like those of a weak base may be mentioned the electric conductivity method. It was stated that a solution of the free base is a very bad conductor; when, therefore, the hydrochloride is dissolved in such a large amount of water as to be practically completely hydrolyzed, the conductivity of this solution must be equal to that of a solution of pure hydrochloric acid of the same molecular concentration. But if the solution is not so dilute, an equilibrium is attained:

$$H^{\cdot} + Cl' + \underset{\text{Dimethylpyrone}}{C_7H_8O_2} \rightleftarrows \underset{\text{Cation of dimethylpyrone}}{[C_7H_8O_2{\cdot}H]^{\cdot}} + Cl'.$$

In this case there is not as great a number of free H-ions, which are much more mobile than other cations, and therefore conduct the current much better. The conductivity of the solution must, therefore, be smaller than that of hydrochloric acid of the same concentration, and must decrease as the equilibrium tends to the right-hand side, that is, as the solution becomes more concentrated. This has, in fact, been verified by experiment.

The power of forming oxonium salts does not seem to be limited to dimethylpyrone and analogous compounds. BAEYER and VILLIGER have shown that compounds containing oxygen, belonging to various classes of organic bodies, such as alcohols, aldehydes, esters, etc., are able to yield crystalline compounds with complex acids, such as ferrocyanic acid; it is possible, though not fully established, that these are oxonium salts. They also attempted to obtain trimethyloxonium iodide, $(CH_3)_3O \cdot I$, analogous to the tetra-alkylammonium salts, but were unsuccessful. They are of opinion that GRIGNARD's ether compounds of alkyl magnesium iodides (**82**), such as $CH_3MgI + (C_2H_5)_2O$, must be regarded as oxonium derivatives,



$$\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix} > O < \begin{matrix} MgCH_3 \\ I \end{matrix}.$$

The power of forming true salts by the addition of acids is especially developed in the alkyl-compounds of the elements of the nitrogen group. Examples of this are also known with sulphur compounds: an alkyl sulphide, such as $(C_2H_5)_2S$, can unite with an alkyl iodide to form $(C_2H_5)_3SI$, trialkylsulphonium iodide, from which the free base can be obtained by the action of moist silver oxide. It remains to be investigated to what extent elements of other groups of the periodic system are capable of forming analogous compounds.

CYANOGEN DERIVATIVES.

Cyanogen, C_2N_2.

241. When mercuric cyanide, $Hg(CN)_2$, is heated, it splits up into mercury, and a gas, *cyanogen*. At the same time a brown, amorphous polymer, *paracyanogen*, $(CN)_x$, is formed, which is converted on heating to a high temperature into cyanogen. A better method for the preparation of the latter is the interaction of solutions of potassium cyanide and copper sulphate; cupric cyanide is formed, and at once decomposes into cuprous cyanide and cyanogen:

$$4KCN + 2CuSO_4 = 2K_2SO_4 + Cu_2(CN)_2 + (CN)_2.$$

This reaction is analogous to that between potassium iodide and a solution of copper sulphate, in which cuprous iodide and free iodine are formed.

Cyanogen is nearly related to oxalic acid; when ammonium oxalate is heated with a dehydrating-agent, such as phosphorus pentoxide, cyanogen is produced; inversely, when cyanogen is dissolved in hydrochloric acid, it takes up four molecules of water, with formation of ammonium oxalate. These reactions prove cyanogen to be the nitrile of oxalic acid, so that its constitutional formula is $N \equiv C—C \equiv N$.

Cyanogen is also somewhat analogous to the halogens, as is indicated by the second method of preparation given above. The following facts also support this view: potassium burns in cyanogen in the same way as in chlorine, with formation of potassium cyanide, KCN; when cyanogen is passed into caustic potash, potassium cyanide, KCN, and potassium cyanate, KCNO, are produced, the process being analogous to the formation of potassium chloride, KCl, and potassium hypochlorite, KClO, by the action of chlorine on caustic potash ("Inorganic Chemistry," **56**). Silver cyanide, like silver chloride, is in consistence a cheese-like substance, insoluble in water and dilute acids, and soluble in ammonium hydroxide.

At ordinary temperatures cyanogen is a gas of pungent odour, its boiling-point being −20·7°. It is excessively poisonous. It is stable at high temperatures, but its aqueous solution decomposes slowly at ordinary temperatures, depositing a brown, amorphous, flocculent precipitate of *azulminic acid*. Cyanogen is inflammable, burning with a peach-blossom coloured flame.

Hydrocyanic Acid, HCN.

242. The salts of *hydrocyanic acid* ("prussic acid") are formed when carbon, nitrogen, and a strong base are in contact at a red heat; for example, by strongly heating a mixture of carbon and potassium carbonate in a stream of nitrogen. *Cyanides* are also produced when nitrogenous organic substances are heated with an alkali or alkali-metal (**4**). Ammonium cyanide results when ammonia-gas is led over red-hot carbon.

When sparks from an induction-coil are passed through a mixture of acetylene and nitrogen, hydrocyanic acid is formed, and, since acetylene can be obtained by direct synthesis (**133**), this reaction furnishes a method of building up hydrocyanic acid from its elements. It is usually prepared by heating potassium ferrocyanide (**243**) with dilute sulphuric acid, anhydrous hydrocyanic acid being obtained by fractional distillation of the aqueous distillate. It is a colourless liquid with an odour resembling that of bitter almonds; it boils at 26°, and in the solid state melts at −14°.

When pure, hydrocyanic acid is stable, but its aqueous solution decomposes with formation of brown, amorphous, insoluble substances; the solution contains various compounds, among them ammonium formate.

Like most cyanogen derivatives, hydrocyanic acid is an excessively dangerous poison. The inhalation of hydrogen peroxide, or of air containing chlorine, is employed as an antidote. Its toxic effect depends upon the degree of ionization, as it does for the mercury compounds ("Inorganic Chemistry," **274**), so that it must be the cyanogen ions that exert the poisonous action. Other evidence leads to the same conclusion; thus, potassium ferrocyanide, whose aqueous solution contains no cyanogen ions, is non-poisonous.

Hydrocyanic acid must be looked upon as the nitrile of formic acid: $H \cdot COOH \rightarrow H \cdot CN$. Its formation by the distillation of ammonium formate, and the reverse transformation—referred to above—of hydrocyanic acid into ammonium formate by the taking up of two molecules of water favour this view, as does also the formation of hydrocyanic acid when chloroform, $H \cdot CCl_3$, is warmed with alcoholic ammonia and caustic potash (**151**). Methylamine is obtained by reduction of hydrocyanic acid:

$$H \cdot C \equiv N + 4H = H_3C \cdot NH_2.$$

Hydrocyanic acid is one of the weakest acids, its aqueous solution having but low electric conductivity.

Hydrocyanic acid is present in considerable amounts in certain plants; it can be obtained from a vegetable product, *amygdalin*, $C_{20}H_{27}NO_{11}$, which is a glucoside (**218**), and is found in bitter almonds and other substances. In contact with water, amygdalin is decomposed by an enzyme (**222**), *emulsin*, also present in bitter almonds, into benzaldehyde, hydrocyanic acid, and glucose:

$$\underset{\text{Amygdalin}}{C_{20}H_{27}NO_{11}} + 2H_2O = \underset{\text{Benzaldehyde}}{C_7H_6O} + HCN + \underset{\text{Glucose}}{2C_6H_{12}O_6}.$$

Cyanides.

243. The cyanides of the alkali-metals and of the alkaline-earth-metals, and cyanide of mercury, are soluble; other cyanides are insoluble. All have a great tendency to form complex salts, many of which, particularly those containing alkali-metals, are soluble in water, and crystallize well. The preparation and properties of some of these salts are described in "Inorganic Chemistry," **308**.

Potassium cyanide, KCN (or KCy), is obtained by heating potassium ferrocyanide, $K_4Fe(CN)_6$ (or K_4FeCy_6), to redness:

$$K_4Fe(CN)_6 = 4KCN + FeC_2 + N_2.$$

(The symbol Cy is sometimes used to denote the radicle CN.)

Potassium cyanide is readily soluble in water, and with difficulty in strong alcohol; it can be fused without undergoing decomposition. The aqueous solution is unstable; the potassium cyanide takes up two molecules of water, slowly at ordinary temperatures and quickly on boiling, with elimination of ammonia, and production of potassium formate:

$$KCN + 2H_2O = HCOOK + NH_3.$$

Potassium cyanide always has an odour of hydrocyanic acid, owing to the fact that it is decomposed by the carbon dioxide of the atmosphere into this compound and potassium carbonate.

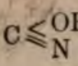
The aqueous solution of potassium cyanide has a strongly alkaline reaction, the salt being partially hydrolyzed to hydrocyanic acid and caustic potash ("Inorganic Chemistry," **239**). Evidence of this decomposition is also afforded by the possibility of saponifying esters with a solution of potassium cyanide, this furnishing at the same time a method of determining the extent of the hydrolytic decomposition of the salt.

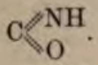
Potassium ferrocyanide ("yellow prussiate of potash"), $K_4Fe(CN)_6$, crystallizes in large, sulphur-yellow crystals, with three molecules of water, which can be driven off by the application of gentle heat, leaving a white powder. It has been stated (**242**) that this substance is not poisonous. On warming with *dilute* sulphuric acid it yields hydrocyanic acid. When heated with *concentrated* sulphuric acid, carbon monoxide is evolved; in presence of the sulphuric acid, the hydrocyanic acid first formed takes up two molecules of water, with production of ammonia and formic acid, the latter being immediately decomposed by the concentrated sulphuric acid into carbon monoxide and water (**88**). This method is often used for the preparation of carbon monoxide.

Cyanic Acid, HCNO.

244. *Cyanic acid* is obtained by heating its polymer, *cyanuric acid* (**247**), and passing the resulting vapours through a freezing-mixture. It is a colourless liquid, stable below 0°. If the flask containing it is removed from the freezing-mixture, so that the temperature rises above 0°, vigorous ebullition begins, sometimes accompanied by loud reports, and the liquid is converted into a white, amorphous solid. This transformation was first observed by LIEBIG and WÖHLER, by whom the product was called "insoluble cyanuric acid", or *cyamelide*, which is a polymer of cyanic acid of unknown molecular weight, $(HCNO)_x$. It has, however, been recently shown by SENIER that the transformation-product contains only about 30 per cent. of cyamelide, the remainder being cyanuric acid; these can be separated by treatment with water, in which cyamelide is only very sparingly soluble, and much less so than cyanuric acid. Above 0° an aqueous solution of cyanic acid changes rapidly into carbon dioxide and ammonia:

$$HCNO + H_2O = H_3N + CO_2.$$

The constitution of cyanic acid itself is unknown, but it yields two series of derivatives which may be regarded as being respectively derived from *normal cyanic acid*,  $C\begin{array}{l}\diagup OH\\ \equiv N\end{array}$, and from *isocyanic acid*,


$C\begin{array}{l}\diagup\!\!\diagup NH\\ \diagdown O\end{array}$.

Cyanogen chloride, CNCl, may be looked upon as the chloride of normal cyanic acid. It is a very poisonous liquid, and boils at 15·5°; it can be obtained by the action of chlorine on hydrocyanic acid, and polymerizes readily to *cyanuric chloride*, $C_3N_3Cl_3$. Cyanogen chloride is converted by the action of caustic potash into potassium chloride and potassium cyanate:

$$CNCl + 2KOH = CNOK + KCl + H_2O.$$

Esters of cyanic acid have not been isolated; they are probably formed in the first instance by the action of sodium alkoxides upon cyanogen chloride, since the polymer, *cyanuric ester*, $(CNOC_2H_5)_3$, can be readily separated from the reaction-product (**247**).

Esters of isocyanic acid, on the other hand, are well known, and are obtained by the action of an alkyl halide on silver cyanate:

$$CO{:}N\boxed{Ag + I}C_2H_5 = CO\cdot NC_2H_5 + AgI.$$

The isocyanic esters are volatile liquids, with a powerful, stifling odour; they, too, polymerize readily, yielding *isocyanuric esters*, such as $(CONC_2H_5)_3$ (**247**).

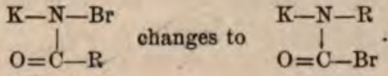
The constitution of the isocyanic esters follows from their decomposition into carbon dioxide and an amine, by treatment with water, or better with dilute alkalis:

$$CO{:}N\cdot CH_3 + H_2O = CO_2 + NH_2\cdot CH_4.$$

This reaction was first applied by Würtz to the preparation of primary amines, whereby they are obtained pure, and free from secondary and tertiary amines.

> It has been stated (**104**) that primary amines can be obtained from acid amides by the action of bromine and caustic potash. This is more economically effected by distilling a mixture of the acid amide and bleaching-powder with lime-water. The mechanism of the reaction has been investigated by Hoogewerff and van Dorp. The first product has been isolated; it is a substituted amide, with bromine in union with nitrogen: $R\cdot CO\cdot NH_2 \rightarrow R\cdot CO\cdot NHBr$. The hydrogen of the amido-group can be replaced by metals, owing to the influence of the acid-

residue, and this replacement is considerably facilitated by the introduction of a Br-atom. The caustic potash present causes the formation of a compound, $R\cdot CO\cdot NKBr$, which is unstable, but can be isolated. This potassium bromamide readily undergoes an intramolecular transformation, similar to the BECKMANN transformation (**112**):



$$\begin{matrix}K-N-Br\\ |\\ O=C-R\end{matrix} \quad \text{changes to} \quad \begin{matrix}K-N-R\\ |\\ O=C-Br\end{matrix}.$$

Potassium bromamide

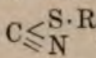
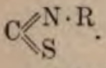
This transformation-product loses KBr, with formation of an isocyanic ester, $\begin{matrix}N\cdot R\\ \|\\ OC\end{matrix}$, which is decomposed by the water present into a primary amine and CO_2.

Thiocyanic Acid, HCNS.

245. *Thiocyanic acid* (*sulphocyanic acid*) resembles cyanic acid in its properties, but is much more stable towards water. It can be obtained by treatment of barium thiocyanate with the calculated proportion of dilute sulphuric acid. When the solution is fractionated under diminished pressure, and the vapour passed over calcium chloride to free it from water, into a vessel cooled by a freezing-mixture, the anhydrous acid is obtained in the form of a very volatile, pungent-smelling liquid, which changes quickly to a solid polymer after removal from the freezing-mixture. When warmed with dilute sulphuric acid, thiocyanic acid takes up one molecule of water, and decomposes similarly to cyanic acid (**244**), with production of carbon oxysulphide, COS, instead of CO_2:

$$HCNS + H_2O = H_3N + COS.$$

Potassium thiocyanate is obtained by boiling a solution of potassium cyanide with sulphur. Among other applications it is used in VOLHARD'S method of silver-titration. When silver nitrate is added to a solution of potassium thiocyanate, *silver thiocyanate*, AgCNS, is deposited in the form of a white, cheese-like precipitate, insoluble in diluto mineral acids. *Ferric thiocyanate*, $Fe(CNS)_3$, has a dark blood-red colour; its formation is used as a test for ferric salts. The red colour is due to the non-ionized molecules $Fe(CNS)_3$, since neither the ferric ion nor the thiocyanic ion are coloured in solution, and the colour is intensified if ionization is diminished, for example, by the addition of more of the ferric salt or of the thiocyanate. The red colour is removed by shaking up with ether, whereas ions cannot be extracted by this means. *Mercury thiocyanate* has the property of swelling up when decomposed by heat ("Pharaoh's serpents").

The constitution of thiocyanic acid, like that of cyanic acid, is unknown, and it resembles the latter in giving rise to two series of esters, the *thiocyanic esters*,  $\mathrm{C}\lessgtr^{\mathrm{S\cdot R}}_{\mathrm{N}}$, and the *isothiocyanic esters*,  $\mathrm{C}\langle^{\mathrm{N\cdot R}}_{\mathrm{S}}$.

Thiocyanic esters are obtained by the action of alkyl iodides upon the salts of thiocyanic acid:

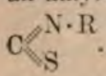
$$\mathrm{CN\cdot S}\boxed{\mathrm{K + I}}\mathrm{C_2H_5} = \mathrm{CN\cdot SC_2H_5} + \mathrm{KI}.$$

They are liquids, insoluble in water, and characterized by a leek-like odour. That the alkyl-group in these compounds is in union with sulphur is proved by the nature of the products obtained both by reduction and oxidation. Reduction yields mercaptans and hydrocyanic acid, methylamine being obtained from the latter by further reduction:

$$\mathrm{CN\cdot SC_2H_5} + 2\mathrm{H} = \mathrm{CNH} + \mathrm{HS\cdot C_2H_5}.$$

Alkyl-sulphonic acids, such as $\mathrm{C_2H_5\cdot SO_2OH}$ (**68**), are obtained by oxidation.

Under the influence of heat the thiocyanic esters are transformed into isothiocyanic esters; thus, distillation of allyl thiocyanate, $\mathrm{CN\cdot SC_3H_5}$, brings about this change.

The isothiocyanic esters are also called *mustard-oils*, after allyl isothiocyanate, to which the odour and taste of mustard-seeds are due. The following reactions prove that these compounds contain an alkyl-group in union with nitrogen, and have the constitution  $\mathrm{C}\langle^{\mathrm{N\cdot R}}_{\mathrm{S}}$. When treated with concentrated sulphuric acid, they take up water, yielding a primary amine and carbon oxysulphide:

$$\mathrm{R\cdot N{:}CS} + \mathrm{H_2O} = \mathrm{R\cdot NH_2} + \mathrm{COS}.$$

They are converted by reduction into a primary amine and *trithiomethylene*, $\mathrm{(CH_2S)_3}$, the latter probably resulting from the polymerization of the thiomethylene, CH_2S, first formed, which is unknown in the free state:

$$R \cdot N:CS + 4H = R \cdot NH_2 + CH_2S.$$

Addition-products of the mustard-oils will be described later (**254** and **255**).

Cyanamide, $CN \cdot NH_2$, is obtained in various reactions; for instance, by the action of ammonia upon cyanogen chloride; it is a crystalline, hygroscopic solid, and polymerizes readily. Its hydrogen atoms can be replaced by metals; for example, silver yields *silver cyanamide*, $CN \cdot NAg_2$, which is yellow, and insoluble in dilute ammonium hydroxide, wherein it differs from the majority of silver compounds.

Fulminic Acid.

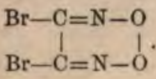
246. Salts of *fulminic acid* are obtained by the interaction of mercury or silver, nitric acid, and alcohol, in certain proportions. The best known of these is *mercury fulminate*, $HgC_2N_2O_2$, which is prepared on a large scale, and employed for filling percussion caps, and for other purposes. It has been mentioned (**231**) that guncotton can be exploded by the detonation of a small quantity of this substance; and it produces the same result with other explosives, so that the so-called "fulminating mercury" plays an important part in their application.

First ex. of isomerism was this a HCNO.

Silver fulminate, Ag(CNO), is much more explosive than the mercury salt, and hence is not employed technically. The explosion of these salts has a *brisant*, though only local, effect; this enabled HOWARD, the discoverer of mercury fulminate, to explode a small quantity in a balloon without injury to the latter, the only effect being to shatter the leaden shells containing the explosive.

Free fulminic acid is a very unstable, volatile substance; it has an odour resembling that of hydrocyanic acid, and is excessively poisonous.

According to NEF, the formula of fulminic acid is $C{=}N \cdot OH$, containing a divalent carbon atom; when mercury fulminate is treated with acetyl chloride, a compound of the formula $CH_3 \cdot CO(CNO)$ is obtained. In presence of hydrochloric acid the fulminate takes up water, with formation of hydroxylamine and formic acid. It is converted by bromine into a compound, $Br_2C_2N_2O_2$, with the constitutional formula



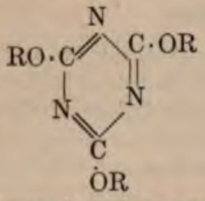
$$\begin{array}{l} Br{-}C{=}N{-}O \\ \quad\;\, | \qquad\;\; | \\ Br{-}C{=}N{-}O \end{array}.$$

Cyanuric Acid and Isocyanuric Acid.

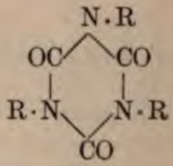
247. *Cyanuric bromide*, $C_3N_3Br_3$, is obtained by heating potassium ferricyanide with bromine at 220°. By heating with water, the bromide is converted into cyanuric acid, $(CNOH)_3$. The latter, however, is usually prepared by the action of heat on urea (**252**). Two series of esters are derived from this acid, the *normal* and the *isocyanuric esters*, the former being called "O-esters," and the latter "N-esters."

The normal cyanuric esters are obtained by the action of sodium alkoxides on cyanuric chloride or bromide. The formation of alcohol and cyanuric acid on saponification proves the alkyl-group in these esters to be in union with oxygen; for this reason constitutional formula I is assigned to them.

I.



II.



The isocyanuric esters result when silver cyanurate is heated with an alkyl iodide. Their alkyl-group is linked to nitrogen, since, on boiling with alkali, they yield a primary amine and carbon dioxide, a decomposition accounted for in constitutional formula II. The O-esters are formed when an alkyl iodide reacts with silver cyanurate at ordinary temperatures, but their conversion into the N-esters when heated explains the difference in the products obtained at ordinary and at elevated temperatures.

Klason has suggested that cyamelide (**244**) is *iso*cyanuric acid, and is related to the *iso*cyanuric esters in the same way as cyanuric acid is related to the normal cyanuric esters. The formation of cyanuric chloride by the action of phosphorus pentachloride on the normal esters and normal cyanuric acid and the fact that the *iso*-esters, and, as Senier has recently shown, cyamelide, do not yield chlorides under this treatment, support this view.

Important evidence in favour of the imino-formula for cyanuric acid has been furnished by Chattaway and Wadmore, who have succeeded in replacing the metal in potassium cyanurate by chlorine. They regard the compound formed as $(O:C:N\cdot Cl)_3$.

FINISH FOR REVIEW

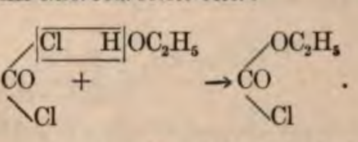
DERIVATIVES OF CARBONIC ACID.

248. *Carbonic acid*, H_2CO_3 or $CO(OH)_2$, is not known in the free state, but is supposed to exist in the solution of carbon dioxide in water; it decomposes very readily into its anhydride, carbon dioxide, and water. It is dibasic, and is generally described, with its salts, in inorganic chemistry ("Inorganic Chemistry," **184**). Some of its organic derivatives are dealt with in this section.

Carbonyl Chloride, $COCl_2$.

249. *Carbonyl chloride* (*phosgene*) is obtained by the action of chlorine on carbon monoxide. It was called phosgene by Sir Humphry Davy, under the impression that its formation by this means can only take place in presence of sunlight, a view since proved to be incorrect. Carbonyl chloride is a gas with a powerful, stifling odour; its solution in benzene, in which it is readily soluble, is a commercial product. It is employed in syntheses, both in the laboratory and in the arts.

The reactions of carbonyl chloride indicate that it is the chloride of carbonic acid. It is slowly decomposed by water, yielding hydrochloric acid and carbon dioxide. With alcohol at ordinary temperatures it first forms *chlorocarbonic ester:*



$$CO\begin{matrix}\diagup\boxed{Cl\quad H}OC_2H_5\\ \\ \diagdown Cl\end{matrix} + \quad \rightarrow CO\begin{matrix}\diagup OC_2H_5\\ \\ \diagdown Cl\end{matrix}.$$

By more prolonged treatment with alcohol, and also by the action of sodium alkoxide, *carbonic ester*, $CO(OC_2H_5)_2$, is produced. By the action of ammonia, the two Cl-atoms in carbonyl chloride can be replaced by amido-groups, with formation of the amide of carbonic acid, *urea*, $CO(NH_2)_2$ (**252**). All these reactions are characteristic of acid chlorides.

The chlorocarbonic esters, also called *chloroformic esters*, are colourless liquids of strong odour, and distil without decomposition. They are employed for the introduction of the group —$COOC_2H_5$ into compounds (**240**).

The carbonic esters are also liquids, but are characterized by the possession of an ethereal odour; they are insoluble in water, and are very readily saponified.

Carbon Disulphide, CS_2.

250. *Carbon disulphide* is manufactured synthetically by passing sulphur-vapour over red-hot carbon. The crude product has a very disagreeable odour, which can be removed by distilling from fat, the pure product being an almost colourless, highly refractive liquid of ethereal odour. It is insoluble in water, boils at 46°, and has a specific gravity of 1·262 at 20°. Carbon disulphide is poisonous, and, as it is highly inflammable, must be handled with great care. It is an excellent solvent for fats and oils, and finds extensive application in the extraction of these from seeds. It is also employed in the process of vulcanizing indiarubber.

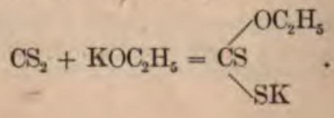
Carbon disulphide is a stable compound, and resists the action of heat, although it is an endothermic substance ("Inorganic Chemistry," **119**). It is, however, possible to make its vapour explode by means of mercury fulminate. The halogens have little action on it at ordinary temperatures, but in presence of a halogen-carrier chlorine and bromine can effect substitution, with production of carbon tetrachloride and tetrabromide respectively.

Carbon disulphide, like carbon dioxide, is the anhydride of an acid, or an anhydrosulphide. With alkali-sulphides it yields *trithiocarbonates:*

$$BaS + CS_2 = \underset{\text{Barium trithiocarbonate}}{BaCS_3}.$$

This barium salt is yellow, and dissolves in cold water with difficulty. By the addition of dilute acids to its salts, free *trithiocarbonic acid*, H_2CS_3, can be obtained in the form of an oil which decomposes readily. The potassium salt is employed in the destruction of vine-lice.

The potassium salt of *xanthic acid* is formed by the action of potassium ethoxide on carbon disulphide:



$$CS_2 + KOC_2H_5 = CS\begin{matrix} \diagup OC_2H_5 \\ \diagdown SK \end{matrix}.$$

This is effected by shaking up carbon disulphide with a solution of caustic potash in absolute alcohol, when potassium xanthate separates in the form of yellow, glittering needles. Free xanthic acid is very unstable; it owes its name (ξανθός, yellow) to its cuprous salt, which has a yellow colour, and results from the spontaneous transformation of the brownish-black cupric salt, precipitated from a solution of copper sulphate by the addition of a xanthate.

Carbon Oxysulphide, COS.

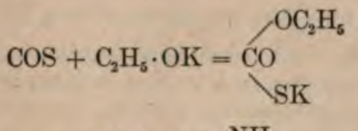
251. Carbon oxysulphide is a colourless, odourless, inflammable gas, and is obtained by the action of sulphuretted hydrogen on isocyanic esters:

$$2CO \cdot NC_2H_5 + H_2S = COS + CO(NHC_2H_5)_2.$$

Mention has been made (**245**) of its formation from isothiocyanic esters. It is also produced when a mixture of carbon monoxide and sulphur-vapour is passed through a tube at a moderate heat.

Carbon oxysulphide can also be obtained by a remarkable reaction; when carbon-disulphide vapour is passed over red-hot kaolin (aluminium silicate), which plays the part of an oxidizing-agent, one S-atom of the CS_2 is replaced by oxygen, and silicon disulphide, SiS_2, simultaneously formed.

Carbon oxysulphide is but slowly absorbed by alkalis. It yields salts with metallic alkoxides; these may be looked upon as derived from carbonates by simultaneous exchange of oxygen for sulphur:



$$COS + C_2H_5 \cdot OK = CO\begin{cases} OC_2H_5 \\ SK \end{cases}$$

Urea, $CO<^{NH_2}_{NH_2}$.

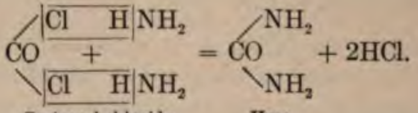
252. *Urea* owes its name to its occurrence in urine, as the final decomposition-product of the albumins in the body.

An adult excretes about 1500 grammes of urine, containing approximately 2 per cent. of urea, in twenty-four hours, so that the daily production of this substance amounts to about 30 grammes. To obtain urea from urine, the latter is first concentrated by evaporation, after which nitric acid is added; *urea nitrate*, $CO(NH_2)_2 \cdot HNO_3$, (**253**) is precipitated, and, on account of impurities, has a yellow colour. These colouring-matters are removed by dissolving the precipitate in water and oxidizing them with potassium permanganate. The urea is set free from the solution of the nitrate by treatment with barium carbonate:

$$\underset{\text{Urea nitrate}}{2CON_2H_4 \cdot HNO_3} + BaCO_3 = 2CON_2H_4 + Ba(NO_3)_2 + H_2O + CO_2.$$

On evaporation to dryness, a mixture of urea and barium nitrate is obtained from which the organic compound can be separated by solution in strong alcohol.

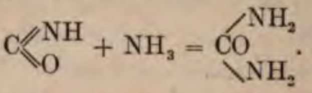
It has been stated (**249**) that urea is to be looked on as the amide of carbonic acid, on account of its formation from the chloride of this acid, carbonyl chloride, $COCl_2$, this reaction proving its constitution:



$$\underset{\text{Carbonyl chloride}}{CO\begin{cases}Cl \quad H\,NH_2 \\ \quad + \\ Cl \quad H\,NH_2\end{cases}} = \underset{\text{Urea}}{CO\begin{cases}NH_2 \\ NH_2\end{cases}} + 2HCl.$$

A confirmation of this view of the constitution of urea is its formation by the action of ammonia on carbonic ester.

Urea is formed by addition of ammonia to isocyanic acid:



$$C\begin{cases}NH \\ O\end{cases} + NH_3 = CO\begin{cases}NH_2 \\ NH_2\end{cases}.$$

Ammonium isocyanate dissolved in water is transformed into urea on evaporation of the solution. This is the method by which Wöhler effected his classic synthesis of urea (**1**).

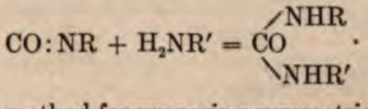
This reaction, which has an important bearing upon the history of organic chemistry, has been studied in detail by James Walker and Hambly. Their researches have shown that the reverse transformation of urea into ammonium isocyanate occurs also, since, on addition of silver nitrate, a solution of pure urea in boiling water yields a precipitate of silver cyanate. An equilibrium is attained:

$$\underset{\text{Urea}}{CO(NH_2)_2} \rightleftarrows \underset{\text{Ammonium isocyanate}}{CON \cdot NH_4}.$$

When this is reached, the solution only contains a very small percentage of isocyanate. It is almost independent of the temperature, proving that the transformation of the systems into one another is accompanied by but slight calorific effect (**100**).

The following is a proof that the formation of urea is occasioned by the interaction of NH_4-ions and CON-ions. The reaction would be unimolecular if it were caused by molecules of ammonium isocyanate, and if it were, on the other hand, a reaction between ions, the velocity equation for bimolecular reactions (**101**) would apply ("Inorganic Chemistry," **51**), as is actually the case. It has also been observed that addition of both ammonium sulphate (NH_4-ions) and potassium isocyanate (CNO-ions) accelerates the transformation into urea by an amount equal to that deduced from the increase in concentration of the ions.

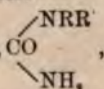
253. It was mentioned (**244**) that isocyanic esters are decomposed by water, with formation of primary amines and carbon dioxide. If the primary amine formed is brought into contact with a second molecule of isocyanic ester, addition takes place, with production of a *symmetrical dialkyl-urea:*

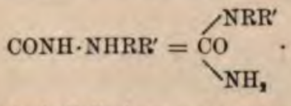


$$\mathrm{CO{:}NR + H_2NR' = CO}\begin{matrix}\diagup\mathrm{NHR}\\ \diagdown\mathrm{NHR'}\end{matrix}.$$

This is a general method for preparing symmetrical dialkyl-ureas.

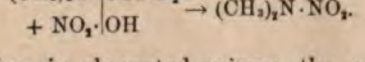
A *monoalkyl-urea* is obtained by the action of ammonia, instead of an amine, upon an isocyanic ester.

Unsymmetrical dialkyl-ureas,  $\mathrm{CO}\begin{matrix}\diagup\mathrm{NRR'}\\ \diagdown\mathrm{NH_2}\end{matrix}$, are prepared by the action of isocyanic acid on secondary amines; the method of procedure is analogous to that employed in WÖHLER's synthesis of urea, and consists in warming a solution of the isocyanate of a secondary amine:



$$\mathrm{CONH{\cdot}NHRR' = CO}\begin{matrix}\diagup\mathrm{NRR'}\\ \diagdown\mathrm{NH_2}\end{matrix}.$$

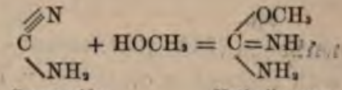
The unsymmetrical dialkyl-ureas are converted by treatment with absolute (100%) nitric acid into nitro-compounds, which were discovered by FRANCHIMONT, and are called *nitramines:*



$$\begin{matrix}\mathrm{(CH_3)_2N{\cdot}}\\ \mathrm{+\ NO_2{\cdot}}\end{matrix}\left|\begin{matrix}\mathrm{CONH_2}\\ \mathrm{OH}\end{matrix}\right. \rightarrow \mathrm{(CH_3)_2N{\cdot}NO_2}.$$

Urea crystallizes in elongated prisms, the crystals resembling those of potassium nitrate; they are very soluble in water, and melt at 132°. Like the amines, urea forms salts by addition of one molecule of a monobasic acid: of these the *nitrate*, $CON_2H_4{\cdot}HNO_3$, and the *oxalate*, $2CON_2H_4\cdot C_2H_2O_4$, dissolve with difficulty in solutions of the corresponding acids.

In some of its reactions, particularly in certain condensation-processes, urea behaves as though it had the structure $\begin{array}{l}\;/\!\!/NH\\ C{-}OH.\\ \;\backslash NH_2\end{array}$ An ether of this *isourea* is obtained by addition of methyl alcohol to cyanamide, the reaction being facilitated by the presence of hydrochloric acid :



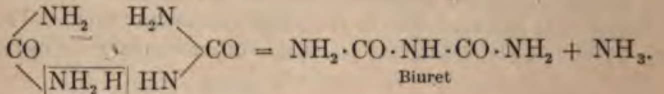
$$\begin{array}{l}\;/\!\!/N\\ C\\ \;\backslash NH_2\end{array} + HOCH_3 = \begin{array}{l}\;/OCH_3\\ C{=}NH\\ \;\backslash NH_2\end{array}$$

Cyanamide Methylisourea

This method of formation indicates the constitution of the compound, which can also be deduced in other ways, such as the production of methyl chloride on heating with hydrochloric acid, which indicates that the CH_3-group is not in union with nitrogen, since under this treatment *methylurea*, $\begin{array}{l}\;/NH_2\\ CO\\ \;\backslash NHCH_3\end{array}$, splits off methylamine, $CH_3\cdot NH_2$.

When heated, urea melts; it then begins to evolve a gas, consisting principally of ammonia, but also containing carbon dioxide; after a time the residue solidifies. The following reactions take place.

Two molecules of urea lose one molecule of ammonia, with production of *biuret* :

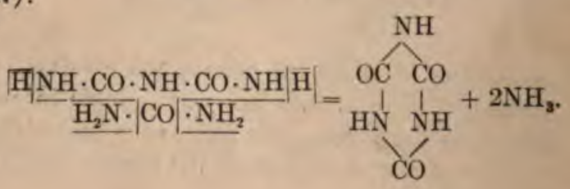


$$\begin{array}{l}\;/NH_2\\ CO\\ \;\backslash\boxed{NH_2\,H}\end{array}\;\begin{array}{l}H_2N\diagdown\\ \qquad\quad CO\\ HN\diagup\end{array} = NH_2\cdot CO\cdot NH\cdot CO\cdot NH_2 + NH_3.$$

Biuret

This is a crystalline substance which melts at 190°, and gives a characteristic red colouration when copper sulphate and caustic potash are added to its aqueous solution.

On further heating, biuret unites with a molecule of unaltered urea, with elimination of ammonia, and formation of cyanuric acid (**247**):



$$\begin{array}{c}\boxed{H}\underline{NH\cdot CO\cdot NH\cdot CO\cdot NH}\boxed{H}\\ \underline{H_2N\cdot}\boxed{CO}\underline{\cdot NH_2}\end{array} = \begin{array}{c}NH\\ OC\quad CO\\ |\qquad\;|\\ HN\quad NH\\ CO\end{array} + 2NH_3.$$

Like the acid amides, when heated with bases urea decomposes, yielding carbon dioxide and ammonia.

The *quantitative estimation of urea in urine* is an operation of considerable importance in physiological chemistry, and is effected by different methods. BUNSEN's process depends upon the decomposition of urea into carbon dioxide and ammonia, on heating with an ammoniacal solution of baryta; the carbon dioxide is thus converted into barium carbonate, which can be collected and weighed. In KNOP's method the nitrogen is quantitatively set free by treatment of the urea solution with one of caustic potash and bromine (German, *Bromlauge*), in which potassium hypobromite is present; the quantity of urea can be calculated from the volume of nitrogen liberated. LIEBIG's titration-method is based upon the formation of a white precipitate of the composition $2CON_2H_4 \cdot Hg(NO_3)_2 \cdot 3HgO$, when mercuric nitrate solution is run into a dilute solution of urea (of about 2 per cent. concentration). When excess of the mercury salt has been added, a drop of the liquid brought into contact with a solution of sodium carbonate gives a yellow precipitate of basic nitrate of mercury. Urine contains substances which interfere with these methods of estimation; an account of the mode of procedure by which the correct percentage of urea can be ascertained will be found in text-books of physiological chemistry.

start

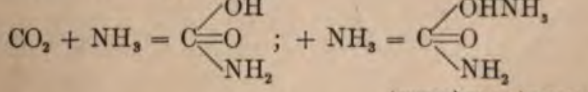
Potassium cyanate and hydrazine hydrate, $H_2N \cdot NH_2 + H_2O$, react together, with formation of *semicarbazide*, $NH_2 \cdot CO \cdot NH \cdot NH_2$, a base which melts at 96°, and combines with aldehydes and ketones similarly to hydroxylamine:

$$R_2 \cdot C\boxed{O + H_2}N \cdot NH \cdot CO \cdot NH_2 \rightarrow R_2 \cdot C:N \cdot NH \cdot CO \cdot NH_2.$$

The compounds thus formed are called *semicarbazones*; they sometimes crystallize well, and are employed in the identification and separation of aldehydes and ketones.

Derivatives of Carbamic Acid.

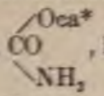
254. *Carbamic acid*, $NH_2 \cdot CO \cdot OH$, which is the semi-amide of carbonic acid, is not known in the free state, but only as salts, esters, and chloride. The *ammonium salt* is formed by the union of dry carbon dioxide with dry ammonia:



$$CO_2 + NH_3 = C\begin{cases} OH \\ =O \\ NH_2 \end{cases}; + NH_3 = C\begin{cases} OHNH_4 \\ =O \\ NH_2 \end{cases}$$

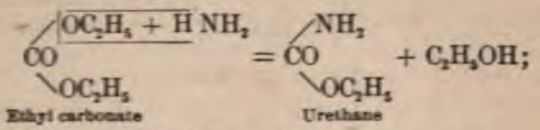
Ammonium carbamate

No precipitate is formed when carbon dioxide is passed into an ammoniacal solution of calcium chloride, since the resulting *calcium carbamate*, $\mathrm{CO}\begin{matrix}\diagup \mathrm{Oca}^{*}\\ \diagdown \mathrm{NH_2}\end{matrix}$, is soluble in water.

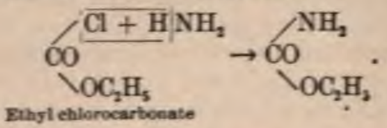


When the salts of carbamic acid are heated in solution, they readily take up water, forming carbonates.

The *esters of carbamic acid* are called *urethanes*. They are formed by the action of ammonia or amines upon the esters of carbonic acid or chlorocarbonic acid:

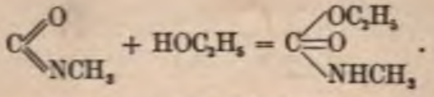


$$\underset{\text{Ethyl carbonate}}{\mathrm{CO}\begin{matrix}\diagup \boxed{\mathrm{OC_2H_5 + H}}\,\mathrm{NH_2}\\ \diagdown \mathrm{OC_2H_5}\end{matrix}} = \underset{\text{Urethane}}{\mathrm{CO}\begin{matrix}\diagup \mathrm{NH_2}\\ \diagdown \mathrm{OC_2H_5}\end{matrix}} + \mathrm{C_2H_5OH};$$



$$\underset{\text{Ethyl chlorocarbonate}}{\mathrm{CO}\begin{matrix}\diagup \boxed{\mathrm{Cl + H}}\,\mathrm{NH_2}\\ \diagdown \mathrm{OC_2H_5}\end{matrix}} \rightarrow \mathrm{CO}\begin{matrix}\diagup \mathrm{NH_2}\\ \diagdown \mathrm{OC_2H_5}\end{matrix}.$$

Urethanes also result from the action of alcohol upon isocyanuric esters:



$$\mathrm{C}\begin{matrix}\nearrow \mathrm{O}\\ \searrow \mathrm{NCH_3}\end{matrix} + \mathrm{HOC_2H_5} = \mathrm{C}\begin{matrix}\diagup \mathrm{OC_2H_5}\\ = \mathrm{O}\\ \diagdown \mathrm{NHCH_3}\end{matrix}.$$

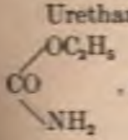
Urethanes are also obtained by boiling acid azides (**105**) with alcohol:

$$\mathrm{R{\cdot}CON_3 + C_2H_5OH = R{\cdot}NHCOOC_2H_5 + N_2}.$$

Since the azides are easily prepared from the corresponding acids, and the urethanes readily yield the corresponding amines, the carboxyl-group can by this means be easily replaced by the amido-group:

$$\underset{\text{Acid}}{\mathrm{R{\cdot}COOH}} \rightarrow \underset{\text{Ester}}{\mathrm{R{\cdot}COOC_2H_5}} \rightarrow \underset{\text{Hydrazide}}{\mathrm{R{\cdot}CONHNH_2}} \rightarrow \underset{\text{Azide}}{\mathrm{R{\cdot}CON_3}} \rightarrow$$
$$\rightarrow \underset{\text{Urethane}}{\mathrm{R{\cdot}NHCOOC_2H_5}} \rightarrow \underset{\text{Primary amine}}{\mathrm{R{\cdot}NH_2}}.$$

Urethanes distil without decomposition; ordinary urethane, $\mathrm{CO}\begin{matrix}\diagup \mathrm{OC_2H_5}\\ \diagdown \mathrm{NH_2}\end{matrix}$, melts at 51°, and is very readily soluble in water. When



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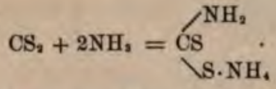
*ca = $\frac{1}{2}$Ca.

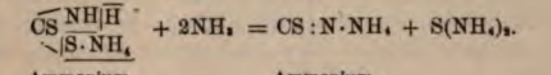
boiled with bases, it decomposes into alcohol, carbon dioxide, and ammonia.

Corresponding sulphur derivatives can be prepared by analogous methods; carbon disulphide and alcoholic ammonia yield *ammonium dithiocarbamate :*



$$\mathrm{CS_2 + 2NH_3 = CS}\begin{cases}\mathrm{NH_2}\\ \mathrm{S\cdot NH_4}\end{cases}.$$

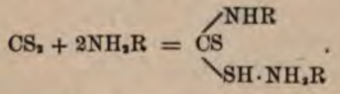
This salt is unstable, and on treatment with more ammonia readily loses sulphuretted hydrogen, forming *ammonium thiocyanate :*



$$\mathrm{CS}\begin{cases}\mathrm{NH|\overline{H}}\\ \mathrm{|\underline{S\cdot NH_4}}\end{cases} + \mathrm{2NH_3 = CS:N\cdot NH_4 + S(NH_4)_2}.$$

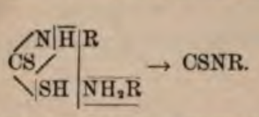
Ammonium dithiocarbamate — Ammonium thiocyanate

Primary amines also add on CS_2, in a manner analogous to ammonia:



$$\mathrm{CS_2 + 2NH_2R = CS}\begin{cases}\mathrm{NHR}\\ \mathrm{SH\cdot NH_2R}\end{cases}.$$

In presence of mercuric or ferric chloride, these substituted dithiocarbamates also lose sulphuretted hydrogen readily, yielding *mustard-oils* (**245**) :



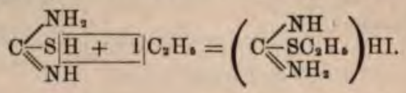
$$\mathrm{CS}\begin{cases}\mathrm{N|\overline{H}|R}\\ \mathrm{SH\,|\underline{NH_2R}}\end{cases} \rightarrow \mathrm{CSNR}.$$

This reaction is used as a test for primary amines, since traces of the mustard-oils can be readily detected by their characteristic odour.

Thiourea, $CS(NH_2)_2$.

255. Ammonium iso*thio*cyanate yields *thiourea* in a manner analogous to the formation of urea from ammonium isocyanate (**252**). The transformation of the thio-compound can in this instance be effected by heating it in the dry state, but is no more complete than that of ammonium cyanate, since thiourea is converted by heat into ammonium isothiocyanate. Alkyl-derivatives of thiourea result from addition of ammonia or amines to the mustard-oils, the reaction being similar to the formation of alkyl-substituted ureas from isocyanic esters (*loc. cit.*).

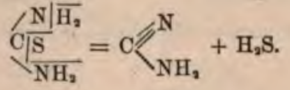
These modes of formation prove that the constitution of thiourea is expressed by the formula $CS(NH_2)_2$, being similar to that of urea. Derivatives of thiourea are also known, however, which indicate the existence of a tautomeric form $C\begin{matrix}/NH_2\\ -SH\\ \backslash\!\!\backslash NH\end{matrix}$ (**253**); thus, on addition of an alkyl iodide, compounds are obtained in accordance with the equation



$$C\begin{matrix}NH_2\\ S|\overline{H + I}|C_2H_5\\ NH\end{matrix} = \left(C\begin{matrix}NH\\ SC_2H_5\\ NH_2\end{matrix}\right)HI.$$

The alkyl-group in this compound is in union with sulphur; for it decomposes with formation of mercaptan, and on oxidation yields a sulphonic acid.

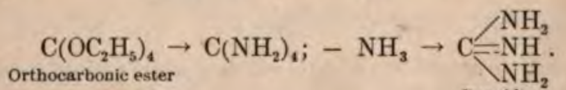
Thiourea forms well-defined crystals, melting at 172°, and readily soluble in water, but with great difficulty in alcohol. On treatment with mercuric oxide, it loses sulphuretted hydrogen, forming cyanamide:



$$C\begin{matrix}N|\overline{H_2}\\ |S\\ \underline{NH_2}\end{matrix} = C\begin{matrix}\equiv N\\ -NH_2\end{matrix} + H_2S.$$

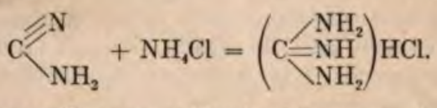
Guanidine, CN_3H_5.

256. *Guanidine* is formed by the interaction of ammonia and orthocarbonic esters or chloropicrin (**151**). This probably takes place through addition of four amido-groups to the carbon atom, the compound formed then losing one molecule of ammonia:



$$\underset{\text{Orthocarbonic ester}}{C(OC_2H_5)_4} \rightarrow C(NH_2)_4; - NH_3 \rightarrow \underset{\text{Guanidine}}{C\begin{matrix}NH_2\\ =NH\\ NH_2\end{matrix}}.$$

This method of preparing guanidine proves it to have the constitutional formula indicated, a view which finds support in the synthesis of this compound from ammonia and cyanamide effected by heating the latter with an alcoholic solution of ammonium chloride:

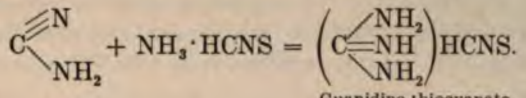


$$C\begin{matrix}\equiv N\\ -NH_2\end{matrix} + NH_4Cl = \left(C\begin{matrix}NH_2\\ =NH\\ NH_2\end{matrix}\right)HCl.$$

Guanidine is generally prepared by heating ammonium thiocyanate at 180°–185°, when it is obtained in the form of guanidine thiocyanate, the reaction taking place in stages:

$$\underset{\text{Ammonium thiocyanate}}{SCNH\cdot NH_3} \rightarrow \underset{\text{Thiourea}}{CS(NH_2)_2} \rightarrow \underset{\text{Cyanamide}}{H_2N\cdot CN}.$$

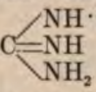
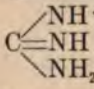
The cyanamide unites with a molecule of the unaltered ammonium thiocyanate:



$$C\begin{matrix}\equiv N\\ \diagdown NH_2\end{matrix} + NH_3\cdot HCNS = \left(C\begin{matrix}\diagup NH_2\\ =NH\\ \diagdown NH_2\end{matrix}\right)HCNS.$$

Guanidine thiocyanate

Guanidine is a colourless, crystalline substance, and readily absorbs moisture and carbon dioxide from the atmosphere. It is a strong base, unlike urea, which has a neutral reaction: the strengthening of the basic character, occasioned by exchange of carbonyl-oxygen for an imido-group, is worthy of notice. Guanidine yields many well-defined, crystalline salts.

Nitroguanidine,  $C\begin{matrix}\diagup NH\cdot NO_2\\ =NH\\ \diagdown NH_2\end{matrix}$, is obtained by the action of fuming nitric acid upon guanidine; when the solution in the strong acid is poured into water, the slight solubility of the nitroguanidine causes its precipitation. On reduction, it yields *aminoguanidine*,  $C\begin{matrix}\diagup NH\cdot NH_2\\ =NH\\ \diagdown NH_2\end{matrix}$, which, on boiling with dilute acids or alkalis, decomposes with formation of carbon dioxide, ammonia, and *diamide* or *hydrazine*, $H_2N\cdot NH_2$ ("Inorganic Chemistry," **114**), a reaction which proves the constitution of nitroguanidine and aminoguanidine.

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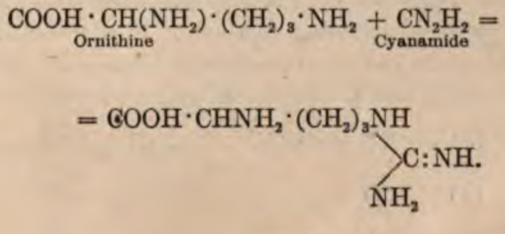
An important derivative of guanidine is *arginine*, $C_6H_{14}N_4O_2$, obtained from proteïd compounds. It can be synthesized by the action of cyanamide on ornithine (**200**):



$$\underset{\text{Ornithine}}{COOH\cdot CH(NH_2)\cdot(CH_2)_3\cdot NH_2} + \underset{\text{Cyanamide}}{CN_2H_2} =$$

$$= COOH\cdot CHNH_2\cdot(CH_2)_3NH\begin{matrix}\diagdown\\ \diagup\end{matrix}C:NH.\quad (NH_2)$$

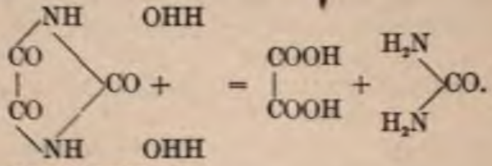
Arginine

It is, however, not quite certain whether the cyanamide adds itself to the ω-NH_2-group, as represented here, or to the α-NH_2-group.

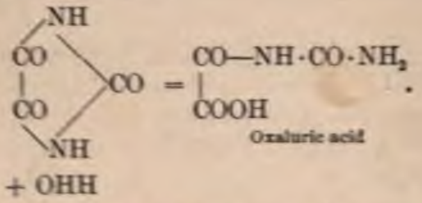
FINISH

257. *Uric acid*, $C_5H_4N_4O_3$, derives its name from its presence in small amount in urine; it is the central point of an important group of urea derivatives. It is closely related to the *ureïdo-acids* and the *acid-ureïdes* (*ureïdes*), which are amino-acids and acid amides, containing the urea-residue, $NH_2\cdot CO\cdot NH—$, instead of the NH_2-group.

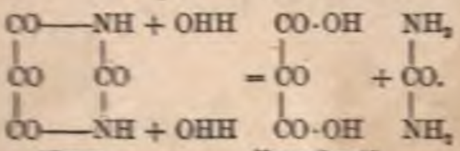
Parabanic acid, $C_3H_2N_2O_3$, may be cited as one of the acid-ureïdes; it is obtained by the oxidation of uric acid. When warmed for a long time with alkalis, parabanic acid takes up two molecules of water, forming urea and oxalic acid, a reaction which proves it to be *oxalylurea:*


Parabanic acid (Oxalylurea)

On careful treatment with alkalis, it takes up only one molecule of water, yielding *oxaluric acid:*


Oxaluric acid

Alloxan, $C_4H_2N_2O_4$, is an important decomposition-product of uric acid, from which it is obtained by oxidation with nitric acid; it can also be prepared by other methods. It is to be looked on as *mesoxalylurea*, since, on treatment with alkalis, it takes up two molecules of water, with production of urea and mesoxalic acid:

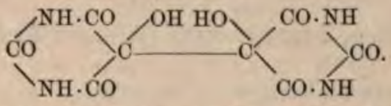


$$\begin{array}{llcllcl} CO & —NH + OHH & & CO\cdot OH & & NH_2 \\ | & | & & | & & | \\ CO & CO & = & CO & + & CO. \\ | & | & & | & & | \\ CO & —NH + OHH & & CO\cdot OH & & NH_2 \end{array}$$

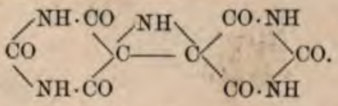
Alloxan Mesoxalic acid

Carbon dioxide and parabanic acid are produced by the oxidation of alloxan with nitric acid.

Alloxan is converted by reduction into *alloxantine*, the reaction being analogous to the formation of pinacone from acetone (**156**); alloxantine has therefore the structure

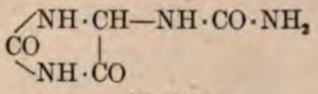


Alloxantine is also formed directly from uric acid by evaporating it to dryness with dilute nitric acid. When treated with ammonia, it forms a purple-red dye, *murexide*, the ammonium salt of *purpuric acid;* to this acid is assigned the constitution



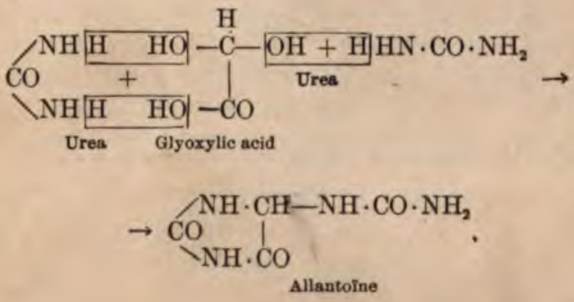
This formation of murexide is employed as a *test for uric acid.* Alloxantine is only soluble with considerable difficulty in cold water, and gives a fine blue colour with baryta-water.

