OUTLINES OF
ORGANIC CHEMISTRY

A BOOK DESIGNED ESPECIALLY
FOR THE
GENERAL STUDENT

BY

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SECOND EDITION REWRITTEN
TOTAL ISSUE FOURTEEN THOUSAND

NEW YORK
JOHN WILEY & SONS, Inc.
London: CHAPMAN & HALL, Limited
1915

Stanhope Press
F. H. GILSON COMPANY
BOSTON, U.S.A.

PREFACE TO SECOND EDITION.

THE present edition represents a thorough revision of the text in which, however, the original point of view has been strictly retained. The attempt has been made to have all statements accord strictly with the results of the latest and most reliable investigations, and the opportunity has been taken to introduce several topics of practical interest which had hitherto been omitted. Among these may be mentioned citric acid, the fulminates, the synthesis of india-rubber, and the chemistry of tannin. The chapter devoted to the compounds of cyanogen has been brought more nearly in accord with modern technical practice, and that dealing with stereoisomerism has been largely rewritten in the interest of clearness.

The author desires to express his thanks to all those who have called attention to inaccuracies or loose statements in the first edition, and hopes that he may rely upon them for similar favors in the future. He is especially indebted to his colleague, Professor W. T. Hall, for valuable assistance in reading the proofs.

F. J. MOORE.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
June, 1914.

PREFACE TO FIRST EDITION.

DURING the past few years, it has been one of the author's most agreeable duties at the Massachusetts Institute of Technology, to deliver a course of about thirty lectures upon the underlying principles of Organic Chemistry. Those attending this course have been, almost exclusively, candidates for the bachelor's degree in Physics, Biology, and Sanitary Engineering. The experience thus gained has produced the conviction that, for such students, a selection of topics is desirable which is somewhat different from that given to those who are fitting themselves to become organic chemists, and consequently different from that outlined in most text-books designed for both classes of students.

The material which has been found suitable for presentation in these lectures is here put in book form, in the hope that it may prove useful to others who study Organic Chemistry from the non-professional point of view.

In selecting from the vast number of organic substances those best adapted for study in a work of this kind, compounds have, as a rule, been included, either because they are themselves of practical importance, or because they serve as the most convenient examples for illustrating fundamental principles which elucidate the chemical character of substances which are of practical importance. The word "practical" has been abused in so many ways, that some definition is desirable. For the purposes of this book those substances have been considered of practical importance which have a wide technical application, like acetylene or linseed oil; those which are important factors in vital processes, like glycogen or urea; those which are familiar in the operations of daily life, like sugar or starch; or, finally, those which throw light upon some important theory. Theories and processes have been selected upon a similar basis. The attempt has been made to present these in a thoroughly scientific manner, no important subject being omitted merely on account of inherent difficulties of presentation or comprehension. Numerous subjects of the greatest importance to the professional organic chemist have, however, been omitted without scruple, if their inclusion did not seem called for on the basis of the principle already laid down. The professional will look in vain for any mention of a subject as important to him as the aceto-acetic ester synthesis or the Grignard reaction, and he will find no mention of the broad subject of *cis-trans* isomerism. Optical isomerism has, however, been dealt with in considerable detail, because so many important natural products are optically active.

It has been the same in the matter of constitutional proof. All will agree that it serves no good purpose to present a constitutional formula unless it is at the same time made clear how such a formula serves as an epitome of the whole general chemical character and behavior of a compound. To give a rigid proof in the case of every substance mentioned would, on the other hand, lead far beyond the limits of a book of this character. The attempt has been made to meet these difficulties in the following way: For simple and important compounds, well adapted for purposes of illustration, proof has been presented in considerable detail, in order that the student may clearly understand just what is meant by this important element in a chemist's work. With more complicated substances and derivatives, the chemistry of the compounds has usually been discussed with sufficient fullness to make the formula plausible. In some isolated cases the author must plead guilty to having presented formulæ without any evidence at all. Where this has been done, it has been done as a choice of evils. In the case of such compounds as pinene, camphor, or uric acid, for example, it seems at least equally undesirable either to omit formulæ altogether, or, on the other hand, to marshal for their support a host of unfamiliar and, for every other purpose, useless facts, each of which is as difficult to remember as the formula it is intended to establish. The semi-philosophical question of the limit of information conveyed by a graphic formula and the validity of the valence theory are discussed in the last chapter as critically as seems appropriate in addressing non-professional students. The chapter which touches upon Physiological Chemistry stands, scientifically, upon a somewhat different footing from the rest of the book, but this difference has been perhaps sufficiently emphasized in the text.

F. J. MOORE.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
May, 1910.

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OUTLINES OF ORGANIC CHEMISTRY.

CHAPTER I.

INTRODUCTORY.

THE division of the subject of Chemistry into two great fields called respectively Organic and Inorganic Chemistry, like all such classifications in science, is merely a matter of practical convenience. The distinction grew up historically from the tendency to classify substances according to their origin; thus those which were obtained directly or indirectly from plant or animal sources were ranked as organic, all others as inorganic. In the first class were placed such substances as sugar, alcohol, and acetic acid; in the second, those like salt, sulphur, or lead. In earlier times the distinction between these classes seemed more fundamental than at present, because as yet no process was known by which an organic compound could be prepared from an inorganic one, or built up from its constituent elements in the laboratory. Since such processes have been devised, and the synthetic method has assumed so much importance in the study of organic compounds, the arbitrary nature of the old classification has become more apparent. The old names have, however, been retained with a somewhat altered significance. We now define Organic Chemistry as that portion of the science which treats of the compounds of carbon. This element occurs so universally in substances of animal or vegetable origin that most compounds included in the old classification are retained in the new, the subject-content of Organic Chemistry remaining much the same.

Not only does the great number of the carbon compounds — probably exceeding those formed by all the other elements combined — justify the separate treatment of this important branch, but the methods of study show well-defined differences, both in mechanical technique and in theoretical point of view. It is, of course, true that the same laws govern chemical action in the one field as in the other. On the other hand, the every-day processes carried out in laboratory practice involve the habitual use of different operations, and the theoretical considerations which govern the work are, as a general rule, quite different. For example, the fundamental theoretical conception which is constantly in the mind of the organic chemist in planning his researches is the valence theory. This has proved a far less serviceable guide in the inorganic field.

Among those properties of organic compounds which are most likely to impress the beginner as differing from inorganic ones, the following may be mentioned as typical.

1. Instability at High Temperature. While many inorganic compounds can be heated to incandescence without undergoing chemical change, nothing of the kind is to be observed among organic compounds. These, almost without exception, undergo decomposition by the time the temperature has been raised to dull redness, while a large proportion decompose at a much lower temperature. This decomposition by heat is usually accompanied by deposition of free carbon, and this phenomenon, known as 'charring,' is therefore one of the most common analytical tests for the presence of 'organic matter.'

2. Solubility. We seldom have occasion to work with the more common inorganic compounds in any other than aqueous solution; the majority of organic compounds, however, are practically insoluble in water, most of these being soluble to a greater or less extent in such media as alcohol, ether, acetone, chloroform, carbon bisulphide, and the like. Most of the reactions carried on in the organic laboratory take place to best advantage in such solvents. The division of substances between two non-miscible solvents is also an operation frequently employed.

3. Velocity of Reaction. Most of the inorganic compounds with which we are most familiar are electrolytes, that is, they are dissociated in aqueous solution into ions; hence the reactions which take place in such solutions are usually those between ions. As a result these reactions are practically instantaneous in character. The greater number of organic compounds, on the contrary, are not electrolytes, and the reactions between them, though often rapid, are frequently extremely slow, requiring hours, and sometimes even days or weeks, for completion. As a result, the long digestion of reaction-mixtures at elevated temperatures is quite the rule in organic operations.

It must be understood that no one of the distinctions which have been mentioned is in any sense absolute. Many organic compounds are electrolytes, many inorganic compounds are soluble in non-aqueous solvents, many reactions between organic substances take place with great velocity, and many inorganic substances decompose at no very high temperature. What has been said is only intended to show enough of the broad differences between the two subjects to justify an independent treatment. The name 'Organic Chemistry' is also well justified, for although no one any longer believes that any mysterious 'vital force' makes the operations of chemical affinity something different in the one class of compounds from what it is in the other, yet two things do remain true: first that, in practice, most organic compounds are still obtained directly or indirectly from organized bodies (animal or vegetable) and second, that the vital processes themselves are, as we shall see in more detail later, reactions between organic compounds.

The Purification of Organic Compounds.

The fact that small amounts of impurities have a marked effect upon the physical properties, and sometimes upon the chemical behavior, of organic substances makes it imperative, in most cases, that compounds be subjected to processes of purification before they can be analyzed or employed for synthetic operations. This makes it necessary to discuss those tests which may be looked upon as furnishing criteria of purity for an organic substance. Those most commonly employed are the determination of the melting-point in the case of solids, and the boiling-point in that of liquids. The knowledge of other physical constants, such as the crystalline form, the specific gravity, the electric conductivity, and the refractive index, is also extremely useful either as a means of identification or as furnishing tests for purity. These latter determinations are, however, much less frequently made in laboratory practice.

To return to the tests first mentioned, a liquid is usually regarded as pure when its boiling-point is constant, that is, when the whole of it will distill at a constant temperature. It should be stated at once that such a conclusion is not justifiable in all cases. Certain mixtures of definite composition also distill at a constant temperature for a given pressure. In such a case, changing the pressure reveals the presence of a mixture of this kind, for then the boiling-point will no longer remain constant.

The boiling-point of a liquid is usually obtained by distilling it, — a process also very useful for purposes of purification. The apparatus employed consists of a flask provided with a side-neck which passes to a condenser. (Fig. 1.) Through the stopper of the flask a thermometer is introduced in such a way that the bulb comes just opposite the opening of the side-neck. It thus measures the temperature of the vapors passing over. This gives the boiling-point of the distillate at any given moment. It is frequently desirable to carry out a distillation under diminished pressure. This operation is commonly spoken of as 'distillation in vacuum.' For this purpose all joints in the apparatus are made air-tight, and the receiver is attached to some form of vacuum pump. A manometer is usually connected to the apparatus to indicate the pressure.

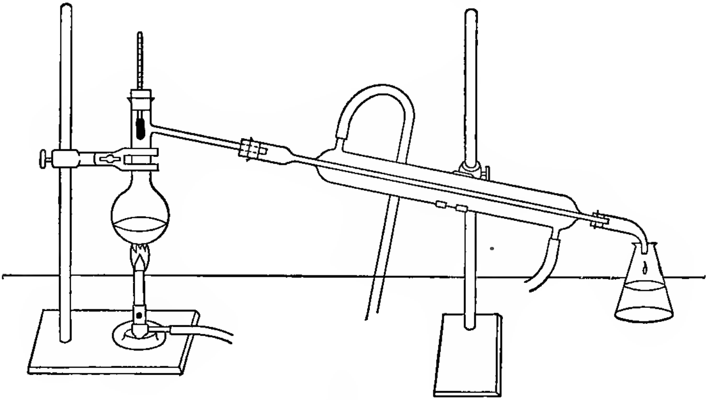

Fig. 1.

The melting-point of a solid is a characteristic property. A small amount of an impurity will frequently depress the melting-point many degrees, so that, in practice, when dealing with an unknown substance, processes of purification are repeated until the melting-point of the material has reached a maximum.

The melting-point of a solid is determined as follows: a little of the finely powdered substance is introduced into a thin-walled tube closed at one end. (Fig. 2.) The tube used should be about five centimeters long and one millimeter in diameter. It is attached to a thermometer in such a way that the substance is just beside the bulb of the latter. Both are now heated slowly in a bath of some transparent liquid — usually concentrated sulphuric acid — until the substance is seen to melt. The temperature is then read off on the thermometer.

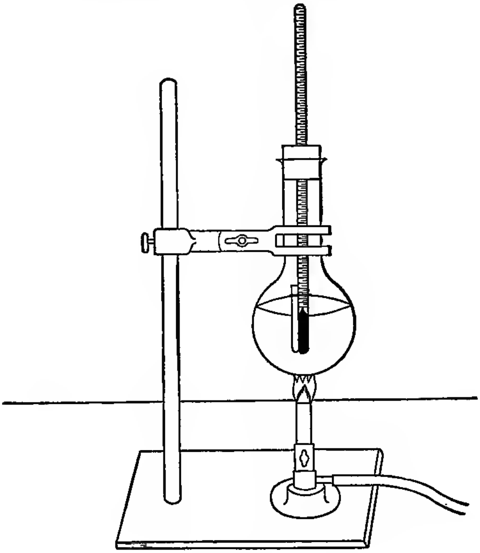

Fig. 2.

Solids are most frequently purified by crystallization. This operation is so constantly carried out in an organic laboratory that it should be described in some detail. The substance to be recrystallized is heated with such a quantity of an appropriate solvent that the boiling solution is nearly saturated. The hot solution is rapidly filtered, in order to remove any insoluble impurities, and the filtrate is allowed to cool slowly. When cold the crystals which have been deposited are filtered off and washed with a little of the pure solvent. The adhering solvent is then removed as far as possible by suction, and the product finally dried, either by heat or by leaving it in a vacuum-desiccator (Fig. 3) which also contains some substance capable of absorbing the vapors of the solvent. For this purpose concentrated sulphuric acid is generally used, as it will absorb the vapors of water, alcohol, ether, and many other liquids. In carrying out the above operation, one of the most important things is the selection of a proper solvent. One should be used from which the solid will be deposited in well-formed crystals, easily washed. In order to secure a good yield, it is also extremely desirable that the substance be but sparingly soluble in the cold solvent, but quite freely soluble at a higher temperature. In many cases, of course, these conditions can be but imperfectly realized.

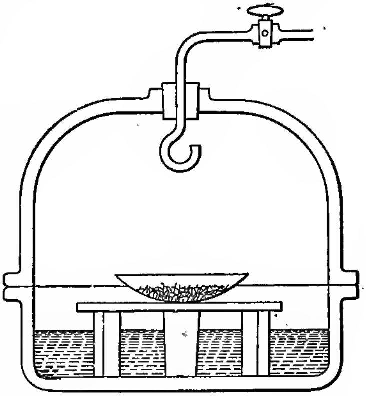
Fig. 3.

A problem frequently met with is the separation of two or more liquids which are miscible in all proportions, but which have different boiling-points. If it does not so happen that the liquids form a mixture boiling at a constant temperature, it is possible to separate them by fractional distillation. When a mixture of water and methyl alcohol, for example, is boiled, the portion which first volatilizes is relatively richer in alcohol than the liquid from which it distills. As the distillation proceeds, the percentage composition of the distillate progressively changes, so that the later portions contain relatively more water than the original mixture. If now, instead of collecting the whole distillate in one receiver, the receivers are changed repeatedly, a series of fractions of varying concentrations will be obtained. If each of these fractions is again distilled, further changes of concentration in the same sense take place, so that, by repeated distillations, it is possible to effect a practically complete separation of the two components.

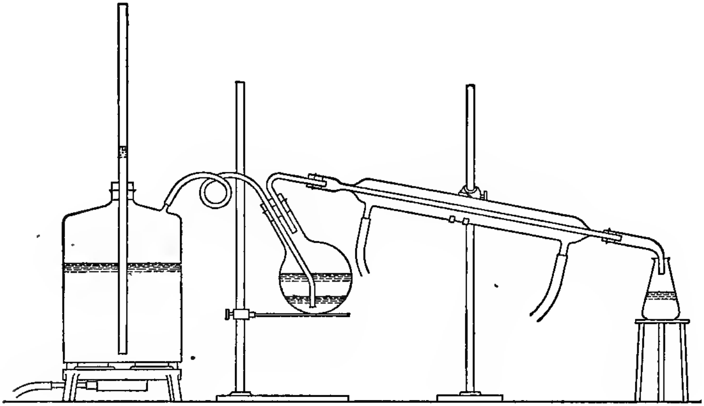

Fig. 4.

Another operation of constant application is distillation with steam. (Fig. 4.) Many substances insoluble in water distill readily in a current of steam, although their own boiling-points may be a hundred degrees or more higher than that of water. The process is chiefly employed for the purpose of removing from a reaction-mixture some one component which alone is volatile with steam.

Another operation which serves the same purpose depends upon the differing solubilities of substances in two liquids which are not miscible. If some substance, for example, is formed in an aqueous solution which is more soluble in ether than in water, its separation and purification may be effected by shaking the reaction mixture with ether. Later, when the two layers have been allowed to separate, the substance sought is found in the ethereal layer, whence it may be readily obtained by distilling off the ether. This operation of 'shaking out with ether' is of constant application, and is usually performed in a piece of apparatus called a 'separatory-funnel' (Fig. 5) which permits the lower layer of liquid to be drawn off through a stopcock at the bottom. Other liquids which do not mix with water may, of course, be substituted for the ether in special cases. Were any substance absolutely insoluble in one liquid and very soluble in another, it is clear that all of the material might be obtained by one operation. As a rule, however, several treatments are necessary, because the conditions of solubility hinted at above are never realized in practice.

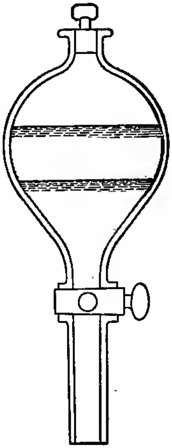

Fig. 5.