Allantoïne is a decomposition-product of uric acid, a fact which has an important bearing on the constitution of this compound, from which it results on oxidation with potassium permanganate. It has the structure

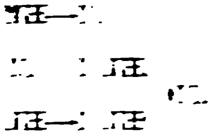


Allantoïne

since it can be obtained synthetically by heating glyoxylic acid with urea:



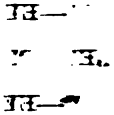
[illegible] gives an [illegible] indicating the presence [illegible] the second, the presence [illegible] These [illegible]



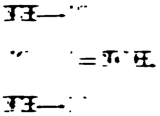
[illegible]

This [illegible] gives [illegible] to the other chemical proper-ties [illegible]

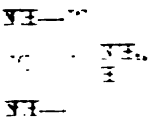
The [illegible] of the [illegible] of the [illegible] acid and [illegible] to [illegible] acid:



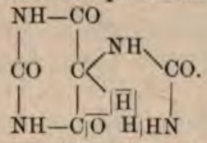
[illegible] with [illegible] acid, [illegible] yields an [illegible] which [illegible] from [illegible] and hydroxyl-[illegible] acid:



On [illegible] acid gives [illegible] acid.



which, like the amines, adds on one molecule of isocyanic acid when brought into contact with potassium cyanate, forming

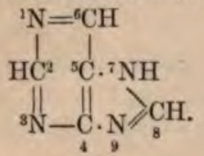


This substance is *pseudo-uric acid*, and only differs from uric acid in containing the elements of another molecule of water, which, by boiling with a large excess of hydrochloric acid of 20 per cent. strength, can be split off in the manner indicated in the formula; this treatment yields a substance with the constitution assigned to uric acid, and identical with this compound.

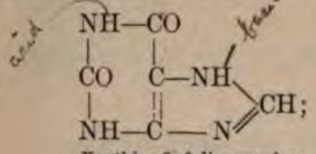
Uric acid dissolves with great difficulty in water, but is soluble in concentrated sulphuric acid, from which solution it is precipitated by addition of water. It forms two series of salts, by exchange of one or two hydrogen atoms respectively for metals. *Neutral sodium urate*, $C_5H_2N_4O_3Na_2 + H_2O$, is much more readily soluble in water than *acid sodium urate*, $2C_5H_3N_4O_3Na + H_2O$. The *neutral lithium salt* is moderately soluble in water.

Uric acid is present in urine, and is the principal constituent of the excrement of birds, reptiles, and serpents; it can be conveniently prepared from serpent-excrement. In certain pathological diseases of the human organism, such as gout, uric acid is deposited in the joints in the form of sparingly soluble acid salts. On account of the solubility of lithium urate, lithia-water is prescribed as a remedy.

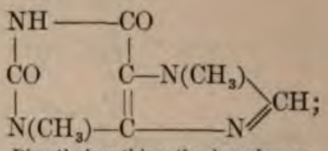
258. A considerable number of compounds, containing the same carbon-nucleus as uric acid, occur in nature, partly in the animal, and partly in the vegetable, kingdom. To the former belong *hypoxanthine*, $C_5H_4N_4O$; *xanthine*, $C_5H_4N_4O_2$; and *guanine*, $C_5H_5N_5O$; to the latter belong the vegetable bases *theobromine*, $C_7H_8N_4O_2$; and *caffeïne*, $C_8H_{10}N_4O_2$. In order to assign a rational nomenclature to these substances and other members of the same group, EMIL FISCHER regards them as derivatives of *purine* (p. 333), whose C-atoms and N-atoms are numbered as indicated in the formula



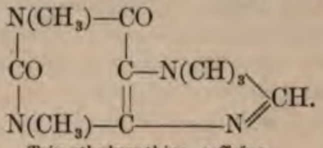
Xanthine, theobromine, and caffeïne have the following structural formulæ and rational names:



Xanthine 2:6-dioxypurine



Dimethylxanthine, theobromine, or 3:7-dimethyl-2:6-dioxypurine



Trimethylxanthine, caffeïne, or 1:3:7-trimethyl-2:6-dioxypurine

Theobromine and caffeïne result from the introduction of methyl-groups into xanthine.

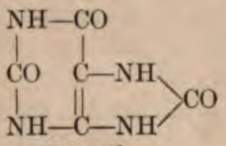
Xanthine, $C_5H_4N_4O_2$, is present in all the tissues of the human body. It is a colourless powder, soluble with difficulty in water, and possessing a weak basic character. On oxidation, it yields alloxan and urea.

Theobromine, $C_7H_8N_4O_2$, exists in cocoa, and is prepared from this source. It is only slightly soluble in water, and is converted by oxidation into *monomethylalloxan* and *monomethylurea*.

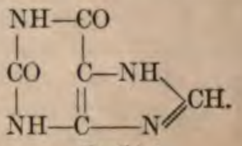
Caffeïne or *theïne*, $C_8H_{10}N_4O_2$, is a constituent of coffee and tea. It crystallizes with one molecule of water in long, silky needles, and is moderately soluble in water. It is generally prepared from tea-dust. On careful oxidation it yields *dimethylalloxan* and *monomethylurea*.

The position of the methyl-groups in theobromine and caffeïne is proved by the formation of these oxidation-products.

There is an evident resemblance between the constitution of uric acid and those of xanthine, theobromine, and caffeïne:



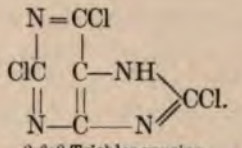
Uric acid



Xanthine

These formulæ indicate the possibility of obtaining xanthine by the reduction of uric acid, and up to the year 1897 numerous unsuccessful attempts were made to prepare it by this method, a reaction ultimately effected by EMIL FISCHER in that year. He has discovered several methods of converting uric acid into the three compounds mentioned above, including one by which the manufacture of the therapeutically important bases, theobromine and caffeïne, seems to be possible.

To convert uric acid into xanthine, it is first treated with phosphorus oxychloride, yielding 8-*oxy*-2:6-*dichloropurine;* this, on further careful treatment with the same reagent, is converted into 2:6:8-*trichloropurine:*



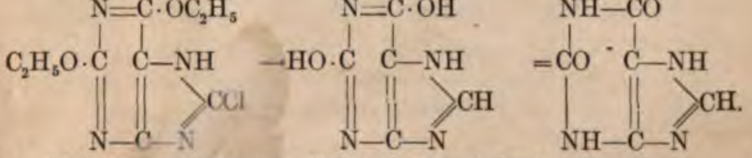
2:6:8-Trichloropurine

At 0° and in presence of hydriodic acid and phosphonium iodide this trichloropurine changes into *di-iodopurine:*

$$C_5HN_4Cl_3 + 4HI = C_5H_2N_4I_2 + 3HCl + 2I.$$

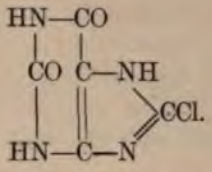
Reduction of the aqueous solution of di-iodopurine with zinc-dust yields *purine*, a white crystalline substance, melting at 216°-217°, and very readily soluble in water. It is a weak base, since it does not turn red litmus blue.

The Cl-atom 8 in trichloropurine is very stable towards alkalis, while the Cl-atoms 2 and 6 are displaced with comparative ease; when trichloropurine is treated with sodium ethoxide, the Cl-atoms 2 and 6 are exchanged for ethoxyl-groups. On heating the compound thus obtained with a solution of hydriodic acid, the ethyl-groups are replaced by hydrogen, the Cl-atom 8 being simultaneously exchanged for an H-atom, with formation of xanthine:



2:6-Diethoxy-8-chloropurine Xanthine (tautomeric form) Xanthine

When 2:6-diethoxy-8-chloropurine is heated with hydrochloric acid, only the ethyl-groups are replaced by hydrogen, with production of a compound of the formula



On methylating this substance, its three H-atoms are exchanged for methyl-groups, yielding *chlorocaffeïne*, which can be converted by nascent hydrogen into caffeïne. This is, therefore, a method of preparing caffeïne from uric acid.

Emil Fischer has discovered a very characteristic and simple mode of effecting this methylation—agitating an alkaline, aqueous solution of uric acid with methyl iodide, whereby the four hydrogen atoms are readily replaced by methyl-groups, with formation of a tetramethyluric acid. On treating this with phosphorus oxychloride, $POCl_3$, chlorocaffeïne is formed in accordance with the equation

$$3C_5N_4O_3(CH_3)_4 + POCl_3 = 3C_5N_4O_2(CH_3)_3Cl + PO(OCH_3)_3,$$

and can be converted by nascent hydrogen into caffeïne.

Electro-reduction of Purine Derivatives.

Tafel has stated that caffeïne, xanthine, uric acid, and other similar compounds, reducible with difficulty by the ordinary methods, readily add on hydrogen evolved by electrolysis. For this purpose the compounds are dissolved in sulphuric acid, the strength of which is varied to suit the particular compound, and lies between 50 and 75 per cent. This solution is contained in a porous cell, and a lead cathode immersed in it. This cell is placed in sulphuric acid of 20 to 60 per cent. strength, which contains the anode. The hydrogen evolved at the cathode by the current readily effects the reduction of the above-mentioned compounds.

Xanthine and its homologues take up four atoms of hydrogen, becoming transformed into *deoxy-derivatives:*

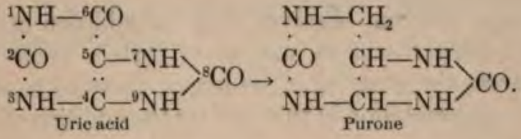
$$\underset{\text{Caffeïne}}{C_8H_{10}O_2N_4} + 4H = \underset{\text{Deoxycaffeïne}}{C_8H_{12}ON_4} + H_2O.$$

These are stronger bases than the original substances, which have very weakly basic properties.

The reduction of uric acid is somewhat remarkable, requiring six hydrogen atoms, and yielding purone:

$$\underset{\text{Uric acid}}{C_5H_4O_3N_4} + 6H = \underset{\text{Purone}}{C_5H_8O_2N_4} + H_2O.$$

It is the carbon atom 6 whose oxygen atom is replaced by hydrogen; at the same time, two hydrogen atoms are added at the double linking of the uric acid molecule:



$$\underset{\text{Uric acid}}{\begin{array}{l} {}^1NH-{}^6CO \\ {}^2CO \quad {}^5C-{}^7NH \\ {}^3NH-{}^4C-{}^9NH \end{array}} > {}^8CO \rightarrow \underset{\text{Purone}}{\begin{array}{l} NH-CH_2 \\ CO \quad CH-NH \\ NH-CH-NH \end{array}} > CO.$$

This structure is proved by the fact that purone yields two molecules of CO_2 on heating with baryta-water, so that it must contain two unaltered urea-residues, which necessitates the presence of the carbonyl-groups 2 and 8. The carbonyl-group 6 can be proved to be the one reduced in xanthine and its homologues.

Purone is neither a base nor an acid, and is not attacked by oxidizing-agents. When warmed with a 10 per cent. solution of caustic soda, it is transformed into *isopurone*, which has acidic properties, and is readily oxidized.

The application of the electro-reduction method was at first attended by many difficulties, greatly varying yields being obtained, even when the process was apparently carried out in exactly the same way. TAFEL has both discovered the cause of this anomaly, and indicated a method by which the process can be kept under control. His investigations are of general interest, and are worth describing in some detail.

In order to have a method of observing the course of the reduction process, TAFEL closed the porous cell with a stopper, through which the cathode and a delivery tube for the gas were introduced, care being taken to make the connections air-tight. A second apparatus, exactly similar to that used for the reduction, but containing acid alone, without the purine derivative, was introduced into the same circuit. Periodically, the gas from both was collected at the same time during a space of one minute. The difference between these quantities of gas is a direct measure of the course of the reduction during that minute, since it indicates the quantity of hydrogen used for the reduction.

When this quantity is represented graphically, the abscissæ standing for the time which has elapsed since the beginning of the experiment, and the ordinates for the quantity of hydrogen used for the reduction, the normal course of the latter must be indicated by Fig. 70, since the quantity of hydrogen absorbed in the unit of time must diminish in the same proportion as the quantity of unreduced purine derivative.

Tafel has, however, observed that the addition of traces of a platinum or copper salt, as well as of certain other salts, very quickly reduces the quantity of hydrogen absorbed to nearly zero, the graphic representation in this case for the addition of 0·04 milligrammes of platinum for each 100 square centimetres of cathode-surface is shown in Fig. 71. This indicates that the slightest contamination of the lead of the cathode by certain other metals is sufficient to almost wholly stop the electro-reduction.

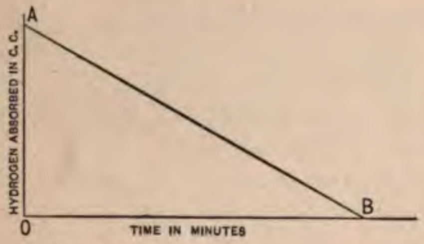


Fig. 70.—Normal Reduction Curve.

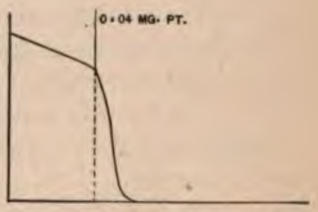


Fig. 71.—Abnormal Reduction Curve.

The following considerations afford an insight into the cause of this phenomenon. Hydrogen is only evolved by the passage of an electric current through dilute sulphuric acid when the difference of potential of the electrodes exceeds a certain value. This is a minimum when platinum electrodes are used, and very nearly coincides with the potential difference to be expected on theoretical grounds for a reversible hydrogen–sulphuric-acid–oxygen-element.

When the cathode is made of other metals, the difference of potential is greater before the evolution of hydrogen; for this a *supertension* (German, *Überspannung*) is necessary. This has a very large value for lead, but as soon as the least trace of platinum or of certain other metals is brought into contact with the surface of the lead cathode, the supertension disappears, and with it the power possessed by the evolving hydrogen of reducing purine derivatives.

This has a deeper lying cause. The difference of potential regulates the energy with which the discharged ions can react, for the pressure under which a discharged ion leaves the solution depends only upon the difference of potential. Nernst states that by varying the difference of potential it is possible to obtain pressures from the smallest fraction of an atmosphere up to many millions of atmospheres. Hence, reductions which are unattainable by other methods and without supertension are possible at cathodes where it exists.

SECOND PART.

THE AROMATIC COMPOUNDS, AND SUBSTANCES RELATED TO THEM.

INTRODUCTION.

259. With but few exceptions, the compounds described in the first part of this book contain an open chain. As examples of these exceptions, closed-chain compounds such as the lactones, the anhydrides of dibasic acids, and the uric acid group may be mentioned. The closed chain of these compounds is very readily opened, and the close relationship of their methods of formation and properties with those of the open-chain derivatives, makes it desirable that they should be included in a description of the fatty compounds.

There exists, however, a large number of substances containing closed chains of great stability towards every kind of chemical reagent, and whose properties differ in many important respects from those of the fatty compounds. Chief among these is *benzene*, C_6H_6, with its derivatives. The molecule of benzene contains a closed chain of six carbon atoms (**263**); this substance and its derivatives constitute the group of *aromatic compounds*. Benzene can take up six hydrogen atoms, with formation of *hexamethylene*, C_6H_{12}, a compound which also contains a closed carbon chain of six atoms, but approximates in properties to the fatty much more than to the aromatic group. Compounds of the formula C_nH_{2n} are also known, containing a closed chain of four or five carbon atoms, and they, too, have similar properties to the fatty compounds.

The closed chain, ring, or *nucleus*, in benzene and its derivatives, and in the closed-chain hydrocarbons C_nH_{2n}, consists of the atoms of a single element, carbon. Compounds of this kind are called *homocyclic*.

Closed chains containing atoms of two or more elements are also known: *pyridine*, C_5H_5N, and its derivatives, have a ring containing five C-atoms and one N-atom; *furfuran*, C_4H_4O, four C-atoms and one O-atom; *pyrrole*, C_4H_5N, four C-atoms and one N-atom; *thiophen*, C_4H_4S, four C-atoms and one S-atom; *pyrazole*, $C_3H_4N_2$, three C-atoms and two N-atoms; and numerous other examples might be cited. Such substances are classed together as *heterocyclic* compounds.

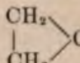
There exists another class of compounds containing *condensed rings*, or two closed chains with atoms common to each. A type of these is *naphthalene*, $C_{10}H_8$, containing two benzene-nuclei. Two dissimilar rings can also have atoms in common, as in *quinoline*, C_9H_7N, which contains a benzene-nucleus and a pyridine-nucleus.

Since numerous derivatives of all these compounds are known, the scope of this—the aromatic—division of organic chemistry is much more extended than that of the fatty series. The description of the aromatic group is, however, greatly simplified by the fact that in it the properties of alcohols, aldehydes, acids, etc., already described for the fatty compounds, are again met with.

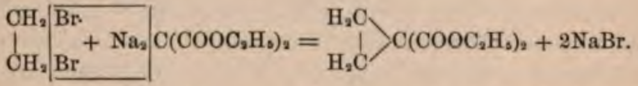
The most important of the closed-chain compounds are benzene and its derivatives, and these will be described after a brief consideration of the compounds of the formula C_nH_{2n}, containing rings of three, four, or five carbon atoms.

POLYMETHYLENE DERIVATIVES.

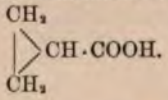
I. TRIMETHYLENE DERIVATIVES.

260. *Trimethylene*, C_3H_6 = , is obtained by the action of sodium on trimethylene bromide, $CH_2Br \cdot CH_2 \cdot CH_2Br$ (**154**). It is a gas, which liquefies at a pressure of from five to six atmospheres, and is not identical with propylene, $CH_2 : CH \cdot CH_3$, since with bromine it forms an addition-product only very slowly under the influence of sunlight, yielding trimethylene bromide. This reaction, together with its synthesis, proves it to have the above constitution.

Derivatives of trimethylene are obtained by the action of ethylene bromide on sodiomalonic ester:

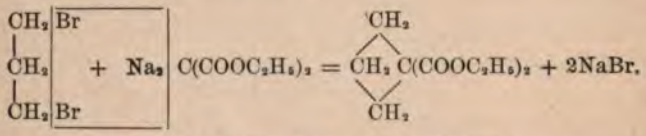


By saponification of this ester a dibasic acid is obtained which splits off CO_2 when heated, with formation of *trimethylenecarboxylic acid:*



II. TETRAMETHYLENE DERIVATIVES.

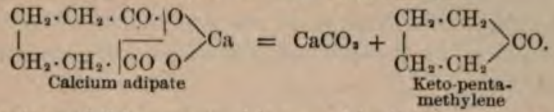
261. Tetramethylene itself is not known, but its derivatives are obtained analogously to trimethylene compounds. When sodiomalonic ester reacts with trimethylene bromide, the ester of a *tetramethylenedicarboxylic acid* is formed:



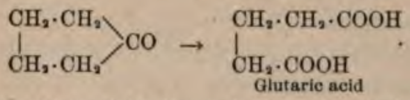
III. PENTAMETHYLENE DERIVATIVES.

262. Pentamethylene derivatives can be obtained by a similar method, the action of tetramethylene bromide on sodiomalonic ester.

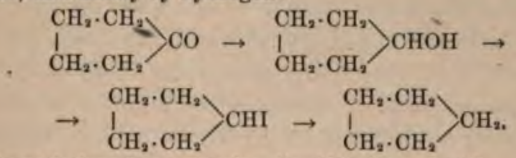
When the calcium salt of adipic acid is submitted to dry distillation, a keto-derivative of pentamethylene is formed:



The structure of this compound is proved by its oxidation to glutaric acid:



Pentamethylene is obtained by the reduction of this keto-derivative, the carbonyl-group taking up two H-atoms, with formation of a CHOH-group. By treatment with hydriodic acid, hydroxyl is first replaced by iodine, and finally by hydrogen:



Pentamethylene is a colourless liquid boiling at 50°.

According to the "tension theory" of BAEYER (**129**), the formation of a trimethylene-ring and a tetramethylene-ring necessitates an alteration in the direction of the affinities, since only in a chain of five carbon atoms are the affinities sufficiently near to one another to form a ring without being bent from their direction (**169**). It follows from this that the pentamethylene-ring must be very stable, while the tetramethylene-ring, and still more the trimethylene-ring, have a tendency to open, so as to bring back the bonds to their original direction. These conclusions are fully supported by experiment. Trimethylene forms an addition-product with bromine (**260**), and with other substances, such as hydriodic acid, whereby the closed chain is opened. The reaction does not take place so readily as the addition of bromine to substances containing a double bond, such as propylene, because the bonds of such compounds are more altered in direction, and are therefore more easily broken, than those of the closed chain of trimethylene. Pentamethylene does not yield an addition-product with bromine, and displays the same stability towards nitric acid and sulphuric acid as a saturated hydrocarbon; it thus shows no tendency to opening of the ring.

A consideration of the great resemblance between the properties of pentamethylene and of the saturated open-chain hydrocarbons leads to the important conclusion that *the formation of a ring does not in itself make any alteration in the properties of compounds* (**378**).

Analogous to the production of ketopentamethylene by the dry distillation of calcium adipate (p. 341) is that of ketopolymethylene derivatives from the calcium salts of the higher saturated dibasic fatty acids; thus, calcium pimelate, $C_7H_{10}O_4Ca$, yields *ketohexamethylene*, and calcium suberate, $C_8H_{12}O_4Ca$, yields *ketoheptamethylene* or *suberone*. The yield of the different homologues obtained completely agrees with BAEYER's theory; for the closed-chain compound with five C-atoms it is theoretical, and diminishes rapidly for its higher homologues with increase in the number of C-atoms, a proof of the instability of the rings containing six, seven, or more carbon atoms, of which further evidence is afforded by the conversion of hexamethylene compounds and aromatic derivatives into pentamethylene compounds by hydriodic acid at a high temperature.

Hexamethylene derivatives are described later (**270**).

FINISH

CONSTITUTION OF BENZENE.

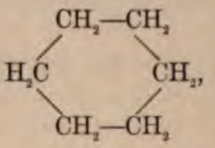
263. Certain substances found in the vegetable kingdom are characterized by the possession of an agreeable aroma; such are *oil of bitter almonds, oil of carraway, oil of cumin, balsam of Tolu, gum-benzoïn, vanilla,* etc. These vegetable-products consist principally of substances of somewhat similar character, which differ from the fatty compounds in containing much less hydrogen in proportion to the other elements: thus, *cymene,* $C_{10}H_{14}$, is obtained from oil of carraway; *toluene,* C_7H_8, from balsam of Tolu; and *benzoïc acid,* $C_7H_6O_2$, from gum-benzoïn. The saturated fatty compounds with the same number of C-atoms have the formulæ $C_{10}H_{22}$, C_7H_{16}, and $C_7H_{14}O_2$, respectively.

Before the nature of the so-called *aromatic* compounds had been closely investigated, and on account of their external similarity, it was customary to regard them as members of a single group, just as ordinary butter and "butter of antimony," $SbCl_3$, were classed together because of their similarity in consistency. This method of classification is still adopted for compounds with analogous properties, but of imperfectly understood constitution, such as the bitter principles, vegetable alkaloids, and many vegetable dyes.

A closer study of the aromatic compounds has shown that the old and somewhat arbitrary classification according to external resemblance is well founded, since all these substances may be looked upon as derivatives of one hydrocarbon, *benzene,* C_6H_6. just as the fatty compounds are to be regarded as derived from methane, CH_4. Thus, on oxidation, toluene yields benzoïc acid, whose calcium salt is converted into benzene by distillation with lime. The dibasic terephthalic acid, $C_8H_6O_4$, is formed by the oxidation of cymene, and can be similarly transformed into benzene.

The discovery of this relation by KEKULÉ brought into prominence the question of the constitution of benzene, the basis of all the aromatic compounds. When its formula, C_6H_6, is compared with that of the saturated paraffin containing six C-atoms, hexane, C_6H_{14}, it is seen that it contains a much smaller percentage of hydrogen, since there are eight H-atoms fewer in its molecule. It might be suggested that benzene, like other hydrocarbons poor in hydrogen, such as C_6H_{12} and C_6H_{10},contains multiple carbon bonds,but the properties of benzene do not admit of this assumption. Compounds containing a multiple carbon bond readily form addition-products with the halogens, are very sensitive to oxidizing-agents, and easily react with BAEYER's reagent (**123**): benzene lacks these properties. It yields halogen addition-products very slowly, whereas compounds with a multiple carbon bond form them instantaneously. It must, therefore, be concluded that benzene does not contain multiple carbon bonds, and that the carbon atoms in its molecule are linked together in a special manner.

Other considerations lead to the same conclusion. BAEYER has discovered certain dibasic acids, derivable from hexamethylene (cyclohexane),



by exchange of hydrogen for carboxyl. Removal of two or four hydrogen atoms from these hexamethylene derivatives yields compounds whose behaviour shows that they contain a multiple carbon bond. It would be expected that the abstraction of six hydrogen atoms would produce a compound of an even more unsaturated character, but a benzene derivative lacking all the properties conferred by a double bond is formed instead. The elimination of the third pair of hydrogen atoms from the hexamethylene derivative, unlike that of the first and second pair, occasions a sudden and complete change in properties.

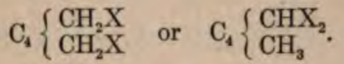
In order to understand the manner of linking of the benzene carbon atoms, it is first necessary to know the relative distribution of its hydrogen and carbon atoms. Two facts suffice to determine this. First, *no isomers of the monosubstitution-products of benzene exist.* Second, *the disubstitution-products exist in three isomeric forms.* Hence, there is only one monobromobenzene, C_6H_5Br; but three dibromobenzenes are known, and are distinguished by the prefixes *ortho*, *meta*, and *para*.

It follows from the first of these facts that *the six hydrogen atoms of benzene are of equal value;* that is, replacement of any one of them yields the same monosubstitution-product. Three formulæ, in which the six hydrogen atoms are of equal value, are possible for benzene:

$$\text{I. } C_4(CH_3)_2. \qquad \text{II. } C_3(CH_2)_3. \qquad \text{III. } (CH)_6.$$

It has now to be considered which of these formulæ agrees with the second fact stated above.

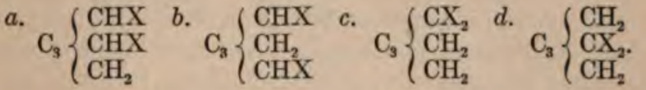
A disubstitution-product of a compound with formula I can be either



$$C_4\left\{\begin{matrix}CH_2X\\CH_2X\end{matrix}\right. \quad \text{or} \quad C_4\left\{\begin{matrix}CHX_2\\CH_3\end{matrix}\right..$$

No other isomers are possible, so that this formula is inadmissible, as leading to two, instead of to three, isomers.

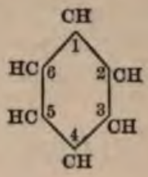
With formula II four isomers seem possible:



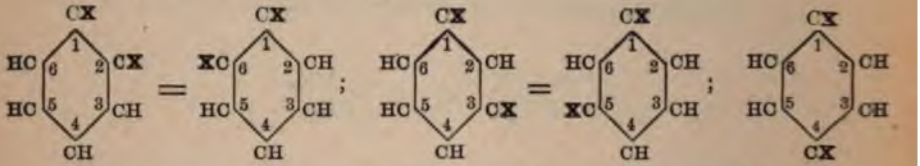
$$a.\ C_3\left\{\begin{matrix}CHX\\CHX\\CH_2\end{matrix}\right. \quad b.\ C_3\left\{\begin{matrix}CHX\\CH_2\\CHX\end{matrix}\right. \quad c.\ C_3\left\{\begin{matrix}CX_2\\CH_2\\CH_2\end{matrix}\right. \quad d.\ C_3\left\{\begin{matrix}CH_2\\CX_2\\CH_2\end{matrix}\right..$$

Since the hydrogen atoms in benzene are equivalent, the CH_2-groups in the benzene molecule must be similarly linked, so that $a = b$, and $c = d$; in other words, the number of possible isomers is reduced to two. Formula II cannot be accepted either, since it also fails to explain the formation of three isomeric disubstitution-products.

There remains only formula III, in which *each carbon atom is in union with one hydrogen atom.* The question of the constitution of benzene therefore narrows itself to this: given a compound C_6H_6, in which each carbon atom is linked to one hydrogen atom, the problem is to find a formula which accounts for the equivalence of all the hydrogen atoms, the formation of three disubstitution-products, and the absence of double or multiple bonds. It is evident that an open carbon-chain formula cannot fulfil the prescribed conditions, since the hydrogen atoms attached to such a chain containing terminal and intermediate CH-groups could not be equal. The six hydrogen atoms can only be of equal value with a closed chain of six C-atoms:

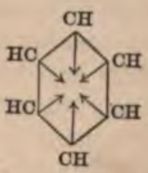


This arrangement of the CH-groups also fulfils the second condition, as is evident from the scheme:



in which the compounds $C_6H_4X_2$, 1:2 = 1:6, 1:3 = 1:5, and 1:4 are isomeric; the formation of three isomers is, therefore, also accounted for.

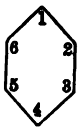
In this scheme, each carbon atom is in union with one hydrogen atom and two other carbon atoms, so that three bonds of each carbon atom are accounted for; it only remains to ascertain the mode of linking of the fourth carbon bond. A hypothetical explanation suggested by **Armstrong**, and also by **Baeyer**, is now regarded as affording the most probable explanation of the observed facts. They assume that the direction of the fourth bond of each C-atom is towards the centre of the benzene-ring, and that each bond is kept in equilibrium by the others, their mutual attraction causing the stability of the closed chain. This *centric* formula for benzene is



Such a mode of linking is unknown in the fatty series, so that it must be the cause of the properties peculiar to aromatic compounds, and lacked by those of the fatty series. Hence, this structural formula not only accounts for the isomerism of the derivatives of benzene, but also explains the "aromatic" character peculiar to them.

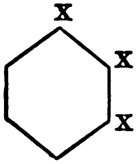
Nomenclature and Isomerism of the Benzene Derivatives

264. The different isomeric disubstitution-products are distinguished by the prefixes *ortho*, *meta*, and *para*, or the positions of their substituents are denoted by numbers:

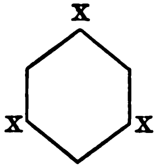


1:2 = 1:6 substitution-products are called *ortho*-compounds.
1:3 = 1:5 „ „ „ „ *meta*-compounds.
1:4 „ „ „ „ *para*-compounds.

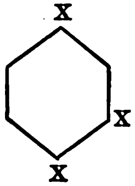
The number of isomeric substitution-products is the same for two similar or dissimilar substituting-groups, but not for three. Three isomers exist when the three groups are similar:



Adjacent or Vicinal
1:2:3



Symmetrical
1:3:5



Asymmetrical
1.3:4

When one of the groups is dissimilar to the other two, different vicinal derivatives result by substitution at 2 and at 3 respectively, and, for the asymmetrical compound, substitution at 3 produces a different compound from that resulting on exchange at 4. For four similar groups, the same number (three) of isomers is possible as for two, since the two remaining hydrogen atoms can be in the *ortho*-position, *meta*-position, or *para*-position to one another. The number of isomers possible in other cases can be readily determined.

An alkyl-radicle or other group linked to a benzene-residue, as in $C_6H_5 \cdot CH_3$, or $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CH_3$, is called a *side-chain,* the benzene-residue being called the *nucleus.* Substitution can take place both in the nucleus and in the side-chain; when in the former, it is usual to refer to the *position* of the substituent relative to those already present, the determination of which is called the *determination of position,* or *orientation,* of the substituents. The methods adopted for this will be found in **352** to **356.**

PROPERTIES CHARACTERISTIC OF THE AROMATIC COMPOUNDS: SYNTHESES FROM FATTY COMPOUNDS.

265. The saturated hydrocarbons of the fatty series are not attacked by concentrated nitric or sulphuric acid, and but slightly by oxidizing-agents; their halogen-substituted derivatives react very readily. The aromatic differ from the aliphatic hydrocarbons in all these points.

1. The aromatic hydrocarbons are readily attacked by concentrated nitric acid, with formation of *nitro-compounds:*

$$C_6H_5 \cdot \boxed{H + HO} NO_2 = \underset{\text{Nitrobenzene}}{C_6H_5 \cdot NO_2} + H_2O.$$

On reduction, these yield amino-derivatives, which proves them to be true nitro-compounds.

2. On treatment with concentrated sulphuric acid, the aromatic compounds yield *sulphonic acids:*

$$C_6H_5 \cdot \boxed{H + HO} \cdot SO_3H = \underset{\text{Benzenesulphonic acid}}{C_6H_5 \cdot SO_3H} + H_2O.$$

The sulphur of the SO_3H-group is linked to a carbon atom of the benzene-nucleus, since thiophenol, $C_6H_5 \cdot SH$, also yields benzenesulphonic acid on oxidation:

$$C_6H_5 \cdot SH \rightarrow C_6H_5 \cdot SO_3H.$$

3. The aromatic hydrocarbons with side-chains are readily oxidized to acids, the whole side-chain being usually oxidized back as far as the carbon atom in union with the nucleus, with formation of carboxyl.

4. Chlorobenzene and bromobenzene have their halogen atoms so strongly attached to the phenyl-group, C_6H_5, that they are almost incapable of taking part in double decompositions with such compounds as metallic alkoxides, salts, etc.

266. Various syntheses of aromatic from aliphatic compounds are known; some of them are very readily effected.

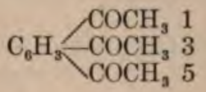
1. When the vapours of volatile fatty compounds are led through a red-hot tube, aromatic substances are among the products. The condensation of acetylene, C_2H_2, to benzene by this means is a typical example. A synthesis of benzene from carbon monoxide is described in **315.**

2. On treatment with sulphuric acid, acetone is converted into *mesitylene*, or 1:3:5-trimethylbenzene (**269**):

$$3C_3H_6O - 3H_2O = C_9H_{12}.$$

Other ketones condense similarly to aromatic hydrocarbons.

3. When liberated from its sodium compound, acetoacetaldehyde, $CH_3\cdot CO\cdot CH_2\,C\genfrac{}{}{0pt}{}{H}{O}$, at once changes into 1:3:5-triacetylbenzene,



$$C_6H_3\begin{cases} COCH_3 & 1 \\ COCH_3 & 3 \\ COCH_3 & 5 \end{cases}.$$

Acetoacetaldehyde can be obtained from acetone and formic ester by CLAISEN's condensation-method (**203**).

The inverse reaction, the conversion of aromatic into fatty compounds, is also possible.

1. When benzene-vapour is led through a red-hot tube, acetylene is produced. Since acetylene under the same conditions is converted into benzene, it follows that both reactions are incomplete.

2. *Catechol*, $C_6H_4(OH)_2$ (1:2), is oxidized by nitrous acid to *dihydroxytartaric acid*, $COOH\cdot C(OH)_2\cdot C(OH)_2\cdot COOH$. The constitution of this acid (**155**) follows from its combining with two molecules of hydroxylamine or of phenylhydrazine, which proves it to be a diketone, just as chloral hydrate, $CCl_3\cdot CH(OH)_2$, possesses nearly all the properties of aldehydes (**204**). On reduction, dihydroxytartaric acid yields tartaric acid, while on treatment with a concentrated solution of sodium hydrogen sulphite, it loses two molecules of carbon dioxide, and forms the sulphite derivative of glyoxal.

BENZENE AND THE AROMATIC HYDROCARBONS WITH SATURATED SIDE-CHAINS.

Gas-manufacture and its By-products ; Tar.

267. The aromatic hydrocarbons are used in large quantities in the manufacture of aniline dyes, and are obtained from coal-tar, a by-product in the manufacture of gas. A short description of this process will not be out of place, since it also yields other products of great importance in the manufacture of organic chemicals.

Coal is gradually heated in iron or clay retorts of a ⌓-shaped cross-section, being finally raised to a red heat; the gases and vapours are removed as completely as possible by means of exhausters. *Coke* remains in the retorts, and is employed as fuel, and in many metallurgical processes, although for the latter purpose the coke has usually to be prepared by special means.

The distillate contains three main products. 1. Gases (illuminating-gas). 2. An aqueous liquid, containing ammonia and other basic substances, such as pyridine bases. 3. Tar. These are separated from one another as completely as possible by a series of treatments. The crude gas is passed over iron ore, to remove the cyanogen derivatives. The purifying-material is employed for the preparation of potassium ferrocyanide (**243**), an important source of the cyanogen compounds.

Tar is a thick, black liquid with a characteristic odour. Its colour is due to suspended particles of carbon. It is a complicated mixture of neutral, acidic, and basic substances. The first are principally hydrocarbons, chiefly belonging to the aromatic series. About 5–10 per cent. of the tar consists of naphthalene, and 1–1·5 per cent. of a mixture of benzene and toluene. Phenol is the principal acidic constituent of tar. Basic substances are only present in small quantities, the chief being pyridine and quinoline, and their homologues.

In the synthesis of Friedel and Crafts more than one alkyl-group is generally introduced, the monosubstitution-products and the higher substitution-products being simultaneously formed; the homologues are separated by fractional distillation.

This reaction constitutes a method both for the building up and breaking down of a hydrocarbon. When toluene, $C_6H_5\cdot CH_3$, is treated with aluminium chloride, benzene, C_6H_6, and xylene, $C_6H_4(CH_3)_2$, are formed. The alkyl-groups of one hydrocarbon are exchanged for the hydrogen of the other. This reaction can also be brought about by the action of concentrated sulphuric acid upon aromatic hydrocarbons with a number of side-chains.

3. Like the saturated fatty hydrocarbons, the aromatic hydrocarbons are obtained by the distillation of the calcium salts of the aromatic acids with soda-lime:

$$C_6H_5\cdot\boxed{CO_2ca^* + caO}H = CaCO_3 + C_6H_6.$$

4. Benzene and its homologues can be obtained by heating the sulphonic acids with sulphuric or hydrochloric acid, the decomposition being facilitated by the introduction of superheated steam:

$$C_6H_3(CH_3)_2\boxed{SO_3H + HO}H = C_6H_4(CH_3)_2 + H_2SO_4.$$

This method can be employed in the separation of the aromatic hydrocarbons from the paraffins. When warmed with concentrated sulphuric acid, the former are converted into sulphonic acids soluble in water; the paraffins are unacted on and are insoluble in water, so that a mechanical separation is thus possible.

This method can also be applied to the separation of the aromatic hydrocarbons themselves, since some of them are more readily converted into sulphonic acids than others.

5. By heating an alcohol, an aromatic hydrocarbon, and zinc chloride at 270°–300°. The zinc chloride plays the part of a dehydrating-agent:

$$C_6H_5\boxed{H + HO}\cdot C_5H_{11} = C_6H_5—C_5H_{11} + H_2O.$$

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* ca = ½ Ca.

Individual Members.

269. Benzene and the aromatic hydrocarbons with saturated side-chains are colourless, highly refractive substances, liquid at ordinary temperatures, and possessing a characteristic odour. They are immiscible with water, but mix in all proportions with strong alcohol. Some of their physical properties are indicated in the table:

Name.	Formula.	Boiling-point.	Specific Gravity.
Benzene........................	C_6H_6	80·4°	0·874 (20°)
Toluene........................	$C_6H_5{\cdot}CH_3$	110°	0·869 (16°)
m-Xylene.................. ...	$C_6H_4<\begin{matrix}CH_3 & 1\\ CH_3 & 3\end{matrix}$	139°	0·881 (0°)
Mesitylene....................	$C_6H_3(CH_3)_3$ (1:3:5)	164°	0·865 (14°)
Ethylbenzene.................	$C_6H_5{\cdot}C_2H_5$	136°	0·883 (0°)
Isopropylbenzene (Cumene)...	$C_6H_5{\cdot}CH(CH_3)_2$	153°	0·866 (16°)
p-Methylisopropylbenzene (Cymene)...	$C_6H_4<\begin{matrix}CH_3 & 1\\ CH(CH_3)_2 & 4\end{matrix}$	175°	0·856 (20°)

Benzene was discovered by FARADAY in 1825 in a liquid obtained by submitting coal-gas to pressure.

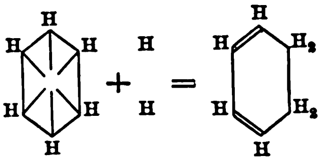
Xylene, or dimethylbenzene, exists in three isomeric forms; m-*xylene* is the principal constituent of the xylene in tar, being 70–85 per cent. of the whole.

The isomeric xylenes can only be separated with difficulty; their boiling-points lie very close together, that of *o*-xylene being 142°, while *m*-xylene and *p*-xylene boil at 139° and 138° respectively. This makes their separation by fractional distillation impracticable, but it can be effected by treating them with sulphuric acid at ordinary temperatures; *m*-xylene and *o*-xylene go into solution as sulphonic acids, while *p*-xylene remains undissolved. The sulphonic acids of the *meta*-compound and *ortho*-compound can be separated by fractional crystallization of their sodium salts, the *ortho*-salt crystallizing first.

Cymene, $C_{10}H_{14}$, is closely related to the terpenes, $C_{10}H_{16}$, and to the camphors, $C_{10}H_{16}O$, since it can be obtained from them in various ways. Cymene is a constituent of certain ethereal oils, such as *oil of carraway*, *oil of thyme*, and *oil of eucalyptus*.

Hydrogen Addition-products of the Aromatic Hydrocarbons.

270. When the aromatic hydrocarbons take up two or four hydrogen atoms, they lose their aromatic character and acquire properties peculiar to unsaturated compounds (**263**). The centric bonds may be supposed to be broken, with formation of double bonds (**316**):



Dihydrobenzene

Dihydrobenzene, C_6H_8, for example, reacts with a solution of permanganate and sodium carbonate, and also adds on four bromine atoms. *Tetrahydrobenzene*, C_6H_{10}, readily adds on two bromine atoms.

When six hydrogen atoms are taken up by benzene, there results *hexamethylene*, which melts at 2° and boils at 80·8°; it has the character of a saturated hydrocarbon of the fatty series. Hexamethylene, $(CH_2)_6$ or C_6H_{12}, and some of its isomers, are present in Russian petroleum; they are called *naphthenes*. They can be recognized as addition-products of the aromatic hydrocarbons from their yielding nitro-derivatives of these hydrocarbons on treatment with nitric acid. They differ from the isomeric olefines in not possessing the power of forming addition-products, and in their stability towards Baeyer's reagent (**123**).

Hexamethylene and its homologues can be obtained by the catalytic action of freshly-reduced nickel on a mixture of hydrogen and benzene or its homologues, the reaction taking place at a comparatively low temperature (**29**, **125**, and **133**).

W. H. Perkin, Jun., has prepared hexamethylene synthetically in the following manner. Chlorobromotrimethylene reacts with sodium ethoxide, yielding a chloro-ether:

$$Cl\cdot CH_2\cdot CH_2\cdot CH_2\cdot Br + NaOC_2H_5 \rightarrow Cl\cdot CH_2\cdot CH_2\cdot CH_2\cdot OC_2H_5.$$

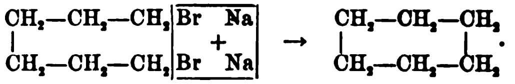
This compound is treated with sodium:

$$2C_2H_5O\cdot CH_2\cdot CH_2\cdot CH_2\cdot \boxed{Cl + Na_2} \rightarrow C_2H_5O\cdot (CH_2)_6\cdot OC_2H_5.$$

This double ether is then treated with hydrobromic acid,

$$C_2H_5O\cdot(CH_2)_6\cdot OC_2H_5 + 2HBr \rightarrow Br\cdot(CH_2)_6\cdot Br.$$

With sodium, the resulting dibromide yields hexamethylene:



$$\begin{array}{l}CH_2-CH_2-CH_2\\ |\\ CH_2-CH_2-CH_2\end{array}\boxed{\begin{array}{cc}Br & Na\\ & +\\ Br & Na\end{array}} \rightarrow \begin{array}{l}CH_2-CH_2-CH_2\\ |\qquad\qquad\quad\;\; |\\ CH_2-CH_2-CH_2\end{array}.$$

FINISH

MONOSUBSTITUTION-PRODUCTS OF THE AROMATIC HYDROCARBONS.

I. MONOSULPHONIC ACIDS.

271. The formation of these compounds has been described already (**265**); they are produced by the action of concentrated sulphuric acid upon aromatic compounds. In order to separate them from the excess of sulphuric acid, use is made of the ready solubility of their calcium and barium salts in water; the process is similar to the separation of ethyl hydrogen sulphate from sulphuric acid (**60**). They can also be separated from their concentrated solution containing sulphuric acid by the addition of common salt until no more will dissolve, when the sodium salt of the sulphonic acid separates in the solid state. This is dissolved in water, the equivalent quantity of mineral acid added, and the free sulphonic acid isolated by extraction with ether.

The sulphonic acids are colourless, crystalline substances, generally hygroscopic, and readily soluble in water. They can be reconverted into the aromatic hydrocarbons by treatment at a high temperature with hydrochloric acid, or with superheated steam (**268**, 4).

Most of the sulphonates crystallize well, and are employed in the purification of the sulphonic acids. On treatment with phosphorus pentachloride, the latter are converted into chlorides:

$$C_6H_5 \cdot SO_2 \cdot OH \rightarrow C_6H_5 \cdot SO_2 \cdot Cl.$$

The *sulphonic chlorides* are very stable towards cold water, being but slowly reconverted into sulphonic acids.

The *sulphonamides* are formed by the action of ammonium carbonate on the chlorides:

$$C_6H_5 \cdot SO_2Cl \rightarrow C_6H_5 \cdot SO_2 \cdot NH_2.$$

They are well-crystallized compounds; the determination of their

Individual Members.

Monochlorobenzene is a colourless liquid; it boils without decomposition at 132°, and has a specific gravity of 1·106 at 20°. *Monobromobenzene*, B.P. 157°, sp. gr. 1·491 at 20°. *Monoiodobenzene*, B.P. 188°, sp. gr. 1·861 at 0°.

Benzyl chloride is a colourless liquid of stupefying odour, intensified by warming; it boils at 178°, and has a specific gravity of 1·113 at 15°. *Benzyl iodide* is prepared by heating benzyl chloride with potassium iodide; it melts at 24°, and decomposes when boiled. It has a powerful and unbearably irritating odour, productive of tears.

Iodobenzene, and other iodine compounds, substituted in the nucleus, can add on two atoms of chlorine, with formation of compounds such as *phenyliodide chloride* or *iodobenzene dichloride*, $C_6H_5 \cdot ICl_2$. When digested with alkalis, these give *iodoso-compounds*, such as *iodosobenzene*, $C_6H_5 \cdot IO$, which are amorphous, yellowish solids. When heated, or oxidized with bleaching-powder, these compounds yield *iodoxy-compounds* (German, *Iodoverbindungen*),

$$2C_6H_5 \cdot IO = C_6H_5 \cdot I + \underset{\text{Iodoxybenzene}}{C_6H_5 \cdot IO_2}.$$

Iodoxybenzene is crystalline and explodes when heated.

The constitution of these compounds is inferred from their ready conversion into iodobenzene, this being effected for iodosobenzene by means of potassium iodide, and for iodoxybenzene by hydrogen dioxide, with evolution of oxygen. These substances would not be so readily converted into iodobenzene if the oxygen were attached to the benzene-nucleus.

FINITA

III. MONOHYDRIC PHENOLS AND AROMATIC ALCOHOLS.

274. The hydroxyl-compounds of the aromatic hydrocarbons display the same characteristic difference, occasioned by the union of the substituent with the nucleus or with the side-chain as the halogen derivatives (**272**). The OH-group in *phenol* (carbolic acid), $C_6H_5 \cdot OH$, is in union with the nucleus, and possesses a character unknown in the fatty series. A compound such as *benzyl alcohol*, $C_6H_5 \cdot CH_2OH$, whose constitution follows from its oxidation to benzoïc acid, $C_6H_5 \cdot COOH$, displays most of the properties characteristic of the aliphatic alcohols.

A. PHENOLS.

Phenol and some of its homologues, such as *cresol*, etc., are found in coal-tar, by the fractional distillation of which they are accumulated in the carbolic and creosote oils (**267**). They are isolated by shaking these fractions up with caustic alkali, which dissolves the phenols, leaving the hydrocarbons behind. They are liberated from the solution with sulphuric acid, and are then separated by fractional distillation. By far the larger proportion of the phenol found in commerce is obtained from this source.

Phenol and its homologues can further be obtained by the following methods.

1. By fusion of the salt of a sulphonic acid with alkali:

$$C_6H_5 \cdot SO_3K + 2KOH = C_6H_5 \cdot OK + K_2SO_3 + H_2O.$$

2. By the action of nitrous acid on aromatic amines, a method analogous to the preparation of alcohols of the fatty series from amines (**72**). But whereas on acting upon an aliphatic amine with nitrous acid the alcohol is produced directly, in this case very important intermediate products, the diazonium compounds (**302**), can be isolated.

3. By the action of oxygen upon benzene in presence of aluminium chloride, phenol is formed.

Properties of the Phenols.

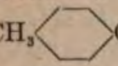
275. The phenols are in some respects comparable with the tertiary alcohols, since in both the hydroxyl is linked to a carbon atom in direct union with three others, although in the phenols one of these bonds is of a special kind. Like the tertiary alcohols, therefore, they cannot be oxidized to aldehydes, ketones, or acids containing the same number of C-atoms. The phenols exhibit many of the characteristics of the aliphatic alcohols; they are capable of forming ethers, when alkyl halides react with their alkali-salts; they produce esters, forming acetates, for example, with acetyl chloride. Phosphorus pentachloride substitutes Cl for their OH, although not so readily as in the fatty series. But in addition to these, the phenols possess special properties due to their much stronger acidic character. When describing the separation of phenol from carbolic oil (**267**), it was mentioned that they dissolve in caustic alkalis, forming *phenoxides*, such as $C_6H_5 \cdot ONa$. The alcohols of the fatty series do not possess this property in the same degree. Those which are insoluble in water do not dissolve in caustic alkalis, and are only converted into metallic alkoxides by the action of the alkali-metals. This increase in acidic character can only be occasioned by the presence of the phenyl-group; in other words, *the phenyl-group has a more negative character than an alkyl-group.* In other respects, the phenols are weak acids; their aqueous solutions are bad conductors of electricity, and the phenoxides are decomposed by carbonic acid.

It is thus seen that the properties of the hydroxyl-group are considerably modified by union with the phenyl-group. Inversely, the influence of the hydroxyl-group on the benzene-nucleus is equally marked, making the remaining hydrogen atoms much more readily substituted. Benzene is only slowly attacked by bromine at ordinary temperatures, but addition of bromine-water to an aqueous solution of phenol at once precipitates *tribromophenol*—a reaction employed in its quantitative estimation. The conversion of benzene into nitrobenzene necessitates the use of concentrated nitric acid, but phenol yields nitrophenol on treatment with the dilute acid. Phenols are also much more readily oxidized than the aromatic hydrocarbons.

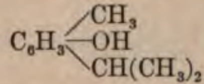
On distillation with zinc-dust, the phenols are reduced to the corresponding hydrocarbons. They can be detected by the formation of a violet colouration when ferric chloride is added to their aqueous solutions.

Individual Members.

276. *Phenol,* or *carbolic acid,* is a colourless substance, crystallizing in long needles. It melts at 39·6°, and boils without decomposition at 181°. It has a characteristic odour, and strong antiseptic properties. It was formerly largely employed in surgery, but to a great extent its place has been taken by mercuric chloride, or corrosive sublimate, $HgCl_2$. Phenol is soluble in water, 1 part dissolving in 15 at 16°; it can also dissolve water. On account of the small molecular weight of water, and the high molecular lowering of the freezing-point of phenol (75), a small percentage of water causes phenol to be liquid at ordinary temperatures (**14**). It follows from the equation $AM = 75$, in which M is the molecular weight of water (18), that A, the lowering of the freezing-point occasioned by the presence of 1 per cent. of water, is about 4·2°.

The hydroxytoluenes, $CH_3 \cdot C_6H_4 \cdot OH$, are called *cresols;* they are present in coal-tar, but are usually prepared from the corresponding amino compounds, or sulphonic acids. On oxidation, they are completely decomposed, but when the hydrogen of the hydroxyl-group is replaced by alkyl or acetyl, they can, like toluene itself, be oxidized to the corresponding acids. The cresols resemble phenol in their behaviour towards bromine-water. p-*Cresol*, CH_3OH, is a decomposition-product of albumin.

Thymol, which is also used as an antiseptic, is hydroxycymene,



$$C_6H_3\begin{cases}CH_3\\OH\\CH(CH_3)_2\end{cases}$$

1 - 1
2 - 3
4 - 4

Carvacrol =

Acid sulphuric esters of phenol are present in urine; they result from the fermentation (putrefaction) of albumins, since the quantity of them present depends upon the extent of this process.

B. AROMATIC ALCOHOLS.

277. A type of these compounds is *benzyl alcohol*, $C_6H_5 \cdot CH_2OH$, which possesses nearly all the properties of an aliphatic alcohol. It can be obtained by treatment of benzyl chloride with potassium acetate, and saponification of the ester of acetic acid thus formed. It reacts readily with phosphorus pentachloride, yielding benzyl chloride, and forms esters, ethers, etc.; being a primary alcohol, it can be oxidized to the corresponding aldehyde, *benzaldehyde*, and also to *benzoïc acid*. It differs from the aliphatic alcohols in its behaviour towards sulphuric acid, which causes resinification, instead of the formation of the corresponding sulphuric ester. Benzyl alcohol possesses no phenolic properties; it is insoluble in alkalis, and does not yield the characteristic phenol colouration with ferric chloride.

Benzyl alcohol is a liquid which dissolves with difficulty in water; it boils at 206°, and possesses only a faint odour.

IV. SULPHUR DERIVATIVES.

Thiophenol, $C_6H_5 \cdot SH$, can be obtained by heating phenol with phosphorus pentasulphide, P_2S_5, or by reduction of the chloride of benzenesulphonic acid. It has all the properties of the mercaptans, particularly the power of forming salts. Like most volatile sulphur compounds, it has a disagreeable odour.

for the preparation of aromatic nitro-compounds. The substance is treated with a mixture of nitric and sulphuric acids:

$$C_6H_5\cdot\boxed{H + HO}\cdot NO_2 = C_6H_5\cdot NO_2 + H_2O.$$

The water formed in the nitration would dilute the nitric acid and retard the action if the sulphuric acid were not present. The more alkyl-groups there are in union with the benzene-nucleus, the more readily is the introduction of nitro-groups effected.

Properties.

280. The mononitro-compounds are very stable, and can be distilled without decomposition; their nitro-groups are very firmly attached. Unlike the primary and secondary nitro-compounds of the fatty series, the aromatic nitro-derivatives do not contain hydrogen replaceable by metals, since the nitro-group in them is linked to a tertiary carbon atom; such an exchange is therefore impossible (**76**). On reduction, the nitro-compounds yield amines, and the reaction can be so carried out that various intermediate products are isolated (**289**).

Most of the nitro-compounds have a pale-yellow colour, and an agreeable odour; they are usually liquids heavier than water, in which they are insoluble. They are volatile with steam.

Individual Members.

Nitrobenzene is manufactured in large quantities in the aniline-dye industry. Cast-iron vessels fitted with a stirring-apparatus, and kept cool by water, are employed. They are charged with benzene into which a mixture of nitric and sulphuric acids is allowed to flow. At the end of the reaction, the nitrobenzene floating on the surface of the sulphuric acid, which contains only small quantities of nitric acid, is washed with water, and purified by distillation with steam.

Nitrobenzene is a yellowish liquid, with an odour resembling that of bitter almonds, for which reason it is used in perfumery. Its boiling-point is 208°, its melting-point 5·5°, and its specific gravity

1·1987 at 25°. Its preparation on the large scale is carried out in order to obtain *aniline* by its reduction (**283** and **292**).

Nitrotoluenes.—When toluene is nitrated, the chief products are the *ortho*-compound and *para*-compound, the *meta*-compound being only formed in traces. Which of the two isomers is produced in greater quantity depends upon the method of nitration employed. Para-*nitrotoluene*, $C_6H_4<\substack{CH_3\ 1\\ NO_2\ 4}$, is solid, melting at 51°, and can be obtained pure from the liquid mixture of the isomers on cooling; the preparation of the pure *ortho*-compound is more troublesome.

Phenylnitromethane and the Pseudo-acids.