The rule is that after equilibrium has been reached, the ratio of the concentrations of the solute in two non-miscible solvents is constant.* This ratio is called the 'distribution

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* An apparent exception to the rule is to be found in the case where the dissolved substance is dissociated in one of the solvents. Here, however, we are really dealing with at least three solutes, — the undissociated substance and its ions. Association may also cause anomalous results.

coefficient' and is usually approximately equal to the ratio of the solubilities of the dissolved substance in the two liquids considered separately.

Qualitative Analysis.

A complete system of analysis, such as we find in use for the study of inorganic substances, is at the present time lacking in Organic Chemistry. We have as yet no standard methods which can be relied upon to reveal all the components in any mixture of organic substances, and owing to the close resemblance which exists between the members of the various classes of organic compounds, and the multitude of classes which exist, it is probable that such a general system can be developed only in the distant future. It follows that for the present, when dealing with mixtures, special methods must be employed which are suitable to particular kinds of mixtures. When these are unfamiliar, new methods must be worked out by the experimenter. Such work requires a wide knowledge of Organic Chemistry, and therefore cannot be discussed at all here. A practical problem which comes up constantly in organic work is the following: Given a pure homogeneous organic compound, to detect the elements which it contains, and to determine the percentage of each which is present. The processes involved in the solution of this problem are, in theory at least, extremely simple, and may well be taken up at this point. The operation, as a whole, is spoken of as the 'elementary,' or more frequently as the 'ultimate,' analysis of an organic compound.

The elements which usually occur in organic compounds are comparatively few in number. The only ones which need to be considered here are carbon, hydrogen, oxygen, nitrogen, chlorine, bromine, iodine, and sulphur. The vast majority of compounds contain no element outside of the first four in the list.

To test for carbon, the substance is merely heated in a tube closed at one end. The presence of carbon is revealed by charring, with the simultaneous evolution of what is commonly called a 'burnt odor.' A few organic substances are so volatile that they do not show this test well. In such cases it is necessary to completely oxidize the substance. This can usually be best effected by heating with copper oxide. If carbon is present the gases evolved will then contain carbon dioxide, and this can be readily detected by the turbidity which it produces in lime water.

A test for hydrogen is usually superfluous after having tested for carbon, since practically all organic compounds contain hydrogen. If any test is desired, the formation of water on heating or by combustion is sufficient.

For combined oxygen, Chemistry still lacks any universally applicable qualitative test, or any good general method for its quantitative determination.

The other elements mentioned — that is, nitrogen, the halogens, and sulphur — are most conveniently detected after total decomposition of the organic material. For this purpose the substance is heated with metallic sodium in a small tube closed at one end, until decomposition has taken place, as witnessed by abundant charring. The tube is then broken under water, and the solution boiled and filtered.

The chemical results of this operation may be summarized as follows: Most of the carbon which the substance contains is deposited directly as such. If nitrogen also is present, this combines with some of the carbon and some of the sodium to form sodium cyanide. Similarly, if the halogens and sulphur are present, they unite with the sodium to form the corresponding binary compounds. Hence a solution prepared as above indicated would contain sodium cyanide if the substance analyzed contained nitrogen, sodium sulphide if it contained sulphur, and sodium chloride, bromide, or iodide, if these halogens were present in the original material. In this solution, then, which now contains no organic matter, the above anions may be tested for according to any of the methods commonly employed in the qualitative analysis of inorganic compounds. In order to test for the presence of a cyanide, for example, the alkaline solution is treated with a few drops of a solution containing iron in both the ferrous and ferric conditions, and the mixture digested for a few minutes. Then, upon acidification, a precipitate of Prussian blue results if nitrogen was originally present in the organic substance.

$$6\,NaCN + FeSO_4 = Na_4Fe(CN)_6 + Na_2SO_4.$$
$$FeCl_3 + 3\,NaOH = Fe(OH)_3 + 3\,NaCl.$$
$$\begin{aligned}4\,Fe(OH)_3 + 3\,Na_4Fe(CN)_6 &+ 12\,HCl \\ &= 12\,NaCl + Fe_4[Fe(CN)_6]_3 + 12\,H_2O.\end{aligned}$$

Chlorides, bromides, and iodides may be recognized by the precipitates which they give with silver nitrate in dilute nitric acid solution. They may be further distinguished by the fact that chlorine-water liberates free bromine from bromides,

$$Cl_2 + 2\,NaBr = 2\,NaCl + Br_2,$$

and free iodine from iodides. The former imparts a red or yellow color to carbon bisulphide according to the concentration, the latter gives a violet color.

If sulphides are present, they may be recognized by the black precipitates which they give with silver nitrate or lead acetate:

$$Na_2S + Pb\overline{Ac}_2 = 2\,Na\overline{Ac} + PbS.$$

A more sensitive test, however, is that effected by adding a dilute solution of sodium nitroprusside, $Na_2(NO)Fe(CN)_5$. This reagent gives a violet color with soluble sulphides.

When two or more of the elements just mentioned are present at the same time, the analysis is a little more complicated. Such cases are, however, exceptional in practice. For dealing with them, the student is referred to any work upon Qualitative Analysis.

Quantitative Analysis.

The principles involved in the quantitative determination of the elements in an organic compound are also extremely simple. The determination of carbon and hydrogen is almost always combined in one operation. This is commonly spoken of as an 'organic combustion,' and in its practical execution it makes very considerable demands upon the manipulatory skill of the analyst. A weighed portion of the substance to be analyzed is burned in a current of air or oxygen, the substance being at the same time surrounded by considerable quantities of copper oxide. Advantage is here taken of the fact that copper oxide, when heated to a temperature of dull redness with an organic substance, gives up its oxygen to the latter, being itself reduced to metallic copper. This insures complete oxidation at a lower temperature than would be possible by the use of air or oxygen alone.

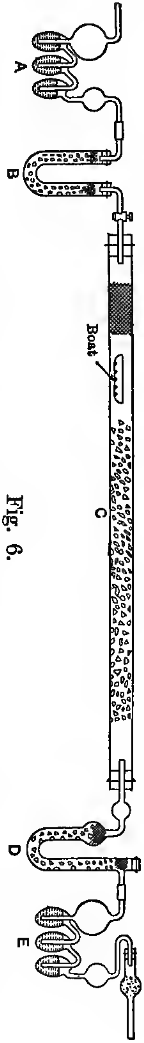


Fig. 6.

Fig. 6 is an outline sketch of the apparatus employed. The actual combustion is carried out in the long tube *C*, which is heated by a furnace not shown in the drawing. *D* is a tube containing calcium chloride which absorbs the water formed by burning the substance, while potassium hydroxide in *E* absorbs the carbon dioxide.

$$KOH + CO_2 = KHCO_3.$$

The tubes *A* and *B*, similar to *E* and *D*, serve to remove water and carbon dioxide from the air or oxygen used in the operation.

The difference between the weight of the calcium-chloride-tube *D* before and after the combustion must represent the weight of water formed by the oxidation of the sample. In the same way the difference in the weight of the potash-bulb *E* gives the weight of carbon dioxide formed in the combustion. From these data, the weights and percentages of carbon and hydrogen in the substance may be determined.

This may be made clearer by a specific example.

Suppose that 0.2 gram of an organic substance is burned in oxygen and that during the combustion the calcium-chloride-tube gains 0.12 gram in weight and the potash-bulb 0.2933 gram.

The gain in the calcium-chloride-tube means the formation of 0.12 gram of water. Now the formula for water, H_2O, indicates that it contains two parts of hydrogen by weight to sixteen of oxygen, or that the proportion of hydrogen which it contains is $\frac{2}{18}$ or $\frac{1}{9}$ of the whole. Now $\frac{1}{9}$ of 0.12 is 0.0133, which is the weight of hydrogen in the water formed in the combustion. This hydrogen is, however, the same hydrogen which was originally in the substance used for the analysis. The percentage of hydrogen in the latter must therefore be $\frac{0.0133}{0.2} \cdot 100$, or 6.66.

Similarly, the weight of carbon dioxide formed in the combustion is 0.2933 gram. The formula CO_2 shows that in carbon dioxide there are twelve parts by weight of carbon to thirty-two parts of oxygen, that is, the carbon constitutes $\frac{12}{44}$ or $\frac{3}{11}$ of the whole. $\frac{3}{11}$ of 0.2933 is 0.07999 gram carbon. Hence $\frac{0.0799}{0.2} \cdot 100$, or 40, is the percentage of carbon in the substance.