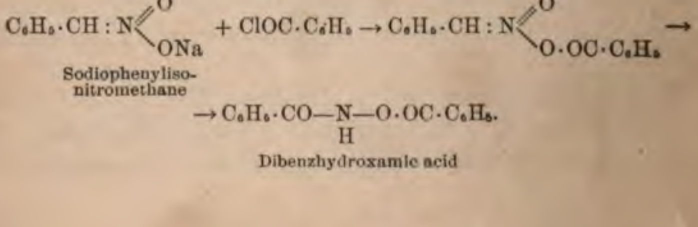
281. *Phenylnitromethane*, $C_6H_5 \cdot CH_2NO_2$, is an aromatic compound with a nitro-group in the side-chain; this is evident from its formation by the action of benzyl chloride or iodide on silver nitrite:

$$C_6H_5 \cdot CH_2\boxed{Cl + Ag}NO_2 = C_6H_5 \cdot CH_2NO_2 + AgCl.$$

It can be reduced to benzylamine, which proves it to be a true nitro compound. Phenylnitromethane, and its derivatives with substituents attached to the nucleus, possess the remarkable property of existing in two modifications which are readily transformed into each other. Phenylnitromethane is a liquid, whose aqueous solution does not react with ferric chloride. When it is converted into its sodium derivative by the action of sodium alkoxide, and subsequently set free by the addition of a strong mineral acid, a crystalline substance of the same composition as phenylnitromethane separates out; the aqueous solution of this compound gives a colouration with ferric chloride. After some hours, these crystals are completely reconverted into ordinary liquid phenylnitromethane. It is very probable that the sodium compound and the unstable modification corresponding to it have the constitution

$$C_6H_5 \cdot CH : NO \cdot OH$$

The presence of a hydroxyl-group is proved by the formation of *dibenzhydroxamic acid* on treatment with benzoyl chloride:



$$C_6H_5 \cdot CH : N\begin{matrix} \nearrow O \\ \searrow ONa \end{matrix} + ClOC \cdot C_6H_5 \rightarrow C_6H_5 \cdot CH : N\begin{matrix} \nearrow O \\ \searrow O \cdot OC \cdot C_6H_5 \end{matrix} \rightarrow$$

Sodiophenyliso-nitromethane

$$\rightarrow C_6H_5 \cdot CO\text{—}\underset{H}{N}\text{—}O \cdot OC \cdot C_6H_5.$$

Dibenzhydroxamic acid

Another proof of the presence of a hydroxyl-group is that isonitro-compounds, unlike ordinary nitro-compounds, react vigorously with phenyl isocyanate (**288**) at low temperatures.

From the preceding it may be deduced that when phenylnitromethane, $C_6H_5\cdot CH_2NO_2$, is converted into a salt, it first changes to an isomeric modification. Inversely, when it is set free from its sodium compound, the iso-modification is first produced, and slowly changes to the ordinary form.

The dilute aqueous solution of the *meta*-nitro-derivative of phenylnitromethane affords a striking example of this phenomenon. This compound is colourless, but its sodium salt has a deep-yellow colour. On the addition of an equivalent quantity of hydrochloric acid to its deeply tinted solution, the yellow colour disappears somewhat slowly, indicating the conversion of the iso-compound into the normal.

The discharge of the colour is attended by another phenomenon; the electric conductivity of the liquid is considerably greater immediately after the addition of the hydrochloric acid than it is several minutes later, when the colour has nearly vanished. The explanation of this is that the iso-form is a true acid, and is therefore a conductor in aqueous solution, while the solution of the normal modification is a non-conductor, and therefore possesses no acidic character.

Compounds which change to an iso-modification on formation of metallic derivatives, are called *pseudo-acids*. In addition to phenylnitromethane and its ring-substituted derivatives, other pseudo-acids are known, most of which are nitro-compounds.

Besides the properties indicated above, the pseudo-acids possess others by which they may be detected. It has just been stated that the addition of a strong acid to a pseudo-acid salt liberates the pseudo-acid, and that it is slowly converted into the normal modification. Inversely, the addition of an equivalent quantity of caustic alkali to the normal modification results in its gradual neutralization. This "slow neutralization" is a characteristic of the pseudo-acids.

Another criterion for them is illustrated by dinitroethane, which, after being liberated from its sodium salt in accordance with the equation

$$CH_3\cdot C{<}^{NO_2}_{NO\cdot ONa} + HCl = \underset{\text{Isodinitroethane}}{CH_3\cdot C{<}^{NO_2}_{NO\cdot OH}} + NaCl,$$

is so rapidly converted into the normal compound, $CH_3\cdot CH{<}^{NO_2}_{NO_2}$, that a change in the electric conductivity of the solution can scarcely be observed even at 0°. The neutral reaction of the alkali-derivatives of the non-conducting or weakly-conducting hydrogen compound nevertheless indicates the existence of a pseudo-acid. An acid which is so weak that its solution is a bad conductor of electricity, yields alkali-salts which undergo strong hydrolytic dissociation, and therefore have a strongly alkaline reaction ("Inorganic Chemistry," **239**). Such a substance as sodiodinitroethane, whose solution is not alkaline, must therefore be derived from an acid other than dinitroethane, since this substance has a neutral reaction and is a non-conductor in aqueous solution.

Among the other methods of detecting pseudo-acids, the adding on of ammonia may be mentioned. A true acid, when dissolved in benzene or another hydrocarbon, combines instantaneously with dry ammonia to form an insoluble ammonium salt. A pseudo-acid, on the contrary, either does not add on NH_3, or only slowly, being in the latter case first converted into a true acid.

VII. MONOAMINO-COMPOUNDS.

282. The amino-compounds of the aromatic series, with the NH_2-group attached to the ring, are almost exclusively obtained by reduction of the corresponding nitro-compounds. This is effected by the action of tin and hydrochloric acid, iron-filings and acetic or hydrochloric acid, or by other reagents. On the manufacturing scale it is usual to employ iron-filings and hydrochloric acid.

Amines can be obtained from phenols by heating them at 300° with ammonium zinc chloride.

The aromatic amines are colourless liquids of high boiling-point, or solids, and have a characteristic odour. With water, the aliphatic amines form stronger bases than ammonia, but the aqueous solutions of the aromatic amines possess only weakly basic properties; thus, they do not turn red litmus blue, and scarcely conduct an electric current. The aromatic amines yield salts, however, although these have an acid reaction in solution, on account of partial hydrolysis. The negative character of the phenyl-group, already alluded to in connection with phenol (**275**), considerably modifies the nature of the amido-group; the behaviour of diphenylamine and triphenylamine in particular betrays this influence. With strong acids the former can yield salts, which, however, are completely hydrolyzed by addition of much water; the second no longer unites with acids.

Substitution of the amido-group for hydrogen produces the same effect upon the benzene-nucleus as substitution of the hydroxyl-group for hydrogen, making the rest of the hydrogen atoms of the nucleus much more easily replaced; thus, aniline is readily converted by bromine-water into tribromoaniline. Moreover, the amines are much more readily oxidized than the hydrocarbons.

By means of an alkyl halide, the hydrogen atoms in the amido-group of the primary aromatic amines, like those in the amido-group of the primary aliphatic amines, can be replaced by an alkyl-group:

$$C_6H_5 \cdot NH_2 + CH_3I = C_6H_5 \cdot NH(CH_3) \cdot HI.$$

Secondary and tertiary bases and also strongly basic quaternary ammonium bases, such as $C_6H_5 \cdot N(CH_3)_3 \cdot OH$, are known.

The *anilides* are derivatives of aniline, $C_6H_5 \cdot NH_2$, and its homologues; they are acid amides, in which one amido-hydrogen atom is replaced by a phenyl-group. *Acetanilide*, $C_6H_5 \cdot NH \cdot COCH_3$, employed as a febrifuge under the name "antifebrine," is a type of these compounds. The anilides are produced by boiling aniline with the corresponding acid; acetanilide is obtained by heating aniline with glacial acetic acid:

$$C_6H_5 \cdot NH\boxed{H + HO}OC \cdot CH_3 = C_6H_5 \cdot NH \cdot COCH_3 + H_2O.$$

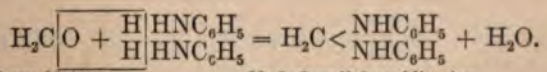
Menschutkin found that the velocity of formation of acetanilide is much less for an excess of aniline than for an excess of glacial acetic acid, although on theoretical grounds the velocity of formation should be the same in both cases; for at each moment it should be proportional to the product of the concentrations of the glacial acetic acid (c) and of the aniline (c'), being therefore expressed by

$$s = k \cdot cc',$$

in which k is constant.

The difference between theory and experiment can be variously explained; for instance, on the ground that the reaction in the two cases takes place in different media. The important influence of the medium has been mentioned (**71**).

Aldehydes react with aromatic amines with elimination of water:



$$H_2C\boxed{O + \begin{matrix}H\\H\end{matrix}}\begin{matrix}HNC_6H_5\\HNC_6H_5\end{matrix} = H_2C<\begin{matrix}NHC_6H_5\\NHC_6H_5\end{matrix} + H_2O.$$

Formaldehyde Methylenediphenyldiamine

Primary aromatic amines show the carbylamine reaction; with nitrous acid they yield diazonium compounds (**302**).

Aniline.

283. Aniline was first obtained by the dry distillation of indigo (*anil*); hence its name. It is manufactured by the action of hydrochloric acid and iron-filings on nitrobenzene contained in a cast-iron cylinder fitted with a stirring-apparatus:

$$C_6H_5NO_2 + 3Fe + 6HCl = C_6H_5NH_2 + 2H_2O + 3FeCl_2.$$

It is remarkable that in this process only about one-fortieth of the hydrochloric acid required by the equation is needed for the reduction. This is probably because iron-filings and water are able to effect the reduction in presence of ferrous chloride. Lime is added as soon as the reduction is complete, and the aniline is distilled with steam.

Aniline is also obtained by the electro-reduction of nitro-benzene (**292**).

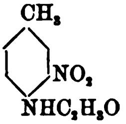
Aniline is a colourless liquid, and, unless perfectly pure, turns brown in the air, the colour change being probably due to the presence of traces of sulphur compounds. It is only slightly soluble in water; it boils at 189°, and has a specific gravity of 1·024 at 16°. It can be reconverted into nitrobenzene by certain oxidizing-agents, various intermediate products, such as nitrosobenzene, $C_6H_5 \cdot NO$, being obtained. Aniline undergoes oxidation somewhat readily; the compounds thus obtained will be described later (**289**).

An aqueous solution of free aniline gives a deep-violet colouration with bleaching-powder solution; an aniline salt in acid solution is coloured dark-green to black by potassium dichromate. These two reactions, and that with wood (**230**), serve as tests for aniline. The bleaching-powder reaction is particularly delicate.

Homologues of Aniline.

Ortho-*toluidine* and para-*toluidine*, $CH_3 \cdot C_6H_4 \cdot NH_2$, are formed by the reduction of the corresponding nitro-compounds; the *ortho*-compound is a liquid, B.P. 199·4°; the *para*-compound is solid, M.P. 42·5°. The different solubilities of their oxalic-acid salts are made use of to separate them.

m-Toluidine can only be obtained indirectly. *p*-Toluidine is converted into its acetyl-derivative, $CH_3\cdot C_6H_4\cdot NHC_2H_3O$, which on nitration yields



The acetyl-group in this compound is split off by boiling with hydrochloric acid, after which the amido-group is eliminated by the method described in **303**, 3. On reduction, the *m*-nitrotoluene thus formed yields *m*-toluidine.

The monoamino-derivatives of the xylenes are called *xylidines*. Six isomers are possible, due to differences in the relative positions of the methyl-groups and the amido-group in the ring. Some of the toluidines and the xylidines are employed in making aniline dyes, and are, therefore, manufactured in large quantities.

Secondary Amines.

284. *Diphenylamine*, $C_6H_5\cdot NH\cdot C_6H_5$, is a type of the true secondary aromatic amines. They are formed by heating the hydrochlorides of the primary amines with the free amines:

$$C_6H_5\boxed{NH_2\cdot HCl + H}HN\cdot C_6H_5 = NH_4Cl + HN(C_6H_5)_2.$$

Diphenylamine can also be obtained by the action of bromobenzene on potassium anilide, $C_6H_5\cdot NHK$.

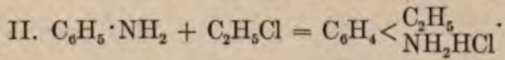
Diphenylamine is a solid, M.P. 54°; it has an agreeable odour, resembling that of some flowers.

Diphenylamine is a very sensitive reagent for the detection of nitric acid, liquids containing which produce a deep-blue colour with its solution in concentrated sulphuric acid. This reaction can only be used to detect nitric acid in the absence of other oxidizing-substances, such as bromine-water, permanganate, etc., with many of which diphenylamine also gives a blue colouration.

The method of formation of the mixed aromatic-fatty amines, such as *methylaniline*, $C_6H_5\cdot NH\cdot CH_3$, has been already indicated current of hydrochloric-acid gas, the alkyl-groups are split off, with formation of aniline and alkyl chlorides. When the hydrochlorides of the alkyl-anilines are strongly heated, the alkyl-groups linked to nitrogen are transferred to the benzene-ring; this can be explained by assuming that decomposition into alkyl chloride and aniline first takes place as just described:

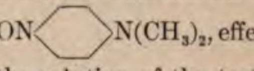
$$\text{I. } C_6H_5 \cdot NH(C_2H_5)HCl = C_6H_5 \cdot NH_2 + C_2H_5Cl.$$

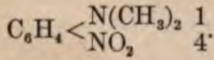
This is then followed by the reaction indicated in equation II:



$$\text{II. } C_6H_5 \cdot NH_2 + C_2H_5Cl = C_6H_4 < \begin{matrix} C_2H_5 \\ NH_2HCl \end{matrix} .$$

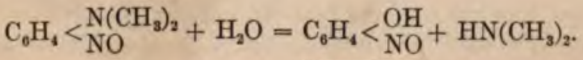
These reactions explain the formation of the hydrochloride of *p*-toluidine, by the interaction of methyl alcohol and aniline hydrochloride at a high temperature. By this process it is possible to obtain even *pentamethylaminobenzene*, $C_6(CH_3)_5 \cdot NH_2$.

Dimethylaniline and other dialkyl-anilines possess the remarkable property of having their *p*-H-atom readily replaceable by different groups. Thus, dimethylaniline reacts readily with nitrous acid, with formation of *nitrosodimethylaniline*, , effected by the addition of potassium nitrite to the solution of the tertiary base in hydrochloric acid. This nitroso-compound crystallizes in well-defined leaves of a fine green colour. It melts at 85°, and yields a hydrochloride crystallizing in yellow needles. On oxidation with potassium permanganate, the nitroso-group is converted into a nitro-group, with formation of p-*nitrodimethylaniline*,



$$C_6H_4 < \begin{matrix} N(CH_3)_2 & 1 \\ NO_2 & 4 \end{matrix} .$$

On boiling with caustic soda, the amido-group of nitrosodimethylaniline is completely split off, with formation of dimethylamine and nitrosophenol:

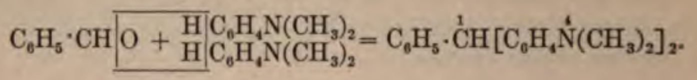


$$C_6H_4 < \begin{matrix} N(CH_3)_2 \\ NO \end{matrix} + H_2O = C_6H_4 < \begin{matrix} OH \\ NO \end{matrix} + HN(CH_3)_2.$$

Nitrosophenol.

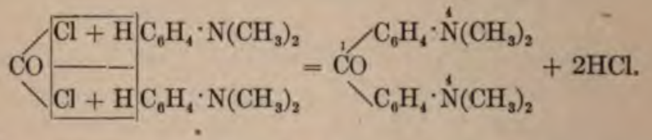
This reaction is employed in the preparation of pure dimethylamine (**72**).

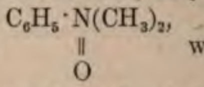
The *p*-hydrogen atom of dimethylaniline can react with substances other than nitrous acid; thus, aldehydes readily yield a condensation-product:



$$C_6H_5\cdot CH\boxed{O+\begin{matrix}H\\H\end{matrix}}\begin{matrix}C_6H_4N(CH_3)_2\\C_6H_4N(CH_3)_2\end{matrix}=C_6H_5\cdot\overset{1}{C}H[C_6H_4\overset{4}{N}(CH_3)_2]_2.$$

The constitution of this compound is deduced from its relation to *triphenylmethane*, $CH(C_6H_5)_3$ (**366**). With dimethylaniline, carbonyl chloride yields a *p*-derivative of benzophenone, $C_6H_5\cdot CO\cdot C_6H_5$:



When dimethylaniline, and other analogous tertiary amines, are treated with hydrogen peroxide at 60°–70°, they yield compounds such as *dimethylaniline oxide*,  $\overset{C_6H_5\cdot N(CH_3)_2,}{\underset{O}{\|}}$ whose constitution follows from its being readily reducible to dimethylaniline.

Quaternary Bases.

286. Quaternary bases are formed by the addition of alkyl halides to the tertiary aromatic-fatty amines, and treatment of the salts thus formed with moist silver oxide. These substances are strong bases. On heating, they split up into an alcohol and a tertiary amine, wherein they differ from the aliphatic ammonium bases (**73**).

Attempts have been made to split up the quaternary ammonium bases containing four dissimilar groups into optically active components. These compounds of the type $NR_1R_2R_3R_4X$, in which X is an acid-radicle, would owe their optical activity to the presence of an *asymmetric nitrogen atom*. This decomposition has been recently effected by POPE. *Benzylphenylallylmethylammonium hydroxide*,

$$HO\cdot N(CH_2C_6H_5)(C_6H_5)(C_3H_5)(CH_3),$$

unites with the strongly optically active *d*-camphorsulphonic acid; the salt obtained is fractionally crystallized from acetone, a solvent which is not so likely to decompose it into alcohol and tertiary base as solvents containing a hydroxyl-group. By this means the base can be split up into its dextro-rotatory and lævo-rotatory components. A complete demonstration of the position and direction of the bonds of the pentavalent nitrogen atom has not yet been given.

That certain tertiary amines possess the property of forming addition-products with alkyl halides, while others do not, is probably also explicable on stereochemical grounds. Thus, to account for the fact that, although triphenylamine and diphenylmethylamine do not form addition-products with methyl iodide, tribenzylamine is capable of doing so, it is assumed that the phenyl-groups of the two former compounds are so situated in relation to the nitrogen atom that no space is left for CH_3I to approach it. If, however, the three benzene-nuclei of triphenylamine are removed to a distance from the N-atom by the introduction of three CH_2-groups, as in tribenzylamine, sufficient space is left for CH_3I to approach the N-atom.

Benzylamine, $C_6H_5 \cdot CH_2 \cdot NH_2$.

287. *Benzylamine* is a type of the amines with NH_2 in the side-chain. It can be obtained by the various methods employed in the preparation of aliphatic amines, such as the action of benzyl chloride upon ammonia, by which *dibenzylamine* and *tribenzylamine* are also formed; addition of hydrogen to benzonitrile, $C_6H_5 \cdot CN$; reduction of phenylnitromethane, $C_6H_5 \cdot CH_2 \cdot NO_2$; etc. Its methods of formation and its properties prove that benzylamine belongs to the primary amines of the fatty series: thus, it does not yield diazonium compounds; and its aqueous solution has a strongly alkaline reaction, proving it to be a much stronger base than aniline, in which the NH_2-group is under the direct influence of the phenyl-group.

Benzylamine is a liquid of ammoniacal odour; it boils at 185°, is volatile with steam, and has a specific gravity of 0·983 at 19°. It absorbs carbon dioxide from the air.

Carbonic Acid Derivatives of Aniline.

288. Only a few of the numerous compounds of this class can be described here. *Phenylurethane*, $C_6H_5 \cdot NH \cdot CO \cdot OC_2H_5$, is formed by the interaction of chlorocarbonic ester and aniline; it is a solid, and melts at 52°. When distilled with phosphorus pentoxide, it yields *phenyl isocyanate*, $C_6H_5\cdot N:C:O$, a colourless liquid productive of tears, which boils at 166°. It is sometimes employed in the detection of OH-groups or NH_2-groups in compounds, since in presence of these, substituted urethanes and urea respectively are obtained. With water it yields symmetrical *diphenylurea*, $CO(NH\cdot C_6H_5)_2$, a crystalline substance melting at 235° (**253**).

Sulphur Derivatives of Aniline.

Sulphur derivatives of aniline, similar to the compounds described in **245** and **255**, are also known. One of these is *phenyl mustard-oil*, $C_6H_5\cdot N:C:S$, which boils at 222°. It is obtained by boiling *diphenylthiourea*, $CS(NH\cdot C_6H_5)_2$, with hydrochloric acid: diphenylthiourea itself is formed by heating carbon disulphide with aniline:

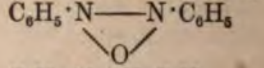
$$CS_2 + 2H_2N\cdot C_6H_5 = H_2S + CS(NH\cdot C_6H_5)_2.$$

FINISH

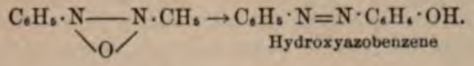
VIII. INTERMEDIATE PRODUCTS IN THE REDUCTION OF AROMATIC NITRO-COMPOUNDS.

289. On reduction, the nitro-compounds of the aliphatic series yield amines directly, from which the alkyl-groups are split off by oxidation; ethylamine, for example, is converted into acetic acid and ammonia. In the aromatic series, on the other hand, intermediate products can be obtained both in the reduction of nitro-compounds, and sometimes also in the oxidation of the amines. Only the compounds derived from nitrobenzene and aniline will be described here, although numerous substitution-products of the same type are known.

In acid solution, the nitro-compounds are directly reduced to the corresponding amino-derivatives, but in alkaline solution yield substances containing two benzene-residues. Nitrobenzene yields in succession

1. Nitro-compound	$C_6H_5\cdot NO_2 \quad O_2N\cdot C_6H_5$
2. Azoxy-compound	 $C_6H_5\cdot N\text{——}N\cdot C_6H_5$ with O bridging below
3. Azo-compound	$C_6H_5\cdot N{=}N\cdot C_6H_5$
4. Hydrazo-compound	$C_6H_5\cdot NH\text{—}NH\cdot C_6H_5$
5. Amino-compound	$C_6H_5\cdot NH_2 \quad H_2N\cdot C_6H_5$

290. *Azoxybenzene* is obtained by boiling nitrobenzene with alcoholic potash, and is also formed in the oxidation of aniline with potassium permanganate in alcoholic solution. It forms light-yellow crystals melting at 36°. When warmed with concentrated sulphuric acid, it is transformed into *hydroxyazobenzene*:



$$C_6H_5\cdot N\overset{O}{—}N\cdot C_6H_5 \rightarrow C_6H_5\cdot N{=}N\cdot C_6H_4\cdot OH.$$

Hydroxyazobenzene

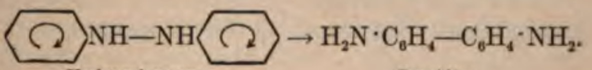
It is readily attacked by various reducing-agents.

291. *Azobenzene*, $C_6H_5\cdot N:N\cdot C_6H_5$, is formed by the reduction of nitrobenzene with a solution of stannous chloride in excess of caustic potash, and also by distilling azoxybenzene with iron-filings. It is produced along with azoxybenzene by the oxidation of aniline with potassium permanganate.

Azobenzene forms well-defined, orange-red crystals, melting at 68°, and boiling without decomposition at 295°. It is a very stable compound, and is insoluble in water. Its constitution follows from its yielding aniline on reduction.

Hydrazobenzene, $C_6H_5\cdot NH—NH\cdot C_6H_5$, is formed by the action of zinc-dust and alcoholic potash upon azobenzene or nitrobenzene. It is a colourless, crystalline substance, and melts at 126°. Strong reducing-agents convert it into aniline; on the other hand, it is readily oxidized to azobenzene, this transformation being slowly effected by atmospheric oxygen. It is also oxidized to the azo-compound by ferric chloride.

The most characteristic reaction of hydrazobenzene is its conversion into *benzidine*, whereby the benzene-nuclei are, as it were, turned end for end; this is effected by the action of strong acids:

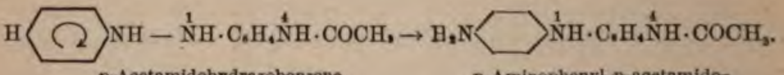


Hydrazobenzene Benzidine

That a diaminodiphenyl is thus formed is proved by the conversion of benzidine into diphenyl, $C_6H_5\cdot C_6H_5$. The amido-groups occupy the *para*-positions:

By reducing azobenzene in acid solution, benzidine is formed directly. It is characterized by the sparing solubility in cold water of its sulphate.

The amido-groups in benzidine are proved in various ways to occupy the *para*-position; for example, a hydrazobenzene whose *p*-hydrogen atoms have been substituted cannot be converted into benzidine. In certain instances compounds of this kind can undergo a remarkable intramolecular transformation, known as the *semidine-transformation*, forming derivatives of diphenylamine by the turning of only one of the benzene-nuclei:



p-Acetamidohydrazobenzene

p-Aminophenyl-*p*-acetamido-phenylamine

Electro-reduction of Nitro-compounds.

292. There is reason to believe that in the future electric methods will be used more and more, for the electric current affords a means of varying the pressure and concentration of the compounds taking part in reactions in the preparation of organic compounds, which is not otherwise attainable. By its aid it is possible to effect new syntheses or to improve those already known. An explanation of the mode of altering this pressure and concentration is necessary here.

It was stated (**258**) that alteration in the difference of potential of the electrodes causes considerable variation in the pressure at which the discharged ions leave the solution. In reduction-processes the same effect is attained by using different reducing-agents. When a compound yields a series of intermediate products on treatment with different reducing-agents of increasing strength, this can also be effected by increasing the potential at the cathode, where hydrogen is evolved.

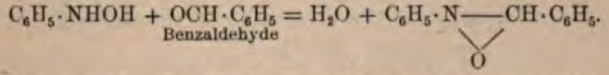
Regarding variation in the concentration, it must be remembered that the electrolytic process takes place only in the immediate neighbourhood of the electrodes. When the surface-area of the electrodes is altered, the strength of the current remaining the same, the number of ions discharged at unit surface varies in direct proportion; it is therefore possible, by selecting suitable electrodes, to cause the concentration of the ions discharged at them to vary within wide limits. The "strength" of the reducing-agent depends upon the difference of potential, but its concentration is controlled by the density of the current (**168**). In reactions in which the discharged ions must act on one another, as in the synthesis of dibasic acids (*loc. cit.*), a current of high density is necessary; on the other hand, in reductions which must take place as far as possible at all parts of the liquid, large cathodes, which give a current of small density, must be used.

On reduction, the nitro-compounds ultimately yield amines, but a number of intermediate reduction-products can be isolated. For this reason the electro-reduction of nitrobenzene and its derivatives is of both theoretical and practical importance; it has been found possible to give a complete and satisfactory explanation of the mechanism of this process.

A distinction must be drawn between primary and secondary reduction-products. The primary process is

$$\underset{\text{Nitrobenzene}}{C_6H_5\cdot NO_2} \rightarrow \underset{\text{Nitrosobenzene}}{C_6H_5\cdot NO} \rightarrow \underset{\text{Phenylhydroxylamine}}{C_6H_5\cdot NHOH} \rightarrow \underset{\text{Aniline}}{C_6H_5\cdot NH_2}.$$

The presence of nitrosobenzene can be detected by the addition of hydroxylamine to the liquid, with which it reacts with loss of one molecule of water, and formation of diazonium hydroxide, $C_6H_5\cdot N_2\cdot OH$; on adding α-naphthol, an azo-dye is produced (**320**). The formation of phenylhydroxylamine can be proved by adding benzaldehyde, with which it yields benzylidenephenylhydroxylamine:



$$C_6H_5\cdot NHOH + \underset{\text{Benzaldehyde}}{OCH\cdot C_6H_5} = H_2O + C_6H_5\cdot \underset{\diagdown O \diagup}{N\text{——}CH}\cdot C_6H_5.$$

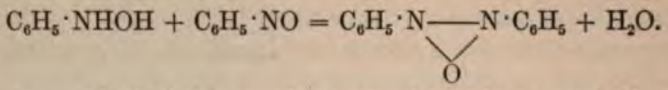
On rapid reduction of nitrobenzene dissolved in moderately concentrated sulphuric acid, with addition of alcohol to increase the solubility, the primary process just described takes place, about 90 per cent. of the theoretical yield of aniline being obtained. In a strongly acid solution, however, the phenylhydroxylamine is very quickly converted into *p*-aminophenol:

$$C_6H_5\cdot NHOH \rightarrow HO\cdot C_6H_4\cdot NH_2.$$

This substance is not further reduced. Since phenylhydroxylamine undergoes the same transformation, though much more slowly, in presence of more dilute acid, it is evident that in the latter case the theoretical yield of aniline cannot be quite obtained, even when the velocity of reduction is great.

In alcoholic-alkaline solution the electro-reduction of nitrobenzene is accompanied by two secondary processes.

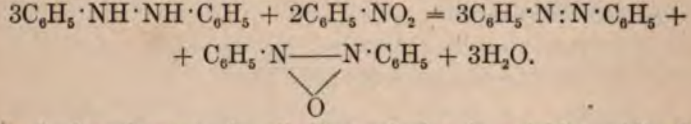
1. Nitrosobenzene reacts with phenylhydroxylamine, yielding azoxybenzene:



$$C_6H_5\cdot NHOH + C_6H_5\cdot NO = C_6H_5\cdot \underset{\underset{O}{\diagdown\diagup}}{N\!\!-\!\!-\!\!N}\cdot C_6H_5 + H_2O.$$

In presence of alkali this reaction proceeds much more quickly than the further reduction of phenylhydroxylamine, so that only small quantities of aniline are formed, and higher reduction-products of azoxybenzene, chief among these being hydrazobenzene, obtained as the main part of the yield.

2. Hydrazobenzene is attacked by the unreduced nitrobenzene with formation of azobenzene and azoxybenzene:



$$3C_6H_5\cdot NH\cdot NH\cdot C_6H_5 + 2C_6H_5\cdot NO_2 = 3C_6H_5\cdot N:N\cdot C_6H_5 + \\ + C_6H_5\cdot \underset{\underset{O}{\diagdown\diagup}}{N\!\!-\!\!-\!\!N}\cdot C_6H_5 + 3H_2O.$$

Since hydrazobenzene in alkaline solution is quickly oxidized by atmospheric oxygen to azobenzene, the yield of the latter is very good.

A much higher tension is required at the cathode to reduce hydrazobenzene to aniline, so that in alkaline solution the reduction-process ceases with the production of the former.

Haber has combined all these primary and secondary reactions in the following scheme, the vertical arrows indicating primary, and the oblique ones secondary, reactions:

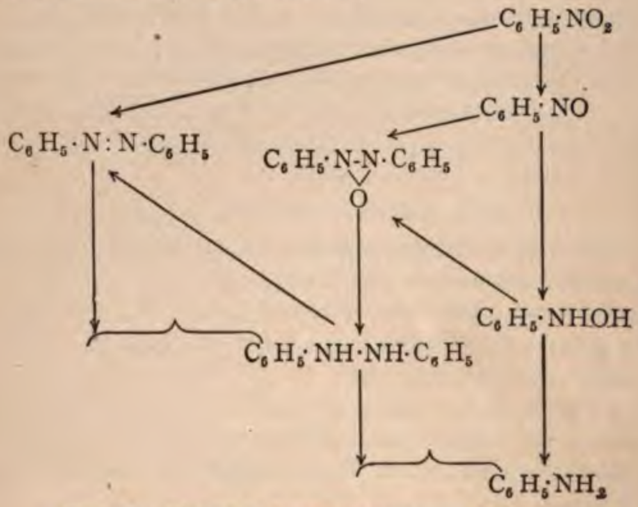


Fig. 72.—Haber's Electro-reduction Scheme.

IX. PHENYL-COMPOUNDS CONTAINING OTHER ELEMENTS

Phosphorus and Arsenic Derivatives.

293. Compounds of phosphorus and arsenic with aromatic hydrocarbons, and having constitutions similar to those of the nitro-compounds, azo-compounds, and amino-compounds, are known.

Phosphinobenzene, $C_6H_5 \cdot PO_2$, cannot be obtained analogously to nitrobenzene, by the interaction of metaphosphoric acid and benzene. It is prepared by the action of *phenylphosphinic acid* upon its chloride:

$$\underset{\text{Phenylphosphinic acid}}{C_6H_5 \cdot PO(OH)_2} + \underset{\text{Chloride}}{C_6H_5 \cdot POCl_2} = 2C_6H_5 \cdot PO_2 + 2HCl.$$

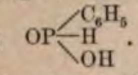
It is a white, crystalline, odourless powder.

Phenylphosphine, $C_6H_5 \cdot PH_2$, is obtained by distilling *phosphenyl chloride*, $C_6H_5 \cdot PCl_2$, with alcohol, in a current of carbon dioxide. It is a liquid with a very penetrating odour. It cannot be obtained by the reduction of phosphinobenzene.

Phosphobenzene, $C_6H_5 \cdot P : P \cdot C_6H_5$, is obtained by treating phenylphosphine with phosphenyl chloride:

$$C_6H_5 \cdot P\boxed{Cl_2 + H_2}P \cdot C_6H_5 = C_6H_5 \cdot P : P \cdot C_6H_5 + 2HCl.$$

It is a pale-yellow powder, insoluble in water, alcohol, and ether. It is energetically oxidized by weak nitric acid, forming *phosphenylous acid*,



$$OP \begin{cases} C_6H_5 \\ H \\ OH \end{cases}.$$

Phosphenyl chloride, $C_6H_5 \cdot PCl_2$, the starting-point in the preparation of these and other aromatic phosphorus derivatives, can be prepared, as can its homologues, by heating aromatic hydrocarbons with phosphorus trichloride and aluminium chloride under a reflux-condenser.

Arsinobenzene, $C_6H_5 \cdot AsO_2$, is obtained by the elimination of water from *phenylarsinic acid*, $C_6H_5 \cdot AsO(OH)_2$, under the influence of heat.

Arsenobenzene, $C_6H_5 \cdot As : As \cdot C_6H_5$, is formed by the reduction of *phenylarsenic oxide*, $C_6H_5 \cdot AsO$, with phosphorous acid. It forms yellow needles, and is converted by oxidation into phenylarsinic acid $C_6H_5 \cdot AsO(OH)_2$.

Comparison of the Aromatic Derivatives of Nitrogen, Phosphorus, and Arsenic.

294. The following compounds are known:

$C_6H_5 \cdot NO_2$ Nitrobenzene	$C_6H_5 \cdot N_2 \cdot C_6H_5$ Azobenzene	$C_6H_5 \cdot NH_2$ Phenylamine
$C_6H_5 \cdot PO_2$ Phosphinobenzene	$C_6H_5 \cdot P_2 \cdot C_6H_5$ Phosphobenzene	$C_6H_5 \cdot PH_2$ Phenylphosphine
$C_6H_5 \cdot AsO_2$ Arsinobenzene	$C_6H_5 \cdot As_2 \cdot C_6H_5$ Arsenobenzene	

Substances in the first column may be looked upon as derived from the *meta*-acids, $HO \cdot NO_2$, $HO \cdot PO_2$, $HO \cdot AsO_2$, by exchange of hydroxyl for phenyl, and hence cannot have acidic properties. The nitrogen acid, H_3NO_4, or $ON(OH)_3$, corresponding to phosphoric acid, H_3PO_4, and arsenic acid, H_3AsO_4, is not known, and accordingly nitrobenzene does not unite with water, while phosphinobenzene and arsinobenzene yield the corresponding acids, phenylphosphinic acid, $C_6H_5 \cdot PO(OH)_2$, and phenylarsinic acid, $C_6H_5 \cdot AsO(OH)_2$. Phosphoric acid does not yield P_2O_5 on heating; arsenic acid yields As_2O_5. Similarly, phosphinobenzene cannot be obtained by heating phenylphosphinic acid, while phenylarsinic acid is converted into arsinobenzene by this treatment.

The methods of formation of the compounds of the second column also differ greatly from one another. They are all coloured, the most deeply tinted being azobenzene. Nitrobenzene and arsinobenzene yield azobenzene and arsenobenzene on reduction; the oxygen of phosphinobenzene is too firmly linked to phosphorus to admit of this reaction. On reduction with hydrogen, azobenzene yields phenylamine; chlorine converts phosphobenzene and arsenobenzene into the corresponding chlorine derivatives, $C_6H_5 \cdot PCl_2$ and $C_6H_5 \cdot AsCl_2$.

The difference between the two compounds in the last column is due to the strong affinity between phosphorus and oxygen. Aniline cannot be oxidized to an acid, while phenylphosphine is very readily converted, even by the oxygen of the atmosphere, into *phenylphosphinous acid*, $C_6H_5 \cdot PO_2H_2$.

Aromatic Metallic Compounds.

295. Mercury, tin, lead, and magnesium are the only metals which yield aromatic compounds, and these are of much less importance than the metallic compounds of the fatty series. *Mercury-phenyl*, $Hg(C_6H_5)_2$, is obtained by the action of sodium amalgam upon bromobenzene. It is crystalline, and resembles the corresponding alkyl-derivatives in its stability when exposed to air. When its vapour is passed through a red-hot tube, it splits up into mercury and diphenyl; the same effect is partially produced by its distillation. When mercury acetate is heated with benzene at 110°, there results phenylmercury acetate, $C_6H_5 \cdot Hg \cdot OOC \cdot CH_3$, the acetic acid salt of the base phenylmercury hydroxide, $C_6H_5 \cdot Hg \cdot OH$.

Aromatic magnesium compounds are referred to in **272.**

BENZOÏC ACID AND ITS DERIVATIVES AND HOMOLOGUES.

Benzoïc Acid, $C_6H_5\cdot COOH$.

296. *Benzoïc acid* can be prepared by a great variety of methods, of which the most important will be described.

1. By the oxidation of any aromatic hydrocarbon with a side-chain:

$$C_6H_5\cdot C_nH_{2n+1} \rightarrow C_6H_5\cdot COOH.$$

Toluene is specially serviceable for this purpose, since it can be readily obtained. In the manufacture of benzoïc acid, toluene is not directly oxidized, but is treated at its boiling-point with chlorine. *Benzotrichloride*, $C_6H_5\cdot CCl_3$, is first formed, and on heating with water is converted into benzoïc acid:

$$C_6H_5\cdot C\left|\begin{array}{lcr} Cl & & H \\ Cl & + & H \\ Cl & & H \end{array}\right|\begin{array}{l} OH \\ OH \\ OH \end{array} - H_2O = C_6H_5\cdot COOH + 3HCl.$$

Benzoïc acid thus prepared often contains traces of *chlorobenzoïc acid*, $C_6H_4Cl\cdot COOH$.

2. By the oxidation of aromatic alcohols or aldehydes, such as benzyl alcohol, $C_6H_5\cdot CH_2OH$, or benzaldehyde, $C_6H_5C<^{H}_{O}$; also by the oxidation of alcohols, aldehydes, or ketones with longer side-chains; in fact, from all compounds containing a side-chain with one carbon atom directly linked to the benzene-nucleus.

3. By the introduction of the nitrile-group into the benzene-nucleus, and hydrolysis of the *benzonitrile*, $C_6H_5\cdot CN$, thus formed. The introduction of the nitrile-group can be effected in two ways.

(*a*) By diazotizing aniline, and treating the diazonium salt with potassium cyanide (**303**, 5).

(*b*) By distilling sodium benzenesulphonate with potassium cyanide:

$$C_6H_5\cdot SO_3K + KCN = C_6H_5\cdot CN + K_2SO_3.$$

4. By the action of carbon dioxide and sodium on bromobenzene, whereby sodium benzoate is formed:

$$C_6H_5Br + CO_2 + 2Na = NaBr + C_6H_5\cdot CO_2Na.$$

5. By the action of various derivatives of carbonic acid, instead of carbon dioxide itself, upon benzene, substances readily convertible into benzoïc acid being formed.

(*a*) Benzene and carbonyl chloride react together in presence of aluminium chloride, with formation of *benzoyl chloride*, the chloride of benzoïc acid, and hydrochloric acid:

$$C_6H_5\boxed{H + Cl}\cdot COCl = \underset{\text{Benzoyl chloride}}{C_6H_5\cdot COCl} + HCl.$$

Benzoyl chloride is readily converted into benzoic acid by treatment with water.

(*b*) Benzene and aluminium chloride react with carbamic chloride, $Cl\cdot CONH_2$ (formed by passing carbonyl chloride over heated ammonium chloride), yielding benzamide, the amide of benzoïc acid:

$$C_6H_5\boxed{H + Cl}\cdot CONH_2 = \underset{\text{Benzamide}}{C_6H_5\cdot CONH_2} + HCl.$$

(*c*) Bromobenzene is converted by sodium and chloro-carbonic ester into benzoïc ester:

$$\begin{matrix} C_6H_5 \\ + \end{matrix}\boxed{\begin{matrix} Br + Cl \\ Na \quad Na \end{matrix}}\cdot COOC_2H_5 = C_6H_5\cdot COOC_2H_5 + NaCl + NaBr.$$

Benzoïc acid is a constituent of many natural resins and balsams, such as gum-benzoïn and Peru and Tolu balsam. It is also present as hippuric acid (**200**) in the urine of horses. It was formerly prepared principally from gum-benzoïn, from which source the benzoïc acid used as a medicament is still sometimes obtained. It is a white solid, crystallizing in leaf-like crystals melting at 121·4°. It sublimes readily, and boils at 250°; it can be purified by distillation with steam, with which it is readily volatile. Its alkali-salts dissolve easily in water, while most of those with other bases are only soluble with difficulty.

The solubility curve ("Inorganic Chemistry," **235**) of benzoïc acid has been the subject of careful investigation, on account of its interesting character (Fig. 73). The solubility increases somewhat rapidly with increase of temperature up to 90° (*AB*). At this temperature, the acid melts beneath the water, so that two liquids result; one is an aqueous solution, containing 11·2% of acid (point *B*); the other consists principally of the acid, of which it contains 95·88% (point *D*). Above this temperature an effect like that described in **74** is produced; the mutual solubility of these layers is represented in the part *BCD* of the curve, of which *BC* corresponds to the aqueous layer, and *DC* to the acid one. The composition of the two layers becomes more and more alike as the temperature rises, since the water dissolves more benzoïc acid, and the acid more water: at 116° they are identical in composition; that is, the liquid has again become homogeneous.

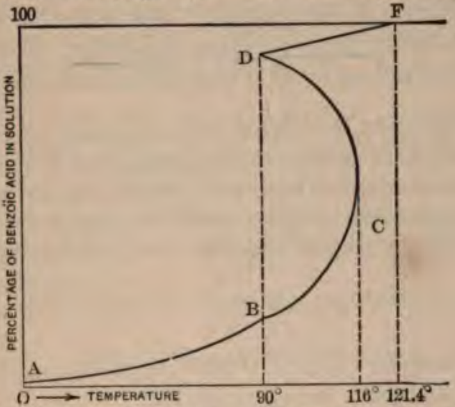


FIG. 73.—SOLUBILITY CURVE OF BENZOÏC ACID IN WATER.

If more benzoïc acid is added to the acid layer only, at 90°, it is necessary to raise the temperature in order to keep all the acid fused; the line *DF* is thus obtained, ending at *F* at the melting-point of pure benzoïc acid, 121·4°. *DF* therefore represents the melting-point curve of the acid, on addition of increasing amounts of water.

Derivatives of Benzoïc Acid.

297. *Benzoyl chloride*, $C_6H_5\cdot COCl$, can be obtained by the action of phosphorus pentachloride or oxychloride upon benzoïc acid, or by the method of **296**, 5*a*; it is a liquid of disagreeable odour, and boils at 194°. It is manufactured by treating benzaldehyde, $C_6H_5\cdot C_{O}^{H}$, with chlorine. Unlike acetyl chloride, which is rapidly decomposed, it is very slowly acted upon by water at ordinary temperatures.

Benzoyl chloride is employed in the introduction of the benzoyl-group, $C_6H_5\cdot CO—$, into compounds. This is readily effected by a method discovered by BAUMANN and SCHOTTEN, which consists in shaking up the substance in alkaline solution with benzoyl chloride.

[illegible]

Benzanilide, $C_6H_5\cdot CO—NH\cdot C_6H_5$, is prepared by dropping small quantities of caustic potash and benzoyl chloride into aniline, and shaking the mixture, which is kept cool. Finally, caustic potash is added with constant shaking until the smell of benzoyl chloride has vanished. The benzanilide is collected on a filter, and is obtained perfectly pure:

$$C_6H_5\cdot NH\boxed{H + Cl}COC_6H_5 + KOH = C_6H_5\cdot NH\cdot COC_6H_5 + KCl + H_2O.$$

Benzoïc anhydride, $C_6H_5CO\cdot O\cdot COC_6H_5$, is formed by the interaction of a benzoate and benzoyl chloride:

$$C_6H_5\cdot CO\cdot O\boxed{Na + Cl}\cdot OCC_6H_5 = NaCl + C_6H_5CO\cdot O\cdot COC_6H_5.$$

At ordinary temperatures it is very stable towards water, but is decomposed when boiled with it, yielding benzoïc acid.

The formation of *ethyl benzoate* is sometimes employed as a test for ethyl alcohol, since it possesses a characteristic peppermint-like odour.

Benzamide, $C_6H_5\cdot CONH_2$, can be prepared by the action of ammonia or ammonium carbonate on benzoyl chloride. It is crystalline and dimorphous, melting at 130°. It was stated (**104**) that, on account of the influence of the negative acetyl-group, the hydrogen atoms of the amido-group in acetamide are replaceable by metals. Benzamide displays this property to an even greater extent, this being due to the more negative character of the benzoyl-group; for the values of the dissociation constants for acetic acid and for benzoïc acid respectively are $K = 0\cdot0018$ and $K = 0\cdot0060$.

When the silver compound of benzamide is treated with an alkyl iodide at ordinary temperatures, an O-ether, *benzoïc iminoether*, $C_6H_5\cdot C\genfrac{}{}{0pt}{}{\diagup OC_2H_5}{\diagdown NH}$, is formed. The constitution of this substance is proved by its yielding ammonia and alcohol, instead of ethylamine and benzoïc acid, when treated with alkalis. When, however, the silver compound is treated with an alkyl iodide at 100°, a N-alkyl, $\mathrm{C_6H_5{\cdot}C}{\lessgtr}\genfrac{}{}{0pt}{}{\mathrm{NHC_2H_5}}{\mathrm{O}}$, is formed. This is proved by the decomposition of the latter substance into ethylamine and benzoïc acid, so that the silver compound must have a different constitution at ordinary temperatures and at 100° (**247**).

Benzonitrile, $\mathrm{C_6H_5{\cdot}CN}$, the methods of producing which were described in **296**, 3, can also be produced similarly to the aliphatic nitriles; for example, by the action of phosphorus pentoxide upon benzamide. It is a liquid with an odour resembling that of bitter almonds, and boils at 191°. It has all the properties characteristic of the aliphatic nitriles.

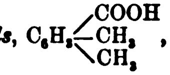
Homologues of Benzoïc Acid.

298. The *toluic acids*, $\mathrm{C_6H_4}{<}\genfrac{}{}{0pt}{}{\mathrm{CH_3}}{\mathrm{COOH}}$, are formed by the oxidation of the corresponding xylenes with dilute nitric acid. *p*-Toluic acid is one of the oxidation-products of the turpentine oils, which are first converted by oxidation into cymene,  The toluic acids only dissolve to a small extent in cold water.

Phenylacetic acid, $\mathrm{C_6H_5{\cdot}CH_2{\cdot}COOH}$, is isomeric with them, and can be obtained by the method indicated in the following scheme:

$$\underset{\text{Benzyl chloride}}{\mathrm{C_6H_5{\cdot}CH_2{\cdot}Cl}} + \mathrm{KCN} \rightarrow \underset{\text{Benzyl cyanide}}{\mathrm{C_6H_5{\cdot}CH_2{\cdot}CN}} \rightarrow \mathrm{C_6H_5{\cdot}CH_2{\cdot}COOH}.$$

It is readily distinguished from the toluic acids by oxidation, which converts it into the monobasic benzoïc acid, while the toluic acids yield the dibasic phthalic acids (**325**).

Xylic acids,  $\mathrm{C_6H_3}\begin{smallmatrix}\diagup \mathrm{COOH}\\ -\mathrm{CH_3}\\ \diagdown \mathrm{CH_3}\end{smallmatrix}$, have properties corresponding to those of benzoïc acid; they, too, are only slightly soluble in cold water.

FINISH

AROMATIC ALDEHYDES AND KETONES.

Aldehydes.

299. *Benzaldehyde*, $C_6H_5\cdot C_{O}^{H}$, is the best-known of the aromatic aldehydes. Like the aliphatic aldehydes, it is formed by the oxidation of the corresponding alcohol, benzyl alcohol, $C_6H_5\cdot CH_2OH$, and by distillation of a mixture of a benzoate and a formate. It is manufactured by heating *benzal chloride*, $C_6H_5CH\cdot Cl_2$, with water and calcium carbonate, a method whose aliphatic analogue is of no practical importance:

$$C_6H_5\cdot CH\boxed{Cl_2 + \begin{matrix}H\\H\end{matrix}}\begin{matrix}OH\\OH\end{matrix} - H_2O = C_6H_5\cdot C_{O}^{H} + 2HCl.$$

The following methods are employed in the preparation of its homologues.

1. Chloro-oxalic ester is allowed to react with an aromatic hydrocarbon in presence of aluminium chloride, when the ester of an α-ketonic acid is produced:

$$C_6H_6 + \underset{\text{Chloro-oxalic ester}}{ClCO{-}COOC_2H_5} = HCl + C_6H_5\cdot CO\cdot COOC_2H_5.$$

The free acid is obtained by saponification, and on dry distillation loses CO_2, with formation of the aldehyde:

$$C_5H_5\cdot CO\cdot CO_2H = C_6H_5\cdot C_{O}^{H} + CO_2.$$

2. An aromatic hydrocarbon is treated with a mixture of carbon monoxide and hydrochloric acid in presence of aluminium chloride and a trace of cuprous chloride. It may be assumed that formyl chloride, HCOCl, is obtained as an intermediate product:

$$CH_3\cdot C_6H_5 + ClOCH = HCl + CH_3\cdot C_6H_4\cdot C_{O}^{H}.$$

3. Anhydrous hydrocyanic acid and hydrochloric acid are brought

into contact with aromatic hydrocarbons, when aldehydes are produced, an *aldime* being formed as an intermediate product:

$$C_6H_6 + CNH + HCl = \underset{\text{Benzaldime hydrochloride}}{C_6H_5\cdot CH:NH\cdot HCl};$$

$$C_6H_5\cdot CH:NH\cdot HCl + H_2O = C_6H_5\cdot C{}^{H}_{O} + NH_4Cl.$$

Benzaldehyde is found in nature as a constituent of amygdalin, $C_{20}H_{27}NO_{11}$ (**242**); on this account, it is called *oil of bitter almonds.* It is a liquid of agreeable odour, is slightly soluble in water, boils at 179°, and has a specific gravity 1·0504 at 15°. It has most of the properties of the aliphatic aldehydes: it is readily oxidized, even by the oxygen of the atmosphere (especially when exposed to sunlight), reduces an ammoniacal silver solution with formation of a mirror, yields a crystalline addition-product with sodium hydrogen sulphite, adds on hydrocyanic acid and hydrogen, forms an oxime and a phenylhydrazone, etc.

There are, however, points in which it differs from the fatty aldehydes. Thus, with ammonia it does not yield a compound like aldehyde-ammonia, but produces *hydrobenzamide*, $(C_6H_5CH)_3N_2$, formed by the union of three molecules of benzaldehyde and two molecules of ammonia:

$$3C_6H_5\cdot C{}^{H}_{O} + 2H_3N = (C_6H_5CH)_3N_2 + 3H_2O.$$

The behaviour of the aromatic aldehydes towards alcoholic potash is characteristic, one molecule of the aldehyde being oxidized, and the other reduced (*cf.*, however, **117**); thus, benzaldehyde yields potassium benzoate and benzyl alcohol:

$$2C_6H_5\cdot C{}^{H}_{O} + KOH = C_6H_5\cdot COOK + C_6H_5\cdot CH_2OH.$$

The aromatic aldehydes condense readily with dimethylaniline or phenols, forming derivatives of triphenylmethane:

$$C_6H_5\cdot C\begin{matrix}H|\\|O\end{matrix} + \begin{matrix}H|C_6H_4OH\\H|C_6H_4OH\end{matrix} = C_6H_5\cdot CH<\begin{matrix}C_6H_4OH\\C_6H_4OH\end{matrix} + H_2O.$$

F 1

It has been observed that during the oxidation of various substances in the air, as much oxygen is rendered "active" as is taken up by the substance under oxidation ("Inorganic Chemistry," **351**); this is true of benzaldehyde. If it is left for several weeks in contact with water, indigosulphonic acid, and air, the same amount of oxygen is used up in oxidizing the indigo derivative as in converting the benzaldehyde into benzoïc acid. BAEYER has shown that benzoyl hydrogen peroxide, $C_6H_5CO \cdot O \cdot OH$, is formed as an intermediate product, and oxidizes the indigosulphonic acid, being itself reduced to benzoïc acid:

$$C_6H_5 \cdot CHO + O_2 = C_6H_5 \cdot CO \cdot O \cdot OH\,;$$

$$C_6H_5 \cdot CO \cdot O \cdot OH + \text{Indigo} = C_6H_5 \cdot COOH + \text{Oxidized indigo.}$$

The oxidation of benzaldehyde in the air must therefore be considered to take place thus:

$$C_6H_5 \cdot CHO + O_2 = C_6H_5 \cdot CO \cdot O \cdot OH\,;$$

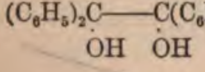
$$C_6H_5 \cdot CO \cdot O \cdot OH + C_6H_5 \cdot CHO = 2C_6H_5 \cdot COOH.$$

BAEYER has, in fact, proved that benzoyl hydrogen peroxide dissolves when added to benzaldehyde, but that the liquid gradually changes to a solid mass of pure benzoïc acid.

Ketones.

300. The *aromatic ketones* can be subdivided into the mixed aromatic-fatty ketones, and the true aromatic ketones. The best-known member of the first class is acetophenone, $C_6H_5 \cdot CO \cdot CH_3$; it can be obtained by distilling a mixture of calcium acetate and benzoate, or more readily by the addition of aluminium chloride to a mixture of benzene and acetyl chloride. It is a crystalline substance of agreeable odour, melting at 20° and boiling at 200°; it is slightly soluble in water, and possesses all the properties of the aliphatic ketones. It is employed as a soporific under the name "hypnone."

Benzophenone, $C_6H_5 \cdot CO \cdot C_6H_5$, is a true aromatic ketone, and can be obtained by the dry distillation of calcium benzoate, or by the action of benzene and aluminium chloride upon benzoyl chloride, or carbonyl chloride. This compound, although a true aromatic derivative, behaves exactly like an aliphatic ketone; on reduction, it yields *benzhydrol*, $C_6H_5 \cdot CHOH \cdot C_6H_5$; *benzpinacone*,



$(C_6H_5)_2\underset{OH}{C}\text{——}\underset{OH}{C}(C_6H_5)_2$, is simultaneously formed (**156**).

Although the mechanism of FRIEDEL and CRAFTS' synthesis (**268**, 2) of the homologues of benzene has not been satisfactorily explained, BÖESEKEN has put forward a complete explanation of the synthesis of aromatic ketones. He has proved that the acid chloride first unites with the aluminium chloride:

$$C_6H_5COCl + AlCl_3 = C_6H_5COCl\cdot AlCl_3.$$

On addition of one molecule of benzene, one molecule of hydrochloric acid is evolved, with formation of a crystalline compound:

$$C_6H_5\cdot COCl\cdot AlCl_3 + C_6H_6 = C_6H_5\cdot CO\cdot C_6H_5\cdot AlCl_3 + HCl.$$

On addition of water, a quantitative yield of the ketone is obtained:

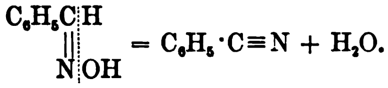
$$C_6H_5\cdot CO\cdot C_6H_5\cdot AlCl_3 + nH_2O = C_6H_5\cdot CO\cdot C_6H_5 + AlCl_3.nH_2O.$$

The reaction therefore takes place in three stages.

Benzophenone exists in two modifications; one of these is unstable and melts at 27°, and the other is stable and melts at 49°. The difference between these two is a purely physical one, since different derivatives of them are unknown.

Oximes.

301. Investigation has shown that some of the oximes of the aromatic aldehydes and ketones exhibit a peculiar kind of isomerism. Thus, there are two isomers of benzaldoxime, *benz*anti*aldoxime*, a liquid boiling without decomposition, and *benz*syn*aldoxime*, which is solid, and on treatment with acetic anhydride readily loses water, forming benzonitrile:

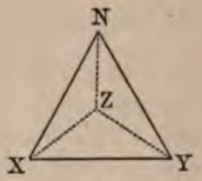


$$\begin{array}{l} C_6H_5C\vdots H \\ \quad\ \ \| \\ \quad\ N\vdots OH \end{array} = C_6H_5\cdot C\equiv N + H_2O.$$

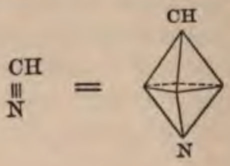
The *anti*aldoxime yields an acetyl-derivative with acetic anhydride.

It has been proved that no isomers of the ketoximes $\frac{R}{R'}{>}C{:}NOH$ exist, when R and R′ are similar; two isomers are known when these groups are dissimilar. Benzophenone oxime and its derivatives furnish examples of this. In spite of many attempts to prepare an isomer, benzophenone oxime is only known in one modification. When, however, hydrogen in one phenyl-group is substituted, two isomeric oximes can be obtained. Monochlorobenzophenone, $C_6H_5 \cdot CO \cdot C_6H_4Cl$, monobromobenzophenone, $C_6H_5 \cdot CO \cdot C_6H_4Br$, tolylphenylketone, $CH_3 \cdot C_6H_4 \cdot CO \cdot C_6H_5$, anisylphenylketone, $CH_3O \cdot C_6H_4 \cdot CO \cdot C_6H_5$, and many others, are examples of ketones which yield two isomeric oximes.

After several ineffectual attempts to explain such isomerism by the ordinary structural formulæ, the following stereochemical explanation of the observed facts has been adopted. It is assumed that the three affinities of the N-atom are directed towards the angles of a tetrahedron, the nitrogen atom itself being situated at the fourth angle:



When the three nitrogen bonds are linked to carbon, as in the nitriles, the following spacial representation is obtained:

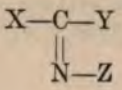


$$\begin{matrix} CH \\ ||| \\ N \end{matrix} =$$

Stereoisomerism is here impossible: experience has shown that none of the numerous nitriles known occurs in two forms due to isomerism in the CN-groups.

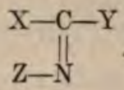
When, however, the nitrogen atom is linked to carbon by two bonds, two isomeric forms become possible:

These can be more readily represented by



$$\begin{array}{l} X-C-Y \\ \quad \| \\ \quad N-Z \end{array}$$

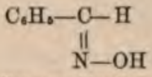
and



$$\begin{array}{r} X-C-Y \\ \| \quad \\ Z-N \quad \end{array}.$$

It will be observed that different configurations for such compounds are only obtained when X and Y are different, since, when they are similar, the figures become identical. This agrees with the facts stated above.

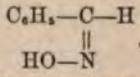
It can also be determined which configuration belongs to each isomer. The two isomeric benzaldoximes have the formulæ



$$\begin{array}{r} C_6H_5-C-H \\ \| \quad \\ N-OH \end{array}$$

Benz*syn*aldoxime
I.

and

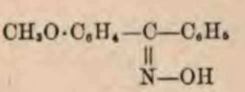


$$\begin{array}{r} C_6H_5-C-H \\ \| \quad \\ HO-N \quad \end{array}.$$

Benz*anti*aldoxime
II.

In formula I, H and OH are nearer together than in formula II, which explains the readiness with which one molecule of water is split off from one aldoxime (*syn*), and not from the other (*anti*). On this account configuration I is assigned to the *syn*aldoxime, and conconfiguration II to the *anti*aldoxime.

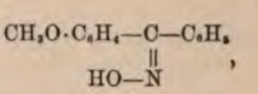
The configuration of the ketoximes can be determined by the BECKMANN transformation (**112**), as is made clear in the following example. Two isomers of anisylphenylketoxime are known,



$$\begin{array}{l} CH_3O\cdot C_6H_4-C-C_6H_5 \\ \qquad\qquad\quad \| \\ \qquad\qquad\quad N-OH \end{array}$$

I.

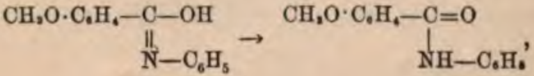
and



$$\begin{array}{l} CH_3O\cdot C_6H_4-C-C_6H_5 \\ \qquad\qquad\quad \| \\ \qquad\qquad HO-N \end{array},$$

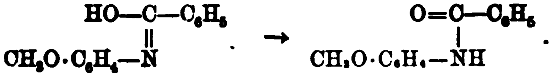
II.

the first melting at 137° and the second at 116°. By the BECKMANN transformation, the oxime of higher melting-point yields the anilide of anisic acid; that of lower melting-point, the aniside of benzoic acid. The former must therefore have configuration I, and the second configuration II, because in I the groups OH and C_6H_5 are next to each other, and exchange places,



$$\begin{array}{l} CH_3O\cdot C_6H_4-C-OH \\ \qquad\qquad\quad \| \\ \qquad\qquad\quad N-C_6H_5 \end{array} \rightarrow \begin{array}{l} CH_3O\cdot C_6H_4-C=O \\ \qquad\qquad\quad | \\ \qquad\qquad\quad NH-C_6H_5 \end{array},$$

producing the anilide of anisic acid, $CH_3O\cdot C_6H_4\cdot COOH$; while in II, anisyl ($CH_3O\cdot C_6H_4$—) and OH are next one another, and exchange places, yielding the aniside of benzoic acid:



$$\begin{array}{rcl}\mathrm{HO{-}} & \mathrm{C} & \mathrm{{-}C_6H_5}\\ & \| & \\ \mathrm{CH_3O\cdot C_6H_4{-}} & \mathrm{N} & \end{array} \rightarrow \begin{array}{rcl}\mathrm{O{=}} & \mathrm{C} & \mathrm{{-}C_6H_5}\\ & | & \\ \mathrm{CH_3O\cdot C_6H_4{-}} & \mathrm{NH} & \end{array}.$$

DIAZO-COMPOUNDS AND HYDRAZINES.

I. DIAZO-COMPOUNDS.

302. The diazo-compounds of the aromatic series, discovered by Griess in 1860, are not merely of theoretical importance, but play an important part in the manufacture of dyes. In the fatty series only amino-compounds of a special kind are capable of yielding diazo-compounds (**201**), while their formation is a general reaction of the primary aromatic amines; *the property of undergoing diazotization is characteristic of aromatic amines.*

Diazo-compounds are substances containing the group $—N_2—$. They are divided into two classes: the diazonium compounds, with properties analogous to ammonium compounds, from which their name is derived; and the true diazo-compounds, in which the group $—N_2—$ has the constitution $—N=N—$.

The diazonium compounds themselves are of slight importance, and are usually not isolated. The numerous transformations which they can undergo, however, with formation of a great number of derivatives, account for the great importance of these substances in the chemistry of the aromatic compounds.

Diazonium compounds are formed by the action of nitrous acid on the salts of aromatic amines:

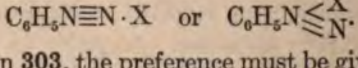
$$\underset{\text{Aniline nitrate}}{C_6H_5 \cdot NH_2 \cdot HNO_3} + HNO_2 = 2H_2O + \underset{\text{Benzenediazonium nitrate}}{C_6H_5 \cdot N_2 \cdot NO_3}.$$

This is usually carried out by adding a solution of sodium nitrite to one containing an equimolecular proportion of the amine-salt and an equivalent quantity of a free mineral acid, the reaction-mixture being cooled by the addition of ice, as the diazonium compounds decompose very readily; a solution of the benzenediazonium salt is thus obtained. In order to isolate such a salt as *benzenediazonium chloride*, $C_6H_5 \cdot N_2 \cdot Cl$, in the solid state, a small quantity of concentrated hydrochloric acid is added to an alcoholic solution of aniline hydrochloride, and then amyl nitrite, whereupon the diazonium chloride crystallizes out. The dry diazonium salts are excessively explosive, and must therefore be handled with great care; they are quite harmless in aqueous solution, and as it is unnecessary to isolate them in order to employ them in reactions, they are seldom prepared in the solid state.

The group N_2X of the diazonium compounds, of which X is an acid-residue, is only linked to one carbon atom of the benzene-nucleus, for all their transformations produce substances containing a group likewise linked to only one carbon atom of the nucleus.

The constitution of the diazonium-group, $—N_2X$, can be deduced from the following considerations. In many respects the group $C_6H_5 \cdot N_2—$ behaves similarly to an alkali-metal, and still more to the ammonium radicle. With strong mineral acids it forms colourless salts of neutral reaction, like KCl and NH_4Cl, while its salts with carbonic acid resemble the alkali-carbonates in having an alkaline reaction, due to hydrolytic dissociation. The conductivity of the diazonium salts of hydrochloric and other acids shows that they are as strongly ionized as KCl and NH_4Cl. Similarly, diazonium chlorides yield platinum double salts, such as $(C_6H_5N_2Cl)_2PtCl_4$, which dissolve with difficulty in water. Other double salts, such as $(C_6H_5N_2Cl)AuCl_3$, have also been obtained. Free *benzenediazonium hydroxide*, $C_6H_5 \cdot N_2 \cdot OH$, is only known in aqueous solution, which has a strongly alkaline reaction. It is obtained by treating the aqueous solution of the chloride with silver oxide, or by the addition of the equivalent quantity of baryta-water to the sulphate. It is colourless, like caustic-potash solution, but through decomposition gradually deposits a flocculent, resin-like substance.

The existence of a pentavalent N-atom in the diazonium salts, just as in those of ammonium, must therefore be assumed, the basic properties of each being due to its presence. Two formulæ are therefore possible:



$$C_6H_5N\equiv N\cdot X \quad \text{or} \quad C_6H_5N\lesseqgtr^{X}_{N}.$$

As will be proved in **303**, the preference must be given to the second.

Reactions of the Diazonium Compounds.

303. Many of the reactions of the diazonium compounds are characterized by the elimination of the group $—N_2—$ as free nitrogen from the molecule, and its replacement by a substituting-group linked by a single bond to the benzene-nucleus. Extended research has revealed the best conditions for obtaining nearly quantitative results in most of these reactions.

1. *Replacement of the N_2-group by hydroxyl.*—This is effected by allowing the aqueous solution of the diazonium salt to stand, or by warming it:

$$C_6H_5\cdot N_2\cdot Cl + HOH = C_6H_5\cdot OH + N_2 + HCl.$$

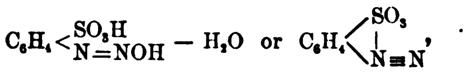
2. *Replacement by an alkoxyl-group,* $—O\cdot C_nH_{2n+1}$.—This is carried out by boiling a diazonium salt with alcohol:

$$C_6H_5\cdot N_2\cdot \boxed{HSO_4 + H}O\cdot C_2H_5 = C_6H_5O\cdot C_2H_5 + N_2 + H_2SO_4.$$

3. *Replacement of the diazonium-group by hydrogen.*—Under certain conditions the diazonium salts do not yield alkoxyl-compounds with alcohols, but produce the corresponding hydrogen compound, the alcohol being converted into aldehyde:

$$\underset{\text{\textit{p}-Nitrobenzenediazonium chloride}}{NO_2\,C_6H_4\cdot N_2\cdot Cl} + C_2H_5OH = \underset{\text{Nitrobenzene}}{NO_2\cdot C_6H_5} + N_2 + HCl + \underset{\text{Acetaldehyde}}{C_2H_4O.}$$

By this treatment, *p*-diazobenzenesulphonic acid,



$$C_6H_4<\begin{matrix}SO_3H\\ N{=}NOH\end{matrix} - H_2O \text{ or } C_6H_4\begin{matrix}\diagup SO_3\\ \quad\;|\\ \diagdown N{\equiv}N\end{matrix},$$

when treated with methyl alcohol under diminished pressure, yields only benzenesulphonic acid, the diazonium-group being therefore only replaced by hydrogen. Under a pressure of 30 atmospheres, however, only anisolesulphonic acid, $C_6H_4<\begin{matrix}SO_3H\\ OCH_3\end{matrix}$, is formed, N_2 being replaced by the methoxyl-group, $—OCH_3$.

4. *Replacement of the diazonium group by halogens.*—This is effected by treatment of a solution of diazonium chloride either with cuprous chloride dissolved in concentrated hydrochloric acid (SANDMEYER), or with finely-divided copper (GATTERMANN);

$$C_6H_5\cdot N_2\cdot Cl = C_6H_5\cdot Cl + N_2.$$

Cuprous chloride, and finely-divided copper, have here a catalytic action ; it is probable that a copper compound is formed as an intermediate product, and is afterwards decomposed.

Replacement by bromine is carried out in the same way: thus, in the preparation of bromobenzene, a solution of potassium bromide is added to an aqueous solution of benzenediazonium sulphate containing free sulphuric acid; on addition of copper-dust to this mixture, nitrogen is evolved, and bromobenzene is formed.

Replacement by iodine takes place readily when a warm solution of potassium iodide is added to a diazonium sulphate solution ; it is unnecessary to employ copper or cuprous chloride.

5. *Replacement of the diazonium group by the* CN-*group*.—This, too, readily takes place in presence of copper compounds. The solution of the diazonium salt is added to one of potassium cuprous cyanide:

$$C_6H_5 \cdot N_2 \cdot Cl + KCN = C_6H_5 \cdot CN + N_2 + KCl.$$

This reaction is of great importance for the synthesis of aromatic acids, which can be got by hydrolyzing the nitriles thus obtained.

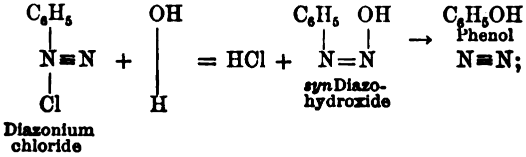
6. *Other reactions* can be carried out by treating diazonium salts with sulphuretted hydrogen, which yields compounds containing sulphur linked to the benzene-nucleus. By this treatment, benzenediazonium chloride yields phenyl sulphide, $(C_6H_5)_2S$, two molecules of the chloride reacting with one of sulphuretted hydrogen.

The N_2-group can also be replaced by aromatic hydrocarbon-residues ; thus, *diphenyl*, $C_6H_5 \cdot C_6H_5$, is obtained by treating dry benzenediazonium chloride with benzene in presence of a small quantity of aluminium chloride :

$$C_6H_5 \cdot N_2 \cdot Cl + H \cdot C_6H_5 = C_6H_5 \cdot C_6H_5 + N_2 + HCl.$$

These reactions illustrate the importance of the diazonium salts as intermediate products in the preparation of numerous substances. Since they are derived from the amines, which are prepared by the reduction of nitro-compounds, it is evident that the nitration of aromatic derivatives is a reaction of great importance, for the nitro-group can be replaced at will by almost all other elements or groups by means of the amino-compounds and diazonium compounds.

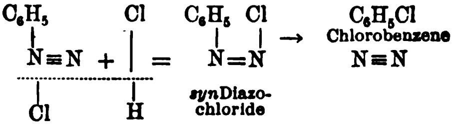
HANTZSCH has explained the reactions of the diazonium compounds by assuming that they themselves do not enter into reaction, but are first converted into a *syn*diazo-compound, which then decomposes with evolution of nitrogen. The formation of phenol must then be represented thus:



$$\begin{array}{c} C_6H_5 \\ | \\ N\equiv N \\ | \\ Cl \end{array} + \begin{array}{c} OH \\ | \\ | \\ | \\ H \end{array} = HCl + \begin{array}{c} C_6H_5 \quad OH \\ | \qquad | \\ N=N \end{array} \longrightarrow \begin{array}{c} C_6H_5OH \\ N\equiv N; \end{array}$$

Diazonium chloride; *syn*Diazo-hydroxide; Phenol

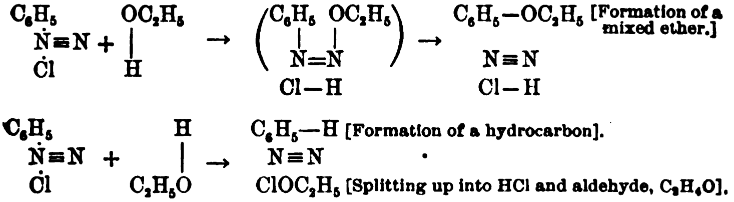
and that of chlorobenzene thus:



$$\begin{array}{c} C_6H_5 \\ | \\ N\equiv N \\ | \\ Cl \end{array} + \begin{array}{c} Cl \\ | \\ | \\ | \\ H \end{array} = \begin{array}{c} C_6H_5 \quad Cl \\ | \qquad | \\ N=N \end{array} \longrightarrow \begin{array}{c} C_6H_5Cl \\ N\equiv N \end{array}$$

*syn*Diazo-chloride; Chlorobenzene

The reactions between diazonium salts and alcohol are explained as follows:

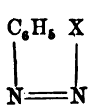


$$\begin{array}{c} C_6H_5 \\ N\equiv N \\ Cl \end{array} + \begin{array}{c} OC_2H_5 \\ | \\ H \end{array} \longrightarrow \left(\begin{array}{c} C_6H_5 \quad OC_2H_5 \\ | \qquad | \\ N=N \end{array}\right) \longrightarrow \begin{array}{l} C_6H_5-OC_2H_5 \text{ [Formation of a mixed ether.]} \\ N\equiv N \\ Cl-H \end{array}$$
$$\begin{array}{c} \\ \\ Cl-H \end{array}$$

$$\begin{array}{c} C_6H_5 \\ N\equiv N \\ Cl \end{array} + \begin{array}{c} H \\ | \\ C_2H_5O \end{array} \longrightarrow \begin{array}{l} C_6H_5-H \text{ [Formation of a hydrocarbon].} \\ N\equiv N \\ ClOC_2H_5 \text{ [Splitting up into HCl and aldehyde, } C_2H_4O]. \end{array}$$

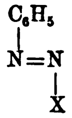
As these transformations of diazonium salts cannot be explained by the other possible structural formula, $C_6H_5\cdot N\equiv N\cdot X$, it is evident that it must be rejected (302).

Most of the *syn*diazo-compounds are very unstable, however; they change readily into *anti*diazo-compounds, in which it is assumed that the phenyl-group and acid-residue are far removed from one another, and can therefore no longer unite:



$$\begin{array}{c} C_6H_5 \quad X \\ | \qquad | \\ N=\!=N \end{array}$$

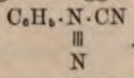
*syn*Diazo-compound; C_6H_5 and X can unite with one another



$$\begin{array}{l} C_6H_5 \\ | \\ N=N \\ \quad\;\; | \\ \quad\;\; X \end{array}$$

*anti*Diazo-compound; C_6H_5 and X cannot unite with one another

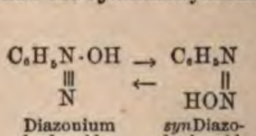
In certain cases, such as that of the diazocyanides, HANTZSCH has been able to isolate these intermediate products, and thus afford a proof of these views. For example, when cyanides are added to diazotized *p*-chloroaniline, $Cl\cdot C_6H_4\cdot NH_2$, *p*-chlorobenzonitrile, $Cl\cdot C_6H_4\cdot CN$, is not immediately formed; it is possible to isolate a yellow intermediate product, $Cl\cdot C_6H_4\cdot N_2\cdot CN$, which yields *p*-chlorobenzonitrile after addition of copper-dust, the action being accompanied by an energetic evolution of nitrogen. This yellow intermediate *p*-chlorobenzene-*syn*diazocyanide is, however, very unstable, and speedily changes to an isomer (the *anti*-compound) which does not react with copper-dust. The stereochemical theory thus affords a satisfactory explanation of the observed phenomena.

It might be suggested that the unstable primary product is diazonium cyanide,  $\begin{array}{l}C_6H_5\cdot N\cdot CN\\ \quad |||\\ \quad N\end{array}$. This cannot be the case, for such a cyanide must have properties analogous to those of potassium cyanide, it must be colourless, like the other diazonium salts, have an alkaline reaction in aqueous solution, and conduct the electric current, whereas the unstable primary product possesses none of these properties.

Moreover, an anisole derivative, $CH_3O\cdot C_6H_4N_2\cdot CN$, was discovered by **Hantzsch**, which must be looked upon as a diazonium cyanide, since its aqueous solution does possess all these properties.

Benzenediazonium hydroxide is a strong base, but reacts with alkalis in a manner quite unknown among the strong mineral bases. When a diazonium salt is added to a strong solution of caustic potash, a potassium derivative, $C_6H_5\cdot N_2\cdot OK$, separates out. The reaction takes place not only in concentrated but also in dilute solutions. When a dilute solution of benzenediazonium hydroxide is treated with an equivalent quantity of caustic soda in dilute solution, the molecular conductivity of the mixture is considerably less than the sum of the two electric conductivities of the solutions separately; it follows that a portion of the ions $(C_6H_5N_2O)' + H^{\cdot}$ and $Na^{\cdot} + OH'$, which have been brought into contact, have changed to the non-ionized state—union of $H^{\cdot}$ and OH'—that is, the formation of a salt must have occurred.

Thus, the diazonium hydroxide, which is a strong base, appears to behave like an acid also. Since this is very improbable, **Hantzsch** assumes that an equilibrium exists in the aqueous solution between the diazonium hydroxide and the *syn*diazohydroxide (p. 399):



$$\begin{array}{ccc} C_6H_5N\cdot OH & \rightleftarrows & C_6H_5N \\ ||| & & || \\ N & & HON \end{array}$$

Diazonium hydroxide   *syn*Diazo-hydroxide

He supposes that the alkali-derivatives are derived from the latter compound.

304. The importance of the diazonium compounds is not confined to reactions in which the nitrogen atoms are eliminated, since important derivatives, in which they are retained, are known.

1. *Diazoamino-compounds* are obtained by the action of primary and secondary amines upon diazonium salts:

$$C_6H_5\cdot N_2\cdot\boxed{Cl + H}NHC_6H_5 = \underset{\text{Diazoaminobenzene}}{C_6H_5\cdot N_2\cdot NHC_6H_5} + HCl.$$

They are also obtained when nitrous acid reacts with free aniline instead of an aniline salt. It may be supposed that in this reaction benzenediazonium hydroxide, or rather benzenediazohydroxide, is first formed, and is at once attacked by a molecule of the aniline still present:

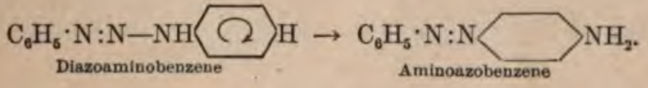
$$\text{I. } C_6H_5\cdot NH_2 + HNO_2 = C_6H_5\cdot N_2\cdot OH + H_2O.$$

$$\text{II. } \underset{\text{Benzenediazohydroxide}}{C_6H_5\cdot N_2\cdot}\boxed{OH + H}NHC_6H_5 = C_6H_5\cdot N:N\cdot NHC_6H_5 + H_2O.$$

The diazoamino-compounds are crystalline and have a yellow colour; they do not unite with acids. In acid solution, they are converted by treatment with nitrous acid into diazonium salts:

$$C_6H_5\cdot N:N\cdot NHC_6H_5+HNO_2+2HCl = 2C_6H_5\cdot N_2\cdot Cl+2H_2O.$$

The most characteristic property of the diazoamino-compounds is their ready transformation into isomers, the *aminoazo-compounds:*



This is best carried out by adding aniline hydrochloride to a solution of diazoaminobenzene in aniline, and warming the mixture on the water-bath.

The amido-group in *aminoazobenzene* is in the *para*-position to the azo-group. When the *para*-position is already occupied, the amido-group takes up the *ortho*-position. Aminoazobenzene and many of its derivatives are dyes (**320**).

The above equation indicates that the transformation of diazoaminobenzene into aminoazobenzene is a unimolecular reaction ("Inorganic Chemistry," **50**). GOLDSCHMIDT proved by experiment that this view is correct. He dissolved diazoaminobenzene in aniline, and determined the quantity of diazoaminobenzene still present after the lapse of known periods of time.

The aniline hydrochloride usually added in carrying out this experiment has merely a catalytic accelerating effect upon the reaction; this is proved by the uniform increase in the velocity constant with increase in the amount of aniline hydrochloride, and in other ways.

It has also been shown that when different salts of aniline are employed, their catalytic influence varies in amount, and is almost proportional to their degree of ionization in aqueous solution. This was proved by GOLDSCHMIDT for the aniline salts of dichloroacetic and trichloroacetic acids.

This phenomenon can be explained by the assumption that aniline salts are decomposed into free acid and aniline when dissolved in aniline, in a manner similar to the setting-free of salts from their water of crystallization when dissolved in water; and by the further assumption that the slight ionization undergone by the free acid in the aniline—such solutions being very poor conductors of the electric current—is proportional to the degree of ionization in aqueous solution.

2. Diazonium salts unite with tertiary amines at the *para*-position:

$$C_6H_5\cdot N_2\cdot\boxed{Cl+H}\underset{\text{Dimethylaniline}}{C_6H_4\cdot N(CH_3)_2} = \underset{\text{Dimethylaminoazobenzene}}{C_6H_5\cdot N:N\cdot C_6H_4\cdot N(CH_3)_2} + HCl.$$

3. They react similarly with phenols, forming *hydroxyazo-compounds*. This takes place in presence of alkalis:

$$C_6H_5\cdot N_2\cdot\boxed{Cl + H}\underset{\text{Phenol}}{C_6H_4OH} = \underset{\text{Hydroxyazobenzene}}{C_6H_5\cdot N:N\cdot C_6H_4OH} + HCl.$$

A number of important dyes are also derived from *hydroxyazobenzene* (**322**).

II. HYDRAZINES.

305. The most important derivative of hydrazine is *phenylhydrazine*, $C_6H_5\cdot NH\cdot NH_2$, which has been referred to several times in the fatty series in connection with its action on aldehydes, ketones, and sugars (**112**, **208**, and **212**.) It is formed by the reduction of the diazonium salts; for example, from benzenediazonium chloride by the action of the calculated quantity of stannous chloride dissolved in hydrochloric acid:

$$C_6H_5{\cdot}N_2{\cdot}Cl + 4H = C_6H_5{\cdot}NH{-}NH_2{\cdot}HCl.$$

It can also be formed by transforming the diazonium salt into a diazosulphonate by means of alkali-sulphite, reducing the diazosulphonate with zinc-dust and acetic acid, and splitting off the sulpho-group by boiling with hydrochloric acid:

$$\text{I. } C_6H_5{\cdot}N_2{\cdot}Cl + Na_2SO_3 = \underset{\text{Sodium diazobenzenesulphonate}}{C_6H_5{\cdot}N{:}N{\cdot}SO_3Na} + NaCl.$$

$$\text{II. } C_6H_5{\cdot}N{:}N{\cdot}SO_3Na + 2H = \underset{\text{Sodium phenylhydrazinesulphonate}}{C_6H_5{\cdot}NH{\cdot}NH{\cdot}SO_3Na}.$$

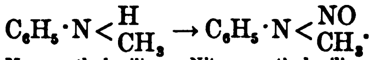
$$\text{III. } C_6H_5{\cdot}NH{\cdot}NH{\cdot}SO_3Na+H_2O = \underset{\text{Phenylhydrazine}}{C_6H_5{\cdot}NH{\cdot}NH_2}+NaHSO_4.$$

This apparently roundabout way is simple in practice, since the intermediate products do not need to be isolated. It is sufficient to mix the solution of the diazonium salt with that of the sulphite, then to add the acetic acid and zinc-dust, and filter off the excess of the latter. The filtrate is then boiled with fuming hydrochloric acid, whereupon the hydrochloride, $C_6H_5{\cdot}NH{\cdot}NH_2{\cdot}HCl$, separates out, since it is soluble with difficulty in water, and almost insoluble in hydrochloric acid.

Phenylhydrazine is a colourless, oily liquid, turning brown in the air. Its melting-point is 17·5°, and its boiling-point 241°; when boiled under ordinary pressure, it undergoes slight decomposition. It is only slightly soluble in water.

Phenylhydrazine is split up by energetic reduction into aniline and ammonia. It is very sensitive towards oxidizing agents, its sulphate being oxidized to the diazonium salt by mercury oxide. Oxidation usually goes further, however, the nitrogen being eliminated from the molecule. For example, an alkaline copper solution converts it into water, nitrogen, and benzene. Phenylhydrazine has a wholly basic character; it yields well-defined crystalline salts.

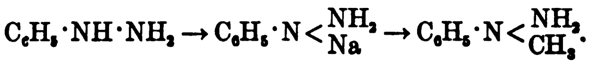
Phenylhydrazine is proved as follows to have the constitutional formula $C_6H_5\cdot NH\cdot NH_2$. A secondary amine is converted by nitrous acid into the corresponding nitrosamine:



$$C_6H_5\cdot N<\genfrac{}{}{0pt}{}{H}{CH_3} \rightarrow C_6H_5\cdot N<\genfrac{}{}{0pt}{}{NO}{CH_3}.$$

Monomethylaniline Nitrosomethylaniline

On careful reduction, this substance yields *methylphenylhydrazine*, $C_6H_5N\cdot<\genfrac{}{}{0pt}{}{NH_2}{CH_3}$, which can also be obtained from phenylhydrazine by the action of sodium, one hydrogen atom being replaced by the metal. On treatment of this sodium compound with methyl iodide, the same methylphenylhydrazine is formed:



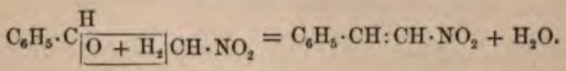
$$C_6H_5\cdot NH\cdot NH_2 \rightarrow C_6H_5\cdot N<\genfrac{}{}{0pt}{}{NH_2}{Na} \rightarrow C_6H_5\cdot N<\genfrac{}{}{0pt}{}{NH_2}{CH_3}.$$

FINISH

COMPOUNDS CONTAINING AN UNSATURATED SIDE-CHAIN.

Hydrocarbons.

306. *Styrole*, $C_6H_5\cdot CH{:}CH_2$, which derives its name from its occurrence in storax, can be obtained by heating cinnamic acid, $C_6H_5\cdot CH{:}CH\cdot COOH$, which splits off CO_2. It is a liquid of agreeable odour, and boils at 146°. It is converted on heating, and also slowly on standing at ordinary temperatures, into a glass-like mass called metastyrole, a polymer of unknown molecular weight. Styrole has the power, characteristic of substances containing a double bond, of forming addition-products. On treatment with nitric acid, it yields *nitrostyrole*, $C_6H_5\cdot CH{:}CH\cdot NO_2$, with the nitro-group in the side-chain. The constitution of this compound follows from its formation by the condensation of benzaldehyde with nitromethane, under the catalytic influence of alcoholic potash:



$$C_6H_5\cdot\overset{H}{C}\boxed{O + H_2}CH\cdot NO_2 = C_6H_5\cdot CH{:}CH\cdot NO_2 + H_2O.$$

Phenylacetylene, $C_6H_5\cdot C\vdots CH$, can be obtained by treating acetophenone with phosphorus pentachloride, and acting on the resulting compound, $C_6H_5\cdot CCl_2\cdot CH_3$, with caustic potash; or from phenylpropiolic acid, $C_6H_5\cdot C\vdots C\cdot COOH$, by slow distillation with aniline. In many respects it resembles acetylene, yielding metallic derivatives, for example. On solution in concentrated sulphuric acid, it takes up one molecule of water, forming acetophenone.

Alcohols and Aldehydes.

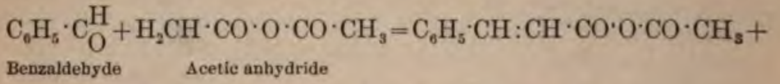
307. *Cinnamic alcohol*, $C_6H_5\cdot CH{:}CH\cdot CH_2OH$, is the only representative of these alcohols which need be mentioned here. It is a crystalline substance with an odour of hyacinths, and is present as an ester in storax. Careful oxidation converts it into cinnamic acid, and more vigorous oxidation into benzoic acid.

308. *Cinnamaldehyde*, $C_6H_5\cdot CH{:}CH\cdot C_{O}^{H}$, is the chief constituent of oil of cinnamon, from which it can be obtained by means of its sulphite compound. It is an oil of agreeable odour, and boils at 246°. It is resinified by strong acids, and yields a compound $N_2(C_6H_5C_3H_3)_3$ with ammonia, in the same way as benzaldehyde (**299**).

Acids.

309. Of these, *cinnamic acid*, $C_6H_5\cdot CH{:}CH\cdot COOH$, is the most important. It is present in some balsams, and in storax. It is manufactured by a synthetic method discovered by W. H. PERKIN, SEN.

Benzaldehyde is heated with acetic anhydride, in presence of sodium acetate as a catalytic agent:

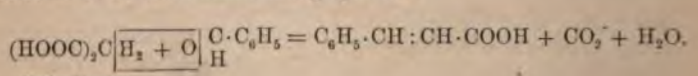


$$\underset{\text{Benzaldehyde}}{C_6H_5\cdot C\overset{H}{\underset{O}{}}} + \underset{\text{Acetic anhydride}}{H_2CH\cdot CO\cdot O\cdot CO\cdot CH_3} = C_6H_5\cdot CH{:}CH\cdot CO\cdot O\cdot CO\cdot CH_3 +$$

$$+ H_2O = \underset{\text{Cinnamic acid}}{C_6H_5\cdot CH{:}CH\cdot COOH} + \underset{\text{Acetic acid}}{HO\cdot CO\cdot CH_3}.$$

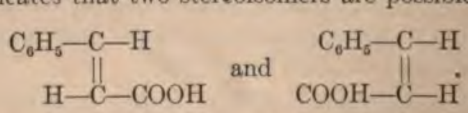
PERKIN'S synthesis can be carried out with substituted benzaldehydes on the one hand, and with homologues of acetic acid or with dibasic acids on the other, so that it is possible to obtain a great number of unsaturated aromatic acids by its aid.

Cinnamic acid can also be obtained by the action of benzal chloride (**312**), $C_6H_5\cdot CHCl_2$, upon sodium acetate. It can further be synthesized by the condensation of malonic acid with benzaldehyde, which takes place readily under the catalytic influence of ammonia, one molecule of carbon dioxide being split off:



$$\underset{\text{Malonic acid}}{(HOOC)_2C}\boxed{H_2 + O}\begin{matrix}C\cdot C_6H_5\\ H\end{matrix} = C_6H_5\cdot CH{:}CH\cdot COOH + CO_2 + H_2O.$$

Cinnamic acid is a crystalline substance, melts at 134°, and dissolves with difficulty in cold water. In all respects it possesses the character of a substance with a double bond, and therefore forms addition-products and reduces BAEYER'S reagent (**123**). Its constitution indicates that two stereoisomers are possible:



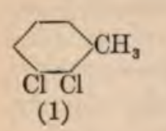
$$\begin{array}{c}C_6H_5—C—H\\ \|\\ H—C—COOH\end{array} \quad\text{and}\quad \begin{array}{c}C_6H_5—C—H\\ \|\\ COOH—C—H\end{array}.$$

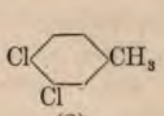
An isomer, *allocinnamic acid*, is known; it is readily transformed into ordinary cinnamic acid.

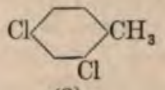
FINISH

POLY-SUBSTITUTED DERIVATIVES CONTAINING SIMILAR SUBSTITUENTS.

310. The number of poly-substituted derivatives of benzene and its homologues is very great. The hydrogen atoms of these hydrocarbons can be replaced not only by two or more similar groups, but also by two or more different groups. For each disubstitution-product and for each trisubstitution-product of benzene three isomers are possible when the substituents are similar. In the homologues of benzene, substitution can take place wholly or partly in the side-chain; thus, the following isomers are theoretically possible for a compound $C_7H_6Cl_2$:


(1)


(2)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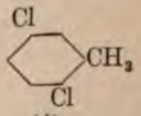
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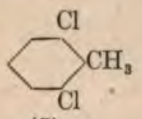
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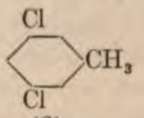
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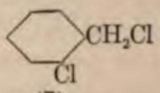
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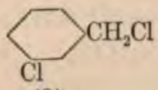
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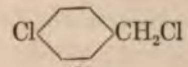
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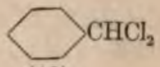

(10)

A large proportion of the numerous compounds theoretically possible is known. Only a few of the chief of them can be considered here.

It would be impossible to describe for each of these compounds how the positions of its substituents (*orientation*) has been determined, so that a summary will be given of the methods of orientation in **352** to **356**.

I. POLYSULPHONIC ACIDS.

311. When benzene and its homologues are treated with fuming sulphuric acid, disulphonic and trisulphonic acids, very similar in properties to the monosulphonic acids, are formed. Under this treatment, benzene yields m-*disulphonic acid*, which, on prolonged heating is partially converted into the p-*disulphonic acid*.

II. POLYHALOGEN DERIVATIVES.

312. These can be obtained by the direct action of chlorine or bromine upon the aromatic hydrocarbons. If one halogen atom is already present, substitution takes place principally in the *p*-position, a small quantity of the *o*-compound being also formed. m-*Dichlorobenzene* or m-*dibromobenzene* is obtained from *m*-dinitrobenzene (**318**) by reducing to diamine and subsequently diazotizing. It has been found possible by prolonged halogenation to replace the six hydrogen atoms of benzene by halogen; C_6Cl_6 (JULINS' *chlorocarbon*) is thus obtained in the form of colourless needles melting at 229°. It has not been possible to replace all the hydrogen atoms in toluene by chlorine; it has only been converted into *tetrachlorobenzotrichloride*, $C_6HCl_4 \cdot CCl_3$, or into *pentachlorobenzal chloride*, $C_6Cl_5 \cdot CHCl_2$. On further chlorination, the molecule splits up. Examples of this phenomenon are also found in the fatty series.

The same methods can be employed in the preparation of the polyhalogen derivatives of the homologues of benzene, as have been described for the monohalogen derivatives (**273**). If it is desired to substitute in toluene the methyl-hydrogen atoms alone, this hydrocarbon is treated with chlorine or bromine at the boiling-point: there are obtained in succession *benzyl chloride*, $C_6H_5 \cdot CH_2Cl$, *benzal chloride*, $C_6H_5 \cdot CHCl_2$, and *benzotrichloride*, $C_6H_5 \cdot CCl_3$. When the object is to substitute hydrogen only in the ring, chlorine is allowed to react at ordinary temperatures in presence of a trace of iodine. To prepare a compound such as $C_6H_4Cl \cdot CH_2Cl$, both methods must be employed in succession.

Benzal chloride, $C_6H_5 \cdot CHCl_2$ (B.P. 206°), and benzotrichloride, $C_6H_5 \cdot CCl_3$ (B.P. 213°), are of technical importance; benzaldehyde (**299**) is obtained from the former, and benzoïc acid (**296**) from the latter.

Benzene and some of its homologues also yield addition-products with chlorine and bromine. From benzene is obtained *benzene hexa-*

chloride, $C_6H_6Cl_6$, and *benzene hexabromide*, $C_6H_6Br_6$. Both are obtained by treating benzene with excess of the halogen in presence of sunlight; the chlorine derivative is known in two isomeric forms.

III. POLYHYDRIC PHENOLS.

313. It was stated in **275** that phenol is much more readily attacked by oxidizing agents than is benzene itself. The polyhydric phenols possess this property to an even greater extent, many of them behaving as powerful reducing-agents when dissolved in alkalis.

Dihydric Phenols.

The *o*-compound, $C_6H_4\begin{matrix}OH\ 1\\OH\ 2\end{matrix}$, *catechol* (pyrocatechol or pyrocatechin), is a constituent of many resins, and can be prepared by fusing *o*-phenolsulphonic acid with caustic potash.

alc ch

Catechol is crystalline and readily soluble in water, alcohol, and ether. It melts at 104°. Its alkaline solution is first turned green by atmospheric oxidation, and then black. Its aqueous solution precipitates metallic silver from silver-nitrate solution at ordinary temperatures, and gives a green colouration with ferric chloride. The monomethyl ether, $C_6H_4<\begin{matrix}OCH_3\ 1\\OH\ \ \ 2\end{matrix}$, is called *guaiacol*; it is present in the tar obtained by the dry distillation of beechwood. When heated with hydriodic acid, guaiacol yields catechol and methyl iodide.

Resorcinol (resorcin), or *m*-dihydroxybenzene, $C_6H_4<\begin{matrix}OH\ 1\\OH\ 3\end{matrix}$, can be obtained by fusing *m*-phenylenedisulphonic acid, $C_6H_4<\begin{matrix}SO_3H\ 1\\SO_3H\ 3\end{matrix}$, with caustic potash: this is the method by which it is manufactured. It yields a deep-violet colouration with ferric chloride; bromine-water converts it into *tribromoresorcinol*. It is a colourless, crystalline substance melting at 118°, and readily soluble in water, alcohol, and ether. It quickly turns brown, owing to the action of the air.

Quinol (hydroquinone), or *p*-dihydroxybenzene, melts at 169°. Its chief characteristic is the loss on oxidation of two hydrogen atoms with formation of *quinone*, $C_6H_4O_2$ (**316**), which is readily reconverted into quinol by reduction. The reducing effect of quinol is employed in photography for the development of negatives. With ammonia it gives a red-brown colouration, due to the formation of complex derivatives. Like its isomers, it is readily soluble in water.

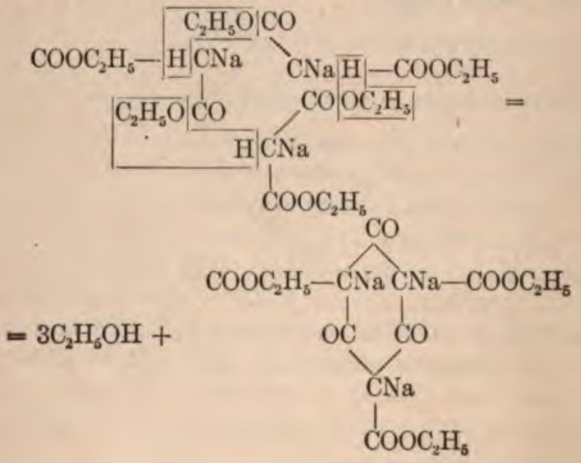
Trihydric Phenols.

314. *Pyrogallol* (pyrogallic acid), $C_6H_3\left\langle\begin{matrix}OH\ 1\\ OH\ 2\\ OH\ 3\end{matrix}\right.$, is obtained by heating *gallic acid* (**345**), CO_2 being split off:

$$\underset{\text{Gallic acid}}{C_6H_2(OH)_3 \cdot COOH} = \underset{\text{Pyrogallol}}{C_6H_3(OH)_3} + CO_2.$$

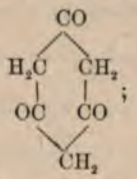
Pyrogallol forms crystals melting at 132°, and is readily soluble in water. It is a strong reducing-agent in alkaline solution; for example. it rapidly absorbs the oxygen of the atmosphere, with formation of a brown colouration. For this reason it is employed in gas-analysis to remove oxygen from mixtures. It is also used as a developer in photography.

Phloroglucinol (symmetrical trihydroxybenzene), $C_6H_3\left\langle\begin{matrix}OH\ 1\\ OH\ 3\\ OH\ 5\end{matrix}\right.$, is formed by fusing various resins with caustic potash. It is crystalline, and gives a deep-violet colouration with ferric chloride. A remarkable synthesis of phloroglucinol has been discovered by Baeyer. When sodiomalonic ester (**166**) is heated, three molecules condense, with elimination of three molecules of alcohol:

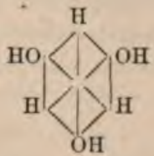


On acidifying this condensation-product, the sodium atoms are replaced by hydrogen, with formation of *phloroglucinoltricarboxylic ester*. When this substance is fused with caustic potash, the ethyl-carboxyl-groups ($—COOC_2H_5$) are abstracted, and replaced by hydrogen, phloroglucinol resulting.

Phloroglucinol should therefore have the constitution



in other words, it is a hexamethylene in which three of the methylene groups, $=CH_2$, have been replaced by carbonyl, $=CO$; it must, therefore, be called *triketohexamethylene*. It has been proved that phloroglucinol does behave as though it had this constitution; thus, with three molecules of hydroxylamine it yields a trioxime. On the other hand, phloroglucinol has the character of a phenol; for example, it yields a triacetate with acetyl chloride. It exists, therefore, in two tautomeric forms, as a hexamethylene derivative and as trihydroxybenzene:



This is a remarkable example of the alteration of the positions of the atoms (the hydrogen of the OH-groups) in the molecule, resulting in the conversion of a benzene derivative into a derivative of hexamethylene.

Higher Phenols.

315 The chief of these is *hexahydroxybenzene*, $C_6(OH)_6$, whose potassium derivative, *potassium carbonyl*, $C_6(OK)_6$, is formed in the preparation of potassium, and develops an explosive character on exposure to the air ("Inorganic Chemistry," **227**). It can be obtained by heating potassium in a current of carbon monoxide, a direct synthesis of a derivative of benzene. Distillation with zinc-dust converts hexahydroxybenzene into benzene. It is a white, crystalline substance, and undergoes oxidation very readily.

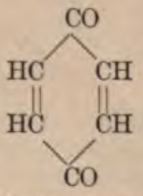
IV. QUINONES.

316. The quinones are substances derived by the elimination of two hydroxyl-hydrogen atoms from aromatic dihydroxy-derivatives:

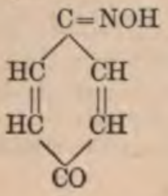
$$\underset{\text{Dihydroxybenzene}}{C_6H_4(OH)_2} - 2H = \underset{\text{Quinone}}{C_6H_4O_2}.$$

The simplest quinone is *benzoquinone*, $C_6H_4O_2$, and is generally called *quinone*. It is obtained by the oxidation of many *p*-derivatives of benzene, such as *p*-aminophenol $C_6H_4{<}\begin{smallmatrix}NH_2 & 1\\ OH & 4\end{smallmatrix}$, sulphanilic acid, $C_6H_4{<}\begin{smallmatrix}NH_2 & 1\\ SO_3H & 4\end{smallmatrix}$, and *p*-phenolsulphonic acid, $C_6H_4{<}\begin{smallmatrix}OH & 1\\ SO_3H & 4\end{smallmatrix}$, and also by the oxidation of aniline with chromic acid—the ordinary method of preparation. It is also formed by the oxidation of quinol (**313**), though the latter is usually prepared by the reduction of quinone. The two other dihydroxybenzenes, (*m*- and *o*-) do not yield quinones on oxidation. This property is possessed only by *p*-dihydroxy-derivatives of benzene and its substitution-products, and by higher phenols containing OH-groups in the *para*-position.

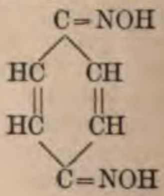
The quinones have usually a yellow colour, and a peculiar, pungent odour; they volatilize with steam with partial decomposition, and have oxidizing properties. The constitution of benzoquinone is best expressed by



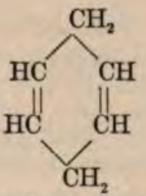
Such a formula requires that benzoquinone should be a diketone, and contain two double bonds; its properties show that it does both. Its ketonic character is inferred from its yielding with hydroxylamine first a *quinone monoxime*, and then a *quinone dioxime*:



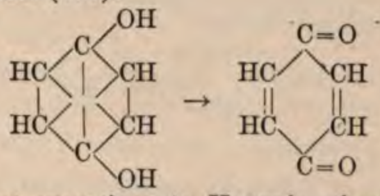
and



The presence of double bonds is proved by its power of forming addition-products; benzoquinone in chloroform solution can take up four atoms of bromine. According to this constitution, benzoquinone is not a true benzene derivative, but the *p*-diketone of a dihydrobenzene:



The formation of benzoquinone from quinol is another example of the conversion of centric bonds into double bonds when two of the former disappear (**270**):



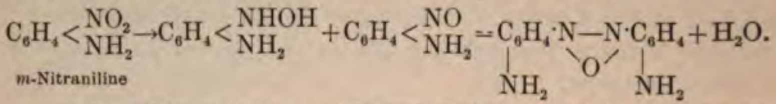
Some apparent exceptions to HABER's scheme (**292**) for the electro-reduction of nitro-compounds may be mentioned here, because they are explained by assuming that quinone derivatives are formed as intermediate products. These exceptions have been observed in the reduction of higher-substituted nitrobenzene derivatives in alcoholic-alkaline solution. According to the scheme, azo-derivatives should be the chief products under these conditions, whereas it is found that in some instances amines are principally produced. Thus, the main product obtained from *p*-nitraniline is *p*-phenylenediamine, while under the same conditions *m*-nitraniline in a normal manner yields *m*-diaminoazobenzene. This difference, however, is readily explained by the fact that *p*-nitraniline gives rise to quinone derivatives, whereas *m*-nitraniline does not; on reduction of *p*-nitraniline to the corresponding hydroxylamine, the latter readily splits off one molecule of water, yielding quinone di-imide:

$$\underset{p\text{-Nitraniline}}{\overset{}{\underset{1}{NH_2}}\cdot C_6H_4\cdot \underset{4}{NO_2}} \rightarrow \underset{p\text{-Aminophenylhydroxylamine}}{NH_2\cdot C_6H_4\cdot NHOH} \rightarrow \underset{\text{Quinone di-imide}}{NH:C_6H_4:NH};$$

and the latter is readily reduced to *p*-phenylenediamine:

$$NH:C_6H_4:NH + 2H = \underset{p\text{-Phenylenediamine}}{H_2N\cdot C_6H_4\cdot NH_2}.$$

m-Nitraniline is unable to form a quinone derivative, and is, therefore, reduced normally in accordance with the scheme

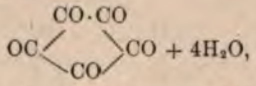


$$C_6H_4{<}\begin{matrix}NO_2\\NH_2\end{matrix}\rightarrow C_6H_4{<}\begin{matrix}NHOH\\NH_2\end{matrix}+C_6H_4{<}\begin{matrix}NO\\NH_2\end{matrix}=\begin{matrix}C_6H_4\cdot N & — & N\cdot C_6H_4\\ | & \diagdown O \diagup & |\\ NH_2 & & NH_2\end{matrix}+H_2O.$$

m-Nitraniline

Tetrachloroquinone, or chloranil, $C_6Cl_4O_2$, is obtained by the action of chlorine on quinone, and also by the oxidation of many organic substances with hydrochloric acid and potassium chlorate. It forms yellow, glistening leaves, and is an oxidizing-agent.

317. Pentamethylene yields remarkable quinones, obtained by the oxidation of hexahydroxybenzene in alkaline solution. Among them is *croconic acid*, $C_5H_2O_5$, which has an intense yellow colour, and is converted by weak reducing-agents into a colourless substance, from which croconic acid can be obtained by oxidation. On oxidation, croconic acid is transformed into *leuconic acid*, $C_5O_5 + 4H_2O$. This compound has the constitution

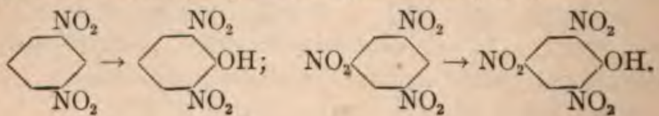


since it yields a pentoxime of the formula $(C: NOH)_5$.

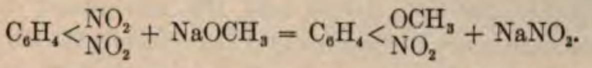
V. POLYNITRO-DERIVATIVES.

318. m-*Dinitrobenzene* is obtained by the nitration of benzene with a mixture of concentrated sulphuric acid and fuming nitric acid; it forms colourless needles melting at 90°. On reduction, it yields m-*phenylenediamine*, and is on this account employed in the preparation of aniline dyes; it is also used in the manufacture of explosives, since it can be exploded by mercury fulminate. In addition to the *m*-compound, small quantities of o-*dinitrobenzene*, and traces of the p-*derivative* are formed. On stronger nitration, effected by a mixture of nitric and fuming sulphuric acids at 140°, *m*-dinitrobenzene is converted into *symmetrical trinitrobenzene* (1:3:5), which melts at 121°.

The hydrogen atoms and nitro-groups in the polynitrobenzenes are much more readily replaced than those in mononitrobenzene. Thus, *m*-dinitrobenzene is converted by oxidation into *dinitrophenol*, and trinitrobenzene into *picric acid*, or trinitrophenol:



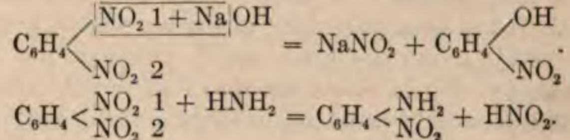
By the action of sodium ethoxide and methoxide respectively, one of the nitro-groups in *o*- and *p*-dinitrobenzene can be quantitatively replaced by OC_2H_5 and OCH_3:



$$C_6H_4<\begin{matrix}NO_2\\NO_2\end{matrix} + NaOCH_3 = C_6H_4<\begin{matrix}OCH_3\\NO_2\end{matrix} + NaNO_2.$$

It is remarkable that this substitution does not take place with *m*-dinitrobenzene.

When boiled with caustic soda, *o*-dinitrobenzene yields ***nitrophenol***, and when heated with alcoholic ammonia, ***nitraniline:***



$$C_6H_4<\begin{matrix}\boxed{NO_2\ 1 + Na}OH\\NO_2\ 2\end{matrix} = NaNO_2 + C_6H_4<\begin{matrix}OH\\NO_2\end{matrix}.$$

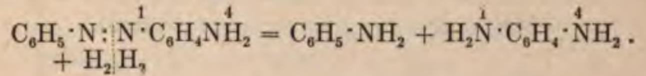
$$C_6H_4<\begin{matrix}NO_2\ 1\\NO_2\ 2\end{matrix} + HNH_2 = C_6H_4<\begin{matrix}NH_2\\NO_2\end{matrix} + HNO_2.$$

Trinitrobutylxylene, containing a tertiary butyl-group, has an odour resembling musk. It is sold under the name "artificial musk."

VI. POLYAMINO-COMPOUNDS AND THEIR DERIVATIVES.

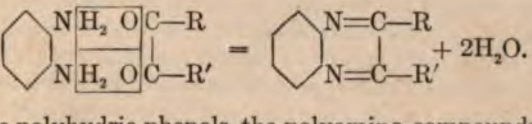
319. These are obtained by the reduction of polynitro-derivatives. m-*Phenylenediamine*, $C_6H_4<\begin{matrix}NH_2\ 1\\NH_2\ 3\end{matrix}$, is got from benzene by nitration and subsequent reduction.

The *p*-derivative can be prepared by the reduction of amino-azobenzene (**304**) with tin and hydrochloric acid, aniline and p-*phenylenediamine* being formed:



$$C_6H_5\cdot \underset{+\,H_2}{N}:\underset{H_2}{\overset{1}{N}}\cdot C_6H_4\overset{4}{N}H_2 = C_6H_5\cdot NH_2 + H_2\overset{1}{N}\cdot C_6H_4\cdot \overset{4}{N}H_2.$$

Ortho-diamino-compounds react readily with 1:2-diketones, yielding *quinoxalines* :



Like the polyhydric phenols, the polyamino-compounds are very readily oxidized. They are colourless, but many of them are turned brown by oxidation in the air.

Azo-dyes.