The method most generally used for the determination of nitrogen in an organic compound is based upon principles entirely similar to those underlying that employed for the determination of carbon and hydrogen. The carbon as before is burned to carbon dioxide, and the hydrogen to water, while the nitrogen is liberated as such. This gas is collected and measured. It is therefore necessary that no other gases should be present which cannot be conveniently separated from nitrogen. In practice, the combustion is accomplished entirely by means of copper oxide in an atmosphere of carbon dioxide.

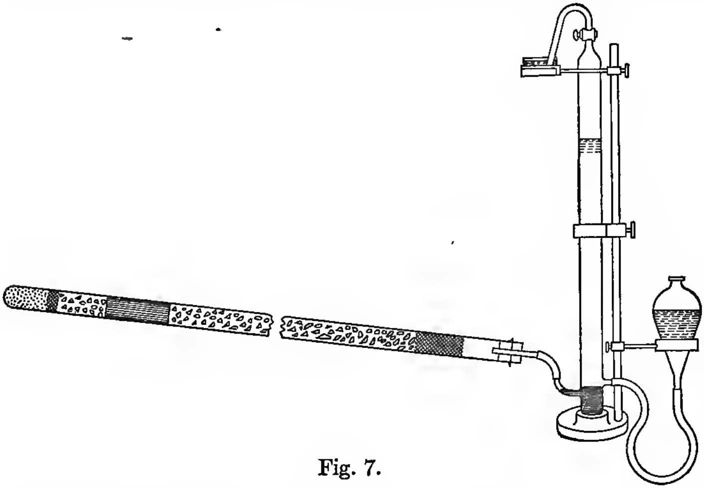


Fig. 7.

Fig. 7 shows the apparatus employed. The combustion tube is similar to that used in the determination of carbon and hydrogen, and it is filled in a similar way, but it is sealed at one end and here is placed some magnesite or manganese carbonate. Either on heating yields carbon dioxide which drives the air out of the tube. The gases now pass to a piece of apparatus called an azotometer, which permits the nitrogen to be collected while the accompanying carbon dioxide is absorbed in a strong solution of alkali. Later it is customary to transfer the gas to a graduated tube over water. The volume of nitrogen obtained is reduced to standard conditions of temperature and pressure and the result multiplied by the weight of one cubic centimeter of nitrogen under those conditions. This gives the weight of nitrogen in the sample, from which the percentage may be calculated.

To take a specific case, let it be supposed that 0.2 gram of an organic substance when treated as above yields 25.6 cubic centimeters of nitrogen at 20° and 782 millimeters pressure as observed by the barometer. This observed volume is reduced to standard conditions by means of the familiar formula $V_0 = \frac{pv}{760\ (1 + 0.00367\ t)}$ in which V_0 represents the volume the gas would occupy at 0° and 760 millimeters, v is the observed volume, t the observed temperature, and p the pressure. Here it has to be remembered that since the gas has been measured over water, the actual pressure under which it stands is equivalent to the atmospheric pressure as registered by the barometer minus the vapor tension of water at the prevailing temperature, in this case 782 minus 17; or 765 millimeters. Having substituted these values in the formula, the result shows that the nitrogen present would occupy 24 cubic centimeters at 0° and 760 millimeters. Under these conditions one cubic centimeter of nitrogen gas weighs 0.001254 gram. Twenty-four cubic centimeters will weigh 0.0301. Hence the percentage of nitrogen in the substance is 0.0301 ÷ 0.2, or 15.05.

When an organic compound contains one of the halogens or sulphur, their determination is effected by a method which also involves the complete oxidation of the carbon and hydrogen. In brief, this method consists in heating the substance in a sealed tube for several hours with fuming nitric acid at a temperature of about 300°. By this treatment, complete oxidation of the organic material is effected, and any sulphur present is oxidized to sulphuric acid. The latter can now be determined in the usual way, by precipitation with barium chloride, forming insoluble barium sulphate. If the substance contains halogen it is customary to seal up with it in the tube an excess of solid silver nitrate. The chlorine, bromine, or iodine is then found as the corresponding insoluble silver halide when the tube is opened. This is filtered off and weighed, subject to the ordinary precautions observed in analytical work. As the percentage of halogen in the silver compounds, as well as that of sulphur in barium sulphate, is readily derived from their formulæ, the calculation of the analyses offers no new difficulties and need not be further discussed here. For the complications which arise when two or more of the above elements are present at the same time, the student is referred to any work upon Quantitative Analysis.

A determination of the oxygen in an organic compound is never made in practice, on account of the lack of any satisfactory method. Instead the percentage of oxygen is obtained by difference, the percentages of the other elements being added together and the sum deducted from 100%. This practice has the serious objection, for one thing, that all the errors of experiment made in the analysis are thrown upon the oxygen. It has also happened in serious scientific investigation that the presence of an element has been entirely overlooked because its atomic weight happened to be a multiple of that of oxygen.

Calculation of the Empirical Formula.

Having obtained the percentages of the different elements in an organic compound, the next step is to determine from these data the empirical formula. This resembles in principle a problem in elementary arithmetic which may be stated thus: "In a pile of cannon balls weighing one hundred pounds, there are thirty pounds of ten-pounders, forty of five-pounders and thirty of two-pounders. How many of each kind of ball are there in the pile?" In this case the total weight of each kind of cannon ball is divided by the weight of one ball of that kind. Similarly, in the chemical problem, the weight of each element present is divided by the atomic weight of that element. There is this difference, however, in the two problems: the weights of the cannon balls are actual weights, while the atomic weights of the elements are relative quantities. The resulting quotients, therefore, in the latter case cannot be the actual number of atoms present in the molecule of the compound, but are simply quantities which stand to each other in the same ratio as those numbers. On this account it is just as well to divide the percentages of the elements by the atomic weights as to employ the actual weights, and in practice this is usually done.

As a concrete example, the case of the compound whose analysis was given on page 14 may be cited. It will be recalled that the analysis showed 40% carbon and 6.66% hydrogen. The sum of these deducted from 100% gives 53.34% oxygen. These percentages divided by the atomic weights of the respective elements yield quotients which stand to each other in the ratio of 1 : 2 : 1.

$$\left.\begin{array}{lrl} \text{C}\ldots\ldots & 40.00 \div 12 & = 3.33 \\ \text{H}\ldots\ldots & 6.66 \div 1 & = 6.66 \\ \text{O}\ldots\ldots & \underline{53.34} \div 16 & = 3.33 \\ & 100.00 & \end{array}\right\} \div 3.33 = \left\{\begin{array}{l} 1 \\ 2 \\ 1 \end{array}\right.$$

Hence it is obvious that a compound of the formula CH_2O would satisfy all the conditions imposed by the analysis. It is clear that these would be equally well satisfied by the formula $C_2H_4O_2$ or $C_3H_6O_3$. In fact, what the analysis of the compound has really given is the formula $(CH_2O)_n$, in which the value of n remains undetermined. This is called the empirical formula of the compound, because its value depends upon no hypothesis as to the nature of matter. No more can be learned from the analysis alone. In order to fix the formula of the compound more definitely it is necessary to determine the molecular weight. A compound of the formula CH_2O must have the molecular weight 12 + 2 + 16 = 30. $C_3H_4O_2$ represents a molecular weight of 24 + 4 + 32 = 60. Similarly the formula $C_3H_6O_3$ corresponds to a weight of 90; and so on. It follows that if a molecular weight determination had yielded the value 60, the formula of the compound would be fixed as $C_2H_4O_2$. This is known as the *molecular* formula of the compound, although it also is frequently spoken of as 'empirical,' in order to distinguish it from the *graphic* or *constitutional* formula.

Determination of the Molecular Weight.

It is fortunately possible to determine the molecular weight of a compound by methods which are based upon its physical properties and which are independent of the results of analysis. The method which is historically the most important, and may be considered the standard, is that based upon the determination of the vapor-density. The only theoretical principle involved is the hypothesis of Avogadro, which states that, under the same conditions of temperature and pressure, equal volumes of all gases contain the same number of molecules. For a full statement of the evidence upon which this important hypothesis is based, the student must be referred to works upon General and Physical Chemistry. Here a single fact will be recalled which has been verified by countless experiments, namely, that equal volumes of the more familiar gases have weights which stand to each other in the same ratio as the molecular weights of the respective compounds. Thus two grams of hydrogen, thirty-two of oxygen, twenty-eight of nitrogen, seventeen of ammonia, and forty-four of carbon dioxide, when measured at 0° and 760 millimeters pressure, all occupy nearly the same volume. This volume is called the molecular volume, and its numerical value is 22.4 liters, a number which it is worth while to remember.

A determination of molecular weight by the vapor-density method consists in volatilizing a known weight of the substance at a temperature well above its boiling-point, and measuring the volume of the gas produced under the conditions of the experiment. From this weight and the volume observed (after applying the proper corrections for temperature and pressure) a simple proportion gives the weight of substance which, in the gaseous state, would occupy a volume of 22.4 liters, and this, as we have just seen, is the molecular weight.

Returning to the case of the compound whose formula was derived on page 18, suppose that 0.1 gram of this substance, when volatilized, yields a volume of gas which, when reduced to 0° and 760 millimeters, would occupy 37.3 cubic centimeters. The following proportion then holds:

$$0.1 : 37.3 :: x : 22{,}400.$$

$$x = \frac{22{,}400}{37.2} = 60,$$

that is, 60 grams of the substance would occupy 22.4 liters, or 60 is the molecular weight of the compound.

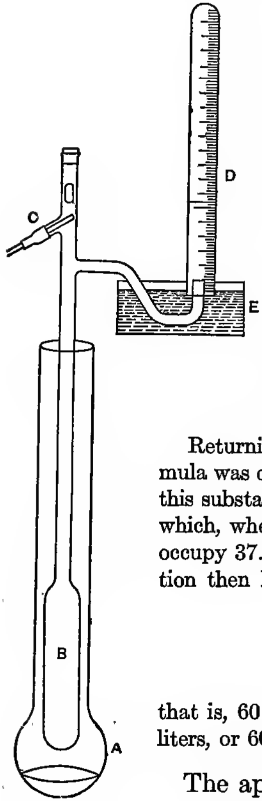


Fig. 8.

The apparatus almost universally employed for the determination of the vapor-density in practical organic work is that shown in Fig. 8. The bulb *B* is heated to a constant temperature by the vapor of a liquid boiling in *A*. The substance to be volatilized is then dropped in by means of the device sketched at

C. Its vapor assumes the volume corresponding to the temperature of *B* and forces out an equal volume of air into *D*. Inasmuch as the air is cooled from the temperature of the bath to the temperature of the room in the course of the transfer, the quantity measured does not represent the volume occupied by the substance at the temperature of the bath, but instead, the volume which the vapor would have occupied, had it been possible for it to exist in the gaseous state at the temperature of the room. This is a great convenience in practice, for it removes the necessity of knowing the exact temperature of the bath, and when this temperature is extremely high, it is not always easy to measure.

The result of the above experiment gives, then, the volume which a given weight of substance would occupy in the gaseous state at the temperature of the laboratory. From this the molecular weight may be calculated according to the methods already indicated. It should be added that the experimental method above outlined is not the most accurate one by which such determinations can be made. It is, however, the most convenient; and for the purposes of the organic chemist, the highest accuracy is not essential in work of this kind. For example, in the case already so frequently employed as an illustration (see page 19) it is only desired to decide between the molecular weights, 30, 60, 90, etc., and it is clear that a method whose experimental error amounted to several units would still be sufficiently accurate for this purpose.

It is obvious that vapor density determinations are only possible in the case of those substances which can be vaporized without decomposition. This applies to only a minority of organic compounds. It is therefore fortunate that molecular weights of substances can be determined in solution at lower temperatures. The fact that this is possible is due to certain analogies which exist between the gaseous state and the state of dissolved substances in solution. For a full account of these extremely important and interesting relations, the student must be referred to works upon Theoretical Chemistry. Here space only suffices for the statement of certain well-established facts which have a direct bearing upon the determination of molecular weights.

It is well known that when a liquid contains another substance in solution, the freezing-point of the solvent is thereby lowered; thus all know that salt water freezes at a lower temperature than fresh. What is, perhaps, not quite so familiar is the fact that, for dilute solutions at least, the depression thus caused is, for the same solute, proportional to the concentration of the solution, and, for different solutes, inversely proportional to their molecular weights. This is frequently stated in the form that equimolar solutions of different substances in the same solvent have the same freezing-point. What is meant by the term 'equimolar' may, perhaps, be best illustrated by a specific example. The molecular weight of cane sugar is 342, of glycerol 92, and of glucose 180. Now if weights of the three substances be taken which are proportional respectively to these three numbers, and dissolved in three equal quantities of water, then these three solutions will be equimolar, and will have the same freezing-point, which will be lower than that of pure water. Had some other solvent been used instead of water, the same would have held true, that is, the freezing-points of the three solutions would still have been equal. The depression of the freezing-point caused in the two solvents would, however, have been different, this constant being dependent upon the nature of the solvent used.

In order to have some numerical system for recording this property of the various solvents, the *molecular de-*

pression of the freezing-point has been defined as the number of degrees which the freezing-point of 100 grams of solvent is depressed by the addition of one mol (the molecular weight expressed in grams) of any solute. In the case of water, the numerical value of this constant is 18.5°. In the terms of the concrete example just mentioned, this means that the freezing-point of 100 grams of water will be depressed 18.5° by dissolving in it 92 grams of glycerol, and that the same effect would be produced by adding, instead, 180 grams of glucose or 342 of cane sugar.

In practice, it is customary to work with far less concentrated solutions. Let it be supposed, for example, that 0.4 gram of an unknown substance, when dissolved in 25 grams of water, is found to depress the freezing-point 0.2°. In the first place, it is obvious that a concentration of 0.4 gram in 25 is equivalent to 1.6 grams in 100. Since, now, 1.6 grams in 100 depress the freezing-point 0.2°, while the molecular weight in grams dissolved in 100 grams of solvent depresses it 18.5°, the molecular weight may be readily found by the simple proportion,

$$1.6 : 0.2 :: M : 18.5,$$

from which $M = 148$.

To put this in more general terms, if the weight of sample be designated by g, the weight of solvent by s, the observed depression by d, and the molecular depression by D, then the molecular weight, M, may be found by the equation,

$$M = \frac{100 \cdot g \cdot D}{s \cdot d}.$$

It should be stated that what has been said up to this point requires some qualification when applied to electrolytes, that is, to those substances like acids, bases, and salts, which, notably in aqueous solution, undergo dissociation into ions. Dissociation produces the same effect as the production of more molecules in the solution. The results obtained by the above method are therefore not directly available for finding the molecular weights of electrolytes, unless they can be controlled by independent determinations of the degree of ionization.

The apparatus employed for determining the molecular weights by the freezing-point method is shown in Fig. 9. It consists of a large test-tube *A*, into which dips a thermometer *C*. *A* is surrounded by a bath *B*, which is kept at a temperature slightly below that of the freezing-point of the solvent used. Both vessels are provided with stirrers in order to maintain a uniform temperature. The thermometer used for this work is of special construction. It has an arbitrary scale so graduated that differences of temperature amounting to only $\frac{1}{1000}$° can be estimated from it. When a molecular weight is to be determined, a quantity of the solvent is weighed out into *A*, the temperature of the apparatus is lowered, and the freezing-point of the pure solvent determined. A weighed portion of the substance to be investigated is then added, and the freezing-point again determined. The difference between the readings is the observed depression. All necessary data for the determination of the molecular weight are now at hand.

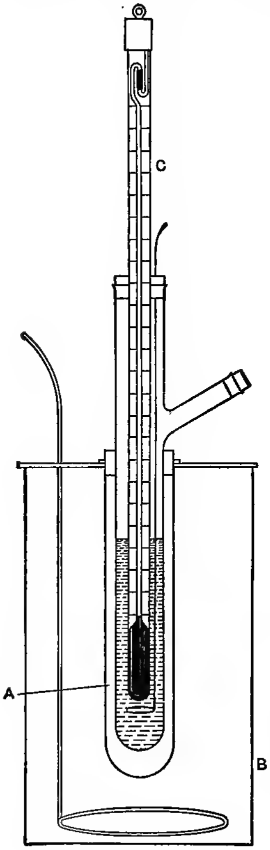


Fig. 9.

It is well known that the presence of a dissolved substance not only depresses the freezing-point of a liquid, but also elevates its boiling-point. This fact has also been made use of for the determination of molecular weights. The method needs no extended discussion here, however, for everything which has been said concerning the one property applies equally well to the other, and the apparatus used is constructed in a manner entirely analogous.

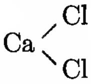
The Graphic Formula

In the preceding pages it has been shown how the molecular formula of a compound could be established from the results of a qualitative and quantitative analysis combined with a determination of the molecular weight. It might at first appear that when this had been accomplished the compound studied would have been thoroughly identified. In the case of organic compounds this is not so. In Inorganic Chemistry such formulæ as H_2O, NH_3, and H_2SO_4 present to the mind certain definite compounds whose properties are familiar. How far this is from being the case in the organic field is best shown by stating the fact that for as simple a formula as $C_4H_6O_3$ there are 26 compounds known to which it applies, and these all differ among themselves in physical properties and chemical behavior. In the case of a formula no more complicated than $C_{10}H_{16}$ it is found that no less than 195 existing compounds are entitled to it. When, as in these cases, two or more substances have the same molecular formula they are called *isomers*, and the relationship itself is known as *isomerism*. It will be obvious that it would be highly desirable if formulæ could be so written that a distinction might be drawn between these different isomers, for only in this way could serious confusion be avoided. It has been found possible to do this by making the fundamental assumption that the difference in properties exhibited by isomers — since it cannot rest upon any qualitative or quantitative difference in their composition — must be due to a difference in the internal arrangement of the atoms within the molecules. Working upon this basis, it has proved possible to formulate compounds in such a way as not only to distinguish the different isomers in a group, but also to give a picture of the whole chemical character of the compound represented. Symbols of this kind are called graphic or constitutional formulæ. By their aid it has been found possible to predict with considerable certainty the properties of compounds as yet unknown, and to devise methods for their actual preparation.