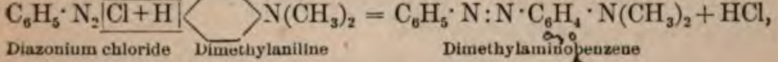
320. The azo-derivatives of the polyamino-compounds are known as *azo-dyes;* they are of great technical importance, being extensively employed in dyeing wool, silk, and cotton. They are azobenzenes in which hydrogen atoms have been replaced by amido-groups. These are not the only dyes; derivatives of azobenzene in which hydrogen is replaced by hydroxyl or by the sulpho-group can likewise be employed in dyeing. Some of these will also be described here.

It is first necessary to state certain facts regarding dyes in general. It has been proved by experience that it is not by any means every colouring-matter which can dye the substances named above; that is, colour them so that the dye cannot subsequently be removed by rubbing, or washing with water or soap. It is, therefore, necessary to make a distinction between coloured substances and dyes; for example, azobenzene has a deep yellowish-red colour, but is not a dye. The introduction of an amido-group, however, converts it into aminoazobenzene, which is a dye. WITT has put forward the theory that the colouring-power of a compound depends upon two factors. The first of these is the presence of certain groups, which he calls *chromophores*, among which are the azo-group, $—N{=}N—$, the nitro-group, and others. Substances containing a chromophore-group, along with NH_2, OH, SO_3H, or in general a group which imparts to them an acidic or basic character, are dyes; this is illustrated by aminoazobenzene. Another example is nitrobenzene, which has a pale-yellow colour, and contains the chromophore nitro-group, but is not a dye; on the other hand, *p*-nitraniline and *p*-nitrophenol are dyes.

321. In many cases it is sufficient to immerse the silk, wool, or cotton to be dyed in a solution of the dye. Since it was dissolved at first, but cannot be removed by washing the fabric after it has been dyed, the dye must have undergone a change. It is assumed that it unites with the constituents of the animal or vegetable fibres to form a compound, a kind of salt, since dyes always have a basic or acidic character. A proof of this will be given for rosaniline (**367**).

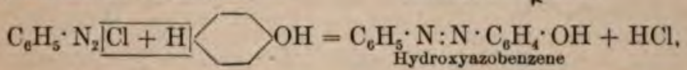
In other cases the fabric does not take up the dye when immersed in its solution; it has been repeatedly observed that dyes which become directly fixed on animal fabrics, such as silk and wool, do not dye vegetable fabrics, like cotton, unless the material to be dyed has undergone a special process, called *mordanting;* that is, a substance must be deposited in the fabric to *fix* the dye, since the latter will not unite with the fibres themselves. Such substances are called *mordants;* they are usually salts of weak bases, or acids; such are aluminium acetate, ferric salts, compounds of tin ("pink salt," $SnCl_4, 2NH_4Cl$). The woven material is thoroughly soaked in a solution of one of these salts, and then spread out and exposed to the action of steam at a suitable temperature. The salt undergoes hydrolytic decomposition, and the base or acid, for example aluminium hydroxide, or stannic acid, is deposited in a fine state of division in the fabric. The dye unites with this base or acid, forming an insoluble compound which is not removed by washing.

322. Azo-dyes are obtained by treating diazonium chlorides with aromatic amines or with phenols:



$$C_6H_5\cdot N_2\boxed{Cl+H}C_6H_4N(CH_3)_2 = C_6H_5\cdot N:N\cdot C_6H_4\cdot N(CH_3)_2 + HCl,$$

Diazonium chloride Dimethylaniline Dimethylaminoazobenzene



$$C_6H_5\cdot N_2\boxed{Cl+H}C_6H_4OH = C_6H_5\cdot N:N\cdot C_6H_4\cdot OH + HCl,$$

Hydroxyazobenzene

when basic and acidic dyes are respectively produced. It was mentioned in **304** that the combination of a diazonium chloride and an aromatic amine sometimes yields the diazoamino-compound as an intermediate product, which can be converted into the aminoazo-derivative by warming with the amine hydrochloride. In this formation of aminoazo-compounds and hydroxyazo-compounds, the *para*-H-atom always reacts with the diazonium chloride; when this atom is replaced by a substituent, the formation of dye either does not take place or is very incomplete.

323. In preparing hydroxyazo-dyes, the solution of the diazonium chloride is kept cool with ice, and is slowly added to the *alkaline* solution of the phenol or its sulphonic acid; care is taken to keep the reaction-mixture slightly alkaline, since otherwise the hydrochloric acid liberated would hinder the formation of the dye. After the solutions have been mixed, the dye is "salted out" by the addition of common salt, which precipitates it in flocculent masses. It is freed from water by means of filter-presses, and put on the market either in the dry state or as a paste.

Aminoazo-dyes are prepared by mixing the aqueous solution of the diazonium chloride with that of the aromatic amine salt, the colouring-matter being subsequently salted out. It is sometimes necessary to employ an alcoholic solution.

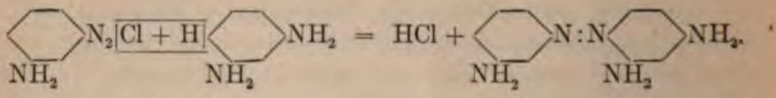
The simplest azo-dyes are yellow; on the introduction of alkyl-groups or phenyl-groups, and in general on increase of molecular weight, their colour changes through orange and red to violet and blue. They are crystalline, and most of them are insoluble in water and soluble in alcohol. Instead of the azo-dyes themselves, it is often better to employ their sulphonic acids, obtainable from them by the usual method—treatment with concentrated sulphuric acid.

324. A short description of some of these dyes may be given here.

Aniline-yellow is a salt of aminoazobenzene; it is now seldom used, its place having been taken by other yellow dyes.

Chrysoïdine or diaminoazobenzene, $C_6H_5\cdot N:N\cdot C_6H_3<^{NH_2}_{NH_2}$, is obtained from benzenediazonium chloride and *m*-phenylenediamine. It yields a hydrochloride, crystallizing in needles of a reddish colour and fairly soluble in water; this salt dyes wool and silk directly, and cotton which has been mordanted.

Bismarck-brown, $NH_2\cdot C_6H_4\cdot N:N\cdot C_6H_3<^{NH_2}_{NH_2}$, (triaminoazobenzene), is manufactured by diazotizing one of the NH_2-groups in *m*-phenylenediamine, and treating the product thus obtained with a second molecule of this base:



Even a very dilute solution of nitrous acid gives a brown colouration with *m*-phenylenediamine, due to the formation of Bismarck-brown or related substances; this reaction furnishes a very delicate test for nitrous acid, and is employed in water-analysis.

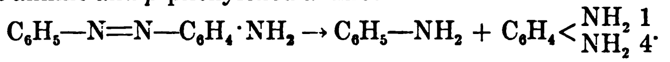
Helianthine, or dimethylaminoazobenzenesulphonic acid, is prepared by the interaction of benzenediazonium sulphonic acid and dimethylaniline hydrochloride in aqueous solution:

$$HO_3S\cdot C_6H_4\cdot N_2\boxed{OH + H}C_6H_4\cdot N(CH_3)_2 =$$
$$= H_2O + HO_3S\cdot C_6H_4\cdot N:N\cdot C_6H_4\cdot N(CH_3)_2.$$

It is not often used as a dye, but its sodium salt, which has a yellow colour, and is turned red by acids, is employed as an indicator in volumetric analysis under the name *methyl-orange*.

Resorcin-yellow, $HO_3S\cdot C_6H_4\cdot N:N\cdot C_6H_3<^{OH}_{OH}$, (dihydroxyazobenzenesulphonic acid), is obtained from resorcinol **(313)** and benzenediazonium sulphonic acid.

The diazo-dyes are split up into amino-compounds by energetic reduction with tin and hydrochloric acid. Thus, aminoazobenzene yields aniline and *p*-phenylenediamine:



$$C_6H_5—N{=}N—C_6H_4{\cdot}NH_2 \rightarrow C_6H_5—NH_2 + C_6H_4{<}\begin{matrix}NH_2 & 1\\ NH_2 & 4\end{matrix}.$$

This decomposition on reduction affords a means of determining the constitution of these dyes, and indicates the methods by which they are obtained. For example, Bismarck-brown is converted by reduction with tin and hydrochloric acid into a mixture of equimolecular amounts of diaminobenzene and triaminobenzene. Since the molecule splits up at the double bond of the azo-group, it follows that the constitution of this compound is

$$NH_2{\cdot}C_6H_4—N:\vdots N—C_6H_3{<}\begin{matrix}NH_2\\ NH_2\end{matrix}.$$

This also indicates that the dye can be obtained by diazotizing a molecule of diaminobenzene, and treating the product with a second molecule of diaminobenzene, in accordance with the equation on page 418.

VII. POLYBASIC ACIDS AND THEIR DERIVATIVES.

DIBASIC ACIDS.

325. The dibasic acids are the most important members of the series of aromatic polybasic acids; they are called *phthalic acids*, a name derived from na*phthal*ene, from which one of them can be obtained. Three isomers are possible, and all of them are known. Like all polybasic acids, they yield neutral and acid esters and salts, acid amides, amino-acids, etc. On distillation with lime, they are converted into benzene.

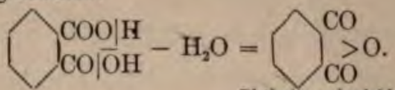
Phthalic Acid.

Phthalic acid is the *ortho*-dicarboxylic acid of benzene, and has the formula, $C_6H_4{<}\begin{matrix}COOH & 1\\ COOH & 2\end{matrix}$. It is obtained by the oxidation of aromatic hydrocarbons with two side-chains in the *ortho*-position, or their derivatives with substituents in the side-chains. It is worthy of note that chromic acid cannot be employed in this oxidation, since it splits up *ortho*-derivatives completely into CO_2 and H_2O. Phthalic acid is employed in the preparation of artificial indigo (**399**), and is manufactured by oxidizing naphthalene (**370**), $C_{10}H_8$, by heating it with very concentrated sulphuric acid.

Phthalic acid is crystalline, and readily soluble in hot water, dicarboxylic anhydrides

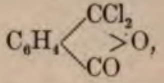
[illegible]

alcohol, and ether; it has no definite melting-point, since on heating it splits off water, yielding *phthalic anhydride*, which sublimes in beautiful, long needles:



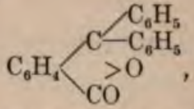
Phthalic anhydride

326. If they followed the ordinary course of the reaction forming acid chlorides, phosphorus pentachloride and phthalic acid would react to produce a chloride of the constitution $C_6H_4<\begin{matrix}COCl\\COCl\end{matrix}$. That they do not, and that *phthalyl chloride* has the structure



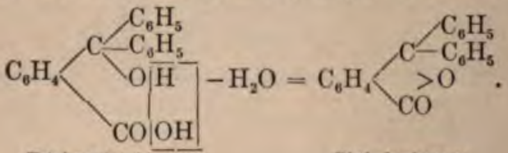
$$C_6H_4<\begin{matrix}CCl_2\\ \\CO\end{matrix}>O,$$

can be proved in various ways. When aluminium chloride reacts with phthalyl chloride in presence of benzene, there results a compound with the formula



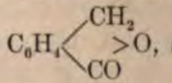
$$C_6H_4<\begin{matrix}C\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\\ \\CO\end{matrix}>O,$$

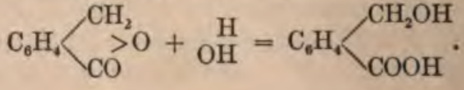
called *phthalophenone*, whose constitution follows from its formation by the elimination of water from triphenylcarbinolcarboxylic acid:



Triphenylcarbinolcarboxylic acid

Phthalophenone

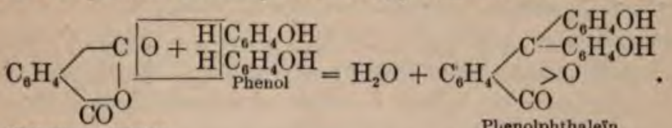
Another proof of the constitution indicated above for phthalyl chloride is the fact that reducing-agents, such as sodium amalgam and water, or zinc and hydrochloric acid, cause the replacement of its halogen atoms by hydrogen, with formation of *phthalide*. This substance has the constitution  $C_6H_4<\begin{matrix}CH_2\\ \\CO\end{matrix}>O$, since on treatment with caustic soda, it yields *hydroxymethylbenzoïc acid*:



$$C_6H_4<\begin{matrix}CH_2\\ \\CO\end{matrix}>O+\begin{matrix}H\\OH\end{matrix}=C_6H_4<\begin{matrix}CH_2OH\\ \\COOH\end{matrix}.$$

This proves it to be a lactone, and not a dialdehyde, $C_6H_4<\begin{smallmatrix}CHO\\CHO\end{smallmatrix}$, as would be expected if the formula of phthalyl chloride were $C_6H_4<\begin{smallmatrix}COCl\\COCl\end{smallmatrix}$.

327. The oxygen of the carbonyl-group in phthalic anhydride can also take part in other reactions; thus, when this substance is heated with phenols and sulphuric acid, *phthaleïns* are formed:



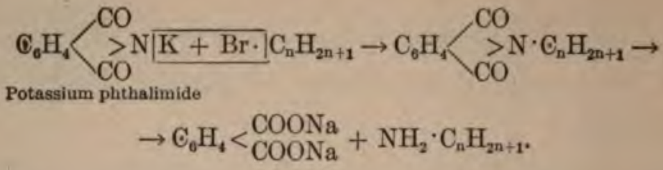
Phthalic anhydride Phenolphthaleïn

Phenolphthaleïn, the simplest member of the phthaleïn series, is a yellow powder; on account of its phenolic character it dissolves in alkaline solutions, with formation of a fine red colour, and is a sensitive indicator for alkalimetry.

Resorcinolphthaleïn or *fluoresceïn* is characterized by the display of an intense yellowish-green fluorescence in alkaline solution. It owes its name to this property, which affords a delicate test for phthalic anhydride, phthalic acid, and resorcinol, since fluorescence is exhibited by mere traces of fluoresceïn. It is prepared by heating together resorcinol and phthalic anhydride at 210°, in presence of zinc chloride as a dehydrating-agent. On treatment with bromine, fluoresceïn yields tetrabromofluoresceïn, whose potassium derivative, $C_{10}H_6Br_4O_5K_2$, is the beautiful dye, *eosin*.

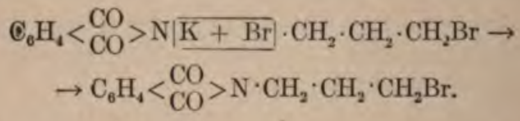
The constitution of the phthaleïns is inferred from their being convertible into derivatives of triphenylmethane (**366**).

328. *Phthalimide*, $C_6H_4\begin{smallmatrix}CO\\CO\end{smallmatrix}>NH$, is of importance on account of its application by GABRIEL to the synthesis of primary amines with substituted alkyl-groups. It is obtained by passing dry ammonia over heated phthalic anhydride. The imido-hydrogen is replaceable by metals; thus, the potassium compound is precipitated by the action of caustic potash upon the alcoholic solution of the imide. When *potassium phthalimide* is treated with an alkyl halide, the metal is replaced by alkyl; on heating with acids or alkalis, a primary amine, free from secondary and tertiary amines, is split off:



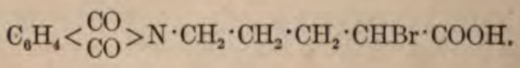
Variously substituted alkyl halides can be employed in this reaction; thus, from ethylene bromide, $CH_2Br\cdot CH_2Br$, is obtained *bromoethylamine*, $NH_2\cdot CH_2\cdot CH_2Br$; from ethylenebromhydrin, $CH_2Br\cdot CH_2OH$, *hydroxyethylamine*, $NH_2\cdot CH_2\cdot CH_2OH$; etc.

Another example is Emil Fischer's synthesis of *ornithine* (**200**). Potassium phthalimide is brought into contact with trimethylene bromide:



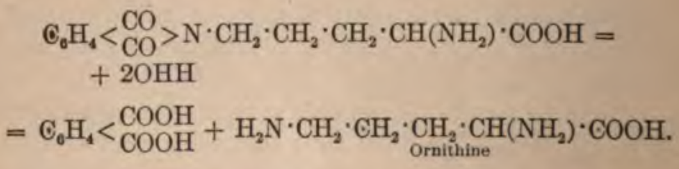
$$C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>N\boxed{K + Br}\cdot CH_2\cdot CH_2\cdot CH_2Br \rightarrow$$
$$\rightarrow C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>N\cdot CH_2\cdot CH_2\cdot CH_2Br.$$

The compound obtained is treated with ethylsodiomalonate, and yields $C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>N\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(COOC_2H_5)_2$, whose tertiary hydrogen atom can be substituted by bromine. Saponification and splitting off of CO_2 give



$$C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>N\cdot CH_2\cdot CH_2\cdot CH_2\cdot CHBr\cdot COOH.$$

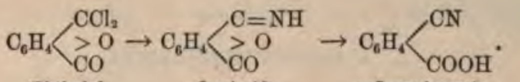
By heating with aqueous ammonia, Br is then replaced by NH_2. Subsequent heating with concentrated hydrochloric acid yields ornithine:



$$C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>N\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(NH_2)\cdot COOH =$$
$$+ 2OHH$$
$$= C_6H_4<\genfrac{}{}{0pt}{}{COOH}{COOH} + \underset{\text{Ornithine}}{H_2N\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(NH_2)\cdot COOH}.$$

These examples make it evident that this method can be applied to the preparation of the most variously substituted primary amines.

329. HOOGEWERFF and VAN DORP found that ammonia reacts with phthalyl chloride, yielding *o-cyanobenzoïc acid*, $C_6H_4<{CN \atop COOH}$; it must be assumed that an ***iso-imide*** of phthalic acid is formed as an intermediate product:



$$C_6H_4\left\langle\begin{array}{l}CCl_2\\>O\\CO\end{array}\right. \rightarrow C_6H_4\left\langle\begin{array}{l}C{=}NH\\>O\\CO\end{array}\right. \rightarrow C_6H_4\left\langle\begin{array}{l}CN\\COOH\end{array}\right. .$$

Phthalyl chloride — Iso-imide — o-Cyanobenzoïc acid

Although they have not been able to isolate the iso-imide itself, they have prepared a number of derivatives in which the imido-hydrogen is replaced by hydrocarbon-residues.

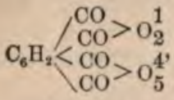
Isophthalic and Terephthalic Acids, $C_6H_4(COOH)_2$ (1:3) and (1:4).

330. *Isophthalic acid* can be obtained by the oxidation of compounds with two side-chains in the *meta*-position, and also by the oxidation of resin (colophonium) with nitric acid. It dissolves with difficulty in water, and does not yield an anhydride.

Terephthalic acid can be prepared by several methods; for example, by the oxidation of turpentine. It is almost insoluble in water, alcohol, and ether. It does not melt under the ordinary pressure, but at high temperatures sublimes without decomposition. Like the iso-acid, it does not form an anhydride.

HIGHER POLYBASIC ACIDS.

331. Tricarboxylic, tetracarboxylic, pentacarboxylic, and hexacarboxylic acids are known. The most remarkable is the last, ***mellitic acid***, on account of its presence in the mineral ***honey-stone***, found in brown-coal seams. Honey-stone is the aluminum salt of mellitic acid, and has the formula $C_{12}O_{12}Al_2 + 18H_2O$; it forms yellow quadratic octahedra. Mellitic acid is produced by the oxidation of wood-charcoal with an alkaline solution of potassium permanganate (**16**). It crystallizes in fine needles, and is readily soluble in water and alcohol. On heating, it loses two molecules of carbon dioxide and two molecules of water, with formation of ***pyromellitic anhydride***,



$$C_6H_2\left\langle\begin{array}{l}\begin{array}{l}CO\\CO\end{array}>O^{1}_{2}\\\begin{array}{l}CO\\CO\end{array}>O^{4'}_{5}\end{array}\right.$$

which takes up water, and yields *pyromellitic acid*, $C_6H_2(COOH)_4$.

FINISH

DERIVATIVES CONTAINING TWO OR MORE DISSIMILAR SUBSTITUENTS.

I. SULPHO-DERIVATIVES.

Halogen Sulphonic Acids.

332. Among these may be mentioned the three *bromobenzenesulphonic acids*, all of which yield resorcinol, $C_6H_4<\begin{matrix}OH & 1\\ OH & 3\end{matrix}$, on fusion with caustic potash. This is one of the comparatively few cases of substitution in which the substituting-group occupies a different position from the one replaced by it. Other similar examples will be referred to later (**352**).

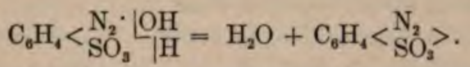
Phenolsulphonic Acids.

333. Ortho-*phenolsulphonic* and para-*phenolsulphonic acids* are obtained by dissolving phenol in concentrated sulphuric acid; the m-*acid* is produced when *m*-benzenedisulphonic acid is fused with caustic potash. The *o*-acid is characterized by being readily converted into the *p*-compound, even on evaporation of its aqueous solution. Phenol is much more readily sulphonated than benzene, its solution in sulphuric acid being transformed into the two above-mentioned acids even at ordinary temperatures.

o-Phenolsulphonic acid is employed as an antiseptic under the name "aseptol," or "sozolic acid." *Di-iodo-*p-*phenolsulphonic acid* is also used for the same purpose, under the name "sozoiodol."

p-Aminobenzenesulphonic Acid or Sulphanilic Acid.

334. *Sulphanilic acid* is obtained by heating aniline with fuming sulphuric acid. Like its isomers, it is soluble with difficulty in cold water. The basic properties of aniline are greatly weakened by the introduction of the sulpho-group into the ring, for sulphanilic acid cannot yield salts with acids, while the sulpho-group reacts with bases, forming salts. The formula of sulphanilic acid is probably $C_6H_4<\begin{matrix}SO_3\\ NH_3\end{matrix}>$; that is, it is an inner salt. On fusion with caustic potash, it does not yield aminophenol, as might be expected, but aniline. Oxidation with chromic acid converts it into quinone. On pouring a mixture of sodium sulphanilate and sodium nitrite in aqueous solution into dilute sulphuric acid, an inner salt of *benzene-diazonium sulphonic acid* is precipitated, as it is nearly insoluble in water:

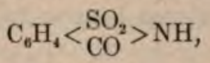


$$C_6H_4<\genfrac{}{}{0pt}{}{N_2\cdot|OH}{SO_3\;\;|H} = H_2O + C_6H_4<\genfrac{}{}{0pt}{}{N_2}{SO_3}>.$$

This compound is of great importance in the preparation of azo-dyes such as *helianthine* (**324**).

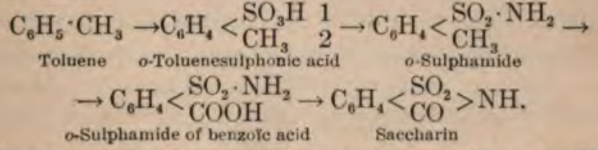
Sulphobenzoïc Acids.

335. The imido-derivative of *o*-sulphobenzoïc acid,



$$C_6H_4<\genfrac{}{}{0pt}{}{SO_2}{CO}>NH,$$

known as *saccharin*, is about three hundred times as sweet as sugar, and on this account is sometimes employed as a substitute for it. Direct sulphonation of benzoïc acid yields m-*sulphobenzoïc acid* almost exclusively, so that saccharin cannot be prepared by this means. It is obtained from toluene, which, on treatment with sulphuric acid, yields a mixture of p- and o-*toluenesulphonic acids*, the former being the chief product. The *o*-acid is converted into its sulphamide, the methyl-group of which is then transformed into carboxyl by oxidation with potassium permanganate. On heating, this oxidation-product loses one molecule of water very readily, forming saccharin:



$$\underset{\text{Toluene}}{C_6H_5\cdot CH_3} \rightarrow \underset{o\text{-Toluenesulphonic acid}}{C_6H_4<\genfrac{}{}{0pt}{}{SO_3H\ \ 1}{CH_3\ \ \ 2}} \rightarrow \underset{o\text{-Sulphamide}}{C_6H_4<\genfrac{}{}{0pt}{}{SO_2\cdot NH_2}{CH_3}} \rightarrow$$

$$\rightarrow \underset{o\text{-Sulphamide of benzoïc acid}}{C_6H_4<\genfrac{}{}{0pt}{}{SO_2\cdot NH_2}{COOH}} \rightarrow \underset{\text{Saccharin}}{C_6H_4<\genfrac{}{}{0pt}{}{SO_2}{CO}>NH.}$$

Saccharin is a white, crystalline powder, soluble with difficulty in cold water, and readily soluble in alcohol and ether. It takes up one molecule of water, yielding the sulphamide of *o*-sulphobenzoïc acid, which does not possess a sweet taste.

II. HALOGEN DERIVATIVES.

Halogen Phenols.

336. Ortho-*chlorophenol* and para-*chlorophenol* are formed by the direct chlorination of phenol, and also by reduction of the halogen nitro-benzenes and subsequent diazotization of the compounds formed. They have a pungent odour. By fusion with caustic potash, the halogen can be replaced by hydroxyl, although it is not always the corresponding hydroxyl-compound which is formed. The introduction of halogen considerably augments the acidic character of the phenols: thus, trichlorophenol decomposes carbonates. It was mentioned in **275** that the presence of hydroxyl in the ring considerably facilitates the substitution of the hydrogen atoms by halogen. Iodine, however, can only substitute in presence of an oxidizing-agent, to remove the hydriodic acid formed; since, unless this were oxidized, it would take away the iodine atom from iodophenol.

Halogen Benzoïc Acids.

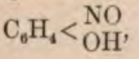
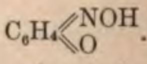
337. The *m*-compound can be obtained by direct chlorination of benzoïc acid, but can be more readily prepared by diazotizing the corresponding amino-compound. This is also the best method for the preparation of the *ortho*-halogen and *para*-halogen benzoïc acids. Phosphorus pentachloride does not react readily with the hydroxybenzoïc acids; hence the halogen benzoïc acids cannot be satisfactorily prepared by its aid.

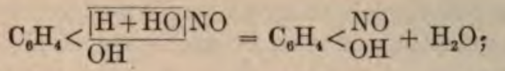
As would be expected, the acidic character of benzoïc acid is strengthened by the introduction of halogen; the dissociation constant K of the halogen benzoïc acids is greater than that of benzoïc acid itself. For benzoïc acid, K is 0·006, for *o*-chlorobenzoïc acid 0·132, for *m*-chlorobenzoïc acid 0·0155, for *p*-chlorobenzoïc acid 0·0093. This shows that the chlorine atom in the *ortho*-position exercises the greatest influence and that in the *para*-position the least, while for the *m*-compound K is intermediate in value.

Combinations of halogen with the sulpho-group are referred to in **332.**

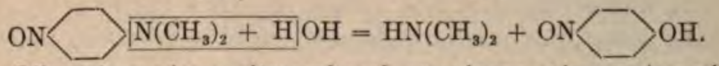
III. HYDROXYL-DERIVATIVES.

Nitrosophenol.

338. This compound reacts in certain respects as though it had the constitution  $C_6H_4<{NO \atop OH}$, although its formation from quinone and hydroxylamine points to the constitution  $C_6H_4\langle{NOH \atop O}$. It is formed by the action of nitrous acid upon phenol, or of caustic ash upon nitrosodimethylaniline:



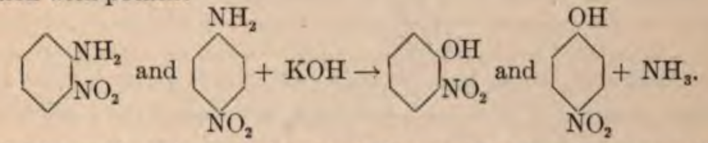
$$C_6H_4<{\boxed{H+HO}NO \atop OH} = C_6H_4<{NO \atop OH} + H_2O;$$



Like other oximes, nitrosophenol, or quinone oxime, unites with bases. It is a colourless compound, crystallizing in needles which soon turn brown on exposure to air. On oxidation and reduction, it behaves as though it were nitrosophenol, yielding nitrophenol and aminophenol respectively.

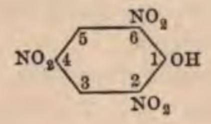
Nitrophenols.

339. The increased readiness with which the hydrogen atoms of the nucleus can be substituted after a hydroxyl-group has been introduced into benzene is illustrated by the behaviour of the phenols towards nitric acid. While it is necessary to employ concentrated nitric acid in order to obtain nitrobenzene from benzene, phenol is converted by dilute nitric acid at low temperatures into *ortho*-nitrophenol and *para*-nitrophenol. These two isomers can be separated by distillation with steam, with which only the *ortho*-compound is volatile. Meta-*nitrophenol* can be prepared from *meta*-nitraniline by the diazo-reaction. *Ortho*-nitraniline and *para*-nitraniline, but not *meta*-nitraniline, yield nitrophenols directly by fusion with potash:



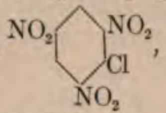
This shows that the substituents in benzene are much more readily replaced when there are several of them than when there is only one. The acidic character of phenol is strengthened in the nitrophenols; they decompose all carbonates, although nitrophenol is precipitated from a solution of an alkali-nitrophenoxide by carbon dioxide.

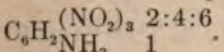
340. The best-known nitrophenol derivative is *picric acid*, or 1:2:4:6-trinitrophenol,



This substance has long been known, and is produced by the action of concentrated nitric acid upon a large variety of substances, such as silk, leather, resins, aniline, indigo, etc. It is prepared by dissolving phenol in concentrated sulphuric acid, and carefully adding small quantities of this solution to concentrated nitric acid of 1·4 sp. gr. An energetic reaction takes place, after which the reaction-mixture is warmed for some time on a water-bath; on cooling, picric acid crystallizes out. It cannot be further nitrated; in other words, it is the final product of the action of nitric acid on phenol. This explains its resulting from the action of nitric acid upon such heterogeneous substances.

Solid picric acid has only a very faint-yellow colour when pure, but its aqueous solution is deep-yellow. It is a strong acid, and, therefore, undergoes considerable ionization when dissolved in water, the yellow colour being characteristic of the anion, since the solution of this acid in petroleum-ether, in which no ionization occurs, is colourless. It is slightly soluble in cold water, and is not volatile with steam. It melts at 122°.

A consideration of the following reactions shows that picric acid is comparable with the carboxylic acids. Phosphorus pentachloride replaces the hydroxyl-group by chlorine, with formation of *picryl chloride*, 

, which has the character of an acid chloride. Thus, it is decomposed by hot water into hydrochloric acid and picric acid, and with ammonia yields *picramide*  $C_6H_2\begin{matrix}(NO_2)_3 & 2:4:6\\ NH_2 & 1\end{matrix}$. Silver picrate and methyl iodide yield the methyl ether; this has the properties of an ester, being saponified by boiling with concentrated caustic alkalis, and yielding picramide on treatment with ammonia. These facts afford further evidence of the remarkable increase in the reactivity of the hydroxyl-group, due to the presence of the three nitro-groups.

Picric acid yields well-defined crystalline salts, of a yellow or red colour, which are explosive. The potassium salt dissolves with difficulty in water, and the ammonium salt explodes by percussion, although the acid itself does not.

Picric acid yields molecular compounds with many aromatic hydrocarbons; for example, with naphthalene a compound of the formula $C_{10}H_8 \cdot C_6H_2(NO_2)_3 \cdot OH$. These crystallize well, and are sometimes employed with advantage in the separation of hydrocarbons, or in their identification by means of the melting-points of these compounds. Picric acid is readily eliminated from them by the action of ammonia.

Picric acid can be tested for with an aqueous solution of potassium cyanide, which yields a red colouration due to the formation of isopurpuric acid.

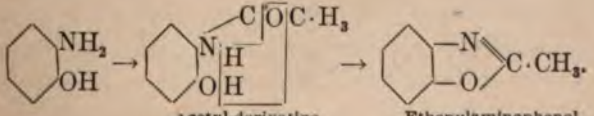
Picric acid is employed as an explosive, usually in the form of its ammonium salt, which leaves no residue on explosion, and is a constituent of "lyddite." It is also used as a dye, imparting a yellow colour to wool and silk.

Styphnic acid, $C_6H\genfrac{}{}{0pt}{}{(OH)_2}{(NO_2)_3}$, is a type of a nitrated dihydroxybenzene, and is obtained by the action of cold nitric acid upon resorcinol, as well as from certain gum-resins by the same means. The conversion of *m*-nitrophenol into styphnic acid by the action of nitric acid is a remarkable reaction, the formation of a hydroxyl-group taking place simultaneously with the nitration.

Aminophenols.

341. Aminophenols are formed by the reduction of nitrophenols. The acidic character in these compounds is so weakened that they do not combine with bases; on the other hand, they yield salts with acids. In the free state the aminophenols are colourless solids, crystallizing in leaflets, and readily turned brown by atmospheric oxidation with formation of a resin. Their hydrochlorides are more stable.

o-*Aminophenol* yields compounds by the substitution of acid-residues in the amido-group; these at once split off water. They are called *anhydro-bases:*



Acetyl-derivative

Ethenylaminophenol,
Anhydro base

On treatment with acids, aminophenol and acetic acid are regenerated.

m. amino phenol with phthalic anhydrid
forms. a fluorescent red dye. (Rhodamines)
ethyl deriv. is Rhodamine

p-*Aminophenol* is obtained by the electro-reduction of nitrobenzene in acid solution (**292**).

The alkaline solution of *p*-aminophenol rapidly acquires a dark colour unless sodium sulphite is present. This solution is sold under the name "rhodinal," and is used as a photographic developer.

Lumière has discovered certain general conditions which aromatic compounds must fulfil to be available as photographic developers. They must either contain ~~some~~ several hydroxyl-groups or amido-groups, or at least one of each. In order that the developing action may not be interfered with when substituents are present in the amido-group and in the hydroxyl-group, not less than two such unsubstituted groups must be present in the molecule.

A derivative of *p*-aminophenol used in medicine is *phenacetin* or *acetylphenetidine*, $C_6H_4<\begin{smallmatrix}OC_2H_5\\NH\cdot C_2H_3O\end{smallmatrix}$, the acetamino-derivative of phenetole, $C_6H_5\cdot OC_2H_5$.

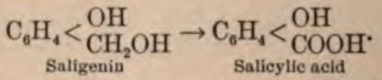
Salts of 1:2:4-diaminophenol are employed as photographic developers under the name "amidol."

Monohydroxy-acids.

342. The most important of the monohydroxy-acids is *o*-hydroxybenzoïc acid, or *salicylic acid*, $C_6H_4<\begin{smallmatrix}OH & 1\\COOH & 2\end{smallmatrix}$. It derives its name from salicin, a glucoside in the bark and leaves of the willow (*salix*); on hydrolysis, this substance splits up into *saligenin* and glucose:

$$\underset{\text{Salicin}}{C_{13}H_{18}O_7} + H_2O = \underset{\text{Saligenin}}{C_7H_8O_2} + \underset{\text{Glucose}}{C_6H_{12}O_6}.$$

Saligenin is the alcohol corresponding to salicylic acid, into which it is converted by oxidation:

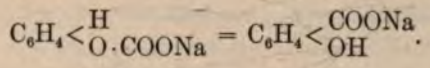


$$\underset{\text{Saligenin}}{C_6H_4<\begin{smallmatrix}OH\\CH_2OH\end{smallmatrix}} \rightarrow \underset{\text{Salicylic acid}}{C_6H_4<\begin{smallmatrix}OH\\COOH\end{smallmatrix}}.$$

Salicylic acid is present as methyl ester in oil of winter-green (*Gualtheria procumbens*), from which the acid is still obtained for pharmaceutical use. It can also be prepared by the action of nitrous acid on anthranilic acid, *o*-aminobenzoïc acid (**351**), by fusing *o*-chlorobenzoïc or *o*-bromobenzoïc acid with caustic potash, and by other methods.

Salicylic acid is manufactured by a process discovered by Kolbe, in which sodium phenoxide is heated with carbon dioxide in an autoclave at 130°. Sodium phenyl carbonate, $C_6H_5\cdot O—COONa$, is formed as an intermediate product, and on heating is converted into sodium salicylate:

$$C_6H_5\cdot ONa + CO_2 = C_6H_5\cdot O\cdot COONa;$$



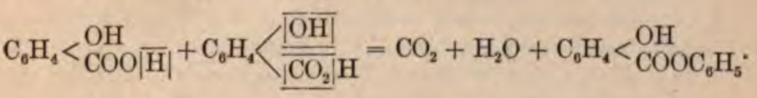
$$C_6H_4{<}\begin{matrix}H\\O\cdot COONa\end{matrix} = C_6H_4{<}\begin{matrix}COONa\\OH\end{matrix}.$$

When CO_2 is passed over potassium phenoxide below 150°, salicylic acid results; but at a higher temperature, 220°, p-*hydroxybenzoïc acid* is formed. Sodium phenoxide, on the other hand, yields only salicylic acid at 220°.

Salicylic acid is a white, crystalline powder, which dissolves with difficulty in cold water, and melts at 159°. When carefully heated, it sublimes, but on rapid heating splits up into phenol and carbon dioxide. With bromine-water it yields a precipitate of the formula $C_6H_2Br_3\cdot OBr$. It gives a violet colouration with ferric chloride, both in aqueous and alcoholic solution, whereas phenol dissolved in alcohol does not. When boiled with calcium chloride and ammonia, a solution of salicylic acid precipitates basic calcium salicylate, $C_6H_4{<}\begin{matrix}COO\\O\end{matrix}{>}Ca$; this affords a means of separating salicylic acid from its isomers, which do not give this reaction.

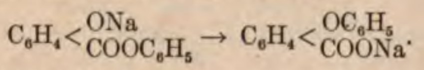
Salicylic acid is a powerful antiseptic, and is employed as a preservative for foods and such beverages as beer. It is not, however, completely innocuous.

When the acid is heated to 220°, it loses carbon dioxide and water, with formation of *salicylic phenyl ester*:



$$C_6H_4{<}\begin{matrix}OH\\COO\boxed{H}\end{matrix} + C_6H_4\Big\langle\begin{matrix}\boxed{OH}\\ \boxed{CO_2}H\end{matrix} = CO_2 + H_2O + C_6H_4{<}\begin{matrix}OH\\COOC_6H_5\end{matrix}.$$

This compound is employed as an antiseptic under the name "salol." By heating to 300°, its sodium derivative is converted into the sodium salt of phenylsalicylic acid:



$$C_6H_4{<}\begin{matrix}ONa\\COOC_6H_5\end{matrix} \rightarrow C_6H_4{<}\begin{matrix}OC_6H_5\\COONa\end{matrix}.$$

The *anhydride* of salicylic acid is proved by the cryoscopic determination of its molecular weight to have a molecule of the formula

$\left(C_6H_4<^{CO}_{O}>\right)_4$; it is obtained by the action of phosphorus oxychloride upon the acid. This anhydride crystallizes with two molecules of chloroform, which are driven off on warming. This process was formerly used in the preparation of pure chloroform.

343. Meta- and para-*hydroxybenzoïc acids* yield no colouration with ferric chloride. Their basic barium salts are insoluble.

From the fact that the monosubstitution-products of benzene are not known in isomeric forms, the conclusion is drawn that the six hydrogen atoms of benzene are of equal value (**263**). The following is a more direct proof of this equality.

Phenol is converted by the action of phosphorus bromide into bromobenzene, which yields benzoïc acid when treated with carbon dioxide and sodium (**296**, 4):

$$C_6H_5 \cdot OH \rightarrow C_6H_5 \cdot Br \rightarrow C_6H_5 \cdot COOH.$$

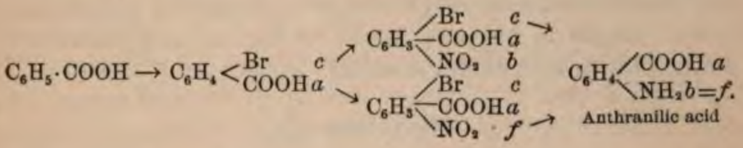
If the position of the hydroxyl-group in phenol is denoted by a, the position of the carboxyl-group in the benzoïc acid obtained from it must also be denoted by a.

There are three isomeric hydroxybenzoïc acids, all of which can be converted into, or obtained from, benzoïc acid; these may be denoted by $a:b$, $a:c$, and $a:d$, a being the position of the carboxyl-group, and b, c, and d of the hydroxyl-group. By elimination of CO_2, all of these yield phenol, proving that the positions of the hydroxyl-groups are of equal value. Moreover, since benzoïc acid is obtained from phenol, a must be equal in value to the other three, so that $a = b = c = d$.

It has still to be proved that the two remaining positions e and f are equal in value to the other four. The starting-point for this second part of the proof is benzoïc acid, the position of whose carboxyl-group may again be indicated by a. On bromination it yields a bromobenzoïc acid (*meta*), which, since it can be converted into a hydroxybenzoïc acid, must have its Br-atom either at b, c, or d. Let it be arbitrarily assumed that it is situated at c. On nitration, this bromobenzoïc acid yields two isomeric bromonitrobenzoïc acids, whose isomerism can evidently only be due to a difference in position of the nitro-group, since, in both, the carboxyl is at a, and the Br at c.

These two bromonitrobenzoïc acids can be so reduced that the nitro-group is converted into an amido-group, and the bromine atom replaced by hydrogen at the same time. The *same* aminobenzoïc acid results from each. This is only possible when the positions occupied by the nitro-groups relative to a are identical. The amino-acid thus obtained is anthranilic acid (**351**), which is readily converted into hydroxybenzoïc acid (salicylic acid). It follows that the nitro-group in one of the isomeric bromonitrobenzoïc acids is at *b*, *c*, or *d*. As it was arbitrarily assumed that the Br-atom is at *c*, then the choice lies between *b* and *d*; suppose it to be *b*.

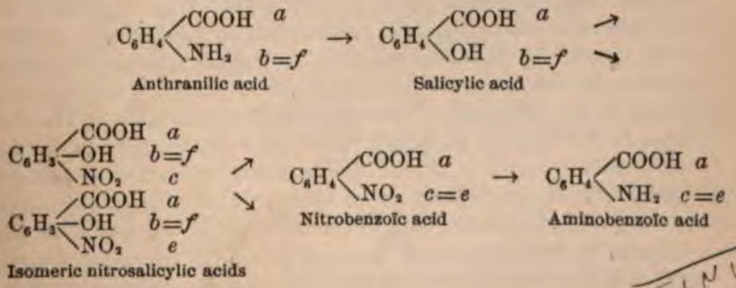
The nitro-group in the other bromonitrobenzoïc acid cannot be situated at *d*, since the aminobenzoïc acid obtained from it would then be $a:d$, and therefore different from the amino-acid $a:b$, just as the hydroxybenzoïc acid $a:d$ differs from $a:b$ and $a:c$; whereas experiment proves that the two amino-acids are identical. The nitro-group in the other bromonitrobenzoïc acid must therefore be at *e* or *f*; let it be arbitrarily supposed to be at *f*, and it follows that $b=f$.



$$C_6H_5\cdot COOH \rightarrow C_6H_4<\begin{matrix}Br & c\\ COOH & a\end{matrix}\;\begin{matrix}\nearrow\\ \searrow\end{matrix}\;\begin{matrix} C_6H_3\begin{cases}Br & c\\ COOH & a\\ NO_2 & b\end{cases}\rightarrow \\ C_6H_3\begin{cases}Br & c\\ COOH & a\\ NO_2 & f\end{cases}\rightarrow\end{matrix}\; C_6H_4\begin{cases}COOH & a\\ NH_2 & b=f.\end{cases}$$

Anthranilic acid

The equality of the position *e* with the others is proved similarly. Anthranilic acid $(a:b=f)$ is converted into hydroxybenzoïc (salicylic) acid, which on nitration yields two isomeric nitrosalicylic acids, whose hydroxyl can be exchanged for hydrogen by a process which need not be described here. Both yield the *same* nitrobenzoïc acid, from which follows the equivalence relative to *a* of the two positions occupied by the nitro-groups in the isomers. One of these positions is *c*, since on reduction this nitrobenzoïc acid yields *m*-aminobenzoïc acid, which can be converted into the above-mentioned *m*-bromobenzoïc acid $a:c$. The nitro-group in the other nitrosalicylic acid cannot be in the position $b=f$, as the nitrobenzoïc acid obtained from it does not yield anthranilic acid on reduction; position *d* is also excluded, since it would not allow the two nitrobenzoïc acids to be identical. There remains therefore only the position *e*, from which it follows that $c=e$. Hence, $a=b=c=d=e=f$:



$$C_6H_4\begin{cases}COOH & a\\ NH_2 & b=f\end{cases} \rightarrow C_6H_4\begin{cases}COOH & a\\ OH & b=f\end{cases}\begin{matrix}\nearrow\\ \searrow\end{matrix}$$

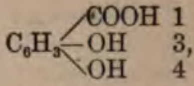
Anthranilic acid — Salicylic acid

$$\begin{matrix}C_6H_3\begin{cases}COOH & a\\ OH & b=f\\ NO_2 & c\end{cases}\\ C_6H_3\begin{cases}COOH & a\\ OH & b=f\\ NO_2 & e\end{cases}\end{matrix}\;\begin{matrix}\nearrow\\ \searrow\end{matrix}\; C_6H_4\begin{cases}COOH & a\\ NO_2 & c=e\end{cases} \rightarrow C_6H_4\begin{cases}COOH & a\\ NH_2 & c=e\end{cases}$$

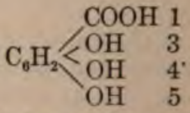
Isomeric nitrosalicylic acids — Nitrobenzoïc acid — Aminobenzoïc acid

FINISH

Dihydroxy-acids.

344. Among these, *protocatechuic acid*,  $C_6H_3{<}\begin{matrix}\text{COOH} & 1\\ \text{OH} & 3\\ \text{OH} & 4\end{matrix}$, may be mentioned. It is obtained from many resins by fusion with potash, and synthetically by heating catechol with ammonium carbonate, the latter method being a striking example of the readiness with which the carboxyl-group can sometimes be introduced into the ring. It is easily soluble in water; it reduces an ammoniacal silver solution but not an alkaline copper one. It gives a characteristic reaction with ferric chloride, yielding a green colour, which changes to blue and finally to red, on addition of a very dilute solution of sodium carbonate.

Trihydroxy-acids.

345. The best known of these is *gallic acid*,  $C_6H_2{<}\begin{matrix}\text{COOH} & 1\\ \text{OH} & 3\\ \text{OH} & 4\\ \text{OH} & 5\end{matrix}$. It is a constituent of gall-nuts, tea, and *divi-divi*, a material used in tanning. It is usually prepared by boiling tannin with dilute acids. It crystallizes in fine needles, readily soluble in hot water. It was mentioned in **314** that the acid loses CO_2 on heating, forming pyrogallol. Gallic acid reduces the salts of gold and silver, and gives a bluish-black precipitate with ferric chloride. In alkaline solution it is turned brown in the air by oxidation, in the same way as pyrogallol.

Gallic acid is used in the manufacture of blue-black ink. For this purpose its aqueous solution is mixed with a solution of ferrous sulphate containing a trace of free sulphuric acid. Without the acid, the ferrous sulphate would quickly oxidize in the air, giving a thick, black precipitate with the gallic acid; this oxidation is retarded in a remarkable manner by the addition of a very small quantity of sulphuric acid. As soon as the solution is brought into contact with paper, the free acid is neutralized by the alumina always present in the latter, and, as oxidation is no longer prevented, the writing in drying turns deep-black. As the mixture of the solutions of ferrous sulphate and gallic acid has only a faint brown colour, which would make the fresh writing almost invisible, indigo-carmine is added to the mixture. This imparts to the ink coming from the pen a dark-blue colour, which changes by the above-mentioned process to a deep black.

The *tannins*, or *tannic acids*, are very closely related to gallic acid, and are widely distributed in the vegetable kingdom. The tannins are compounds which are soluble in water, have a bitter, astringent taste, yield a dark-blue or green precipitate with ferric salts, convert substances containing gelatine—such as animal hides—into leather, and precipitate albumins from their solutions. Some of the tannins are glucosides.

The most typical tanning-material is *tannin* or *tannic acid*, contained in oak-bark. It is a derivative of gallic acid, into which it is converted by boiling with dilute hydrochloric acid. Tannin is optically active, and seems to have a somewhat complicated molecular structure.

It is best obtained from gall-nuts—pathological excrescences on the leaves and branches of the oak, caused by an insect. Turkish gall-nuts are especially rich in tannin, yielding as much as 65 per cent.

Tannin imparts its characteristic bitter taste to many beverages—to tea which has been too long infused, for instance. The addition of milk removes this bitter taste, because the tannin forms an insoluble compound with the albumin present in the milk.

Tannin is a white (sometimes yellowish), amorphous powder readily soluble in water, only slightly in alcohol, and insoluble in ether. It forms salts with two equivalents of the metals, and precipitates many alkaloids, such as strychnine and quinine, from their aqueous solutions (**401**).

A distinction is drawn between the different kinds of tanning-substances, which have properties analogous to those of tannin, but differ from it in composition. They are named after the plants in which they are found; *kino-tannin*, *catechu-tannin*, *moringa-tannin*, *coffee-tannin*, *oak-tannin*, *quinine-tannin*, and others are known.

346. The tannins are used in *medicine* and in the *tanning of hides*.

In making leather, the hide is saturated with the tannin, because without this treatment it cannot be used in the manufacture of shoes, etc., since it soon dries to a hard, horn-like substance, or in the moist condition becomes rotten. When saturated with tannin it remains pliant, and does not decompose.

The skin of an animal consists of three layers, the epidermis, the cuticle, and the fatty-layer. The cuticle being the part made into leather, the two other layers are removed by suspending the hides in running water, when the epidermis and fatty layer begin to decompose, and are easily removed by means of a blunt knife. Alternate horizontal layers of the hides thus prepared and oak-bark or some other material containing tannin are placed in large troughs or vats, which are then filled with water. At the end of six or eight weeks the hides are taken out and placed in a second vat containing fresh bark of stronger quality. This is continued with increasingly concentrated tannin-solutions until the hides are perfectly tanned, the process lasting as long as two or three years, according to the thickness of the hide. Whether a hide is thoroughly saturated or tanned may be judged from the appearance of its cross-section, or by treatment with dilute acetic acid; if this treatment makes it swell up internally, it shows that the conversion into leather is incomplete. It is still a matter of doubt whether tanning is a mechanical or a chemical process. According to some, the tannin is simply deposited mechanically in the hides; according to others, chemical union takes place between the tissue of the hide and the tannin. The first view is held by most chemists.

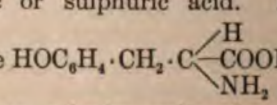
Acids Containing Hydroxyl or Carboxyl in the Side-chains.

347. Three different types are here possible:

1. OH in the side-chain, COOH in the ring;
2. COOH in the side-chain, OH in the ring;
3. OH and COOH both in the side-chain.

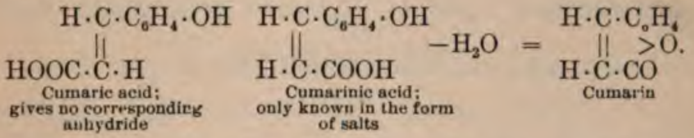
The following are representatives of these three classes.

1. *Hydroxymethylbenzoïc acid,* $C_6H_4<\begin{matrix}CH_2OH & 1\\ COOH & 2\end{matrix}$, was mentioned in **326.** It yields phthalide by separation of water, and is obtained by boiling o-*xylylene chloride,* $C_6H_4<\begin{matrix}CH_2Cl\\ CH_2Cl\end{matrix}$, with water and lead nitrate.

2. p-*Hydroxyphenylpropionic acid,* $C_6H_4<\begin{matrix}OH\\ CH_2\cdot CH_2\cdot COOH\end{matrix}$, is of some importance owing to its relation to *tyrosine* (M.P. 235°)—which derives its name from its presence in old cheese, and is produced when albumins, such as the white of egg, horn, hair, etc., are boiled with hydrochloric or sulphuric acid. Its formula is $C_9H_{11}NO_3$, and its structure  $HOC_6H_4\cdot CH_2\cdot C\begin{matrix}\diagup H\\ -COOH\\ \diagdown NH_2\end{matrix}$; it is the α-amino-acid corresponding to p-hydroxyphenylpropionic acid.

Being an amino-acid, it yields salts with acids as well as with bases.

o-Hydroxycinnamic acid, $C_6H_4<\genfrac{}{}{0pt}{}{OH}{CH:CH\cdot COOH}$, exists in two forms, *cumaric acid* and *cumarinic acid,* which are easily converted into each other. Cumarinic acid is not known in the free state, but only in the form of salts, since it at once loses a molecule of water when set free, yielding *cumarin,* the aromatic principle of wood-ruff (*Asperula odorata*). Cumaric acid, on the other hand, does not yield a corresponding anhydride; removal of water produces cumarin, which is converted into salts of cumarinic acid by treatment with alkalis. This behaviour recalls that of fumaric and maleïc acids (**170**), and it may be assumed that this is a similar case of stereoisomerism. Both acids may then be represented as follows:

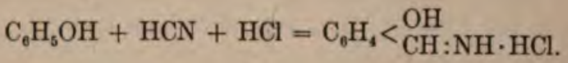


Cumarin can be obtained from salicylaldehyde by Perkin's synthesis (**309**); acetylcumaric acid, $C_6H_4<\genfrac{}{}{0pt}{}{O|\overline{C_2H_3O}}{\overline{CH:CH\cdot COO}|H}$, is first formed, and is converted into cumarin by heating, acetic acid being split off.

3. *Mandelic acid* has both hydroxyl and carboxyl in the side-chain. Its constitution is $C_6H_5\cdot CHOH\cdot COOH$, as its synthesis from benzaldehyde and hydrocyanic acid indicates. The mandelic acid found in nature is lævo-rotatory; the synthetical acid can be split up by the action of cultures obtained from mildew (*Penicillium glaucum*), the dextro-rotatory acid being left intact. The decomposition is also effected by the formation of the cinchonine salts, when the salt of the dextro-rotatory acid crystallizes out first.

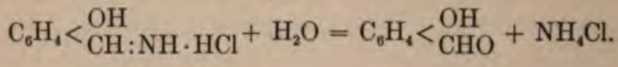
Hydroxy-aldehydes.

348. These can be obtained artificially by a synthetical method generally applicable to the preparation of aromatic hydroxyaldehydes. It consists in treating the phenols in ethereal solution with anhydrous hydrocyanic acid and hydrochloric-acid gas, it being sometimes an advantage to add a small quantity of zinc chloride as a condensing-agent. This mode of synthesis was discovered by GATTERMANN, whose name it bears. The hydrochloride of an imide is formed as an intermediate product, and can sometimes be isolated:



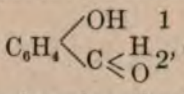
$$C_6H_5OH + HCN + HCl = C_6H_4<{OH \atop CH:NH \cdot HCl}.$$

On treatment with warm water, the imide-salt is converted into the hydroxyaldehyde and ammonium chloride:

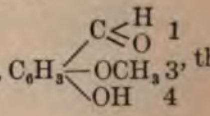


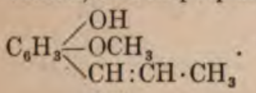
$$C_6H_4<{OH \atop CH:NH \cdot HCl} + H_2O = C_6H_4<{OH \atop CHO} + NH_4Cl.$$

p-*Hydroxybenzaldehyde* is here obtained from phenol.

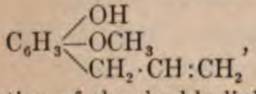
Salicylaldehyde,  $C_6H_4<{OH \quad 1 \atop C<{H \atop O} \quad 2}$, occurs in volatile *oil of spiræa.*

The *o*-hydroxyaldehydes colour the skin deep yellow.