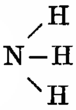
Since neither atoms nor molecules can be subjected to direct observation, it may well be asked how a knowledge of their arrangement is possible. An attempt will be made to deal with the general aspects of this question in the final chapter of the book, when the student has become acquainted with the use of graphic formulæ and their interpretation, and is therefore better prepared than at present for a critical discussion of this interesting subject. Here it is sufficient to state that the object of a graphic formula is not, essentially at least, to picture for us how the smallest particles of matter may be mechanically constructed, but rather to assist us in remembering, recording, and understanding the way in which chemical reactions take place between organic compounds. With this idea well fixed in mind, we may now pass over to a consideration of those fundamental assumptions upon which constitutional formulæ are based. These, on their face at least, suggest a highly mechanical conception of the nature of matter. They are the Atomic Theory and the Valence Theory. Both of these are more or less familiar to the student of Inorganic Chemistry, but it will not be out of place, for the purposes of the present application, to restate them briefly here.

It is assumed by these theories that matter is made up of minute particles called molecules, these being the smallest units which can exist and yet retain the properties of the substance of which they are components. It is further generally assumed that for a given substance the molecules are alike in mass and volume. The molecule, in its turn, is made up of atoms. These are extremely small portions of the elements which may be looked upon as the units of chemical combination. Like the molecule they are regarded as being, for a given element, of equal mass and volume. They are bound together by the force of chemical affinity, acting along or through the agency of certain points of union or attraction, whose number varies with the individual element, and which are variously known as 'valencies,' 'bonds,' 'linkings,' and the like. The atom then, is to be thought of as a minute particle of matter — perhaps spherical — having upon its surface certain points by means of which it may be attached to other atoms. The student may think of a kind of magnetic pole. This, however, is only an analogy, for the number is not limited to two as in the case of true magnets, nor has it been found possible to ascribe to certain ones a positive, and to others a negative polarity, though speculative attempts in this direction have been frequently made.

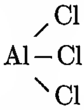
The number of valencies which belong to each atom depends upon its nature and is determined in practice by a study of the composition of the more simple compounds which the element forms with other elements. Hydrogen is taken as the standard and to it is assigned the valence of one. Any other element of which one atom will unite with one atom of hydrogen to form a saturated compound (see page 32) is also given a valence of one. This is the case, for example, with the halogens which form with hydrogen the compounds, HCl, HBr, and HI. Those elements are said to have a valence of two, of which one atom unites with two atoms of hydrogen or of the halogens; thus we have the compounds,

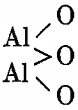
$H - O - H$ and 

calcium and oxygen being bivalent. It follows that all valencies will be satisfied when one atom of a bivalent element unites with one of another bivalent element as in the compound, $Ca = O$. Similarly a trivalent element is one whose atoms possess three points of attachment. Compounds will then be possible which contain one atom of a trivalent element to three of a univalent element, one atom each of two trivalent elements, or three of a bivalent combined with two of a trivalent element. Thus nitrogen, boron, and aluminium are classified as trivalent elements, and we have such compounds as are represented by the following formulæ:

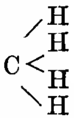


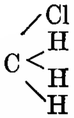
$B \equiv N$

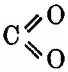


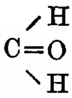


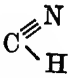
Carbon is the most convenient example of an element with a valence of four, and this is illustrated by the following formulæ:





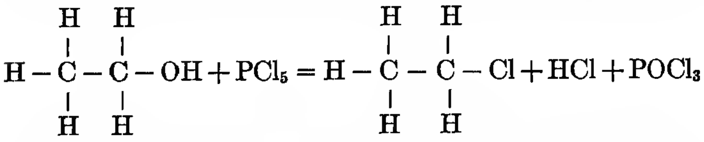






It sometimes happens that, on account of the different compounds which it forms, an element must be assigned a variable valence. Nitrogen, for example, forms certain compounds in which it appears to have a valence of five, whereas, in the majority of cases, as we have already seen, it is customary to ascribe to it a valence of three. Variable valence has been met with so constantly in Inorganic Chemistry that the whole valence theory has been thereby considerably weakened, and in that department of the science its usefulness has proved comparatively limited. In Organic Chemistry, on the other hand, we have, in practice, little to do with any other elements than carbon, hydrogen, oxygen, and nitrogen. The first three rarely show chemical behavior which suggests the possibility of variable valence, while in the case of nitrogen this usually occurs in certain well-understood circumstances intimately associated with the physical and chemical properties of the compounds involved. The student, therefore, need for the present only remember that carbon has the valence four, hydrogen one, oxygen two, and nitrogen three and sometimes five. These four points well fixed in mind, in such a manner that they can be readily and constantly applied, will go far toward making the approach to the detailed study of Organic Chemistry an easy matter.

A word should be added concerning the way in which atomic arrangement is deduced from, or associated with, chemical behavior. Here, again, we are guided by assumptions, which have, however, justified themselves in practice. The chief of these is that when in any chemical reaction an element or group is substituted by another, the substituting atom or group attaches itself to the same carbon atom to which the substituted element or radicle was originally united. This may be illustrated by the following equation:



$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-OH+PCl_5=H-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-Cl+HCl+POCl_3$$

In this case oxygen and hydrogen leave an organic compound and chlorine enters it. If now the original compound had the constitution represented, the formula of the product is thereby determined, the chlorine being represented as taking the place in the organic molecule which was vacated by the hydroxyl group.

It is freely conceded that all these assumptions concerning the arrangement of the atoms within the molecules are themselves highly hypothetical, and never have been, and perhaps never can be, susceptible of proof by direct observation. Considered, however, as a working hypothesis, the valence theory has proved one of the most fruitful in Natural Science. Historically, the whole subject of Organic Chemistry has been developed upon this basis, and the organic chemist habitually thinks in these terms. It is, therefore, essential that the student should, at the outset, familiarize himself with this point of view, and accustom himself, from the start, to associate every chemical reaction of an organic compound with its graphic formula. It may further be added that this method of study will be found an invaluable aid to the memory, and will make easy what might otherwise become a difficult subject.

The student is particularly warned against attempting to memorize empirical or molecular formulæ. This is a temptation under whose influence those unfamiliar with the subject are especially likely to fall. Empirical formulæ have their uses for the professional as long as no others are available, but the beginner should pay them absolutely *no attention.* They are all so similar in form as to be practically impossible to remember, and, as has already been pointed out, the same formula applies to so many different substances that it is ambiguous in meaning, and therefore, even if memorized, entirely useless to the student. When, for any reason, such formulæ are desired, they can always be derived at a moment's notice from the graphic formulæ. The latter, because they take up more room, often appear more formidable to the beginner, but if he will, at the outset, learn to associate them with chemical behavior, he will be astonished to see how many will cling to his mind without effort.

CHAPTER II.

THE SATURATED ALIPHATIC HYDROCARBONS.

ORGANIC compounds are usually divided into two great classes, called respectively *aliphatic* and *aromatic* compounds. Unfortunately, it is not possible to give any adequate definition of either of these words at this point. Both illustrate very well something which will frequently be found exemplified in the nomenclature of Organic Chemistry. Certain groups of compounds or phenomena acquire names founded upon some outstanding characteristic, either of the group or of some prominent member. Later, with the rapid growth of the science, the name comes to be used in such a way as to include a much larger number of objects, and, on account of other characteristics which these possess, the name itself acquires a meaning quite foreign to its original one. For example, the word 'aromatic' was originally given to a group of compounds which possessed an odor to which this adjective might be appropriately applied. Later, there came to be classed with these, on account of analogies in chemical behavior, other compounds which did not have this odor. Gradually the word 'aromatic' became more associated with the chemical properties of the larger group than with anything else, and it is only in this latter sense that it is now employed in Organic Chemistry. It is the same with the word, 'aliphatic.' This is derived from the Greek word ἀλίφη, meaning 'fat,' and was originally applied to those substances which were chemically closely allied to the fats. At the present time, however, although the fats are still classed among the aliphatic compounds, they can no longer be considered as the most important members of the group, nor, indeed, as being typical, either in point of physical properties or chemical behavior. In short, the names have become outgrown, and as they have remained in use, they have been forced to become conventional symbols for ideas not associated with their original significance. Something similar is, of course, to be met with almost everywhere in the history of words, but in the development of Organic Chemistry the changes of meaning have been more rapid, perhaps, than almost anywhere else.