To this class of substances belongs *vanillin*,  $C_6H_3\begin{cases} C<{H \atop O} & 1 \\ OCH_3 & 3 \\ OH & 4 \end{cases}$, the methyl ether of pyrocatechualdehyde. It is the aromatic principle of vanilla, and is prepared on the large scale by oxidizing *isoeugenol*,



$C_6H_3\begin{cases} OH \\ OCH_3 \\ CH:CH \cdot CH_3 \end{cases}$. This substance is obtained by boiling *eugenol*,



$C_6H_3\begin{cases} OH \\ OCH_3 \\ CH_2 \cdot CH:CH_2 \end{cases}$, with alcoholic potash, which alters the position of the double linking in the side-chain. Eugenol is the chief constituent of oil of cloves.

For compounds containing the hydroxyl-group and the sulpho-group or the halogens, *cf.* respectively **333** and **336.**

IV. COMPOUNDS WITH THE NITRO-GROUP AND AMIDO-GROUP.

Nitranilines.

349. These compounds can be obtained by the partial reduction of dinitro-compounds, by means of ammonium sulphide. Another method for their production consists in the nitration of anilines, though if nitric acid is allowed to act directly on this base the resulting products are mostly those of oxidation. If nitration is to be carried out, the amido-group must be "protected" against the action of this acid, either by first converting the aniline into acetanilide, or by causing the nitric acid to react in presence of a large quantity of sulphuric acid. When the acetyl-compound is employed, p-*nitraniline* is the chief product, o-*nitraniline* being formed when sulphuric acid is used.

In these substances there is a weakening of the basic character, m-*nitraniline*, for example, yielding salts which are decomposed by water.

The *o*-, *m*-, and *p*-nitranilines, $C_6H_4<{NO_2 \atop NH_2}$, are yellow, crystalline compounds, readily soluble in alcohol. Their melting-points are respectively 71°, 114°, and 147°.

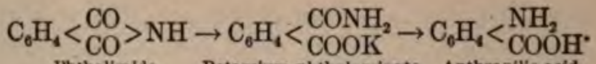
Nitrobenzoïc Acids.

350. The *meta*-compound is the principal product obtained by nitrating benzoïc acid; some of the *ortho*-acid and a very small quantity of the *para*-acid are formed at the same time. The *ortho*-compound is best obtained by the oxidation of *ortho*-nitrotoluene, and is characterized by an intensely sweet taste.

The introduction of the nitro-group causes a large increase in the value of the dissociation constant K, which for benzoïc acid itself is 0·006, for *o*-nitrobenzoïc acid 0·616, for the *m*-acid 0·0345, and for the *p*-acid 0·0396. The melting-points of these acids are respectively 148°, 141°, and 241°.

Aminobenzoïc Acids.

351. The most important of these is the *o*-acid, called *anthranilic acid*, first obtained by the oxidation of indigo. It has quite the character of an amino-acid, yielding salts with both acids and bases. It possesses a sweet taste, and slightly antiseptic properties. It is obtained by the method of HOOGEWERFF and VAN DORP (**244**), by treating phthalimide with bromine and caustic potash; the potassium salt of phthalaminic acid is first formed, and then changes into anthranilic acid:



$$C_6H_4<{CO \atop CO}>NH \rightarrow C_6H_4<{CONH_2 \atop COOK} \rightarrow C_6H_4<{NH_2 \atop COOH}.$$

Phthalimide — Potassium phthalaminate — Anthranilic acid

Anthranilic acid melts at 145°, and can be sublimed without composition; it is readily soluble in water and in alcohol. By the thod given above it is prepared technically for the synthesis of ligo, bleaching-powder being substituted for the caustic potash d bromine.

FINISH

ORIENTATION OF AROMATIC COMPOUNDS.

352. Orientation is the determination of the positions which the side-chains or substituents in the benzene-ring occupy in relation to one another. A description of a number of the most important substituted benzene derivatives having been given in the foregoing pages, it becomes necessary to furnish an insight into the methods by which orientation is carried out.

These rest on two main principles.

1. *Relative determination of position.*—The compound, the position of whose substituents is unknown, is converted into another with known positions; from this it is inferred that the first compound has its substituents arranged similarly to the second. If, for example, the constitution of one of the three xylenes is required, the hydrocarbon can be oxidized; the particular phthalic acid formed indicates the positions of the methyl-groups in the xylene under examination, provided the positions of the carboxyl-groups in the three phthalic acids are known.

In order to apply this method, it is necessary to know the positions of the substituents in a small number of compounds, and it is further assumed that the positions of the substituents remain the same during the course of the reactions which have to be made use of. Experience has shown that this is true in most cases, although the position of the side-chain does alter in a few reactions.

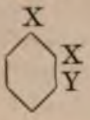
> It was stated in **332** that the three bromo-sulphonic acids are converted into resorcinol by fusion with caustic potash. There are other examples of change of position when the sulpho-group is replaced by the hydroxyl-group, by fusion with caustic alkalis.

In order to avoid erroneous conclusions, it is, therefore, desirable in cases of doubt to check the determination of position by converting the substance into another compound.

2. *Absolute determination of position.*—This is the determination of the positions of the substituents without having recourse to other compounds the positions of whose substituents are

known. A general method is afforded by KÖRNER's *principle*, by which it is possible to ascertain whether substances $C_6H_4X_2$, containing two substituents, are *ortho-*, *meta-*, or *para*-compounds; this is effected by determining the number of trisubstitution-products corresponding to them.

When a third group, Y, is introduced into an *ortho*-compound, $C_6H_4X_2$, whether Y is the same as or different from X, only *two* isomers can be formed,



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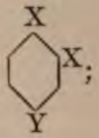
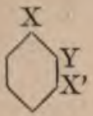
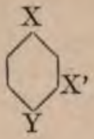


the introduction of a third group into a *meta*-compound renders possible the formation of *three* isomers,





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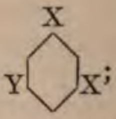
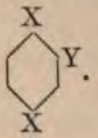


while in the case of a *para*-compound the introduction of a third group yields only *one* trisubstitution-product,

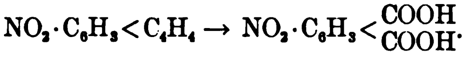


In addition to this general method, there are others for special cases, several of which may be mentioned here; it will be observed that they fully substantiate the conclusions already arrived at by KÖRNER's method.

1. Absolute determination of position for *ortho*-compounds.

353. For the *ortho*-series, the structure of a dibromobenzene melting at $-1°$ is determined by means of KÖRNER's principle; this body yields two isomeric nitrodibromobenzenes. The constitution of a *xylene* boiling at 142° and melting at $-28°$, has also been established by this method; it gives rise to two isomeric nitroxylenes when treated with nitric acid. This xylene is converted into phthalic acid by oxidation, showing that the latter is an *ortho*-compound.

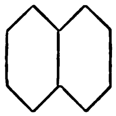
That the carboxyl-groups of this acid are in the *ortho*-position was also determined by a different method, by means of the oxidation of naphthalene, $C_{10}H_8$, a hydrocarbon which is converted into phthalic acid by this treatment. This fact shows that its structure must be $C_6H_4 < C_4H_4$, in which the group C_4H_4 is linked to two positions in the benzene-ring. When naphthalene is treated with nitric acid, nitronaphthalene is formed, and is converted by oxidation into nitrophthalic acid. The group C_4H_4 has, therefore, been converted into two carboxyl-groups in this case also:



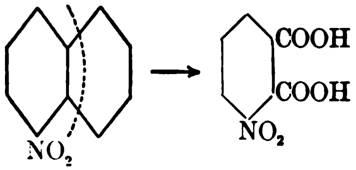
$$NO_2 \cdot C_6H_3 < C_4H_4 \rightarrow NO_2 \cdot C_6H_3 < \begin{matrix} COOH \\ COOH \end{matrix} .$$

Nitronaphthalene **Nitrophthalic acid**

If, however, the nitro-group is reduced, and the aminonaphthalene thus obtained oxidized, phthalic acid is formed. Hence, it follows that the group C_4H_4 forms a second benzene-ring with the two carbon atoms of the benzene-ring, so that naphthalene must be represented thus:



The oxidation of nitronaphthalene and aminonaphthalene is expressed as follows:



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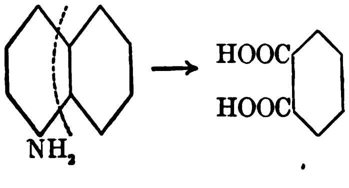
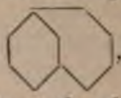
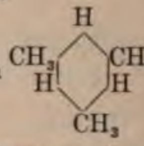


This shows that phthalic acid must be an *ortho*-compound, because if it be assumed to have the *meta*-structure, for example, naphthalene must be represented by the formula , which leads at once to a contradiction, since there could not then be a benzene derivative produced by the oxidation of *both* nitronaphthalene and aminonaphthalene.

2. Absolute determination of position for *meta*-compounds.

354. The proof that mesitylene is symmetrical trimethylbenzene (1:3:5) is stated by Ladenburg as follows.

If this compound has the constitution 

, the three hydrogen atoms directly linked to the benzene-ring must be of equal value. If this can be proved, the structure of mesitylene is established.

The proof of the equality is as follows. On nitrating mesitylene a dinitro-compound is obtained. If the hydrocarbon is represented by

$$\text{I.}\quad C_6(CH_3)_3\overset{a}{H}\overset{b}{H}\overset{c}{H},$$

the dinitro-compound may be arbitrarily assumed to be

$$\text{II.}\quad C_6(CH_3)_3\overset{a}{NO_2}\overset{b}{NO_2}\overset{c}{H}.$$

One of the nitro-groups of the dinitro-compound is reduced, and the resulting amino-compound is converted into an acetyl-derivative; suppose that this acetyl-derivative is

$$\text{III.}\quad C_6(CH_3)_3\overset{a}{NO_2}\overset{b}{NH(C_2H_3O)}\overset{c}{H}.$$

This substance can be again nitrated, when there must result

$$C_6(CH_3)_3\overset{a}{NO_2}\overset{b}{NH(C_2H_3O)}\overset{c}{NO_2}.$$

It is possible to eliminate the acetylamido-group, $NH(C_2H_3O)$, from this compound by saponification, subsequent diazotization, etc. In this way a dinitromesitylene with the formula

$$C_6(CH_3)_3\overset{a}{NO_2}\overset{b}{H}\overset{c}{NO_2}\cdot$$

is obtained, and is found to be identical with the former dinitro-product, the nitro-groups of which are at *a* and *b*. From this it follows that

$$H^b = H^c.$$

Nitromesidine, *a* : *b*, whose acetyl-compound is represented by formula III, furnishes a further proof that $H^a = H^c$.

When the amido-group is eliminated from this by means of the diazo-reaction, there is formed

$$\text{IV.}\quad C_6(CH_3)_3\overset{a}{NO_2}\overset{b}{H}\overset{c}{H}.$$

This is reduced and converted into an acetyl-compound, acetylmesidine,

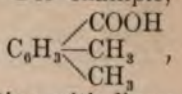
$$C_6(CH_3)_3NH(\overset{a}{C_2H_3O})\overset{b}{H}\overset{c}{H}.$$

This compound can be again nitrated, yielding

$$C_6(CH_3)_3NH(\overset{a}{C_2H_3O})\overset{b}{NO_2}\overset{c}{H},$$

in which it is of no consequence whether the nitro-group is in the position *b* or *c*, since the equality of these positions relative to *a* has been already proved.

On eliminating the acetylamido-group from the substance last obtained, a mononitromesitylene is produced, identical with the compound IV; it follows that $a = b = c$, which completes the proof of the equality of the three hydrogen atoms.

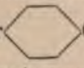
From the known constitution of mesitylene it is possible to deduce the structure of many other compounds. For example, partial oxidation converts it into *mesitylenic acid*,  $C_6H_3\begin{cases}COOH\\CH_3\\CH_3\end{cases}$, which is in turn converted into xylene by distillation with lime; this compound must be *meta*-xylene. Oxidation converts this *m*-xylene into isophthalic acid, showing that the carboxyl-groups in the latter occupy the *meta*-position. These determinations of position have been fully substantiated by the application of Körner's principle. Thus, Nölting has prepared three isomeric nitroxylenes, in which the relative positions of the methyl-groups are the same as in the xylene obtained from mesitylenic acid.

Among other *meta*-compounds in which the position of the groups has been independently established, there may be mentioned a dibromobenzene boiling at 220°. Körner proved that corresponding to this substance are three isomeric tribromobenzenes and three nitrodibromobenzenes. In conclusion, it may be mentioned that the phenylenediamine which melts at 62° can be obtained from three different diaminobenzoïc acids by elimination of CO_2, so that it also must be a *meta*-compound.

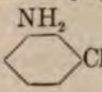
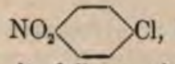
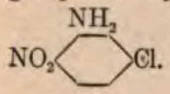
3. Absolute determination of position for *para*-compounds.

355. KÖRNER's principle has been of great service in determining the constitution of some members of the *para*-series. For example, from the xylene boiling at 138°, and melting at 13°, it was only possible to obtain one nitroxylene; the phenylenediamine melting at 140° can only be obtained from one diaminobenzoïc acid by splitting off CO_2; etc.

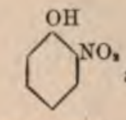
These determinations of position have been confirmed in another way. Thus, a hydroxybenzoïc acid melting at 210° has been proved to have the *para*-constitution. It is obtained from a bromobenzoïc acid, which can be got from ordinary bromotoluene, the latter being convertible into a xylene from which terephthalic acid can be obtained by oxidation. *p*-Hydroxybenzoïc acid affords, therefore, a valuable basis for orientation.

The proof can be stated as follows. The starting-point is bromobenzoïc acid, obtained directly by the bromination of benzoïc acid. On nitration, two isomeric nitrobromobenzoïc acids are formed, either of which yields on reduction the same aminobenzoïc acid, anthranilic acid; this can be converted into salicylic acid by means of the diazo-reaction. It follows that in both the isomers the nitro-group must be situated symmetrically to the carboxyl-group: at 2 or 6, or at 3 or 5, if the carboxyl-group is at 1. The same reasoning establishes the position of the hydroxyl-group in salicylic acid. Concerning the position of the bromine atom, it is evident that it cannot be at 4, because two isomeric nitro-compounds which would yield the same aminobenzoïc acid on reduction, could not be obtained from BrCOOH. The bromine atom must, therefore, occupy the *meta*-position or *ortho*-position to the carboxyl-group. A hydroxybenzoïc acid melting at 200°, obtained by this means, must therefore be *meta* or *ortho*. Since the isomeric salicylic acid can also be only a *meta*-compound or an *ortho*-compound, there remains no possibility, except the *para*-structure, for the third hydroxybenzoïc acid melting at 210°.

Determination of position for the Trisubstituted and higher-substituted derivatives.

356. This can usually be effected by ascertaining the relation in which they stand to the diderivatives of known constitution. For example, since a certain chloronitroaniline, $C_6H_3Cl(NO_2)(NH_2)$, is obtained by nitrating *m*-chloroaniline, , and yields *p*-chloronitrobenzene, , by exchange of the amido-group for hydrogen, it follows that it has the constitution .

A more complicated example of orientation is afforded by the way in which the positions of the groups in *picric acid* are ascertained. Careful nitration converts phenol into two mononitrophenols,

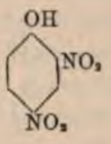


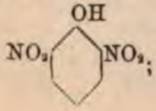
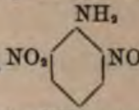
and

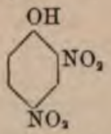
M.P. 45° M.P. 114°

One of these must be the *ortho*-compound and the other the *para*-compound, because the third nitrophenol can be obtained from *m*-dinitrobenzene—the constitution of which has been proved by its reduction to *m*-phenylenediamine (**354**)—by reduction to *meta*-nitraniline, and subsequent exchange of NH_2 for OH by diazotizing.

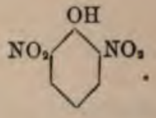
When further nitrated, both nitrophenols yield the same dinitrophenol, which can therefore only have the formula



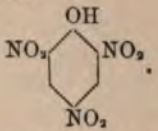
The mononitrophenol, which melts at 114°, is converted by oxidation into quinone, and must, therefore, be the *para*-compound. For the body melting at 45° there remains only the *ortho*-structure. On nitration this *o*-nitrophenol yields, in addition to the 1 : 2 : 4-dinitrophenol (OH at 1), another dinitrophenol with its groups at 1 : 2 : 6, ; for on conversion of this into its methyl ether, and heating the latter with alcoholic ammonia, the group OCH_3 is replaced by NH_2; and this substance, which has the formula , is converted by the substitution of hydrogen for the NH_2-group into the ordinary, or *meta-*, dinitrobenzene. Thus, we have two dinitrophenols of known structure,



and



Further nitration converts both of these into picric acid, which must, therefore, have the constitution

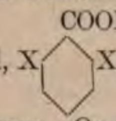


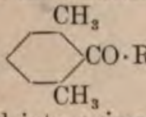
From the known constitution of picric acid may be inferred the position of the groups in ordinary trinitrobenzene, since this compound is readily oxidized to picric acid (**318**). This trinitrobenzene must, accordingly, have the symmetrical structure.

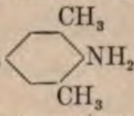
Influence of the substituents on each other.

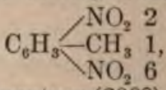
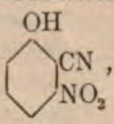
357. This influence is very important, and manifests itself in various ways. It affects the position which the substituents take up in relation to one another, when introduced simultaneously or in succession into the benzene-nucleus. Let us consider first the simplest case, the introduction of a second atom or group into a monosubstituted compound C_6H_5X. It is found that one of the three possible isomers is always obtained as the chief product, the second isomer being produced in less quantity, while the yield of the third isomer is very small. For example, when benzoïc acid is nitrated at 0°, 80·2 per cent. of *meta-*, 18·5 per cent. of *ortho-*, and only 1·3 per cent. of *para-*nitrobenzoïc acid are formed. On nitration at 30°, nitrobenzene yields 90·9 per cent. of the *meta-*, 8·1 per cent. of the *ortho-*, and 1 per cent. of the *para-*compound. It has often been stated that the introduction of a second group results in the formation of only one or two isomers; but when a careful examination has been made as to the presence of the third isomer, it has been shown to be present in minute quantity; so that it is

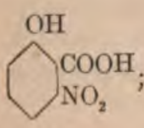
Ortho-groups sometimes exert a remarkable influence in retarding or partially preventing reactions which otherwise take place readily. Among others which have been observed, the following are examples.

It is known that when an acid is dissolved in excess of absolute alcohol it can be almost quantitatively converted into an ester by passing through it a current of hydrochloric-acid gas (**99**). VICTOR MEYER and his pupils found, however, that esterification of acids containing two groups in the *ortho*-position relative to carboxyl, 

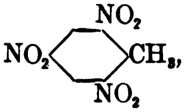
, was by no means complete when carried out in this manner. On the other hand, when the acid has been converted into an ester (by means of the silver salt and an alkyl halide) the ester so formed can only be saponified with great difficulty. When the two substituents occupy any of the other positions, these peculiarities do not manifest themselves, or at least not to the same extent. Ketones substituted in the two *ortho*-positions, 

, where R is an alkyl-radicle, cannot be converted into oximes, wherein they differ from all other ketones. *o-o*-Dimethylaniline, 

, is not converted by treatment with an alkyl iodide into a quaternary base; pentamethylbenzonitrile, $C_6(CH_3)_5CN$, cannot be saponified to the corresponding acid; the methyl-hydrogen in *o-o*-dinitrotoluene, 
$C_6H_3\begin{cases}NO_2 & 2\\ CH_3 & 1\\ NO_2 & 6\end{cases}$, cannot be replaced by halogens even at a high temperature (200°); this is also true of 1:2:4-dinitrotoluene; AUWERS and JAMIESON WALKER were unable, in spite of numerous attempts, to effect the hydrolysis of *o*-nitrosalicylic nitrile, 

, to the corresponding acid, 

; etc.

Groups occupying positions further removed sometimes exert a similar effect. One of the NO_2-groups of symmetrical trinitrobenzene is easily replaced by OCH_3 through the action of sodium methoxide, but for trinitrotoluene, , this is not found possible: the methyl-group prevents exchange of the nitro-group even in the *para*-position.

FINISH

TERPENES AND CAMPHORS.

358. All the terpenes have the empirical composition C_5H_8, but most of those which have been examined have the molecular formula $C_{10}H_{16}$. The *true terpenes*, $C_{10}H_{16}$, will therefore be described here, and the *semi-terpenes*, C_5H_8, as well as the *poly-terpenes*, $(C_5H_8)_x$, left almost out of account.

Most camphors have the formula $C_{10}H_{16}O$, but some varieties of the formulæ $C_{10}H_{18}O$ and $C_{10}H_{20}O$ are known.

Both the terpenes and camphors, which are nearly related to one another, are widely distributed throughout the vegetable kingdom; the species of *Pinus* are particularly rich in terpenes, and yield oil of turpentine, a mixture of these hydrocarbons, when distilled with steam. Common or *Japan camphor*, $C_{10}H_{16}O$, is obtained in the same way from the camphor tree (*Laurus camphora*) and *Borneo camphor* or borneol, $C_{10}H_{18}O$, from *Dryobalanops camphora*. Many ethereal oils consist chiefly of compounds $C_{10}H_{16}$ and $C_{10}H_{16}O$.

The terpenes are chiefly liquids—very few are solids—which boil at temperatures ranging from 158° to 190°. They have a characteristic odour, are tolerably stable towards alkalis, but are easily decomposed on treatment with acids, or on being heated to a high temperature. Some of them are optically active.

The camphors are solid, crystalline substances, and are very volatile even at ordinary temperatures. They can be sublimed, and are characterized by a peculiar odour. Some varieties are optically active. The convertibility by various means of the terpenes and the camphors into aromatic bodies betrays their relation to the latter. Thus, *p*-toluic acid and terephthalic acid, along with other compounds, are obtained on oxidizing terpenes with nitric acid. In particular they are related to *cymene;* this aromatic hydrocarbon can be obtained from the terpenes by the action of iodine, for example, and from camphor by means of dehydrating-agents, such as phosphorus pentoxide:

$$\underset{\text{Terpene}}{C_{10}H_{16}} + I_2 = \underset{\text{Cymene}}{C_{10}H_{14}} + 2HI; \ \underset{\text{Camphor}}{C_{10}H_{16}O} - H_2O = \underset{\text{Cymene}}{C_{10}H_{14}}.$$

Terpenes.

359. The natural ethereal oils $C_{10}H_{16}$ have different physical and chemical properties, according to the particular plant from which they have been obtained. In default of methods by which the isomers could be sharply distinguished from one another, it was formerly supposed that there was a great number of compounds with the formula $C_{10}H_{16}$. WALLACH succeeded in preparing well-defined crystalline derivatives of the compounds $C_{10}H_{16}$, and thus in distinguishing the existing isomers. It was found by this means that the natural ethereal oils are principally mixtures of such isomers, of which fifteen have been identified. They are classified into two main groups.

1. Substances with the formula $C_{10}H_{16}$, which form addition-products with only one molecule of HCl or with two Br-atoms.

2. Substances with the formula $C_{10}H_{16}$, which form addition-products with two molecules of HCl or with four Br-atoms.

Some particulars regarding the individual members are given below.

Pinene is the most widely distributed of all the terpenes; it is the principal constituent of German and American oil of turpentine. The first contains chiefly a lævo-rotatory, and the second a dextro-rotatory, modification. The boiling-point of this substance is 158°–161°, and its specific gravity 0·86–0·89. With nitrosyl chloride, NOCl, pinene yields an addition-product, $C_{10}H_{16}NOCl$, from which HCl is split off by heating with alcoholic potash, yielding a compound, $C_{10}H_{15}NO$, *nitrosopinene*. This can be reduced to a base, $C_{10}H_{15}NH_2$, *pinylamine*, whose hydrochloride on heating readily decomposes into ammonium chloride and cymene, $C_{10}H_{14}$. Pinene unites with one molecule of HCl to form a solid crystalline mass, $C_{10}H_{17}Cl$, melting at 125°; this substance is called *artificial camphor*, and strongly resembles natural camphor in its external appearance and odour.

On heating artificial camphor, $C_{10}H_{17}Cl$, with anhydrous sodium acetate and glacial acetic acid (a general method for splitting off hydrochloric acid from terpene hydrochlorides), there is formed *camphene*, one of the few solid compounds having the composition $C_{10}H_{16}$. It is crystalline, melts at 50°, and is known both in the dextro-rotatory and lævo-rotatory modifications; it has an odour like turpentine and camphor, and is not a natural product. Oxidation with chromic acid converts camphene into camphor. It is likewise obtainable in the reverse way from camphor: borneol is converted into camphene by the splitting off of water. Camphene forms an addition-product with only one molecule of HCl, the compound $C_{10}H_{17}Cl$ which is formed being isomeric with artificial camphor.

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360. Among the substances $C_{10}H_{16}$ which add on two molecules of HCl and four bromine atoms, *limonene* and *dipentene* deserve special mention. Limonene is the principal constituent of the ethereal oil obtained from orange-rind, and is also present in numerous other ethereal oils, such as oil of citron, oil of bergamot, etc. Dipentene appears to exist as such only in *Oleum cinæ*, but is formed by heating limonene and other terpenes to 250° to 300°. It is, therefore, present in ethereal oils in whose preparation a high temperature has been employed, as is the case with Russian and Swedish turpentine.

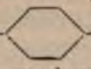
Limonene is strongly dextro-rotatory, and its tetrabromide is also optically active. On the other hand, dipentene and its tetrabromide are optically inactive, and the addition-products which limonene and dipentene yield with the hydrogen halides are identical and inactive. The latter yield dipentene by the splitting off of hydrogen halide, so that limonene can in this way be converted into dipentene.

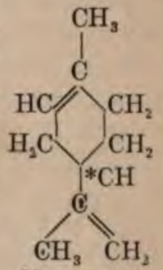
WALLACH discovered in pine oil a hydrocarbon, $C_{10}H_{16}$, which rotates the plane of polarization to the left to the same extent as limonene to the right, and which from its general character is to be looked upon as the optical antithesis of limonene. When this *lævo-limonene* is mixed with the dextro-modification, *dipentene* is formed, from which it follows that dipentene is to be regarded as the racemic modification of the limonenes.

Pinene can be converted into dipentene as follows. By the action of water containing nitric acid, it takes up three molecules of water, forming *terpin hydrate*, $C_{10}H_{20}O_2 + H_2O$. On heating, this loses a molecule of water, yielding *terpin*, $C_{10}H_{20}O_2$, which by the usual linkings in its molecule. It is converted by oxidation into an aldehyde, $C_{10}H_{16}O$, *geranial*, showing that it must be a primary alcohol. Geranial is sometimes also called *citral*, owing to its presence in oil of citron. On heating with potassium pyrosulphate, citral easily loses water, being converted into cymene, $C_{10}H_{14}$. Geraniol also loses water when treated with potassium pyrosulphate, yielding a terpene, $C_{10}H_{16}$, *geraniene*, boiling between 172° and 176°. From its additive power, this compound seems to contain three double linkings in the molecule.

Closely related to geraniol are *linalol* (from oil of linalœs), and *rhodinol* (from oil of roses). They have also the formula $C_{10}H_{18}O$, and are converted into citral by oxidation. This is probably accompanied by an alteration in the positions of the double linkings present in the compound.

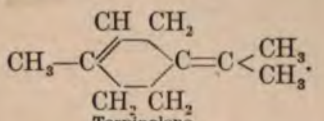
The Constitution of the Terpenes and Camphors.

362. A compound $C_{10}H_{16}$ has six hydrogen atoms less than a saturated fatty hydrocarbon of ten carbon atoms, $C_{10}H_{22}$. An aromatic hydrocarbon with saturated side-chains and ten carbon atoms has the formula $C_{10}H_{14}$. The terpenes, therefore, occupy a position intermediate between the aromatic and the saturated fatty series. Their properties correspond with this view: on the one hand, they are readily converted into aromatic compounds, especially cymene; on the other, they exhibit many of the properties of aliphatic compounds. The difference of six hydrogen atoms between them and the saturated hydrocarbons with ten carbon atoms might be caused by the presence of three double linkings, which, indeed, seem to be present in geraniene. Since, however, the other terpenes do not add six monovalent atoms, but some only four, and others only two such atoms, they must contain one or more closed chains of C-atoms, in addition to double linkings. As in each closed chain there are two atoms of hydrogen less in the molecule than in the corresponding open chain (hexane, C_6H_{14}; hexamethylene, C_6H_{12}), it follows that in the terpenes which add 4Br and 2HCl, there must be one closed chain and two double linkings; and in the terpenes which add 2Br and 1HCl, one double linking and two closed chains. The problem is to determine which are the ring-systems in the different terpenes, and what are the positions of the double linkings in the molecules. These two questions have not yet been satisfactorily answered for all terpenes. For nearly all, two or more constitutional formulæ have been proposed, among which no definite selection has been made up to the present. Owing to the readiness with which many terpenes yield cymene, it is supposed that the carbon-nucleus of this compound, a closed hexagon, is present in them, with methyl and isopropyl in the *para*-position: CH_3—  —$CH(CH_3)_2$. The positions of the double linkings in this nucleus have been determined for terpenes which yield tetra-addition-products; for some of them with considerable certainty. For example, the adjoining formula is almost universally assigned to limonene, one of the double linkings being in the side-chain. This formula explains the different behaviour of the two double linkings, owing to their being situated within and without the ring respectively; limonene adds on only one molecule of HCl by treatment with dry hydrochloric-acid gas; the second double linking is only broken by treatment with moist hydrochloric-acid gas. It further explains the optical activity, since the carbon atom which is marked with an asterisk (*) is asymmetric.



Limonene and dipentene

Terpinolene also gives tetra-addition-products, and has, therefore, two double linkings. One of these is situated in the cymene-nucleus, between two tertiary C-atoms:

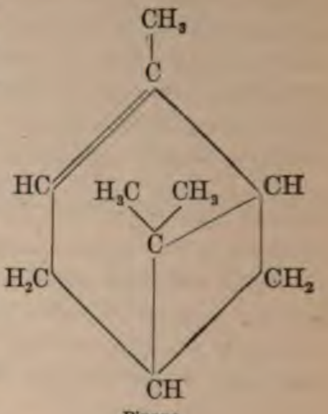


Terpinolene

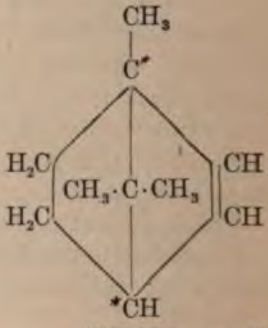
This is proved by the fact that this body yields a crystalline, blue addition-product with nitrosyl chloride. This is a characteristic of compounds which have a double linking between tertiary carbon atoms >C=C<, as has been indicated in the case of several such substances.

Compounds with the formula $C_{10}H_{16}$, which can only take up one molecule of HCl or two halogen atoms, must have two closed rings. A hexagon of carbon atoms is also supposed to exist in these. In the case of pinene the second ring is probably four-sided:

Baeyer assigns to this compound the adjoining formula, in which the isopropyl-group of cymene is linked by its tertiary carbon atom with the *meta*-carbon atom of the hexagon. This formula attributes two six-sided rings and one four-sided ring to pinene. In camphene the tertiary carbon atom of the isopropyl-group is linked to the benzene-ring at the *para*-position, so that it contains one six-sided ring and two five-sided rings. Analogous constitutional formulæ are assigned to the other terpenes, $C_{10}H_{16}$.



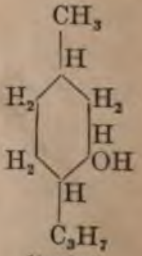
Pinene



Camphene

* = asymmetric

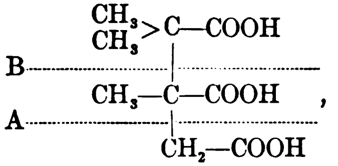
363. It has been mentioned that the camphors have the formula $C_{10}H_{20}O$, $C_{10}H_{18}O$, $C_{10}H_{16}O$. Menthol is an example of a compound with the first of these formulæ. It is an alcohol, and, according to its formula, contains two hydrogen atoms less than a saturated alcohol, $C_{10}H_{22}O$. Since menthol does not form addition-products, it must have the one closed-ring structure. The readiness of its conversion into cymene indicates that it contains a cymene-nucleus, its constitution being expressed by the adjoining formula.



Menthol

A compound with the formula $C_{10}H_{18}O$ can only have an open chain, if it has double or treble linkings in its molecule. This is the case with geraniol, $C_{10}H_{18}O$, which has two double linkings. Borneol, which is isomeric with it, does not possess any additive power, and its deficiency in hydrogen compared to a saturated compound must be caused by the presence of two closed rings, the same being then true of ordinary camphor, $C_{10}H_{16}O$. The oxidation of camphor affords a closer insight into its constitution. Bredt has shown that the first product obtained by its oxidation is *camphoric acid,* which on further oxidation yields *camphanic acid,* the latter yielding *camphoronic acid* on still further oxidation. It may, therefore, be assumed that the two first-named acids, as well as camphor itself, have the same carbon-nucleus as *camphoronic acid.*

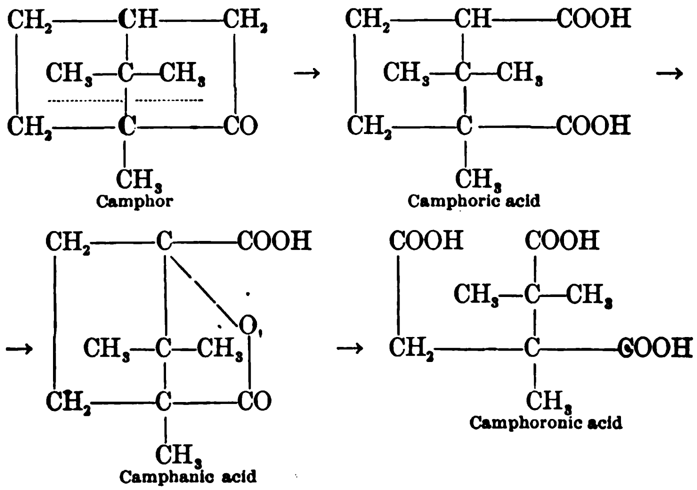
The constitution of the tribasic camphoronic acid follows from the result of its decomposition when submitted to dry distillation, a treatment which splits it up into trimethylsuccinic acid, isobutyric acid, and carbon dioxide. This is accounted for by the formula



$$\begin{array}{l} \quad {}^{CH_3}_{CH_3}{>}C\text{—}COOH \\ B\cdots\cdots\cdots | \cdots\cdots\cdots \\ \quad CH_3\text{—}C\text{—}COOH \quad , \\ A\cdots\cdots\cdots | \cdots\cdots\cdots \\ \qquad CH_2\text{—}COOH \end{array}$$

the formation of the first acid being represented by the decomposition A, and the second by B.

From a consideration of these and other known properties of these substances, Bredt assigns to them the following constitutional formulæ:



Camphor

Camphoric acid

Camphanic acid

Camphoronic acid

The formation of cymene from camphor is indicated in the formula of the latter by a dotted line, showing the breaking of the carbon bond in such a manner that the isopropyl-group takes up the *para*-position to the methyl-group.

Recent work affords confirmation of the correctness of Bredt's formulæ, that of the one for camphor being proved as follows. According to it, there are two asymmetric C-atoms in the molecule, indicated in the formula by bolder type. When, however, the CO-group is transformed into CH_2, the asymmetry of both atoms vanishes, and the molecule must become optically inactive, provided Bredt's formula is correct. This does, in fact, take place.

FINISH

BENZENE-NUCLEI DIRECTLY LINKED TOGETHER, OR INDIRECTLY BY CARBON.

364. The simplest possible compound of this nature is one containing two benzene-nuclei directly linked to one another. In addition to this there are compounds in which the benzene-nuclei are indirectly connected by a carbon atom, or by a chain of carbon atoms. A few of these substances will be described in this section.

Diphenyl, $C_6H_5 \cdot C_6H_5$.

Diphenyl can be prepared by FITTIG'S synthesis (**268**) from bromobenzene and sodium. Another method for the preparation of the derivatives of diphenyl, the conversion of hydrazobenzene into benzidine, was mentioned in **291**. On removing the amido-groups from benzidine by means of the diazo-reaction, diphenyl is formed. This method of formation also affords a proof of the constitution of benzidine.

The preparation of diphenyl is usually effected by passing benzene-vapour through a red-hot tube. It is converted by oxidation into benzoïc acid; this, together with its synthesis by FITTIG'S method, is a proof of its constitution.

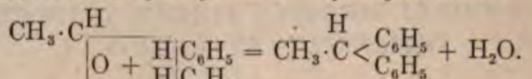
Diphenyl forms large, tabular, colourless crystals, readily soluble in alcohol and ether. It melts at 71°, and boils at 254°.

The isomeric substitution-products of diphenyl are much more numerous than those of benzene; a monosubstitution-product can exist in three isomeric forms, the substituent being in the *ortho-*, *meta-*, and *para*-positions to the bond between the benzene-nuclei; in a disubstitution-product, both substituents may be linked to the same benzene-nucleus, or to different benzene-nuclei, etc.

Benzidine is of technical importance, because many of the azo-dyes are derived from it.

Diphenylmethane, $C_6H_5\cdot CH_2\cdot C_6H_5$.

365. *Diphenylmethane* can be obtained from benzyl chloride, $C_6H_5\cdot CH_2Cl$, or from methylene chloride, CH_2Cl_2, by the action of benzene and aluminium chloride. Its homologues are obtained by the action of benzene and concentrated sulphuric acid upon aldehydes; thus, acetaldehyde yields *as-diphenylethane :*



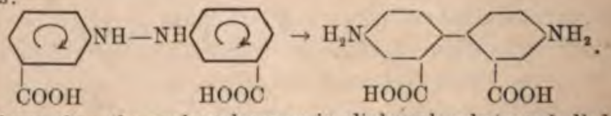
$$CH_3\cdot C^{H}\boxed{O + \begin{matrix}H|C_6H_5\\ H|C_6H_5\end{matrix}} = CH_3\cdot \overset{H}{C}<\begin{matrix}C_6H_5\\ C_6H_5\end{matrix} + H_2O.$$

When derivatives of benzene are substituted for benzene itself, many derivatives of diphenylmethane can be obtained by the application of the syntheses just mentioned.

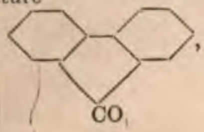
Diphenylmethane is crystalline; it melts at 26°, boils at 262°, and has an odour resembling that of orange-peel. Oxidation with chromic acid converts it into *benzophenone* (**300**).

A derivative of diphenylmethane, in which the benzene-nuclei are still directly linked, is *fluorene*, $\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!\!>CH_2$. It is formed by leading the vapour of diphenylmethane through a red-hot tube. It crystallizes from alcohol in fluorescent leaflets, from which it derives its name. It melts at 113°, and boils at 295°. It yields red needles with picric acid.

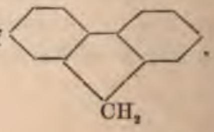
The constitution of fluorene is thus established. It is converted by the action of oxidizing-agents into *diphenyleneketone*, which has the formula $\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!\!>CO$, this being proved by its formation when the calcium salt of *diphenic acid*, $\begin{matrix}C_6H_4\cdot CO|O\\ |\\ C_6H_4\cdot|COO\end{matrix}\!\!>Ca$, is distilled. Diphenic acid, for its part, is obtained from *m*-hydrazobenzoïc acid by the benzidine-transformation (**291**), and subsequent elimination of the amido-groups:



It follows that the carbonyl-group in diphenyleneketone is linked at the *ortho*-position in both the benzene-nuclei; it has, therefore, the structure



, and fluorene itself



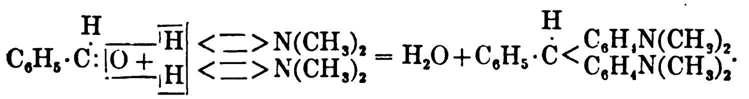
This receives confirmation from the fact that phthalic acid is the only product obtained by its oxidation.

Triphenylmethane and its Derivatives.

366. *Triphenylmethane*, $CH(C_6H_5)_3$, is formed from benzal chloride, $C_6H_5\cdot CHCl_2$, by the action of benzene and aluminium chloride; from benzaldehyde and benzene in presence of a dehydrating-agent, such as zinc chloride; and from the interaction of chloroform and benzene in presence of aluminium chloride. It crystallizes in beautiful, colourless prisms melting at 93°; its boiling-point is 359°.

A series of important dyes, the *rosanilines*, is derived from this hydrocarbon. Triphenylmethane itself is not employed as a basis for their preparation, simpler substances which are converted into its derivatives being used instead. The formation of the dye takes place in three stages; that of *malachite-green* furnishes an example.

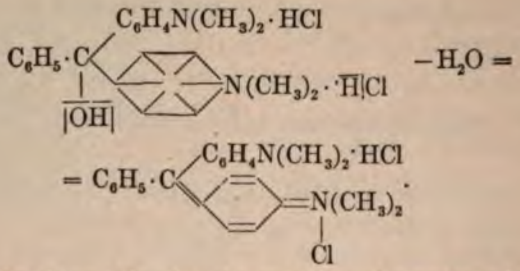
When benzaldehyde and dimethylaniline are heated with zinc chloride, *tetramethyldiaminotriphenylmethane* is formed:



$$C_6H_5\cdot\overset{H}{C}:\boxed{O+\begin{matrix}H\\H\end{matrix}}\begin{matrix}<\!=\!>N(CH_3)_2\\<\!=\!>N(CH_3)_2\end{matrix} = H_2O+C_6H_5\cdot\overset{H}{C}<\begin{matrix}C_6H_4N(CH_3)_2\\C_6H_4N(CH_3)_2\end{matrix}.$$

The carbon atom of the aldehyde group, therefore, furnishes the "methane carbon atom" of triphenylmethane.

This substance is also called *leucomalachite-green*. It is converted by oxidation with PbO_2 in hydrochloric-acid solution, into the corresponding carbinol, $\underset{OH}{C_6H_5C[C_6H_4N(CH_3)_2]_2}$, which is a colourless, crystalline substance, like the leuco-compound from which it is derived. Being an amino-base, it is capable of yielding salts; thus, it dissolves in acids with the formation of colourless salts. When such a solution is warmed, water is split off, and the deep-green dye produced. The latter, either as a double salt with zinc chloride, or as an oxalate, is known as *malachite-green*. This splitting-off of water may be represented in several ways; it is usually supposed to take place thus:



According to this mode of representation, the process is analogous to the formation of quinone from quinol, in which the colourless quinol is converted into the deep-yellow quinone.

The three stages necessary to the formation of the dye may, therefore, be defined as follows.

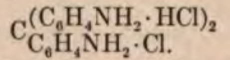
1. Formation of a *leuco-base* (colourless), a derivative of

$$HC(C_6H_4NH_2)_3;$$

2. Formation of a *colour-base* (colourless), a derivative of

$$HO\cdot C(C_6H_4NH_2)_3;$$

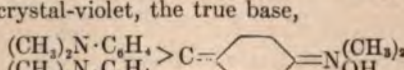
3. Formation of the *dye*, a derivative of



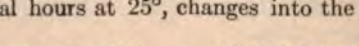
$$C\begin{matrix}(C_6H_4NH_2\cdot HCl)_2\\ C_6H_4NH_2\cdot Cl.\end{matrix}$$

Reduction converts the dyes back again into their leuco-bases, two hydrogen atoms being taken up during the reaction.

Crystal-violet (hexamethyltriaminotriphenylmethane) furnishes an excellent example of a phenomenon also exhibited by other analogous basic substances. When an equivalent quantity of a base is added to a salt of crystal-violet, the liquid still remains coloured, has a strong alkaline reaction, and conducts an electric current; the solution slowly becomes colourless on standing, when it is no longer alkaline, and its power of conducting an electric current has ceased. The liquid now contains a colour-base. These phenomena are analogous to the conversion of acids into pseudo-acids (**281**). For this reason the colour-base may be looked upon as a *pseudo-base*. According to this view, on addition of the equivalent quantity of NaOH to crystal-violet, the true base,



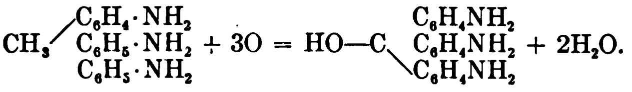
is at first present in the solution; this true base, however, after standing for several hours at 25°, changes into the colour-base (pseudo-base),



$$\begin{matrix}(CH_3)_2N\cdot C_6H_4\\ (CH_3)_2N\cdot C_6H_4\end{matrix}>C<\begin{matrix}C_6H_4\cdot N(CH_3)_2.\\ OH\end{matrix}$$

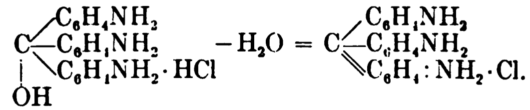
Hantzsch has been able to assign the character of a pseudo-base to certain substances other than those mentioned on p. 464.

Pararosaniline is obtained by the oxidation of a mixture of *p*-toluidine (1 molecule) and aniline (2 molecules) by means of arsenic acid or nitrobenzene. The methyl-group of toluidine is thus converted into the "methane carbon atom" of triphenylmethane:



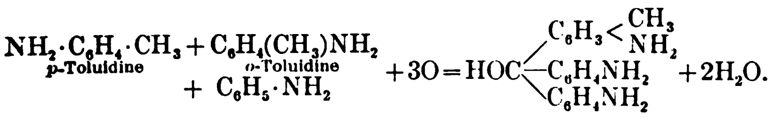
$$\mathrm{CH_3}\diagup\begin{array}{l}\mathrm{C_6H_4\cdot NH_2}\\ \mathrm{C_6H_5\cdot NH_2}\\ \mathrm{C_6H_5\cdot NH_2}\end{array} + 3\mathrm{O} = \mathrm{HO{-}C}\begin{array}{l}\mathrm{C_6H_4NH_2}\\ \mathrm{C_6H_4NH_2}\\ \mathrm{C_6H_4NH_2}\end{array} + 2\mathrm{H_2O}.$$

This colour-base yields a red dye with acids, from which it can be precipitated by alkalis. It is converted by reduction with zinc-dust and hydrochloric acid into *paraleucaniline*, $HC(C_6H_4NH_2)_3$, a colourless, crystalline substance which melts at 148° and is reconverted into the colour-base by oxidation. The constitution of paraleucaniline is shown by its yielding triphenylmethane when its amido-groups are removed by the diazo-reaction. On the other hand, paraleucaniline can be obtained by the nitration of triphenylmethane, and subsequent reduction of the trinitro-derivative thus formed. Paraleucaniline is converted by oxidation into triaminotriphenylcarbinol, which, like malachite-green, splits off water under the influence of acids, forming the dye:



$$\underset{\mathrm{OH}}{\mathrm{C}}\begin{array}{l}\mathrm{C_6H_4NH_2}\\ \mathrm{C_6H_4NH_2}\\ \mathrm{C_6H_4NH_2\cdot HCl}\end{array} - \mathrm{H_2O} = \mathrm{C}\begin{array}{l}\mathrm{C_6H_4NH_2}\\ \mathrm{C_6H_4NH_2}\\ \mathrm{C_6H_4\!:\!NH_2\cdot Cl}.\end{array}$$

Another important dye related to triphenylmethane is *rosaniline*. Its preparation is similarly effected by oxidizing a mixture of aniline, *o*-toluidine, and *p*-toluidine in equimolecular proportions with arsenic acid, mercuric nitrate, or nitrobenzene. In this reaction the methane carbon atom is obtained from *p*-toluidine as follows:



$$\underset{p\text{-Toluidine}}{\mathrm{NH_2\cdot C_6H_4\cdot CH_3}} + \underset{o\text{-Toluidine}}{\mathrm{C_6H_4(CH_3)NH_2}} + \mathrm{C_6H_5\cdot NH_2} + 3\mathrm{O} = \mathrm{HOC}\begin{array}{l}\mathrm{C_6H_3}<\begin{array}{l}\mathrm{CH_3}\\ \mathrm{NH_2}\end{array}\\ \mathrm{C_6H_4NH_2}\\ \mathrm{C_6H_4NH_2}\end{array} + 2\mathrm{H_2O}.$$

The hydrochloride of the rosaniline base containing one equivalent of hydrochloric acid is called *magenta*. This substance forms beautiful green crystals with a metallic lustre, which dissolve in water, yielding a solution of an intense deep-red colour.

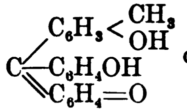
The colour of the magenta-solution is due to the monovalent cation, $(C_{19}H_{18}N_3)^{\cdot}$, because such solutions are almost completely ionized, as is shown by the slight increase of their molecular conductivity on further dilution. Moreover, the solutions of all the magenta salts—chloride, bromide, sulphate, etc.—exhibit the same absorption-spectrum for solutions of equimolecular concentration, which is an indication of the presence of a constituent common to all of them (the cation).

The salts containing three equivalents of acid are yellow, the red, monovalent cation having been converted into the yellow, trivalent one; as a result of this, magenta dissolved in excess of hydrochloric acid, yields a nearly colourless solution. These salts are, however, very readily hydrolyzed, as shown by the reappearance of the red colour when this solution in hydrochloric acid is poured into water.

Many derivatives of pararosaniline and rosaniline are known, in which the hydrogen atoms of the amido-groups have been replaced by alkyl-radicles. They are all dyes. The violet colour becomes deeper as the number of methyl-groups present increases (**323**). Pentamethylpararosaniline is sold under the name "methyl-violet." When one hydrogen atom in each of the amido-groups of rosaniline is replaced by phenyl, a blue dye is formed, called "aniline-blue."

The alkyl-groups were formerly introduced into pararosaniline in the ordinary way, by means of an alkyl chloride or even iodide These methods have long since given place to others, better suited to the preparation of the alkyl-derivatives. For example, methyl-violet is obtained by the oxidation of dimethylaniline with potassium chlorate and cupric chloride; the methane carbon atom is in this case obtained from one of the methyl-groups.

Aniline-blue, or triphenylrosaniline hydrochloride, is obtained by heating rosaniline with analine and a weak acid, such as benzoic acid, where by the amido-groups in the rosaniline are replaced by anilido-groups, the ammonia set free entering into combination with the acid. This process is exactly analogous to the formation of diphenylamine from aniline hydrochloride and aniline (**284**).

367. Dyes formed from hydroxyl-derivatives of triphenylmethane are also known, but are much less valuable than those just described, on account of their being difficult to fix. *Rosolic* *acid,* 

$$C\begin{cases}C_6H_3<^{CH_3}_{OH}\\ C_6H_4OH\\ C_6H_4=O\end{cases}$$

obtained from rosaniline by means of the diazo-reaction, is an example of such dyes.

Malachite-green and the pararosaniline and rosaniline dyes colour wool and silk directly, and calico after it has been mordanted.

It was stated in **321** that the fixing of dyes upon vegetable or animal fibres must be looked upon as a chemical combination of the compounds contained in the fibre with the dye, analogous to the formation of salts. The following is a proof of this. The colour-base of rosaniline is colourless; when, however, wool or silk is immersed in its colourless solution, it becomes gradually coloured, as though an acid had been added. This can only be explained by supposing that a compound in the fibre unites with the colourless base, forming with it a salt of the same colour as a solution of the dye in water.

The phthaleins, dyes related to triphenylmethane, have been mentioned already (**327**).

Gomberg has shown that zinc reacts with *triphenylchloromethane*, yielding a compound with the formula $(C_6H_5)_3C$. This he proved by analysis, and by the cryoscopic determination of its molecular weight. This compound can be precipitated in crystalline form from a benzene-solution by the addition of acetone or ethyl formate.

This substance, *triphenylmethyl*, is very remarkable, for it is the first known instance of a compound containing a trivalent carbon atom. It possesses notable additive-power; thus, it combines at once with the oxygen of the air, with formation of a peroxide, $(C_6H_5)_3C\cdot O—O\cdot C(C_6H_5)_3$; it instantly decolourizes iodine solution, yielding *triphenylmethyl iodide*. With ether it yields a crystalline substance of the composition $2(C_6H_5)_3C+(C_2H_5)_2O$.

Dibenzyl and its Derivatives.

368. *Dibenzyl,* $C_6H_5\cdot CH_2\cdot CH_2\cdot C_6H_5$, can be obtained by the action of sodium upon benzyl chloride:

$$C_6H_5\cdot CH_2|\underline{Cl+Na_2+Cl}|CH_2\cdot C_6H_5=C_6H_5\cdot CH_2\cdot CH_2\cdot C_6H_5+2NaCl.$$

This method of formation shows it to be *symmetrical diphenylethane.* It melts at 52°.

omit

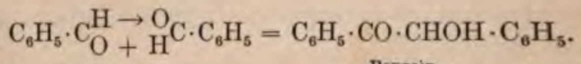
Symmetrical diphenylethylene, $C_6H_5\cdot CH:CH\cdot C_6H_5$, M.P. 125°, is usually called *stilbene*. It can be obtained in various ways, a typical method being the distillation of the phenyl ester of fumaric acid, which eliminates two molecules of CO_2:

$$C_6H_5|\overline{O_2C}|\cdot CH:CH\cdot|\overline{CO_2}|C_6H_5 = 2CO_2 + C_6H_5\cdot CH:CH\cdot C_6H_5.$$

Stilbene forms an addition-product with bromine, from which *tolan*, $C_6H_5\cdot C\equiv C\cdot C_6H_5$, is obtained by splitting off 2HBr. Tolan can be reconverted into stilbene by careful reduction.

p-*Diaminostilbene*, $NH_2\cdot C_6H_4\cdot CH:CH\cdot C_6H_4\cdot NH_2$, can be obtained by treatment of *p*-nitrobenzyl chloride, $ClH_2C\cdot C_6H_4\cdot NO_2$, with alcoholic potash, and subsequent reduction of the p-*dinitrostilbene* thus formed. It is used as a basis for the preparation of certain dyes.

Derivatives of dibenzyl are obtained by the condensation of benzaldehyde in presence of potassium cyanide; for example, *benzoïn* is thus formed:



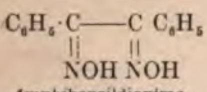
$$C_6H_5\cdot C\genfrac{}{}{0pt}{}{H\rightarrow O}{O+H}C\cdot C_6H_5 = C_6H_5\cdot CO\cdot CHOH\cdot C_6H_5.$$

Benzoïn

It has the character of a ketone alcohol, since it takes up two hydrogen atoms, with formation of a dihydric alcohol, *hydrobenzoïn*, $C_6H_5\cdot CHOH\cdot CHOH\cdot C_6H_5$; on oxidation it yields a diketone, *benzil*, $C_6H_5\cdot CO\cdot CO\cdot C_6H_5$. Benzoïn contains the group —CHOH·CO—, which is present in the sugars (**206**). It also possesses properties characteristic of the sugars; thus, it reduces an alkaline copper solution, and yields an osazone.

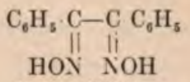
Benzil is a yellow, crystalline substance. As a diketone it unites with two molecules of hydroxylamine to form a dioxime.

369. *Benzildioxime* exists in three isomeric forms, the number theoretically possible from a consideration of the stereoisomerism of nitrogen derivatives (**301**):



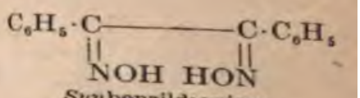
$$\begin{array}{cc} C_6H_5\cdot C & \!\!-\!\!-\; C\; C_6H_5 \\ \| & \| \\ NOH & NOH \end{array}$$

*Amphi*benzildioxime



$$\begin{array}{cc} C_6H_5\cdot C & \!\!-\; C\; C_6H_5 \\ \| & \| \\ HON & NOH \end{array}$$

*Anti*benzildioxime

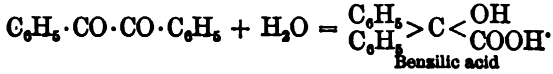


$$\begin{array}{cc} C_6H_5\cdot C & \!\!-\!\!-\!\!-\!\!-\; C\cdot C_6H_5 \\ \| & \| \\ NOH & HON \end{array}$$

*Syn*benzildioxime

One of these oximes very readily yields an anhydride, and is therefore assumed to have the two hydroxyl-groups in close proximity, the *syn*-formula. One of the other dioximes is the most stable of the three compounds, and can be obtained by various means; the third dioxime can be readily transformed into this stable modification. It is probable that the stable dioxime has the symmetrical or *anti*-formula, so that the *amphi*-formula must be that of the unstable modification.

When heated with alcoholic potash, benzil takes up one molecule of water, undergoing an intramolecular transformation, with production of *benzilic acid*, a reaction analogous to the formation of pinacolin from pinacone (**156**):



$$\mathrm{C_6H_5\cdot CO\cdot CO\cdot C_6H_5 + H_2O = \begin{matrix}C_6H_5\\ C_6H_5\end{matrix}\!>C<\!\begin{matrix}OH\\ COOH\end{matrix}.}$$

Benzilic acid

FINISH FOR
2nd Term Exam

CONDENSED BENZENE-RINGS.

370. Condensed-ring compounds contain two or more closed chains, with C-atoms common to both. Such compounds are present in the higher-boiling fractions of coal-tar (**267**). Next to the phenols, *naphthalene* is the principal constituent of the second fraction, carbolic oil, and of the third fraction, creosote oil. The anthracene oil contains *anthracene* and *phenanthrene,* in addition to other hydrocarbons. These three compounds and some of their derivatives will be described here.

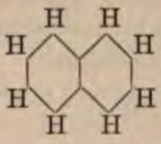
I. NAPHTHALENE, $C_{10}H_8$.

This hydrocarbon is present in considerable quantity in coal-tar, from which it is readily obtained pure. The crude crystals of naphthalene precipitate on cooling from the fraction passing over between 170° and 230°, and are separated from liquid impurities by pressure, which are further eliminated by conversion into non-volatile sulphonic acids on warming the crude product with small quantities of concentrated sulphuric acid, and distilling with steam or subliming, when pure naphthalene comes over.

It crystallizes in shining plates, melting at 80°, and boiling at 218°. It is insoluble in water, but readily soluble in hot alcohol and ether; it dissolves to a very small extent in cold alcohol. It has a characteristic odour, and is very volatile; it is always present in coal-gas, whose illuminating power is to a large extent due to its presence. It is extensively employed in the manufacture of dyes.

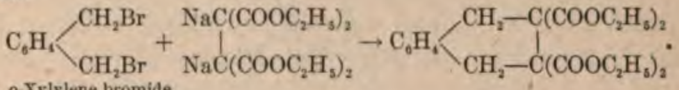
The formation of naphthalene on passing the vapours of many compounds through a red-hot tube, a process somewhat similar to that which takes place in the retorts of the gas-works (**267**), explains its occurrence in coal-tar.

The constitution of naphthalene was proved in **353** to be



This view is confirmed by the two following syntheses.

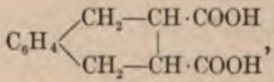
1. *o*-Xylylene bromide is converted by treatment with sodioethanetetracarboxylic ester into *hydronaphthalenetetracarboxylic ester:*



$$C_6H_4\left\langle\begin{array}{l}CH_2Br\\ CH_2Br\end{array}\right. + \begin{array}{l}NaC(COOC_2H_5)_2\\ \quad|\\ NaC(COOC_2H_5)_2\end{array} \rightarrow C_6H_4\left\langle\begin{array}{l}CH_2-C(COOC_2H_5)_2\\ \qquad\quad|\\ CH_2-C(COOC_2H_5)_2\end{array}\right..$$

o-Xylylene bromide

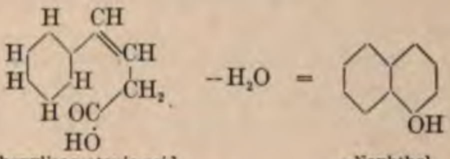
On saponification, this compound splits off two molecules of carbon dioxide, forming *hydronaphthalenedicarboxylic acid:*



$$C_6H_4\left\langle\begin{array}{l}CH_2-CH\cdot COOH\\ \qquad\quad|\\ CH_2-CH\cdot COOH\end{array}\right.,$$

whose silver salt readily loses two molecules of carbon dioxide and two atoms of hydrogen, yielding naphthalene.

2. On heating, phenylisocrotonic acid is converted into *α-naphthol,* a hydroxyl-derivative of naphthalene:



Phenylisocrotonic acid α-Naphthol

Naphthalene behaves in all respects as an aromatic hydrocarbon: with nitric acid it yields a nitro-derivative, with sulphuric acid a sulphonic acid; its hydroxyl-derivatives have the phenolic character; the amino-compounds undergo the diazo-reaction; etc. The great resemblance in properties between benzene and naphthalene indicates similarity of structure, and to the latter is assigned the formula

Partial hydration converts the centric bonds in naphthalene, like those in benzene, into double bonds, since *naphthalene dihydride*, $C_{10}H_{10}$, readily forms an addition-product with bromine, like other substances containing a double bond.

371. Naphthalene yields a much greater number of substitution-products than benzene, the number obtained corresponding to those theoretically possible for a compound with the above formula; this fact supports the constitution indicated.

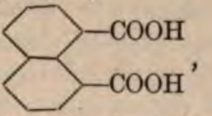
A compound of the formula

must yield *two* isomeric monosubstitution-products. Substitution can take place at a carbon atom directly linked to one of the two C-atoms common to both rings (1, 4, 5, or 8), or at one of the others (2, 3, 6, or 7), which are also similar to one another. Two series of monosubstitution-products are in fact known; those in which the hydrogen at 1, 4, 5, or 8 has been replaced are called α-derivatives; when hydrogen is substituted at 2, 3, 6, or 7, the products are termed β-derivatives.

A great number of disubstitution-products is possible; for two similar substituents it is 10, and for two dissimilar substituents 14: many of these have been obtained. The ten isomers are denoted by the numbers

1:2, 1:3, 1:4, 1:5, 1:6, 1:7, 1:8, 2:3, 2:6, 2:7.

In any other arrangement the grouping is identical with one of these; thus, 2:5 = 1:6, and 3:6 = 2:7, etc. For three similar substituents the number of possible isomers is much greater, and still greater for three dissimilar ones. The disubstitution-products with the substituents in the same ring are called *ortho*, *meta*, and *para;* when they are in different rings, the compounds are usually distinguished by numbers, or sometimes by letters: thus, a compound 4:5 is also indicated by αα′, and one 3:6 by ββ′. The positions 1:8 and 4:5 are also called the *peri*-positions; in certain respects these resemble the *ortho*-positions. For example, peri-*naphthalenedicarboxylic acid*,



resembles *o*-phthalic acid in being able to form an anhydride.

372. On account of the great number of isomers, the orientation of naphthalene derivatives is sometimes very difficult, and the positions occupied by the substituents in many of those which are known are still uncertain. The same method of orientation is employed as for the benzene derivatives, the conversion of compounds whose side-chains occupy unknown positions into others with substituents whose positions have been determined.

Oxidation is another important aid in their orientation, and is employed to determine whether the substituents are attached to the same or to different rings, as well as their position relative to one another. Thus, suppose the position of the nitro-groups in a dinitronaphthalene has to be determined. If it yields phthalic acid on oxidation, the two nitro-groups must be in union with the same ring, that one which has been removed by oxidation. If a dinitrophthalic acid is formed, this also proves that the two nitro-groups are linked to the same ring, and the orientation of these groups in this acid should indicate their relative position in the naphthalene derivative. Lastly, if oxidation yields a mononitrophthalic acid, one nitro-group is attached to each ring, and orientation of the mononitrophthalic acid obtained will determine the position of one of the nitro-groups.

Substitution-products.

373. The homologues of naphthalene—methyl-derivatives, ethyl-derivatives, etc.—are unimportant; they can be prepared by FITTIG's method, or that of FRIEDEL and CRAFTS (**268**, 1 and 2).

α-Methylnaphthalene is a liquid, and boils at 240°-242°; *β*-methylnaphthalene is a solid, and melts at 32°; both are present in coal-tar. On oxidation, they yield *α-naphthoïc* and *β-naphthoïc acid* respectively, which resemble benzoïc acid in their properties, and are converted into naphthalene by distillation with lime.

α-Chloronaphthalene and *α-bromonaphthalene* are respectively formed by the action of chlorine and bromine upon boiling naphthalene. Although their halogen atom is not so firmly linked as that in monochlorobenzene or monobromobenzene (**265**), they are not decomposed on boiling with alkalis. This also holds good for the corresponding β-compounds, which are not obtained by the direct action of halogens upon naphthalene, but can be prepared from other β-compounds, such as amino-derivatives, sulpho-derivatives, etc., by the methods described under benzene (**303**, 4).

374. The product obtained by the action of concentrated nitric acid upon naphthalene is very important for the orientation of the naphthalene derivatives: it is *α-nitronaphthalene*, M.P. 61°, which is proved to belong to the α-series by its conversion into the same naphthol as is obtained from phenylisocrotonic acid (**370**).

The position of the substituents in a great number of monosubstitution-products can be determined from a knowledge of that of the nitro-group in this nitronaphthalene, for the nitro-group can be reduced to an amido-group, which is replaceable by numerous atoms or groups by means of the diazo-reaction. If a monosubstituted naphthalene is known to be an α-compound, its isomer must belong to the β-series.

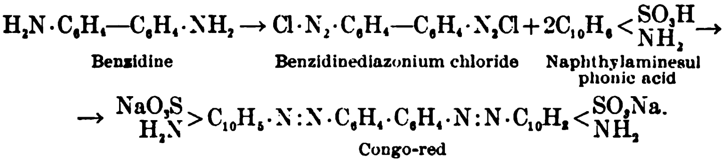
375. On heating naphthalene with concentrated sulphuric acid at a temperature not exceeding 80°, the two isomeric *naphthalenemonosulphonic acids* are formed; at 160° only the β-acid is obtained, owing to the conversion of the α-compound into its β-isomer. Both are crystalline, and very hygroscopic.

On fusion with caustic potash, the naphthalenesulphonic acids are converted into *naphthols*, $C_{10}H_7 \cdot OH$, with properties very similar to those of phenol. They are present in coal-tar. *α-Naphthol* melts at 95°, and boils at 282°; *β-naphthol* melts at 122°, and boils at 288°. The hydroxyl-group in these compounds can be replaced much more readily than that in phenol. They dissolve in alkalis. With ferric chloride α-naphthol yields a flocculent, violet precipitate; β-naphthol gives a green colouration, and a precipitate of *β-dinaphthol*, $HO \cdot C_{10}H_6 \cdot C_{10}H_6 \cdot OH$. The violet precipitate obtained with α-naphthol is possibly an iron derivative of *α-dinaphthol*.

376. *α-Naphthylamine*, and *β-naphthylamine*, $C_{10}H_7 \cdot NH_2$, can be obtained by the reduction of the corresponding nitro-derivatives, but are usually prepared by heating α-naphthol and β-naphthol respectively with the ammonia compound of zinc chloride or of calcium chloride. α-Naphthylamine is a solid, melting at 50°, and has a fæcal odour; β-naphthylamine melts at 112°, and is nearly odourless. A mode of distinguishing between the isomers is afforded by the fact that the salts of the α-compound give a blue precipitate with ferric chloride and other oxidizing-agents, while those of the β-isomer do not.

These bases are of technical importance, since the dyes of the *congo-group* and the *benzopurpurins* are derived from them, and possess the important property of dyeing unmordanted cotton.

Congo-red is formed by diazotizing benzidine, and treating the product with a sulphonic acid of naphthylamine; the dye is the sodium salt of the acid thus formed:



$$\underset{\text{Benzidine}}{H_2N\cdot C_6H_4—C_6H_4\cdot NH_2} \rightarrow \underset{\text{Benzidinediazonium chloride}}{Cl\cdot N_2\cdot C_6H_4—C_6H_4\cdot N_2Cl} + \underset{\text{Naphthylaminesulphonic acid}}{2C_{10}H_6{<}\begin{matrix}SO_3H\\NH_2\end{matrix}} \rightarrow$$

$$\rightarrow \underset{\text{Congo-red}}{\begin{matrix}NaO_3S\\H_2N\end{matrix}{>}C_{10}H_5\cdot N:N\cdot C_6H_4\cdot C_6H_4\cdot N:N\cdot C_{10}H_5{<}\begin{matrix}SO_3Na.\\NH_2\end{matrix}}$$

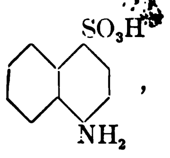
The acid itself is blue.

The benzopurpurins differ from congo-red only in having a methyl-group attached to each benzene-nucleus of the benzidine-group.

377. Some polysubstituted naphthalene derivatives may be mentioned.

Dinitro-α-naphthol is obtained by the action of nitric acid upon the monosulphonic or disulphonic acid of α-naphthol. Its sodium salt is *Martius' yellow;* it dyes wool and silk directly a golden-yellow. Nitration of α-naphtholtrisulphonic acid yields dinitronaphtholsulphonic acid, whose potassium salt is *naphthol-yellow;* it resists the action of light better than Martius' yellow.

Naphthionic acid is one of the longest known naphthalene derivatives: it is 1:4-*naphthylaminesulphonic acid,*



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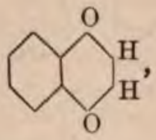
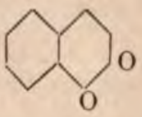
and results from the interaction of α-naphthylamine and sulphuric acid. It is crystalline, and only slightly soluble in water; it is manufactured for the preparation of congo-red and other dyes. Solutions of its salts display an intense reddish-blue fluorescence.

α-Naphthaquinone, $C_{10}H_6O_2$, is formed by the oxidation of many α-derivatives, and of some diderivatives, of naphthalene. It is usually prepared from naphthalene itself by oxidation with a boiling solution of chromic acid in glacial acetic acid, a method of formation which has no parallel among those for the preparation of the corresponding benzene derivatives. It crystallizes from alcohol in deep-yellow needles, melting at 125°. It resembles benzoquinone not only in colour but in its other properties; thus, it has a characteristic, pungent odour, and is very volatile, subliming readily at 100°; it is easily reduced to a dihydroxynaphthalene by sulphurous acid. For these reasons the structural formula



is assigned to it, analogous to that of benzoquinone. In support of this view is the fact that on oxidation it yields phthalic acid, proving both oxygen atoms to be attached to the same ring; moreover, hydroxylamine converts it into an oxime. Knowing the constitution of α-naphthaquinone to be 1:4, it is possible to determine that of other diderivatives. If, on oxidation, they yield this quinone by elimination of the substituents, the latter must occupy the *para*-position.

β-Naphthaquinone, $C_{10}H_6O_2$, is formed by the oxidation of aminonaphthol (1:2) which proves its structure to be

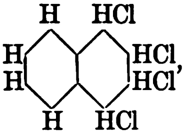


Its properties are very different from those of the α-quinone. It crystallizes in red needles, and decomposes without melting at 115°, being therefore non-volatile; it is also odourless. Sulphurous acid reduces it to 1:2-dihydroxynaphthalene.

Addition-products.

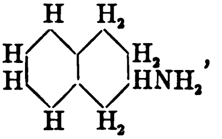
378. Naphthalene and its derivatives yield addition-products somewhat more readily than the benzene derivatives. The best known are those formed by the addition of four monovalent atoms, such as hydrogen or chlorine. It has been proved by the oxidation-method, and in other ways, that the four atoms are always added to the same ring.

On passing chlorine over naphthalene at ordinary temperatures, there results *naphthalenetetrachloride*,

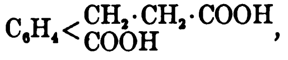


a well-crystallized, colourless substance, melting at 182°. On oxidation it yields phthalic acid, and is converted by alcoholic potash into *dichloronaphthalene*, $C_{10}H_6Cl_2$.

On reduction with sodium and boiling amyl alcohol, β-naphthylamine yields a *tetrahydro-derivative*, $C_{10}H_{11}NH_2$, a compound with most of the properties characteristic of the aliphatic amines: it is strongly alkaline, absorbs carbon dioxide from the air, has an ammoniacal odour, and cannot be diazotized. All four hydrogen atoms are in union with the same ring as the amido-group,



since, on oxidation with potassium permanganate, this substance is converted into *o*-hydrocinnamiccarboxylic acid,

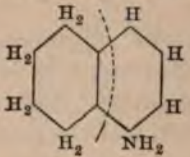


$$C_6H_4<\begin{matrix}CH_2\cdot CH_2\cdot COOH\\COOH\end{matrix},$$

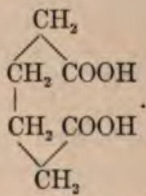
which must evidently result from a tetrahydro-derivative with the above structure if the oxidation takes place at the C-atom linked to the NH_2-group. Moreover, the hydrogen addition-product does not take up bromine, another proof that the four H-atoms are attached to the same benzene-nucleus. The entrance of two hydrogen atoms into each ring must produce a compound with double bonds, which would yield an addition-product with bromine.

The complete resemblance between β-tetrahydronaphthylamine and the aliphatic amines is another confirmation of the view that the ring-structure does not in itself occasion any marked peculiarity in the chemical properties of a compound (**262**). This compound may be looked upon as benzene with a saturated side-chain, $—CH_2 \cdot CH_2 \cdot CH(NH_2) \cdot CH_2—$, linked to two *ortho*-C-atoms.

α-Naphthylamine can also be reduced by amyl alcohol and sodium, but the tetrahydro-derivative formed is quite different from that obtained from β-naphthylamine, for it possesses all the properties characteristic of the aromatic amines: it can be diazotized, and has not an ammoniacal odour. Since it, too, does not form an addition-product with bromine, its constitution is



This proves that the four hydrogen atoms in it also are in union with the same nucleus, but *not* the one linked to the amido-group. In support of this are its completely aromatic character, and the fact that, on oxidation with potassium permanganate, the ring containing the amido-group is removed, with formation of adipic acid (**164**),



Tetrahydro-α-naphthylamine must, therefore, be looked upon as aniline containing a saturated side-chain, $—CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2—$, linked to two *ortho*-C-atoms.

II. ANTHRACENE, $C_{14}H_{10}$.

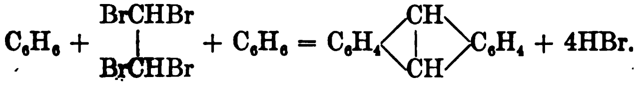
379. *Anthracene* is present only in small proportions in coal-tar, the percentage varying between 0·25 and 0·45 per cent.;

notwithstanding this, it is the basis of the manufacture of an important dye, alizarin (**382** and **383**).

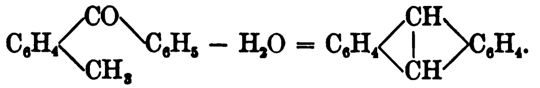
By fractionation of anthracene oil (**267**), the so-called "50 per cent. anthracene" is obtained; this is mixed with one-third of its weight of potassium carbonate, and distilled from an iron retort. This removes certain impurities, among them *carbazole*, $\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!>\!NH$, which is present in considerable proportion in the crude anthracene, and is thus converted into a non-volatile potassium derivative, $(C_6H_4)_2N \cdot K$. The distillate consists almost wholly of anthracene and phenanthrene, which are separated by means of carbon disulphide, in which only phenanthrene is soluble. On crystallization from benzene, the anthracene is obtained pure.

It crystallizes in colourless, glistening leaflets, with a fine blue fluorescence; it melts at 213°, and boils at 351°; it dissolves readily in boiling benzene, but with difficulty in alcohol and ether. With picric acid it yields a compound $C_{14}H_{10} \cdot C_6H_2(NO_2)_3OH$, which melts at 138°.

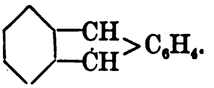
Various modes of preparing anthracene are known which give an insight into its constitution. One of these is its synthesis by ANSCHÜTZ's method from benzene, aluminium chloride, and tetrabromoethane:



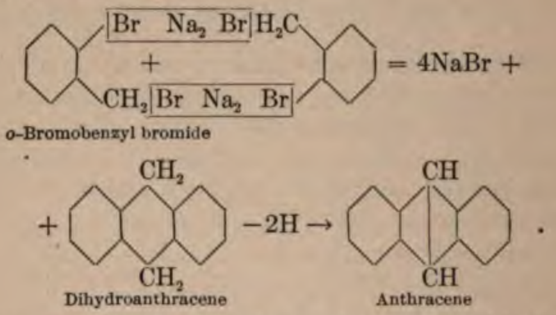
This proves that anthracene contains two benzene-nuclei united by the group C_2H_2, a view further supported by its formation on heating *o*-tolylphenylketone with zinc-dust:



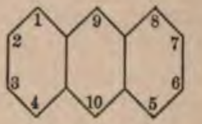
From this it follows that the C_2H_2-group is linked to *ortho*-C-atoms in at least one benzene-nucleus; the formula of anthracene may, therefore, be written



The central group C_2H_2 is also linked to *ortho*-C-atoms in the second benzene-nucleus. This is proved, for example, by the synthesis of anthracene from *o*-bromobenzyl bromide and sodium, in which a dihydro-derivative is first formed, and is readily converted into anthracene by oxidation:



This constitution indicates that anthracene should yield a very large number of isomeric substitution-products, that of the mono-substitution-products being three. Numbering the carbon atoms thus,



,

then 1 = 4 = 5 = 8, 2 = 3 = 6 = 7, and 9 = 10. Fifteen disubstitution-products with similar groups are possible. A very considerable number of anthracene derivatives is known, although it is small in comparison with the enormous number theoretically possible.

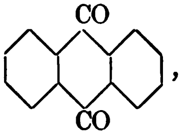
The orientation of the anthracene derivatives is effected similarly to those of naphthalene (**372**), oxidation and a study of the resulting products being an important aid.

FINIS

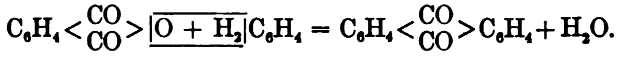
Substitution-products.

380. *Anthraquinone*, $C_{14}H_8O_2$, is one of the most important derivatives of anthracene, from which it is obtained by oxidation with such agents as nitric and chromic acids. Anthracene is so readily converted into anthraquinone by nitric acid that it is not possible to nitrate it.

Anthraquinone is proved to have the structure



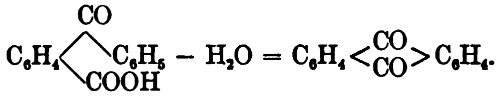
since it is formed by the interaction of phthalic anhydride and benzene in presence of a dehydrating-agent such as aluminium chloride:



$$C_6H_4<\substack{CO\\CO}>\boxed{O + H_2}C_6H_4 = C_6H_4<\substack{CO\\CO}>C_6H_4 + H_2O.$$

Phthalic anhydride

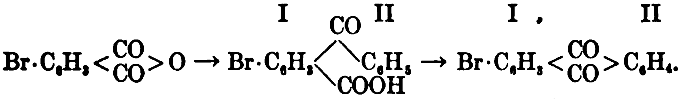
This reaction takes place in two stages: *o*-benzoylbenzoïc acid, $C_6H_4<\substack{CO\cdot C_6H_5\\COOH}$, is first formed, and loses one molecule of water, forming anthraquinone:



$$C_6H_4\underset{COOH}{\overset{CO}{\diagup\diagdown}}C_6H_5 - H_2O = C_6H_4<\substack{CO\\CO}>C_6H_4.$$

381. The central group in anthraquinone can be proved to be in union with two *o*-C-atoms in each benzene-nucleus—another proof that the same is true of anthracene. The same method is employed as in the proof of the constitution of naphthalene (**353**): one of the benzene-nuclei is distinguished by the introduction of a substituent, so as to identify the one broken by the oxidation.

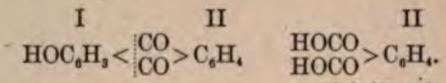
On treatment with benzene and aluminium chloride, bromophthalic anhydride reacts like phthalic anhydride, yielding *bromoanthraquinone* by elimination of water:



$$Br\cdot C_6H_3<\substack{CO\\CO}>O \rightarrow Br\cdot \overset{\text{I}}{C_6H_3}\underset{COOH}{\overset{CO}{\diagup\diagdown}}\overset{\text{II}}{C_6H_5} \rightarrow Br\cdot \overset{\text{I}}{C_6H_3}<\substack{CO\\CO}>\overset{\text{II}}{C_6H_4}.$$

Bromoanthraquinone

Since this compound is derived from phthalic acid, the two CO-groups must be substituted in the *ortho*-position in nucleus I. Its Br-atom can be replaced by a hydroxyl-group, by heating with potassium carbonate at 160°, and the *hydroxyanthraquinone* thus formed oxidized by nitric acid to phthalic acid, the formation of which proves nucleus II to have been unacted upon, and to be also substituted in the *ortho*-position:



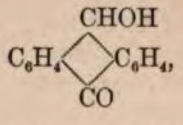
$$\overset{\text{I}}{HOC_6H_3}<\begin{matrix}CO\\CO\end{matrix}>\overset{\text{II}}{C_6H_4} \qquad \begin{matrix}HOCO\\HOCO\end{matrix}>\overset{\text{II}}{C_6H_4}.$$

Phthalic acid

The constitutional formula of anthraquinone indicates that only two isomeric monosubstitution-products are possible. This has been verified by experiment—a further proof that the formula is correct.

382. Anthraquinone crystallizes from glacial acetic acid in light-yellow needles, melting at 277°. At higher temperatures it sublimes very readily, forming long, sulphur-yellow prisms. It is very stable, and is not easily attacked by oxidizing-agents, or by concentrated nitric or sulphuric acid.

The name anthra*quinone* is in some measure incorrect, for this substance lacks some of the properties characteristic of quinones, such as ready reduction, great volatility, pungent odour, etc., and has much more the character of a diketone. With fused caustic potash it yields benzoïc acid, and with hydroxylamine an oxime. On warming with zinc-dust and caustic-soda solution, it forms *oxanthranol*,



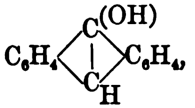
$$C_6H_4\overset{CHOH}{\underset{CO}{\diamond}}C_6H_4,$$

which in alkaline solution is converted into anthraquinone by atmospheric oxidation. Oxanthranol dissolves in alkalis, the solution having a deep blood-red colour.

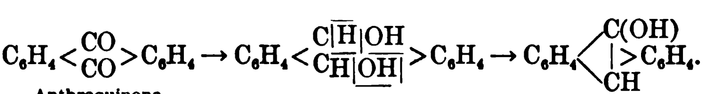
This property of oxanthranol makes its formation a delicate test for anthraquinone. It is carried out by warming the substance to be tested with zinc-dust and caustic-soda solution; if anthraquinone is present, a blood-red colouration is developed, and is destroyed by shaking up the mixture with air.

Oxygen is rendered "active" (**299**) in the oxidation of oxanthranol, hydrogen peroxide being formed in addition to anthraquinone. As in other instances of oxygen being rendered active, for every atom of oxygen employed for oxidation, one atom is used up in the formation of hydrogen peroxide.

On reduction with tin and hydrochloric acid, anthraquinone is converted into *anthranol,*



a substance of weak phenolic character, which is slightly soluble in cold. and readily in boiling, alkalis. Its formation is to be looked upon as resulting from the splitting-off of water from an intermediate product, a dihydric alcohol:

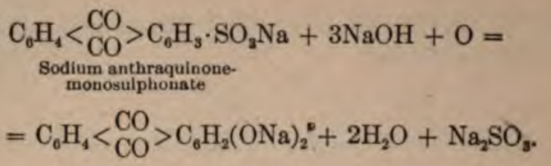


Anthraquinone Anthranol

When anthraquinone is more strongly reduced, by heating with zinc-dust, it yields anthracene.

Alizarin, or dihydroxyanthraquinone, is the most important derivative of anthraquinone, and is a dye of a splendid red colour. It was formerly manufactured from madder-root, which contains a glucoside, *ruberythric acid,* $C_{26}H_{28}O_{14}$, yielding glucose and alizarin on boiling with dilute sulphuric or hydrochloric acid; but it is now prepared almost wholly by a synthetical method. It is one of the organic dyes known to the ancients.

In preparing alizarin, the anthracene is first oxidized to anthraquinone with sodium dichromate and sulphuric acid. Heating with concentrated sulphuric acid at 100° converts various impurities into sulphonic acids, the anthraquinone remaining unchanged; on dilution, these sulphonic acids dissolve, so that pure anthraquinone is left after filtering. This is then heated to 160° with fuming sulphuric acid containing 50 per cent. of sulphur trioxide, the main product being the monosulphonic acid. Its sodium salt is only slightly soluble in water, and separates out when the acid is neutralized with sodium carbonate. On fusing with sodium hydroxide, the sulpho-group is replaced by hydroxyl. A second hydroxyl-group is simultaneously formed, its production being considerably facilitated by the addition to the reaction-mixture of potassium chlorate as an oxidizing-agent:



$$C_6H_4{<}\substack{CO\\CO}{>}C_6H_3\cdot SO_3Na + 3NaOH + O =$$

Sodium anthraquinone-monosulphonate

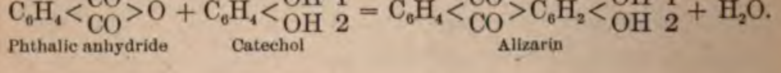
$$= C_6H_4{<}\substack{CO\\CO}{>}C_6H_2(ONa)_2 + 2H_2O + Na_2SO_3.$$

The dye is set free from the sodium salt by addition of an acid.

Alizarin crystallizes in red prisms, and sublimes in orange needles, melting at 289°–290°; it is nearly insoluble in water, and slightly soluble in alcohol. On account of its phenolic character, it dissolves in alkalis. It yields a diacetate. On distillation with zinc-dust, it is converted into anthracene, a reaction which gave the first insight into the constitution of alizarin.

The value of alizarin as a dye depends upon its power of forming fine-coloured, insoluble compounds, called *lakes*, with metallic oxides. When a fabric is mordanted with one of these oxides, it can be dyed with alizarin, the colour depending on the oxide used. The ferric oxide compound of alizarin is violet-black, the chromium oxide compound claret-colour, the calcium oxide compound blue, the aluminium and tin compounds various shades of red (Turkey-red), etc.

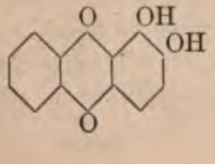
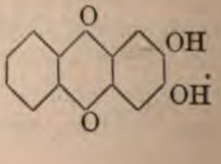
383. The method by which alizarin is prepared proves it to be a derivative of anthraquinone, but it has now to be determined what positions the hydroxyl-groups occupy. The formation of alizarin when phthalic anhydride is heated at 150° with catechol and sulphuric acid proves them to be in the same benzene-nucleus; and, since the hydroxyl-groups in catechol occupy the *o*-position, the same must be true of alizarin:



$$C_6H_4{<}\substack{CO\\CO}{>}O + C_6H_4{<}\substack{OH\ 1\\OH\ 2} = C_6H_4{<}\substack{CO\\CO}{>}C_6H_2{<}\substack{OH\ 1\\OH\ 2} + H_2O.$$

Phthalic anhydride Catechol Alizarin

It follows that the choice lies between the two structural formulæ

I.  and II. 

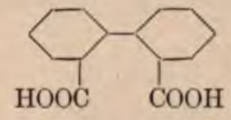
The result of nitration proves that formula I is correct. Two isomeric mononitro-derivatives are obtained, with the nitro-group in the same nucleus as the hydroxyl-groups, since both can be oxidized to phthalic acid. Formula I alone admits of the formation of two such mononitro-derivatives, and must therefore be correct.

> Other hydroxyl-derivatives of anthraquinone are also dyes. This is so only when two hydroxyl-groups are in the *o*-position to one another. In addition to these, derivatives of anthraquinone containing hydroxyl-groups and amido-groups, or only amido-groups, are also valuable dyes.

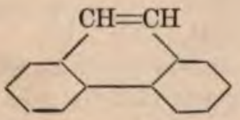
III. PHENANTHRENE, $C_{14}H_{10}$.

384. *Phenanthrene* is isomeric with anthracene, and is present with it in "anthracene oil," they are separated by the method already described (**379**). It crystallizes in colourless, lustrous plates, which dissolve in alcohol more readily than anthracene, the solution having a blue fluorescence. It melts at 96°, and boils at 340°.

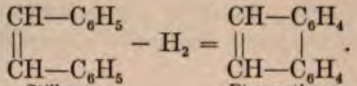
On oxidation with chromic acid, it yields first *phenanthraquinone* (p. 486), and then diphenic acid (**365**),



This proves that phenanthrene possesses two benzene-nuclei directly linked to one another, and is therefore a diphenyl derivative, and also a di-*ortho*-compound. Diphenyl with two hydrogen atoms substituted, $—C_6H_4\cdot C_6H_4—$, or $—C_{12}H_8—$, differs from phenanthrene by C_2H_2. This must link together two *o*-positions, so that phenanthrene has the constitution



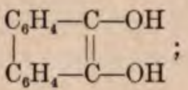
This structure finds support in the conversion of stilbene into phenanthrene, on passing its vapour through a red-hot tube, a method of formation analogous to that of diphenyl from benzene (**364**):



$$\begin{array}{l}CH{-}C_6H_5\\ \|\\ CH{-}C_6H_5\end{array} - H_2 = \begin{array}{l}CH{-}C_6H_4\\ \|\qquad |\\ CH{-}C_6H_4\end{array}.$$

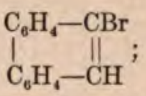
Stilbene Phenanthrene

It is seen from the above constitutional formula that the group CH:CH, which is united with four C-atoms of diphenyl, thus yields a fresh ring of six C-atoms. The question arises whether this is a true benzene-ring; if it is not, the link C_2H_2 must be assumed to contain a double bond. This question is difficult to answer. On the one hand, phenanthrene displays aromatic properties; for example, its yielding phenanthraquinone, which resembles other quinones in being reduced by sulphurous acid to dihydroxyphenanthrene,



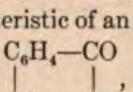
$$\begin{array}{l}C_6H_4{-}C{-}OH\\ |\qquad\ \|\\ C_6H_4{-}C{-}OH\end{array};$$

the existence of a bromophenanthrene, in which the bromine atom is very firmly linked, and is not attacked by alcoholic potash at 170°, and whose structure is proved by its oxidation to phenanthraquinone to be



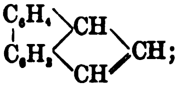
$$\begin{array}{l}C_6H_4{-}CBr\\ |\qquad\ \|\\ C_6H_4{-}CH\end{array};$$

and the fact that phenanthrene is not acted upon by BAEYER's reagent for double bonds (**123**): all point to the aromatic character of this ring. On the other hand, however, the group C_2H_2 adds on bromine very readily, and is attacked when phenanthrene is oxidized—reactions characteristic of an ordinary unsaturated group.

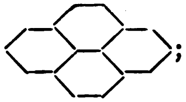
Phenanthraquinone,  $\begin{array}{l}C_6H_4{-}CO\\ |\qquad\ |\\ C_6H_4{-}CO\end{array}$, is a yellow, crystalline substance melting at 200°, and boiling without decomposition above 360°. Its diketonic character follows from its yielding diderivatives with sodium hydrogen sulphite, and with hydroxylamine. It is odourless, and non-volatile with steam.

IV. FLUORANTHENE, PYRENE, AND CHRYSENE

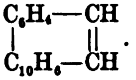
385. Other hydrocarbons possessing condensed rings and a greater number of carbon atoms are also known. Among these are *fluoranthene*, $C_{15}H_{10}$, with the formula



pyrene, $C_{16}H_{10}$, with the probable formula



and *chrysene*, C_{18}, H_{12}, with the formula



$$\begin{array}{l} C_6H_4\text{—}CH \\ \;| \qquad\;\; \| \\ C_{10}H_6\text{—}CH \end{array}.$$

These compounds are present in the coal-tar fractions coming over above 360°, and also in a peculiar substance called "stubb-fat," obtained in the distillation of mercury ores from Idria.

HETEROCYCLIC COMPOUNDS.

386 The compounds hitherto considered all contain a ring of carbon atoms only, and can be classed together under the name *homocyclic* compounds. It was mentioned in **259** that ring-systems are also known possessing not only carbon atoms but also those of other elements. Substances containing rings of this kind are classed together as *heterocyclic* compounds. A few of these and their derivatives will be considered.

I. PYRIDINE, C_5H_5N.

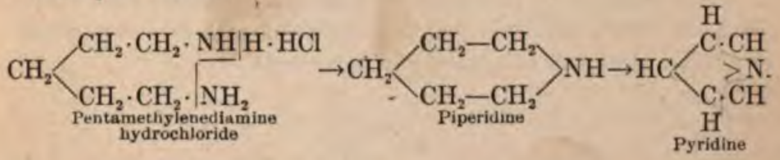
Pyridine and some of its homologues are constituents of coal-tar. On mixing the "light oil" (**267**) with sulphuric acid, they are absorbed by the latter, and separate on addition of sodium carbonate in the form of a dark-brown, basic oil, from which pyridine and its homologues are obtained by fractional distillation. Prepared by this method, pyridine is never quite pure, always containing small proportions of its homologues.

Another source of pyridine is "Dippel's oil," a liquid of extremely disagreeable odour, obtained by the dry distillation of bones which have not been deprived of their fat. It is a very complicated substance, containing, in addition to the pyridine bases and quinoline, many other substances, such as nitriles, amines, and hydrocarbons.

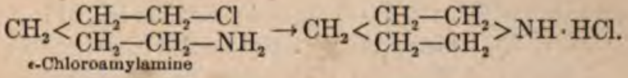
Pyridine is a colourless liquid boiling at 115°, and with a specific gravity of 1·0033 at 0°; it is miscible with water in all proportions, has a strongly alkaline reaction, and a very characteristic odour reminiscent of tobacco-smoke. It is very stable, being unattacked by boiling nitric or chromic acid. It reacts with sulphuric acid only at high temperatures, yielding a sulphonic acid. The halogens have very slight action on it. On very energetic reduction with hydriodic acid at 300°, it yields normal pentane and ammonia.

Being a base, it yields salts with acids, mostly readily soluble in water. The ferrocyanide dissolves with difficulty, and is employed in its purification. With platinum chloride, the hydrochloride yields a double salt, $(C_5H_5N)_2H_2PtCl_6$, freely soluble in water. On boiling this solution, two molecules of hydrochloric acid are eliminated, with production of a yellow compound, $(C_5H_5N)_2PtCl_4$, which is only slightly soluble in water; this reaction affords a delicate test for pyridine. The following test is also very delicate. On warming the base with methyl iodide, an energetic reaction takes place, with formation of an addition-product, $C_5H_5N \cdot CH_3I$. When this is warmed with solid potash, it gives off a very pungent and disagreeable odour.

387. Many methods for the synthesis of pyridine and its homologues are known, although but few of these afford insight into its constitution. Among them is the formation of pyridine from quinoline and pentamethylenediamine (**162**). When the hydrochloride of the latter is submitted to dry distillation, *piperidine*, or hexahydropyridine, is produced, and can be oxidized to pyridine by heating with sulphuric acid:



Another method of preparing pyridine, which is carried out at low temperatures and, therefore, affords even more trustworthy evidence of its constitution, is from ε-chloroamylamine; when an aqueous solution of this substance is heated on a water-bath for some time, it is transformed into the hydrochloride of piperidine:



$$CH_2<\begin{matrix}CH_2-CH_2-Cl\\CH_2-CH_2-NH_2\end{matrix} \rightarrow CH_2<\begin{matrix}CH_2-CH_2\\CH_2-CH_2\end{matrix}>NH \cdot HCl.$$

ε-Chloroamylamine

ε-Chloroamylamine was thus obtained by GABRIEL. γ-Chloropropylphenyl ether, obtained from chlorotrimethylene bromide and sodium phenoxide, reacts thus with sodiomalonic ester:

$$C_6H_5O \cdot CH_2 \cdot CH_2 \cdot CH_2Cl + NaCH(COOC_2H_5)_2 =$$
$$= C_6H_5O \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH(COOC_2H_5)_2.$$

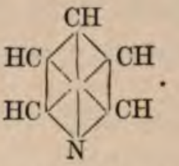
On saponification of this ester, and subsequent heating of the acid obtained, one molecule of carbon dioxide is split off, with formation of δ-phenoxyvaleric acid, $C_6H_5O \cdot (CH_2)_4 \cdot COOH$. When this acid is heated with lead thiocyanate, it is converted into the corresponding nitrile, $C_6H\ O\cdot(CH_2)_4\cdot CN$, which is reduced by sodium and alcohol to ϵ-phenoxyamylamine, $C_6H_5O\cdot(CH_2)_5\cdot NH_2$. On heating with hydrochloric acid, the phenoxyl-group in this amine is replaced by chlorine.

Since pyridine is easily reduced to piperidine by sodium and alchohol, and piperidine can be oxidized to pyridine, it may be assumed that pyridine has the same closed chain as piperidine; that is, one of five C-atoms and one N-atom. Moreover, it can be proved that the N-atom in pyridine is not linked to hydrogen; for, while piperidine possesses the character of a secondary amine, yielding a nitroso-derivative for example, pyridine has that of a tertiary amine; thus, it yields an addition-product with methyl iodide (**386**), and the iodine atom in this substance, like that in other ammonium iodides, can be exchanged for hydroxyl by means of moist silver oxide.

The number of isomeric substitution-products, like that of benzene (**263**), indicates that *each carbon atom is in union with one hydrogen atom.* A substance of the formula

should yield three monosubstitution-products, $2 = 6(\alpha)$, $3=5(\beta)$, and $4(\gamma)$. Moreover, for similar substituents, six disubstitution-products are possible: $2:3 = 6:5$; $3:4 =5:4$; $2:4 = 6:4$; $2:6$, $3:5$, and $2:5 = 6:3$. This agrees with the results of experiment. The mode of linking of three out of the four valencies of each carbon atom is thus established, and that of two of the three nitrogen valencies; it remains only to determine how the fourth valency of each carbon atom and the third of the nitrogen atom are distributed in the molecule.

The same argument which led to the assumption of the centric formula for benzene (**263**) are applicable here. The great stability of pyridine towards energetic chemical reagents proves that it does not possess double bonds. Further analogies with benzene support the assumption of a similar constitution. Only the side-chains of both compounds are attacked by oxidizing-agents; with sulphuric acid, both yield sulphonic acids, which are converted by fusion with caustic potash into hydroxyl-derivatives, and by heating with potassium cyanide into cyanides. The hydroxyl-derivatives of pyridine have a phenolic character: they yield characteristic colourations with ferric chloride. The constitution of pyridine must, therefore, be



It must be looked upon as benzene in which one of the CH-*groups has been replaced by* N.

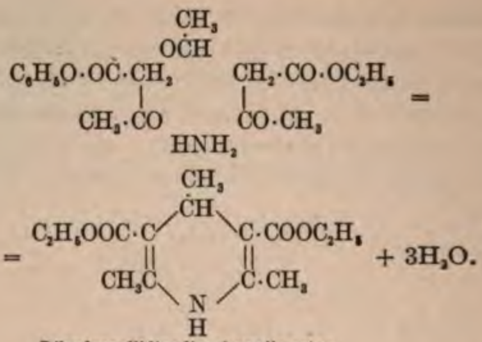
Notwithstanding these analogies, there are great differences in the behaviour of benzene and pyridine, one of these being that pyridine does not admit of nitration.

The principle of the orientation of pyridine is the same as that of benzene—conversion of a compound of unknown structure into one with its side-chains in known positions. The monocarboxylic and dicarboxylic acids have served as the main basis for its orientation: the method of ascertaining the positions occupied by the carboxyl-groups in these compounds is described in **390.**

Homologues of Pyridine.

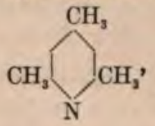
388. The homologues of pyridine are the methylpyridines or *picolines*, dimethylpyridines or *lutidines*, and trimethylpyridines or *collidines*. Many of them can be obtained by more or less complex methods; thus, β-picoline is formed by the distillation of acroleïn-ammonia (**147**), and collidine by the distillation of crotonaldehyde-ammonia. The formation of pyridine and its homologues by the dry distillation of bones depends upon these reactions; under the influence of heat, the fat present yields acroleïn, which reacts with the ammonia resulting from the heating of the albumins, forming pyridine bases.

HANTZSCH has discovered an important synthesis of pyridine derivatives—the condensation of one molecule of aldehyde-ammonia with two molecules of acetoacetic ester:



Dihydrocollidinedicarboxylic ester

On oxidation with nitrous acid, this substance loses two H-atoms; one from the CH-group and one from the NH-group, with formation of collidinedicarboxylic ethyl ester. On saponification of this with caustic potash, and subsequent heating of the potassium salt with quicklime, the carboxyl-groups are split off, and collidine;



distils over.

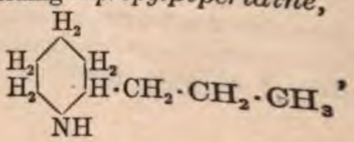
In this synthesis acetaldehyde may be replaced by other aldehydes, and acetoacetic ester by the esters of other β-ketonic acids, so that it affords a method of preparing numerous pyridine derivatives.

Some of the homologues of pyridine can be obtained from it by the action of an alkyl iodide, an addition-product being formed. On heating this to 300°, the alkyl-group becomes detached from the nitrogen atom and links itself to a carbon atom, a reaction analogous to the formation of toluidine by heating methylaniline hydrochloride to a high temperature (**285**).

α-Allylpyridine is of theoretical importance. LADENBURG obtained it by the condensation of α-picoline with acetaldehyde;

$$\underset{\alpha\text{-Picoline}}{NC_5H_4 \cdot CH_3} + \underset{\text{Acetaldehyde}}{OCH \cdot CH_3} = \underset{\alpha\text{-Allylpyridine}}{NC_5H_4 \cdot CH : CH \cdot CH_3} + H_2O.$$

By its aid he effected the first synthesis of a natural alkaloid, that of coniïne, $C_8H_{17}N$ (**403**). α-Allylpyridine was reduced with sodium and boiling alcohol, yielding *α-propylpiperidine*,



which differs only from natural coniïne in being optically inactive, whereas the alkaloid is optically active. This substance was resolved into a dextro-rotatory and a lævo-rotatory modification by fractional crystallization of its tartrate, the dextro-rotatory isomer proving to be identical with natural coniïne.

The constitutional formula of this compound indicates that the carbon atom in union with the propyl-group is asymmetric. β-Propylpiperidine and γ-propylpiperidine do not contain an asymmetric carbon atom, and should therefore be optically inactive, which is a proof of the α-structure of coniïne, as well as of picoline, from which it is derived. A further proof is that coniïne splits up into ammonia and normal octane when strongly heated with hydriodic acid. Thus treated, a β-propylpiperidine or γ-propylpiperidine must yield an octane with a branched side-chain.

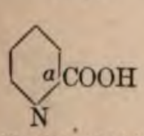
Piperidine is present in pepper in combination as *piperine*, $C_{17}H_{19}NO_3$; on boiling with alkalis, it yields *piperic acid*, $C_{12}H_{10}O_4$, and piperidine, by addition of one molecule of water. Piperine must, therefore, be looked upon as a substituted amide of piperic acid, containing the piperidine-residue, $C_5H_{10}N$—, instead of the NH_2-group:

$$C_5H_{10}N—C_{12}H_9O_3.$$

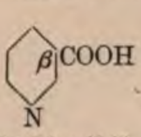
Piperidine is a colourless liquid, boiling at 106°, with a characteristic pepper-like odour and strongly marked basic properties. It is best obtained by the electro-reduction of pyridine.

Pyridinecarboxylic Acids.

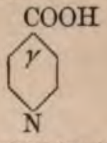
389. Three *pyridinemonocarboxylic acids* are known:



Picolinic acid (α)



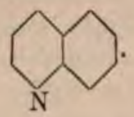
Nicotinic acid (β)



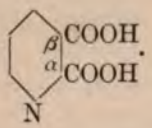
Isonicotinic acid (γ)

The orientation of the carboxyl-groups in these acids can be carried out as follows. It was stated in **368** that the side-chain in coniïne occupies the α-position. On oxidation, this substance yields picolinic acid, by conversion of the propyl-group into a carboxyl-group, and elimination of the six added hydrogen atoms. Picolinic acid is therefore the α-carboxylic acid.

Nicotinic acid is proved to have the β-constitution thus: quinoline (**395**) has the formula



It is naphthalene in which one of the α-CH-groups has been replaced by N. On oxidation, quinoline yields a pyridinedicarboxylic acid, *quinolinic acid,* which must therefore have the structure

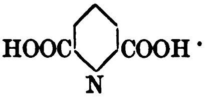


On heating this acid, one molecule of carbon dioxide is eliminated, with formation of nicotinic acid. Since the carboxyl-group in picolinic acid has been proved to occupy the α-position, nicotinic acid must be the β-acid; there remains only the γ-structure for isonicotinic acid.

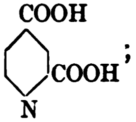
The pyridinemonocarboxylic acids are formed by the oxidation of the homologues of pyridine containing a side-chain. Nicotinic acid derives its name from its formation by the oxidation of nicotine. The monocarboxylic acids are crystalline, and possess both a basic and an acidic character. As bases, they yield salts with acids, and double salts with platinum chloride and mercuric chloride, etc. As acids, they form salts with bases, the copper salts being often employed in their separation.

Picolinic acid can be distinguished from its isomers by two properties: on heating, it splits off CO_2 more readily than they do, with formation of pyridine; and it gives a yellowish-red colouration with ferrous sulphate. Quinolinic acid answers to the same tests; it may, therefore, be concluded that they are applicable to acids with a carboxyl-group in the α-position.

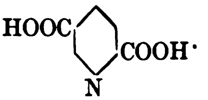
390. By the aid of these reactions it is possible to determine the positions of the carboxyl-groups in the six *pyridinedicarboxylic acids.* On heating with glacial acetic acid, *dipicolinic acid* splits off one molecule of CO_2, forming picolinic acid; on heating alone, it loses two molecules of CO_2, yielding pyridine. It must, therefore, have the αα′-structure



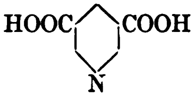
Quinolinic acid was proved in **389** to have the αβ-structure. *Lutidinic acid* answers to the ferrous sulphate test, and, on heating, readily loses one molecule of CO_2, forming isonicotinic acid; this proves it to be an αγ-compound,



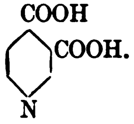
Isocinchomeronic acid also gives the colouration with ferrous sulphate, and is converted by heat into nicotinic acid. It cannot be the αβ-compound, this structure having been proved to be that of quinolinic acid, and must, therefore, have the αβ′-constitution,



The positions of the side-chains in four of the six possible isomers have thus been established. For the two other acids there remain the structures ββ′ and βγ,



and



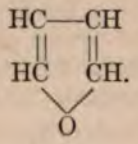
When strongly heated, *cinchomeronic acid* yields isonicotinic acid along with a small proportion of nicotinic acid; under similar conditions *dinicotinic acid* yields only nicotinic acid. They cannot be α-compounds, for they do not give the colouration with ferrous sulphate; it may, therefore, be concluded that cinchomeronic acid has the βγ-structure, and dinicotinic acid the ββ′-structure.

391. Pyridine may be looked upon as derived from benzene by replacement of one CH-group by N. Other closed-chain compounds are known, derived from benzene by replacement of two CH-groups by O, N, or S, respectively. Such are *furfuran*, C_4H_4O; *pyrrole*, C_4H_5N; and *thiophen*, C_4H_4S.

II. **FURFURAN**, C_4H_4O.

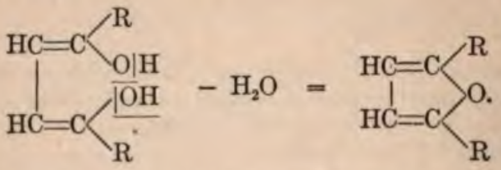
Furfuran, B.P. 36°, is itself of little importance; two of its substitution-products must be considered in some detail.

To furfuran is assigned the ring-formula

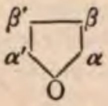


This is supported by the resemblance in properties between some of its derivatives, such as *furfuraldehyde* (*furfural* or *furfurole*), $C_4H_3O\cdot C^{H}_{O}$, and the corresponding benzene derivatives. Moreover, the O-atom can be proved to be linked similarly to that of ethylene oxide (**156**), since on treatment with sodium, hydrogen is not evolved from furfuran, which proves the absence of a hydroxyl-group; and since it is not acted on by hydroxylamine or phenylhydrazine, which indicates that it does not contain a carbonyl-group.

Furfuran derivatives can be obtained from the 1:4-diketones, $R\cdot CO\cdot CH_2\cdot CH_2\cdot CO\cdot R$, by treatment with dehydrating-agents, such as acetyl chloride. This reaction may be looked upon as the result of the conversion of the diketone into an unstable form, $R\cdot\underset{OH}{C}:CH\cdot CH:\underset{OH}{C}\cdot R$, which then splits off water;



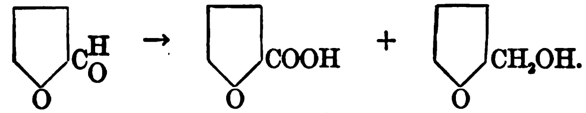
This method yields $\alpha\alpha'$-substituted furfuran derivatives, the C-atoms in furfuran being denoted as in the scheme



This synthesis of furfuran derivatives is likewise a proof of their constitution.

The most important derivatives of furfuran are *furfuraldehyde*, $C_4H_3O\cdot C_{O}^{H}$, and *pyromucic acid*, $C_4H_3O\cdot COOH$, both of which have long been known.

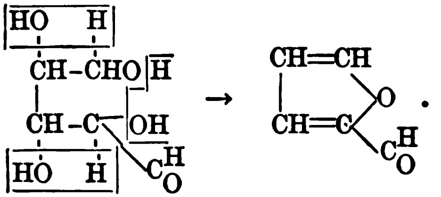
Furfuraldehyde is prepared from pentoses by the method mentioned in **211.** It has the character of an aromatic aldehyde; like benzaldehyde (**299**), it is converted by alcoholic potash into the corresponding acid, pyromucic acid, and the corresponding alcohol, *furfuryl alcohol*, $C_4H_3O\cdot CH_2OH$:



Furfuraldehyde **Pyromucic acid** **Furfuryl alcohol**

With ammonia it yields *furfuramide*, $(C_5H_4O)_3N_2$, analogous in composition to hydrobenzamide (**299**). Just as benzaldehyde condenses in presence of potassium cyanide to benzoïn (**368**), furfuraldehyde under the same conditions yields the similarly constituted *furoïn*, $C_4H_3O\cdot\overset{H}{\underset{OH}{C}}\cdot CO\cdot C_4H_3O$. The resemblance in properties between the two compounds is, therefore, very striking.

Furfuraldehyde is proved to have the α-structure by various means; for example, by its formation from pentoses (**211**), which may be represented thus:

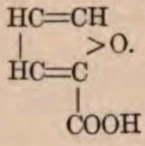


Pentose **Furfuraldehyde**

Furfuraldehyde results from the elimination of three molecules of water under the influence of hydrochloric or sulphuric acid. It is a colourless, oily liquid of agreeable odour, and boils at 162°. A test for it is described in **211**.

As its name indicates, pyromucic acid is formed by the dry distillation of mucic acid (**212**, 6). It can also be obtained by oxidizing furfuraldehyde with silver oxide. It is crystalline, melts at 132°, can be readily sublimed, and dissolves freely in hot water. When heated at 275° in a sealed tube, it splits up into carbon dioxide and furfuran.

Pyromucic acid wholly lacks the character of an aromatic compound: its properties in no way resemble those of benzoïc acid, but are like those of the unsaturated fatty acids. Thus, it easily undergoes oxidation; it almost instantaneously decolourizes Baeyer's reagent (**123**), and readily adds four bromine atoms. Hence, the distinguishing characteristics of the benzene-nucleus are absent, so that the formula

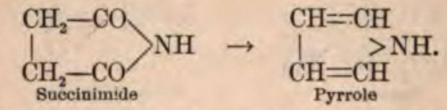


with two double bonds, must be assigned to it.