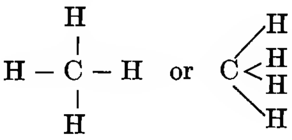
From what has been said, the student must not get the idea that such words as 'aliphatic' and 'aromatic' have become meaningless. On the contrary, they convey many ideas concerning chemical character and behavior which make them extremely useful and significant. These ideas cannot, however, be appropriately set forth in this place. Those substances first taken up in our detailed study will be aliphatic compounds. The student will note that their most general characteristic lies in the fact that their formulæ possess open chains of carbon atoms as distinguished from closed chains or rings. When the aromatic compounds come up for discussion, the more important differences between the classes will be dealt with.

Organic compounds are also classified as *saturated* and *unsaturated.* The fundamental idea underlying the classification is that an unsaturated substance forms addition products just as nitric oxide adds oxygen to form a nitrogen peroxide. This behavior makes it clear that in nitric oxide the whole affinity of nitrogen for oxygen was not brought into play, hence this substance may well be called unsaturated. In organic chemistry it is customary to limit the significance of the term to the carbon, and to define a saturated compound as one in which the combining capacity of carbon is completely utilized.

It is usual to begin the study of organic compounds with the hydrocarbons. These substances contain only the two elements carbon and hydrogen. Their structure is, in some respects, more simple than that of most of the other classes, and this makes it possible to regard them as types from which the other classes may be derived by substitution. On this account the hydrocarbons serve as the basis for a system of nomenclature. For these reasons it is appropriate that they be taken up at the beginning, although the establishment of their constitution may, at times, anticipate a slight knowledge of other classes not yet considered.

There are several kinds of hydrocarbons. The only class which will be considered at present is the one which is named, from its simplest member, the methane series. It is also frequently called the paraffin series (from the Latin *parum affinis* — without affinity).

Methane, as shown by its density and the results of analysis, has the empirical formula CH_4. When it is recalled that carbon shows the valence four and hydrogen one, it is evident that this compound is the simplest saturated one which could be formed by the two elements. Its constitution would therefore be appropriately expressed by the formula:



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

the direction assumed by the various valencies in space being considered, for the present, as a matter of indifference.

Methane is also known under the name of 'marsh-gas' and, as this name indicates, it is sometimes formed by the slow decay of organic matter under water at the bottom of stagnant pools. It is also formed in large quantities in the distillation of coal. The gas which is manufactured in this manner for illuminating purposes contains on the average about 35% of methane, the other chief constituent being hydrogen. Since it is formed by the heating of coal, methane is naturally met with in coal-mines, where it has received from the miners the name of 'fire-damp,' on account of the serious explosions which take place when a mixture of the gas with air is accidentally ignited.

Methane is one of the organic products formed when carbon is heated in an atmosphere of hydrogen at a temperature of 1200°, and this fact, while of no technical importance, is interesting because it shows how this simple hydrocarbon may be synthesized from its elements. It will be seen later that many other organic compounds can be prepared from methane.

Other methods of formation, a little less direct, are the reduction of carbon monoxide by hydrogen in the presence of metallic nickel:

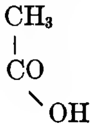
$$CO + 3\,H_2 = H_2O + CH_4,$$

and the reaction between hydrogen sulphide, carbon bisulphide, and metallic copper at red heat:

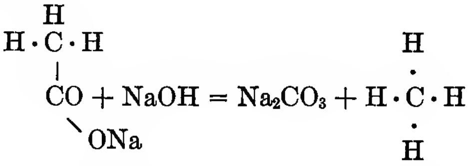
$$CS_2 + 2\,H_2S + 8\,Cu = CH_4 + 4\,Cu_2S.$$

As carbon bisulphide and hydrogen sulphide can be obtained directly from the elements, this constitutes an indirect synthesis of methane.

In the laboratory, methane is usually prepared by heating sodium acetate with soda-lime. Inasmuch as this method is very generally applicable in similar cases, it should be given close attention. Acetic acid has the constitution,



as will be shown later, and if its sodium salt is heated with sodium hydroxide, sodium carbonate is formed and methane is evolved:



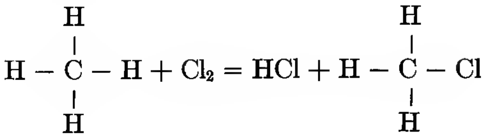
$$\begin{matrix} \mathrm{H} \\ \mathrm{H}\cdot\mathrm{C}\cdot\mathrm{H} \\ | \\ \mathrm{CO} \\ \diagdown\mathrm{ONa} \end{matrix} + \mathrm{NaOH} = \mathrm{Na_2CO_3} + \mathrm{H}\cdot\overset{\overset{\mathrm{H}}{\cdot}}{\underset{\underset{\mathrm{H}}{\cdot}}{\mathrm{C}}}\cdot\mathrm{H}$$

This is a perfectly general reaction; that is, it is almost always possible to prepare a hydrocarbon by heating with an alkali the salt of a certain acid containing one more atom of carbon than the hydrocarbon sought.

Methane is a colorless gas which can be condensed to a colorless liquid by cooling with liquid air at ordinary pressure. The liquid thus produced boils at −164°. By evaporating it under diminished pressure, sufficient cold is produced to cause partial solidification. The gas burns with a scarcely luminous flame, and, as has already been noted, forms explosive mixtures with air and oxygen.

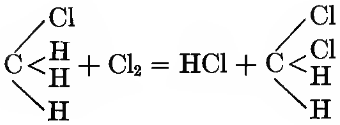
Of the chemical properties of methane it may be said that, except for the fact that it burns in air and oxygen, it is rather inert, being little affected by most ordinary reagents such as concentrated or dilute acids or alkalies. One reaction, however, is of all the more importance, namely, that which takes place with chlorine. The reaction is general and typical. In the dark, the gases react but slowly, while in sunlight the action may become so rapid as to produce explosion. The products formed are a mixture of hydrochloric acid with a series of derivatives of methane which contain chlorine instead of hydrogen. The formation of these compounds may be represented by the following equations:

(1)

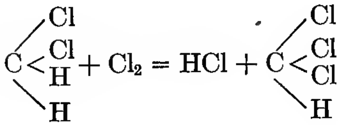


$$\begin{array}{c}H\\|\\H-C-H\\|\\H\end{array}+Cl_2=HCl+\begin{array}{c}H\\|\\H-C-Cl\\|\\H\end{array}$$

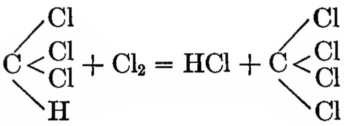
(2)



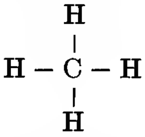
(3)



(4)



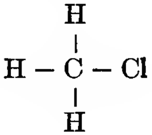
These equations represent a type of reaction extremely common in Organic Chemistry. It is known as *substitution.* As was pointed out in the preceding chapter, it is practically always assumed in such cases that the substituent (in this case chlorine) takes the place just vacated by a hydrogen atom in the organic molecule. It has already been pointed out that methane has the constitution,



$$\begin{array}{c}H\\|\\H-C-H\\|\\H\end{array}$$

that is, that all of the hydrogen atoms are directly connected to carbon. It will therefore be well to remember that capacity for substitution by chlorine is a property quite generally found associated with hydrogen connected directly to carbon.

A few of the properties of the compounds formed by the above reactions may profitably receive some attention at this time. The names, in particular, should be noted carefully, as they illustrate principles constantly applied in organic nomenclature. The product of the first reaction is a methane in which one of the hydrogens has been replaced by chlorine. An appropriate name for the compound is, therefore, *chloromethane*. Another name which is more commonly used should also be mentioned. The combination CH_3 (methane less one hydrogen) is a grouping of the elements which occurs very frequently in the formulæ of organic compounds. It is, therefore, extremely convenient to have a name for this group. It is called *methyl*. Now the compound



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

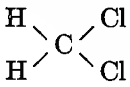
may be looked upon as a binary compound of the radicle methyl with chlorine. It is therefore called *methyl chloride*.

At this point, the student makes his first acquaintance with a peculiarity of Organic Chemistry which he is to meet with constantly in his study of the subject, namely, that one and the same compound may have a number of different names which, if not all applied with equal frequency, are nevertheless all equally correct. The beginner is apt to look upon this as a difficulty and a stumbling-block. Even a limited acquaintance with the subject, however, soon convinces him that it is a matter of great convenience, as it helps him to look at chemical compounds from several points of view, each of which may be associated with a different name for the substance concerned, according to the particular relationship which it is desired to emphasize. It is believed that this will in general be found an aid to the memory rather than the reverse.