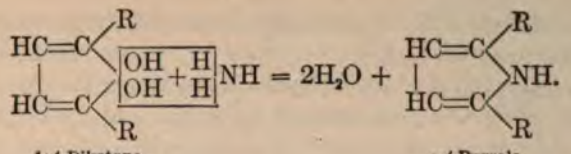
III. PYRROLE, C_4H_5N.

392. *Pyrrole* is present in coal-tar, and in "Dippel's oil" (**386**). It is a colourless liquid of chloroform-like odour, and boils at 131°. The vapours of pyrrole and its derivatives impart a carmine-red colouration to a wood-shaving moistened with hydrochloric acid, due to the formation of an amorphous substance, *pyrrole-red*. This is a delicate test for these compounds.

Pyrrole can be synthesized by distilling succinimide (**169**) with zinc-dust, which proves its constitution:



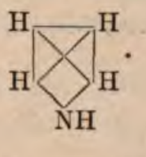
Pyrrole derivatives are obtained from 1:4-diketones by treatment with ammonium acetate, a process analogous to the formation of furfuran derivatives from these substances (**391**):



1:4-Diketone aa'-Pyrrole

Pyrrole has to some extent the character of a secondary amine. The hydrogen linked to nitrogen can be replaced by potassium, with formation of *potassio-pyrrole*, C_4H_4NK, which reacts with alkyl halides, acid chlorides, etc., yielding "N-substitution-products;" that is, pyrrole derivatives with substituents in union with the N-atom.

Pyrrole resembles benzene in properties much more closely than furfuran does, being much more stable than the latter. As a result of this, it does not yield addition-products with halogens. On reduction with zinc-dust and acetic acid, however, it takes up two hydrogen atoms, with formation of *dihydropyrrole** or *pyrroline*, C_4H_6NH, which adds on two atoms of bromine. This behaviour is very like that of benzene and its partially-hydrated derivatives (**270**). For these and other reasons, pyrrole is assumed to possess centric bonds, and its formula becomes



IV. THIOPHEN, C_4H_4S.

393. *Thiophen* has the most aromatic character of the compounds mentioned at the beginning of **391**.

It is present in the crude benzene obtained from coal-tar (**267**) to the extent of about 0·5 per cent.; its homologues, *thiotolen* or methylthiophen, and *thioxen* or dimethylthiophen, are contained in toluene and xylene from the same source.

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* The CHEMICAL SOCIETY OF LONDON employs the name *dihydropyrrole* for the compound C_4H_7N, and *tetrahydropyrrole* for C_4H_9N. In the nomenclature of the GERMAN CHEMICAL SOCIETY the corresponding terms are *pyrrolin* and *pyrrolidin*.—TRANSLATOR.

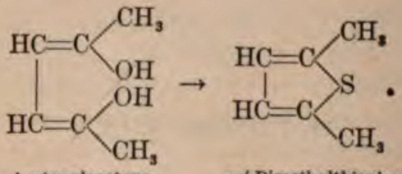
Thiophen was first obtained by Victor Meyer by agitating coal-tar benzene with small amounts of concentrated sulphuric acid till it ceased to give the *indophenin reaction*, a blue colouration with isatin (**398**) and concentrated sulphuric acid. By this treatment the thiophen is converted into a sulphonic acid, from which it can be regenerated by the action of superheated steam.

Thiophen can be synthesized by various methods, the most important being the interaction of succinic acid and pentasulphide of phosphorus. On heating a mixture of these substances, a vigorous reaction ensues, carbon disulphide is evolved, and a liquid, consisting chiefly of thiophen, distils over.

It is a colourless liquid, boiling at 84°, a temperature which differs little from the boiling-point of benzene (80·4°). It has a faint, non-characteristic odour. It is heavier than water, its specific gravity being 1·062 at 23°.

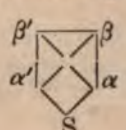
Bromine reacts energetically with thiophen, forming chiefly *dibromothiophen*, $C_4H_2Br_2S$, along with a small proportion of the monobromo-derivative.

The homologues of thiophen can be obtained by Fittig's synthesis (**268**) and by other methods; for instance, by heating 1:4-diketones with pentasulphide of phosphorus, a mode of synthesis which proves the constitution of the thiophen homologues. Thus, acetonylacetone yields *dimethylthiophen:*

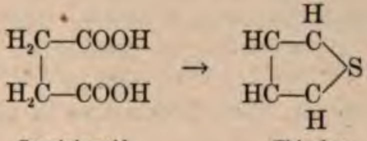


Acetonylacetone (unstable form) αα'-Dimethylthiophen

Since, however, thiophen has all the properties of an aromatic compound, it must also be assumed to possess centric, and not double, bonds, so that its constitution is represented by the following scheme which also shows the mode of denoting the carbon atoms

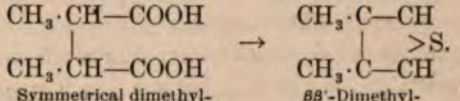


$\alpha\alpha'$-Dialkyl-thiophens are obtained from 1:4-diketones; the β-alkyl-compounds can be prepared by another method. It was stated (p. 500) that thiophen results from the interaction of succinic acid and pentasulphide of phosphorus:



Succinic acid **Thiophen**

Similarly, a monoalkyl-succinic and symmetrical dialkyl-succinic acid respectively yield a β-alkyl-thiophen and a $\beta\beta'$-alkyl-thiophen:

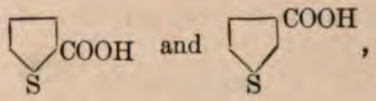


$$\begin{array}{l} CH_3 \cdot CH—COOH \\ \quad\quad | \\ CH_3 \cdot CH—COOH \end{array} \rightarrow \begin{array}{l} CH_3 \cdot C—CH \\ \quad\quad | \quad >S. \\ CH_3 \cdot C—CH \end{array}$$

Symmetrical dimethyl-succinic acid **$\beta\beta'$-Dimethyl-thiophen**

The known structure of these compounds can be employed as a basis for the orientation of the derivatives of thiophen.

The two monocarboxylic acids, *α-thiophencarboxylic acid* and *β-thiophencarboxylic acid*,



possess the remarkable property, when a cold aqueous solution containing both of them is crystallized slowly, of forming a mixture which cannot be resolved into its components. On oxidizing a mixture of α-thiotolen and β-thiotolen, an apparently homogeneous acid is obtained; from its method of formation, however, it can only be a mixture of the corresponding acids.

Thiophenketones are prepared by FRIEDEL and CRAFTS' reaction (**268**); thus, acetothiënone or *α-thiënylmethylketone*. $C_4H_3S \cdot COCH_3$, is obtained from acetyl chloride thiophen, and aluminium chloride. These ketones are readily oxidized to thiophencarboxylic acids, a good method of preparing these compounds.

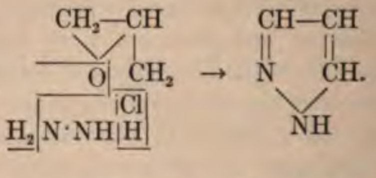
A *thiophensulphonic acid* is also known; it is more easily formed than benzenesulphonic acid, which furnishes a method of separating thiophen and benzene (p. 500). On distillation with potassium cyanide, it forms the corresponding nitrile; but the sulpho-group is not exchanged for hydroxyl by fusion with caustic potash. It is possible, however, to obtain a *thiophenphenol* by the interaction of aminothiophen hydrochloride and nitrous acid, which yields a nitrated hydroxyl-derivative, $C_4H_2S < {}^{NO_2}_{OH}$. This compound greatly resembles *p*-nitrophenol; thus, it dissolves in alkalis, yielding a solution of yellow colour.

On volatilizing thiophen in a current of air, and passing the resulting gaseous mixture into carefully cooled, fuming nitric acid, the principal product is *dinitrothiophen*, although *mononitrothiophen* is also formed. The latter is a solid, melting at 44°, and boiling at 224°; it has an odour like that of nitrobenzene. On reduction, it yields *aminothiophen*, or *thiophenine*, which differs from aniline in being very unstable; it quickly changes to a varnish-like mass, but its hydrochloride is stable. It does not yield diazo-compounds, but reacts with benzenediazonium chloride, forming a crystalline, orange dye.

Many other thiophen derivatives have been obtained, chiefly through the researches of VICTOR MEYER. The examples which have been cited suffice to indicate the great analogy subsisting between the properties of thiophen and those of benzene.

V. PYRAZOLE, $C_3H_4N_2$.

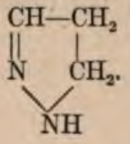
394. *Pyrazole* is obtained by the action of hydrazine, $NH_2 \cdot NH_2$, on epichlorhydrin (**162**):



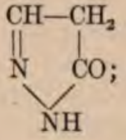
Hydrogen is simultaneously eliminated, which is effected by employing excess of hydrazine; one molecule of this takes up two atoms of hydrogen, forming two molecules of ammonia. This synthesis proves that pyrazole has the above formula, so that it may be regarded as pyrrole in which one of the CH-groups nas been replaced by N.

It is crystalline, melts at 70°, and is very stable. It yields only a weak base, for its aqueous solution has a neutral reaction.

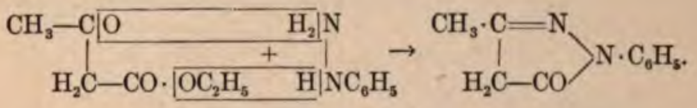
Pyrazole itself does not give important derivatives, but such are obtained from a dihydro-product, *pyrazoline*, $C_3H_6N_2$, formed by the action of hydrazine hydrate on acroleïn. This substance has the formula



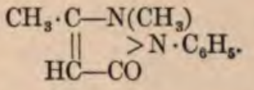
Bromine converts it into pyrazole. A ketonic derivative of pyrazoline is called *pyrazolone*, and has the formula



substitution-products of it are obtained by the interaction of aceto-acetic ester and phenylhydrazine:



Methylphenylpyrazolone is thus formed. Methylphenylhydrazine, $C_6H_5 \cdot NH \cdot NH \cdot CH_3$, condenses similarly with acetoacetic ester, yielding a dimethylphenylpyrazolone with the formula



This is *antipyrine*, $C_{11}H_{12}N_2O$, which was discovered by **Knorr**, and is extensively employed in medicine as a febrifuge. It crystallizes in white leaflets melting at 113°; it cannot be distilled without undergoing decomposition. It is readily soluble in water and alcohol; the aqueous solution gives a red colouration with ferric chloride, and a bluish-green one with nitrous acid.

Antipyrine is manufactured by condensing phenylhydrazine and acetoacetic ester to methylphenylpyrazolone, and subsequently introducing a methyl-group into this compound by heating it with a mixture of methyl alcohol, methyl iodide, and caustic potash.

Many other ring-compounds are known, containing rings of six, as well as of five atoms, but these are beyond the scope of this book.

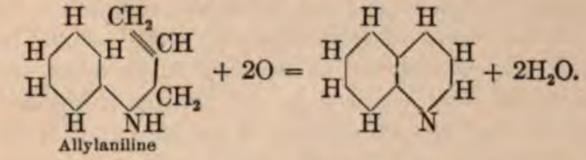
CONDENSATION-PRODUCTS OF BENZENE AND HETEROCYCLIC NUCLEI.

395. Only three of the compounds of this class will be described: *quinoline*, *isoquinoline*, and *indole*. The first two are related to the alkaloids, and the last is important on account of its relation to indigo.

I. QUINOLINE, C_9H_7N.

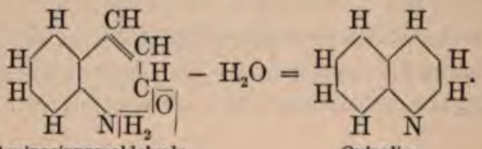
Quinoline is present in coal-tar and bone-oil, but it is difficult to obtain it pure from these sources. It is usually prepared by Skraup's synthesis, which is described below. It is a colourless, highly refractive liquid of characteristic odour; it boils at 236°, and has a specific gravity of 1·1081 at 0°. It has the character of a tertiary base, so that it possesses no hydrogen linked to nitrogen. It yields salts with acids; the dichromate, $(C_9H_7N)_2H_2Cr_2O_7$, dissolves with difficulty in water.

Quinoline can be synthesized by various methods which prove its constitution. Its synthesis was first effected by Königs, by passing allylaniline-vapour over red-hot oxide of lead:



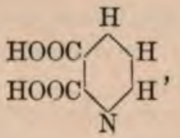
Skraup's synthesis consists in heating together aniline, glycerol, sulphuric acid, and nitrobenzene. In presence of sulphuric acid as a dehydrating-agent, the glycerol loses water, forming acroleïn, which unites with the aniline to acroleïn-aniline, $C_6H_5 \cdot N:CH \cdot CH:CH_2$. In Königs' synthesis the oxidizing-agent is the lead oxide; in this it is the nitrobenzene, which is reduced to aniline. Arsenic acid can be substituted for nitrobenzene.

Baeyer and Drewsen have discovered another method of synthesis which proves the constitution of quinoline; it consists in the reduction of *o*-nitrocinnamaldehyde. This is first converted into an intermediate product, the corresponding amino-compound, the H-atoms of the NH_2-group of this substance being subsequently eliminated along with the O-atom of the aldehyde-group:



o-Aminocinnamaldehyde Quinoline

The last synthesis proves quinoline to be an *ortho*-substituted benzene; the constitution of the ring containing the N-atom has now to be determined. This is effected by oxidation, which produces a dibasic acid, *quinolinic acid*,



which on distillation with quicklime yields pyridine. From these facts it must be concluded that quinoline contains a benzene-nucleus and a pyridine-nucleus, with two *ortho*-C-atoms common to both. *It may be regarded as naphthalene, in which one of the α-CH-groups has been replaced by* N. It was mentioned (**263**, **370**, and **387**) that the assumption of centric bonds is the most probable explanation of the structure of benzene, naphthalene, and pyridine. The analogy between these substances and quinoline is an indication that it, too, possesses centric bonds, so that it has the formula

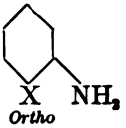
The number of isomeric substitution-products is very large. The seven hydrogen atoms occupy dissimilar positions relative to the nitrogen atom, so that seven monosubstitution-products are possible. Twenty-one disubstitution-products are possible for similar substituents, while the number of triderivatives possible is much greater, etc.

396. There are three methods for the orientation of quinoline derivatives.

First, the relative method (**352**, 1).

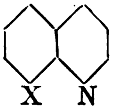
Second, oxidation. This usually removes the benzene-nucleus, leaving the pyridine-nucleus intact, and thus furnishes a means of determining which substituents are present in each of these.

Third, SKRAUP'S synthesis—an important aid to orientation. It can be carried out not only with aniline, but with many of its substitution-products, such as homologues of aniline, nitranilines, aminophenols, and other derivatives. The quinoline compounds thus obtained have their substituents in the benzene-nucleus. But this synthesis also indicates the positions of the side-chains when an *ortho*-substituted or a *para*-substituted aniline is used; thus,



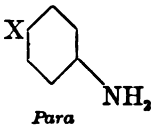
Ortho

can only yield



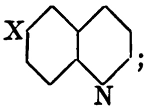
,

and



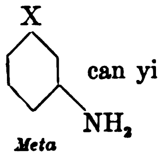
Para

only



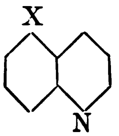
;

while

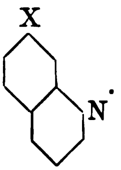


Meta

can yield



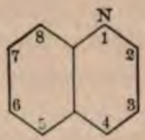
or



.

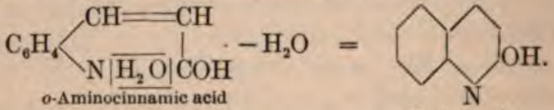
All four possible quinoline derivatives with substituents in the benzene-nucleus can, therefore, be prepared by SKRAUP'S synthesis.

The nomenclature of the quinoline derivatives is indicated in the scheme



Many of the known quinoline derivatives are obtained by SKRAUP's method, a smaller number directly from quinoline. The sulphonic acids are best prepared by the latter method. On fusion with caustic potash, they are converted into hydroxyquinolines; when heated with potassium cyanide, they yield cyanoquinolines, which on hydrolysis give carboxylic acids.

Carbostyril is 2-hydroxyquinoline; it can be synthesized by the elimination of water from *o*-aminocinnamic acid:



o-Aminocinnamic acid

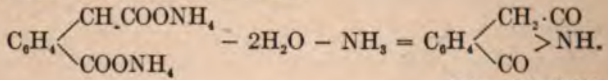
Carbostyril

It has a phenolic character; thus, it dissolves in alkalis, and is reprecipitated by CO_2.

II. ISOQUINOLINE, C_9H_7N.

397. *Isoquinoline* is present in coal-tar, from which HOOGEWERFF and VAN DORP isolated it in the form of its sparingly soluble sulphate. It is a colourless substance with an odour like that of quinoline; it melts at 21°, and boils at 237°.

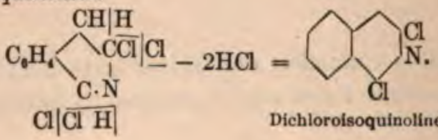
The following synthesis indicates its constitution. On heating, the ammonium salt of *homophthalic acid*, $C_6H_4<\begin{matrix}CH_2\cdot COOH & 1 \\ COOH & 2\end{matrix}$, is converted into *homophthalimide*:



$$C_6H_4\left<\begin{matrix}CH_2COONH_4 \\ COONH_4\end{matrix}\right. - 2H_2O - NH_3 = C_6H_4\left<\begin{matrix}CH_2\cdot CO \\ CO\end{matrix}\right>NH.$$

Homophthalimide

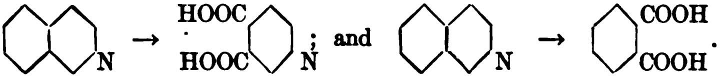
On treating with phosphorus oxychloride, each O-atom is replaced by two Cl-atoms, 2HCl being subsequently split off, with formation of *dichloroisoquinoline*:



Dichloroisoquinoline

Reduction with hydriodic acid and phosphorus converts this substance into isoquinoline, which differs from ordinary quinoline in that the N-atom of the pyridine-nucleus is not directly linked to the benzene-nucleus.

The products obtained by the oxidation of isoquinoline support this view of its constitution. The benzene-ring is removed from one part, and the pyridine-ring from the other, so that cinchomeronic acid (**390**) and phthalic acid are formed:



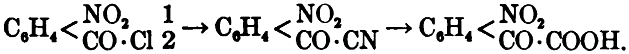
Cinchomeronic acid
Phthalic acid

Since the constitution of isoquinoline is decided by the synthesis described above, it is thus possible to infer from it that of cinchomeronic acid, and this method leads to the same conclusion as that previously arrived at from other considerations (*loc. cit.*).

III. INDOLE, C_8H_7N.

398. The relation between indigo and indole, mentioned at the beginning of **395**, is made evident by the following series of transformations, most of which were discovered by Baeyer.

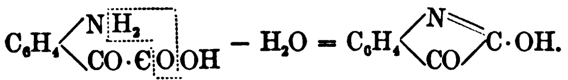
On treatment with nitric acid, indigo, $C_{16}H_{10}N_2O_2$, yields an oxidation-product, *isatin*, $C_8H_5NO_2$, which can also be synthesized by treating *o*-nitrobenzoyl chloride with silver cyanide; on hydrolysis, the resulting nitrile yields *o*-nitrobenzoylformic acid:



$$C_6H_4<\begin{matrix}NO_2\\CO\cdot Cl\end{matrix}\,{}^{1}_{2} \rightarrow C_6H_4<\begin{matrix}NO_2\\CO\cdot CN\end{matrix} \rightarrow C_6H_4<\begin{matrix}NO_2\\CO\cdot COOH.\end{matrix}$$

o-Nitrobenzoyl chloride
o-Nitrobenzoyl cyanide
o-Nitrobenzoylformic acid

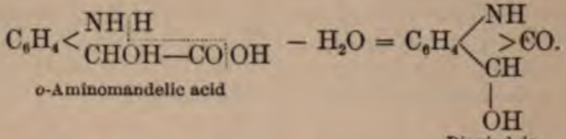
On reduction, the nitro-group in this acid is converted into an amido-group, water being split off simultaneously, and isatin formed. It has therefore the constitution indicated by the equation



$$C_6H_4\left<\begin{matrix}N\boxed{H_2}\\CO\cdot C\boxed{O}OH\end{matrix}\right. - H_2O = C_6H_4\left<\begin{matrix}N\\CO\end{matrix}\right>C\cdot OH.$$

o-Aminobenzoylformic acid
Isatin

On reduction with zinc-dust and hydrochloric acid, isatin takes up two hydrogen atoms, forming *dioxindole*, $C_8H_7NO_2$. This compound also results by the elimination of water from the unstable *o*-aminomandelic acid, which determines its constitution:

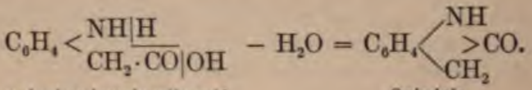


$$C_6H_4<\begin{matrix}NH|H\\ CHOH—CO|OH\end{matrix} - H_2O = C_6H_4\begin{matrix}\diagup NH\\ \\ \diagdown CH\\ \quad|\\ \quad OH\end{matrix}>CO.$$

o-Aminomandelic acid

Dioxindole

On reduction with tin and hydrochloric acid, dioxindole yields *oxindole*, C_8H_7NO, which is also obtained by reduction of *o*-nitrophenylacetic acid and subsequent elimination of water:



$$C_6H_4<\begin{matrix}NH|H\\ CH_2\cdot CO|OH\end{matrix} - H_2O = C_6H_4\begin{matrix}\diagup NH\\ \\ \diagdown CH_2\end{matrix}>CO.$$

o-Aminophenylacetic acid

Oxindole

When distilled with zinc-dust, oxindole is converted into *indole*, C_8H_7N, which must, therefore, have the structure $C_6H_4<\begin{matrix}NH\\ CH\end{matrix}\geqslant CH$; or, written in another way,

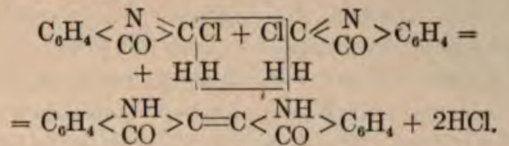
It therefore possesses a benzene-nucleus condensed with a pyrrole-nucleus. It does, in fact, display some of the properties characteristic of pyrrole; thus, it is a very weak base, and gives a red colouration with hydrochloric acid.

β-Methylindole, or *skatole*, $C_6H_4\begin{matrix}\diagup NH\diagdown\\ \\ \diagdown C\cdot CH_3\diagup\end{matrix}\!\!CH$, is present in fæces.

It is also found in a species of wood grown in India, and is formed in the putrefactive decay of albumin, or by fusing albumin with caustic potash. Skatole is characterized by its disagreeable odour.

Indigo.

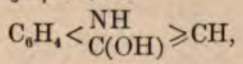
The constitution of indigo is inferred from its formation from *isatin chloride*, obtained by the interaction of isatin and phosphorus pentachloride: on reduction with zinc-dust and acetic acid, it is transformed into indigo:



$$\begin{gathered} C_6H_4<\genfrac{}{}{0pt}{}{N}{CO}\geqslant C\,\overline{Cl + Cl}\,C\leqslant\genfrac{}{}{0pt}{}{N}{CO}>C_6H_4 = \\ +\ H\,\underline{H \quad H}\,H \\ = C_6H_4<\genfrac{}{}{0pt}{}{NH}{CO}>C{=}C<\genfrac{}{}{0pt}{}{NH}{CO}>C_6H_4 + 2HCl. \end{gathered}$$

Since on treatment with sulphuric acid, and subsequent reduction, o-*dinitrodiphenyldiacetylene*, $\underset{NO_2}{C_6H_4}\cdot C{\equiv}C{-}C{\equiv}C\cdot\underset{NO_2}{C_6H_4}$, is converted into indigo, the two isatin-residues in the latter must be united by a carbon bond.

399. Indigo has long been known as one of the finest blue dyes, and is very permanent, being unaffected by light, acids, alkalis, or washing. It is prepared from certain plants, among them *Indigofera tinctoria* and *leptostycha*. These are cultivated on a large scale in Bengal in India—whence the dye derives its name—as well as in Central America, Java, and other countries. Indigo is not present in the plant as such, but in combination as the glucoside *indican*, which is chiefly in the leaves, and can be extracted with hot water. It is crystalline, and has the formula $C_{11}H_{17}NO_6 + 3H_2O$. In addition to the glucoside, the leaves contain an enzyme, whose activity, like that of all enzymes, is destroyed by *boiling* water; hence, when indican itself is to be prepared, hot water must be employed in the extraction. With cold water, both indican and the unchanged enzyme dissolve, and the glucoside splits up into glucose and *indoxyl*, C_8H_7NO, or



$$C_6H_4<\genfrac{}{}{0pt}{}{NH}{C(OH)}\geqslant CH,$$

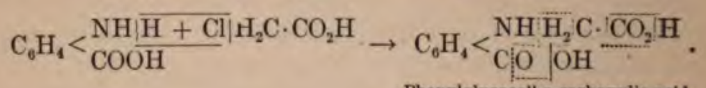
a substance which is moderately stable in acid solution, but in dilute alkaline solution is quickly oxidized to indigo by atmospheric oxygen.

The manufacture of indigo from the plants containing it is carried out by the method indicated. The leaves of the indigo-plant are allowed to remain immersed in lukewarm water for some hours; the aqueous extract is "churned" by a revolving water-wheel with wooden paddles, which aerates it, and thus oxidizes the indoxyl to indigo. The oxidation-process is facilitated by the addition of slaked lime to make the liquid faintly alkaline. The indigo formed sinks to the bottom, is removed by filtration, and dried. It is put on the market in the form of small cubes.

In addition to the blue dye, *indigotin*, commercial indigo contains indigo-gluten, indigo-brown, and indigo-red; these can be extracted by water, alcohol, and alkalis, in which indigotin is insoluble. The latter is a dark-blue powder, which, when rubbed, has a copper-like lustre. It can be sublimed *in vacuo*, so that it is possible to determine its vapour density. It is insoluble in most solvents, but can be crystallized from nitrobenzene or aniline. It dissolves in fuming sulphuric acid, with formation of sulphonic acids.

On account of the great industrial importance of indigo, many attempts have been made to synthesize it. One of these is commercially successful, enabling the artificial product to be sold at the same price as natural indigo. It yields pure indigotin, which is an advantage in some cases.

This method is employed by the BADISCHE ANILIN- UND SODA-FABRIK of Ludwigshafen-on-Rhine. Anthranilic acid, or *o*-aminobenzoïc acid (**351**), $C_6H_4<\genfrac{}{}{0pt}{}{NH_2}{COOH}$, combines with monochloroacetic acid to form phenylglycocoll-*o*-carboxylic acid:



$$C_6H_4<\genfrac{}{}{0pt}{}{NH|\overline{H + Cl}|H_2C\cdot CO_2H}{COOH} \rightarrow C_6H_4<\genfrac{}{}{0pt}{}{NH\,H_2\,C\cdot \overline{CO_2}\,H}{C\,\boxed{O}\,OH}.$$

Phenylglycocoll-*o*-carboxylic acid

On fusion with caustic soda, this compound is transformed into indoxyl, $C_6H_4<\genfrac{}{}{0pt}{}{NH}{C(OH)}\geqslant CH$, which in alkaline solution is converted by atmospheric oxidation into indigo.

The manufacture of indigo by this method has been rendered possible by the discovery of a satisfactory manufacturing-process for anthranilic acid. This substance is obtained by oxidizing naphthalene to phthalic acid (**325**), which can be converted into anthranilic acid, with intermediate production of phthalimide (**351**).

On reduction, indigo takes up two hydrogen atoms, with formation of *indigo-white*, $C_{16}H_{12}N_2O_2$, a white, crystalline substance, whose phenolic character is proved by its solubility in alkalis. In alkaline solution it is speedily reconverted into indigo by atmospheric oxidation, a reaction employed in dyeing with this substance. The dye is first reduced to indigo-white, and the fabric thoroughly soaked in an alkaline solution of this compound; on exposure to the air, the indigo-blue formed is fixed on the fibres. This process is technically known as "indigo-vatting."

The reduction of indigo to indigo-white is variously carried out in the dyeing-industry according to whether wool, silk, or cotton is to be dyed. Reduction is best effected with a salt of hyposulphurous acid, $H_2S_2O_4$ ("Inorganic Chemistry," **83**), for the two first named. The solution is mixed with zinc hyposulphite, and treated with excess of milk of lime, which precipitates zinc hydroxide. The indigo is mixed with water, and warmed to about 60° with this solution of calcium hyposulphite, a concentrated alkaline solution of indigo-white being obtained in a short time. On adding sufficient water to this in the dyeing-vat, the bath is ready for use.

The hyposulphite reduction-process possesses the advantage that the reduction stops at indigo-white, so that almost none of the indigo is lost

ALKALOIDS.

400. Plants of certain families contain substances, usually of complex composition and basic character, called *alkaloids*. Their classification in one group is of old standing, and had its origin in an idea similar to that which prevailed concerning the vegetable acids (**1**) prior to the determination of their constitution. Just as the latter have been subdivided into different classes, such as monobasic, polybasic, aliphatic, and aromatic acids, so it has become apparent that the individual alkaloids can be arranged in very different classes. Most of the alkaloids are, however, related to pyridine, quinoline, or isoquinoline, while a smaller number belong to the aliphatic series. Some of the latter class were described along with the compounds of similar chemical character; among them are betaïne (**200**), muscarine (**232**), choline (**162**), caffeïne and theobromine (**258**). Only alkaloids which are derivatives of pyridine will be described here; to these the name alkaloids, in its more restricted sense, is applied, the other substances being known as vegetable bases.

PROPERTIES.

401. It is seldom that an alkaloid is present in more than one family of plants; many of these do not contain them. Almost all alkaloids are present in dicotyledonous plants. Only a few, such as *coniïne* and *nicotine*, are liquids; most of them are crystalline. Many are optically active and lævo-rotatory, it being very exceptional for them to exhibit dextro-rotation. They have an alkaline reaction and a bitter taste; most of them are insoluble in water, more or less soluble in ether, and readily soluble in alcohol. Most are insoluble in alkalis, but dissolve in acids, forming salts which are sometimes well-defined, crystalline substances.

Oudemans observed that the specific rotatory power (**27**, 2) of the alkaloid salts of strong acids in aqueous solution depends only on the alkaloid, and is not influenced by the nature of the acid-radicle; while for the salts of weak acids it depends on the nature of both the alkaloid and the acid. This is accounted for by the theory of electrolytic dissociation: when dissolved, the salts of strong acids are almost completely ionized, so that in solutions of equimolecular concentration there is always the same amount of the optically active cation present; the salts of weak acids, however, are to a great extent non-ionized, so that they possess a different (smaller) specific rotatory power.

Many alkaloids can be identified by characteristic colour-reactions. Some substances precipitate many of the alkaloids from their aqueous or acid solution; such *general alkaloid-reagents* are tannin (**345**), phosphomolybdic acid, mercuric potassium iodide, $KI \cdot HgI_2$ ("Inorganic Chemistry," **146** and **273**), and others. Some alkaloids are excessively poisonous.

Strong tea is sometimes employed as an antidote, the tannin present precipitating the alkaloid, and rendering it innocuous.

Most of the alkaloids are tertiary amines, so that they yield addition-products with methyl iodide; none of them possesses the character of a primary amine. Many contain acid-residues or methoxyl-groups; the former are split off by saponification, effected by heating with bases or acids, the latter by heating with hydriodic acid, which yields methyl iodide. Hydroxyl-groups can be tested for in the ordinary way with acid chlorides or acetic anhydride (**95** and **96**). On dry distillation, or on heating with zinc-dust, substituted pyridines are sometimes formed.

On account of the complex constitution of the alkaloids, the structures of many of them have not hitherto been determined, so that a rational classification is not yet possible.

402. In the *extraction of the alkaloids from plants* the latter are cut up into fine pieces and lixiviated with acidified water in a conical vat tapering towards the bottom, where there is a layer of some material such as glass-wool or lint. The effect of this is that the acidified water gradually sinks through a thick layer of the substance under extraction, a process technically known as "percolation." Dyes, carbohydrates, inorganic salts, etc., are dissolved out along with the alkaloids. When the alkaloid is volatile with steam, it can be separated by this means from the liquid, after making the mixture alkaline; when it is comparatively insoluble, it can be obtained by filtration. Further purification is always necessary, and is effected by crystallizing the free alkaloid or one of its salts several times.

INDIVIDUAL ALKALOIDS.

Coniïne, $C_8H_{17}N$.

403. The synthesis of *coniïne* is described in **388.** It is present in spotted hemlock (*Conium maculatum*), and is a colourless liquid of stupefying odour. It boils at 167°, is but slightly soluble in water, and is very poisonous.

Nicotine, $C_{10}H_{14}N_2$.

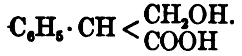
404. *Nicotine* is present in combination with malic and citric acids in the leaves of the tobacco-plant (*Nicotiana tabacum*). It is a colourless, oily liquid, which is lævo-rotatory, and readily soluble in water. It has a tobacco-like odour, which is not nearly so marked in a freshly-distilled sample as in one which has stood for some time. It boils at 246·7°, and is excessively poisonous. It quickly turns brown on exposure to air. It is a ditertiary base; on oxidation with potassium permanganate, it is converted into nicotinic acid (**389**), proving it to be a β-derivative of pyridine. It is assumed to contain a pyridine-nucleus, and a hydrogenated pyrrole-nucleus whose N-atom is in union with a methyl-group.

Atropine, $C_{17}H_{23}NO_3$.

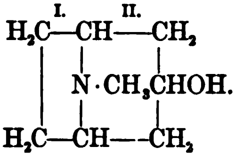
405. *Atropine* is present in the berry of the deadly nightshade (*Atropa belladonna*) and in the thorn-apple, the fruit of *Datura stramonium*. It is crystalline, melts at 115·5°, and is very poisonous. It exercises a "mydriatic" action—that is, when dropped in dilute solution on the eye, it expands the pupil; for this reason it is employed in ophthalmic surgery. It is optically inactive. On heating with hydrochloric acid or caustic soda to 120°, it takes up water and splits up into *tropine* and *tropic acid:*

$$\underset{\text{Atropine}}{C_{17}H_{23}NO_3} + H_2O = \underset{\text{Tropine}}{C_8H_{15}NO} + \underset{\text{Tropic acid}}{C_9H_{10}O_3}.$$

It can be regenerated from these two substances by the action of hydrochloric acid. Atropine is, therefore, the tropine ester of tropic acid, which is α-phenyl-β-hydroxypropionic acid,



$C_6H_5 \cdot CH < \begin{matrix} CH_2OH. \\ COOH \end{matrix}$ The constitution of tropine is probably a carbon ring of seven atoms with a "nitrogen-bridge,"



This formula explains the formation of various substitution-products, derivatives of tetrahydropyrrole * or pyrrolidine (ring I), of piperidine (ring II), and of heptamethylene (external carbon-ring).

Hyoscyamine, $C_{17}H_{23}NO_3$.

406. *Hyoscyamine* is isomeric with atropine, into which it is converted by the action of alcoholic potash; it can also be split up into tropine and tropic acid. The isomerism is probably stereochemical.

Cocaïne, $C_{17}H_{21}NO_4$.

407. On account of its use as a local anæsthetic, *cocaïne* is the best known of the alkaloids present in coca-leaves (*Erythroxylon coca*). It is crystalline, is readily soluble in alcohol, and melts at 98°. On heating with strong acids, a benzoyl-group and a methyl-group are split off, with formation of *ecgonine*, $C_9H_{15}NO_3$, so that the formula of cocaïne may be written $C_9H_{13}NO_2(OCH_3)(COC_6H_5)$; by benzoylating and methylating ecgonine, cocaïne is regenerated. Ecgonine is a carbonyl-derivative of tropine.

Morphine, $C_{17}H_{19}NO_3$.

408. *Morphine* is the longest-known alkaloid; it was obtained from opium in 1806 by SERTÜRNER. Opium is the dried juice of the seed-capsules of *Papaver somniferum*, a variety of poppy. It is a very complicated mixture, containing caoutchouc, fats, resins, gum, sugar-varieties, albumins, mineral salts, meconic acid, some more organic acids, and other substances, together with numerous alkaloids. Twenty of the last-named have been identified; of these morphine is present in largest proportion, and constitutes about 10 per cent. of opium.

Morphine is crystalline, and melts with decomposition at 230°;

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* *Cf.* footnote, p. 499.

it is slightly soluble in water, without odour, and is employed as an anodyne and narcotic. On distillation with zinc-dust, it yields pyrrole, pyridine, quinoline, and phenanthrene. It is a tertiary base, and also possesses a phenolic character, since it is soluble in alkalis.

Narcotine, $C_{22}H_{23}NO_7$.

409. *Narcotine* is present in opium to the extent of about 6 per cent., its percentage being next to that of morphine. It is crystalline, melts at 176°, and is slightly poisonous. It is a weak, tertiary base, its salts readily undergoing hydrolytic decomposition. It contains three methoxyl-groups, so that its formula can be written $C_{19}H_{14}NO_4(OCH_3)_3$. *Nornarcotine* has the formula $C_{19}H_{14}NO_4(OH)_3$. On hydrolysis, narcotine yields the anhydride of meconinic acid, or *meconin*, $C_{10}H_{10}O_4$, and *cotarnine*, $C_{12}H_{13}NO_3$, which is a derivative of isoquinoline. Bromine converts narcotine into dibromopyridine.

Quinine, $C_{20}H_{24}N_2O_2$.

410. The bark of certain trees of the *Cinchona* and *Remya* families contains a great number of alkaloids; of these twenty-four have been isolated, but it is probable that more are present. The most important of them is *quinine*, on account of its anti-febrile effect. *Cinchonine*, $C_{19}H_{22}N_2O_2$, is the next best-known; its physiological action is similar to that of quinine, but less pronounced.

In addition to alkaloids, these barks contain various acids, such as quinic, quinovic, and quinotannic acids; indifferent substances, such as quinovin, quina-red, etc., are also present.

Quinine is very slightly soluble in water, and is lævo-rotatory; in the anhydrous state it melts at 177°, and at 57° when it contains three molecules of water of crystallization. It is a strong base, and both N-atoms are tertiary. It unites with two equivalents of an acid. In dilute solution the salts of quinine exhibit a splendid blue fluorescence, which serves as a test for the base.

The constitution of quinine has been partially elucidated, chiefly through the researches of Königs. It seems to contain two ring-systems, and to possess a hydroxyl-group and a methoxyl-group, so that its formula may be written

$$CH_3O \cdot C_9H_5N—C_{10}H_{15}(OH)N.$$

In accordance with the nomenclature in **396**, the first of these ring-systems is 5-methoxyquinoline, a compound which is obtained by fusing quinine with caustic potash. The second ring is probably similar to the one assumed to be present in tropine (**405**).

Strychnine, $C_{21}H_{22}N_2O_2$.

411. Three extremely poisonous alkaloids, *strychnine*, *brucine*, and *curarine*, are present in the seeds of *Strychnos nux vomica*, as well as in others of the *Strychnos* family. Little is known of the chemical nature of curarine, although it has been much studied from a physiological standpoint; when administered in small doses, it produces total paralysis. Strychnine and brucine cause death, preceded by tetanic spasms—that is, contraction of the muscles; curarine is, therefore, employed as an antidote.

Strychnine is crystalline, and melts at 265°; it is almost insoluble in water. It is a monohydric, tertiary base, only one of its N-atoms exhibiting basic properties. On fusion with caustic potash, it yields quinoline and indole; and when distilled with slaked lime, it is converted into β-picoline (**388**). Heating with zinc-dust produces carbazole (**379**) and other substances.

ALBUMINS.

412. This section contains a short account of the *albumins*, which are compounds of great importance in the animal and vegetable kingdoms, but of such complicated structure that their chemical investigation is a matter of extreme difficulty. Their great physiological importance is made apparent by the fact that the dry material in animal bodies—apart from the mineral constituents and fats—consists almost wholly of albumins, by their being an essential constituent of each living plant-cell, and by their forming the most important part of human and animal food. An animal can exist without fats and carbohydrates for a protracted period, but its death is assured by the withdrawal of albumins from its nourishment.

The investigation of the albumins is rendered difficult not only by their complicated structure, but also by the fact that, with few exceptions, they do not crystallize, and cannot be distilled without undergoing decomposition, so that advantage cannot be taken of these valuable aids in the isolation of individual substances. Moreover, many of the albumins change very readily into other substances, and the distinctions between the different varieties are sometimes by no means marked.

The *albumins*, *proteïds*, and *albuminoids* are closely related, and are classed together under the name *proteins*. The *true*, or *native*, albumins will be first considered. Since they sometimes exhibit great differences in physical and chemical behaviour, it is necessary to first state the general properties characteristic of the albumins.

They contain only five elements, and do not differ much from one another in composition, as the following table shows:

Carbon	50–55	per cent.
Hydrogen	6·5–7·3	,,
Nitrogen	15–17·6	,,
Oxygen	19–24	,,
Sulphur	0·3–2·4	,,

Those of one variety, called *nucleïns*, also contain phosphorus.

Both nitrogen and sulphur are linked in the albumin molecule in more ways than one. A portion of the nitrogen is readily eliminated in the form of ammonia by treatment with a hot, dilute solution of caustic potash, although the greater part is not removed by this means. On warming the albumins with caustic potash, a portion of the sulphur is similarly split off in the form of potassium sulphide, which can be recognized by the formation of a black precipitate of lead sulphide on addition of lead acetate; the remainder of the sulphur can only be detected by completely breaking up the molecule, which is effected by fusion with caustic potash and potassium nitrate. It follows that the albumin molecule must contain at least two atoms of sulphur.

Up to the present it has not been possible to give an empirical formula for albumin; attempts to determine the molecular weight by the cryoscopic method (**14**) lead to the conclusion that it must be very great, the number obtained being about 15,000.

413. The solutions of the albumins are all optically active and lævo-rotatory.

The albumins are colloids ("Inorganic Chemistry," **195**)—that is, do not diffuse through parchment-paper. Advantage is often taken of this in separating them from salts and other crystalloids (*loc. cit.*). Very few have been obtained crystalline, among them serum-albumin; most of them are white, amorphous powders with no definite melting-points. On heating, they carbonize, with evolution of gases.

Some albumins can be "salted out" from their solutions, others cannot. This is an important aid in identifying and separating the different varieties; usually common salt or magnesium sulphate is employed. It is remarkable that not only all albumins, but proteïns in general can be completely "salted out" from their solutions in both neutral and acid liquids by saturation with ammonium sulphate. The native albumins can be fractionally precipitated from aqueous solutions by gradually increasing the concentration of the ammonium-sulphate solution. The point of concentration at which a salt begins to precipitate an albumin is just as characteristic for the latter as, for example, the solubility is for a crystalline substance. When the "salting-out" is effected at ordinary temperatures, it causes no change in the properties of the albumins; their solubilities are the same after as before the operation.

Addition of alcohol precipitates the albumins unchanged from an aqueous solution; strong alcohol *coagulates* them, as also does heating with water. For each native albumin there is a definite coagulation-point; in other words, each albumin coagulates at a definite temperature. On coagulation, the differences in solubility between the albumins vanish; they are all rendered insoluble in neutral solvents, and can be brought into solution again only by treatment with dilute caustic alkalis or with mineral acids. A solution, which behaves exactly like those thus obtained, can be prepared by boiling uncoagulated albumins with a large excess of acetic acid or with caustic alkali.

In this process the native and coagulated albumins undergo a change, which is called *denaturation*. When this is effected with alkali, the product is termed an *albuminate ;* when an acid is employed, a *syntonin* or *acid albumin*. Both these substances differ in composition from the ordinary albumins; since, as mentioned in **412**, when thus treated, they split off ammonia and sulphuretted hydrogen. The albuminate and syntonin are quite insoluble in water, and are, therefore, precipitated by neutralizing their solutions.

414. *Decomposition-products.*—Prolonged boiling with dilute alkalis or mineral acids decomposes the albumins, water being taken up, and ammonia, sulphuretted hydrogen, and a series of amino-acids formed. Since these constitute the decomposition-products of all albumins, it follows that the latter only differ from one another in the proportions in which these are present. These amino-acids are *tyrosine* (**347**)—which proves that the albumin molecule contains benzene-nuclei—*leucine*, *aspartic acid*, *aminoglutaric* or *glutaminic acid* (**200**); diamino-acids, such as *ornithine* (**200**), *arginine* (**256**) and others. are also obtained; of all these leucine is formed in greatest amount. The same amino-acids are produced by the action of the ferment *trypsin*, which is present in the pancreatic gland: decomposition due to putrefactive decay produces aromatic compounds, such as *indole*, *skatole*, *phenylacetic acid*, *phenol*, *cresol*, and so on, in larger proportion. It is probable that the nitrogenous substances are the primary decomposition-products; while such substances as carbonic acid, acetic acid, and its homologues up to caproic acid, formed by an oxidizing action, or by the action of caustic alkalis or of acids, on the albumins, are probably produced by the subsequent decomposition of the amino-acids.

The albumins are precipitated from solution by various substances, either by coagulation or by the formation of compounds insoluble in water. Coagulation is effected by the addition of mineral acids, preferably nitric acid, since an excess of hydrochloric and other acids redissolves the albumin, with formation of a syntonin; this does not take place with nitric acid.

The formation of compounds insoluble in water results on addition of salts of most of the heavy metals, especially copper sulphate, ferric chloride, and an acidified solution of mercuric chloride. The albumins, therefore, behave like weak acids, which with the oxides of these metals yield compounds of the nature of salts. This acidic nature is indicated by the fact that neutral solutions of albumin partly dissolve freshly-precipitated ferric hydroxide. The formation of copper albuminates furnishes a good method of obtaining albumins free from mineral constituents, which are always present to a greater or less extent; on addition of an acid to these copper compounds, the albumin is set free again in the denatured state.

Some weak acids yield insoluble compounds with albumin, which, therefore, behaves also like a base; in this respect it exhibits complete analogy to its main decomposition-products, the amino-acids. Among these weak acids are *tannic acid*, *picric acid*, *phosphotungstic acid*, and others. The albumins are completely precipitated from solution by phosphotungstic acid, a method employed, along with those of coagulation by boiling, and precipitation with alcohol, to separate liquids from the albumin dissolved in them. The acidic and basic properties of the albumins recall those of the pseudo-acids (**281**) and pseudo-bases (**366**); thus, in the free state they have a neutral reaction towards indicators, but the reaction remains neutral when strong acids and bases are added (**281**).

415. Various *tests for albumins* are known, among which the following may be mentioned.

1. *Millon's reagent*, which is a solution of mercuric nitrate containing nitrous acid, yields a red, coagulated mass on boiling.

2. The *xanthroproteïn-reaction*, which consists in the formation of a yellow colouration on treatment with warm nitric acid.

3. The *biuret-reaction*, which depends upon the formation of a fine violet-red colouration when caustic potash is added to albumin, and then a dilute (2 per cent.) solution of copper sulphate drop by drop. This reaction derives its name from the fact that biuret, on similar treatment, gives this colouration (**253**).

The albumins can be classified into the following groups.

1. **Native or true albumins,** which are subdivided into four groups.

(*a*) The *albumins*, including serum-albumin, egg-albumin, milk-albumin, muscle-albumin.

(*b*) *Globulins*, including serum-globulin and vegetable-globulin.

(*c*) *Coagulable albumins*, including fibrinogen, myosin, and gluten-proteïns.

(*d*) *Nucleo-albumins*, including caseïn and vitellin.

2. **Decomposition-products of the true albumins.**

(*a*) *Denatured albumins*, including acid albumins (syntonins) and albuminates.

(*b*) *Albumoses* and *peptones*.

3. **Proteïds,** compounds of albumin with other, usually very complicated, substances.

(*a*) *Nucleo-proteïds*, compounds with nucleïc acid.

(*b*) *Hæmoglobins*.

(*c*) *Gluco-proteïds*, compounds with carbohydrates (mucins).

4. **Albuminoids.**

Some particulars may be given regarding the various classes named.

The *albumins* are the best known and most readily obtained of the albuminous bodies; all of them form well-defined crystals, and are therefore among the few substances of the class which are known to be individual chemical compounds. They dissolve in water, and in dilute acids, alkalis, and salt-solutions.

Their neutral solutions cannot be salted out with sodium chloride, magnesium sulphate, or a semi-saturated solution of ammonium sulphate—a method of separating them from the globulins, which always occurs along with them.

The *globulins* are further distinguished from the albumins by being insoluble in water, although they dissolve in dilute, neutral salt-solutions, and in solutions of alkali-carbonates. At 30° they can be completely salted out by magnesium sulphate, and partly by sodium chloride. They have not been obtained crystalline.

Coagulable albumins have the property of assuming the glareous state, intermediate between solution and coagulation. In this condition they are insoluble in water and salt-solutions, but can be made to coagulate under the influence of heat, strong alcohol, etc.

The *nucleo-albumins* contain phosphorus, and for this reason were formerly classed with the nucleo-proteïds (**416**). They are sharply distinguished from them, however, by yielding xanthine bases among their decomposition-products. The nucleo-albumins have a distinctly acidic character; all of them turn blue litmus red, and in the free state are only slightly soluble in water, though readily soluble in the form of their alkali-salts or ammonium salts. The solutions of their salts do not coagulate, and can be boiled without undergoing any change.

Denatured albumin was referred to in **413**.

Albumoses and *peptones* can be obtained from all proteïns by suitable hydrolysis. They have the albumin character, being insoluble in alcohol, and answering to the xanthoproteïn-test and biuret-test (**415,** 2 and 3). They result from the action of gastric juice on proteïns. They are to be looked upon as intermediate products in the hydrolysis of albumins, the albumoses being nearer the proteïns, and the peptones nearer the amino-acids.

The albumoses are the soluble decomposition-products of albumin; they cannot be coagulated, but can be salted out by salts such as ammonium sulphate.

The peptones are the final, simplest decomposition-products of the native albumins; their colour-reactions (especially the biuret-reaction), their constitution, and their physiological behaviour indicate that they should be classed with the albumins, but they cannot undergo further decomposition without being converted into substances of wholly different character, the amino-acids.

416. Nearly related to the true albumins are the *proteïds,* compounds of albumin with other substances, usually of a very complex nature. Like the true albumins, they are insoluble in alcohol, by which most of them are coagulated.

Nucleo-proteïds derive their name from the fact that they are the principal constituent of the cell-nuclei. They are compounds of albumins with *nucleïns*—that is, compounds of albumin with phosphoric acid or a *nucleïc acid*. A nucleïc acid is phosphoric acid which is partially saturated by union with basic substances, such as hypoxanthine, guanine, xanthine, etc., and is to be looked upon as an amide. The composition of the nucleïns differs considerably from that of the true albumins; they contain about 41 per cent. of carbon, 31 per cent. of oxygen, and 5·7 per cent. of phosphorus.

The nucleïns have a markedly acidic character; they are insoluble in water and dilute acids, but soluble in caustic alkalis. They answer to the same colour-tests as the albumins.

There is not much difference in composition between the nucleo-proteïds and the true albumins, this being due to the small amount of nucleïn-substance present in the former. They contain phosphorus, which is present in the nucleïn, and are more acidic than the albumins, having the character of a dibasic acid.

Hæmoglobins are compounds of albumins with dyes containing iron, hæmoglobin being the dye of red blood-corpuscles. It splits up into albumin and *hæmatin*, and unites very readily with oxygen, forming *oxyhæmoglobin*, from which the oxygen is eliminated by placing it in a vacuum or treating it with reducing-agents. For this reason, hæmoglobin plays an important part in respiration. It unites with carbon monoxide to form *carbonylhæmoglobin*, which is unable to combine with oxygen; on this depends the poisonous action of carbon monoxide.

On treatment with acetic acid and sodium chloride, oxyhæmoglobin yields the hydrochloride of hæmatin, called *hæmin*, which crystallizes in characteristic, microscopic needles of a brown-red colour. This reaction furnishes a delicate test for blood.

Gluco-proteïds are compounds of albumins and carbohydrates. To them belong the *mucins;* these, like the nucleo-albumins, are acidic in character and insoluble in water, but soluble in a small quantity of lime-water or alkali solution. The solution thus obtained is neutral, has a glutinous appearance, and is not coagulated by boiling. Unlike those of the true albumins, these solutions are not precipitated by nitric acid. When boiled with acids or caustic alkalis, they yield either syntonins or peptones, together with carbohydrates. The presence of the nitrogen-free carbohydrates makes the percentage-amount of nitrogen in the mucins considerably less than in the true albumins; its value lies between 11·7 and 12·3 per cent.

417. The *albuminoids* differ somewhat more in composition from the true albumins. They exist only in the animal economy in the undissolved state, being the organic constituent of the skeleton and the epidermis.

They include various substances, among them being *ceratin, elastin,* and *collagen.*

Ceratin is the principal constituent of the epidermis, hair, nails, hoofs, and feathers. It is particularly rich in sulphur, of which it contains between four and five per cent., a portion being readily removed by treatment with boiling water. It can be dissolved only by boiling with caustic alkalis, or by the action of high-pressure steam. Its decomposition-products resemble those of the true albumins. With nitric acid it gives the xanthoproteïn-reaction; this is the origin of the yellow colour developed when nitric acid comes into contact with the skin.

Elastin constitutes the elastic fibres present in tissue, which in some parts of the body are united in the form of ligaments. On warming with dilute caustic potash, *all* the sulphur in it is eliminated, which distinguishes it from other albumins. The decomposition-products obtained by boiling it with concentrated caustic potash have the same qualitative composition as those obtained from the true albumins. It is quite insoluble in dilute acids and caustic alkalis.

The *collagens* are the most widely distributed of the albuminoids. They are among the constituents of cartilage. In some respects they differ from the true albumins. They have a higher percentage of nitrogen (17·9 per cent.). They do not contain aromatic nuclei, so that tyrosine is not formed by their hydrolytic decomposition. Another decomposition-product, glycocoll, is produced, which is not obtained from the albumins; at the same time leucine, aspartic acid, and glutaminic acid are formed. The collagens are further distinguished by not possessing sulphur so readily split off as that in the albumins.

When boiled with water, the collagens take it up, forming *glutin* or *glue*. A solution of glue is not precipitated by nitric acid, or other mineral acids, but is by mercuric-chloride solution in presence of hydrochloric acid. It is also precipitated by tannin.

418. In the inferior orders of animal life a series of substances has been discovered whose chemical properties approximate more or less closely to those of the collagens and also of elastin. Among them is *spongin*, the principal constituent of sponges, which is much more stable towards caustic soda and baryta-water than collagen. On complete hydrolysis by boiling with dilute sulphuric acid, it yields leucine and glycocoll, but no tyrosine, proving it to be a collagen.

On prolonged boiling, silk splits up into *fibroïn*, which is not decomposed by water even at 200°, and *sericin*, or *silk-glue*, which is perhaps a mixture of glue and albumins. Fibroïn dissolves very readily in strong acids, ammonia being simultaneously split off, and *sericoïn* formed. On complete hydrolysis, fibroïn yields tyrosine and glycocoll, but no leucine.

Lastly, *corneïn* may be mentioned; it is the organic constituent of coral. On hydrolysis, it splits up into leucine and an aromatic substance of unknown composition.

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The principal references are in old-style figures.

~~$K_4Fe(CN)_6 + H_2SO_4 = K_2Fe\,Fe(CN)_6 + 3K_2SO_4 + 2HCN$~~

~~Fe_2CN_6~~ + H_2SO_4 = K_2Fe_2 ~~$Fe_2CN_6 + 9K_2SO_4 + 2HCN$~~