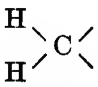
Of the properties of methyl chloride, the only ones to which it is desired to call attention at this time are that it is a gas, and that its halogen atom is quite reactive, that is, it is subject to various metathetical reactions which will be studied more in detail later. Methyl chloride being a gas, it is not very convenient to work with, but the corresponding iodide, which is a liquid, finds constant application in every organic laboratory for the introduction of methyl groups into organic compounds.

This compound is not prepared by the action of iodine upon methane, but from methyl alcohol by another method which cannot be profitably discussed at this point. It should, however, be stated that the hydrocarbons of the methane series may in general be substituted by the direct action of chlorine and bromine, while with iodine this is not practicable.

The next product of the reaction of chlorine upon methane

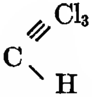


may, in accordance with the principles already laid down, be called either dichloromethane or, more commonly, methylene chloride, 'methylene' being the name commonly used for the bivalent radicle,



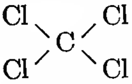
This word is, however, by no means so frequently met with as 'methyl.' Methylene chloride is a colorless oil boiling at 40° and has no further interest for us here.

The third product,



might appropriately be called trichloromethane, but it is universally known as chloroform, a name given it before the valence theory was invented. The importance of this substance as an anæsthetic is familiar to all. Its properties and the technical method for its preparation will be dealt with later.

The final product of the action of chlorine upon methane is

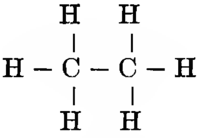


carbon tetrachloride or tetrachloromethane, a methane in which all the hydrogens have been substituted by chlorine. It is a heavy oil boiling at 78.5° which is very useful as a solvent. It has also found use as a non-combustible cleansing material and as a fire extinguisher.

None of these compounds is ever prepared technically in the manner indicated. The action of chlorine upon methane is too difficult to control, and leads to the formation of mixtures which are not easy to separate. The reaction is, however, of great theoretical importance, and the compounds formed have been mentioned here, partly because some of them are employed in reactions which we shall soon have occasion to study, and partly to illustrate two common methods of naming organic compounds. In accordance with the first, substitution-products are named by prefixing to the name of the substance which serves as a type the name of the substituting atom or group. This is illustrated by the name 'chloromethane.' According to the second, the formula of the compound is divided, more or less arbitrarily, into radicles, and named as if the latter were its essential components. Thus the name 'methyl chloride' would indicate that the compound it represents was a binary compound of the radicle methyl with chlorine.

In addition to the names based upon chemical constitution, there remain in use a large number of special names which were applied to well-known compounds before the introduction of the valence theory, and which it has not been found possible in practice to replace by more formal scientific terms.

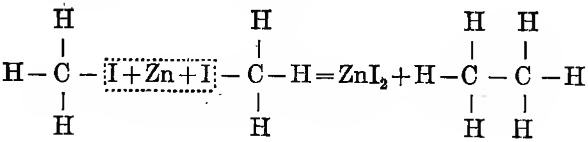
Ethane. If one of the hydrogen atoms in the formula of methane be replaced by a methyl group or (what amounts to the same thing) if two methyl groups be written as directly joined together,



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

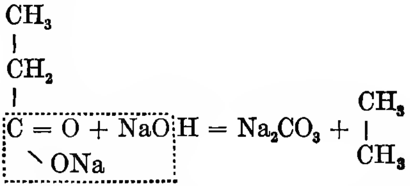
the formula obtained is that of the next hydrocarbon in series, called ethane.

One method for the preparation of this compound serves to establish the constitution which has just been suggested, for if methyl iodide is treated with zinc, a reaction takes place in the sense of the following equation:



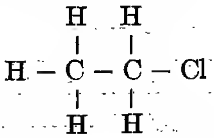
$$\begin{array}{ccccccccccccccc} & & H & & & & H & & & & & H & & H & \\ & & | & & & & | & & & & & | & & | & \\ H & - & C & - & \boxed{I+Zn+I} & - & C & - & H = ZnI_2 + H & - & & C & - & C & - H \\ & & | & & & & | & & & & & | & & | & \\ & & H & & & & H & & & & & H & & H & \end{array}$$

and ethane is formed. Of the properties of ethane little need be said which would not be a repetition of the most essential things which have been said concerning methane. This also is a gas which can be liquefied at a temperature of 4° under a pressure of forty-six atmospheres. It may be prepared by distilling sodium propionate with soda-lime, in a manner entirely analogous to the preparation of methane from sodium acetate:



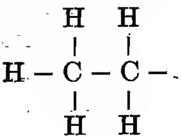
$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ C = O + NaO|H = Na_2CO_3 + \begin{array}{l} CH_3 \\ | \\ CH_3 \end{array} \\ \quad \diagdown ONa \end{array}$$

When treated with chlorine, all of the hydrogen atoms may successively be substituted by that element. The products of this reaction need not be further discussed here except to note that, in names and properties, they are in every way analogous to the corresponding derivatives of methane. The first substitution product has the formula,



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

and is called ethyl chloride, *ethyl* being the name given to the important radicle,

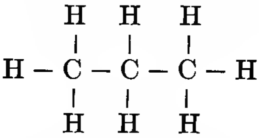


$$\begin{array}{cccccc} & & H & & H & \\ & & | & & | & \\ H & - & C & - & C & - \\ & & | & & | & \\ & & H & & H & \end{array}$$

This stands in the same relation to ethane as methyl does to methane. Ethyl bromide and iodide are very important reagents in the laboratory.

Up to this point, the term 'methane series' has been employed several times without any definition being offered. A comparison of the compounds methane and ethane gives opportunity for a partial explanation. The formula of ethane may be derived from that of methane by substituting one hydrogen atom in the latter by a methyl group. Two compounds whose formulæ stand in the same relation to each other which that of ethane does to that of methane are called *homologues,* and a series of such compounds, in which the successive members stand in the same relationship, is spoken of as a *homologous series.* The student will become acquainted with many such series in the study of Organic Chemistry. The methane series, then, is made up of all those compounds whose formulæ may be derived from methane by the successive substitution of methyl for hydrogen. A moment's thought will show that the number of members in such a series must be, theoretically at least, indefinitely large; and further, that since each member contains one carbon and two hydrogens more than the preceding, the empirical formula of any member of the methane series will correspond to the expression, C_nH_{2n+2}, in which n represents the number of carbon atoms. The members of such homologous series strongly resemble each other both in physical properties and chemical behavior. This is a great convenience for the student, since it enables him to get a good idea of the chemistry of a whole series of compounds by the detailed study of a few members. It is too early to discuss the various properties of homologous series in detail, but speaking generally it may be said that as the molecular weight increases, the compounds are found to have higher melting- and boiling-points and to be more inert in their chemical behavior. These statements require some qualification, but the more important exceptions will be touched upon later as examples arise.

Propane. If one of the. hydrogens in the formula of ethane be substituted by a methyl group, the formula of propane, the next member of the methane series, is obtained:

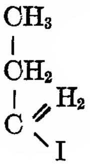


$$\begin{array}{ccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$

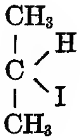
This hydrocarbon may be prepared by heating sodium butyrate with soda-lime in a manner entirely analogous to that described already for the preparation of methane and ethane. It is a gas at ordinary temperatures, but can be more easily liquefied than the two substances just mentioned. To these it shows the closest analogy in all its properties, physical and chemical.

An examination of the formula of propane shows that if one hydrogen be replaced by halogen the substitution can be made in two different ways, according as the hydrogen replaced belongs to a carbon atom at the end or in the middle of the chain. On making such a substitution there would result in the two cases the two following formulæ, for the iodine compound for example:

(1)



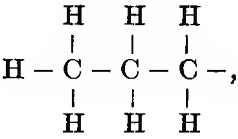
(2)



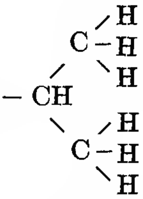
Now as a matter of fact there are two compounds known, both of which, as the analysis and molecular weight determinations show, have the empirical formula of an iodopropane, C_3H_7I. The student will recall that compounds thus related are called isomers, and since this is the first case of isomerism which he has thus far encountered, it will be well to take up at this point the nomenclature of isomers of this kind. The two compounds whose formulæ have just been given are distinguished as 'primary' and 'secondary' propyl iodide, or perhaps more commonly as 'normal' and 'iso'-propyl iodide. The meaning of these words should be made clear at once, as they are of constant occurrence in Organic Chemistry. A primary carbon atom may be defined as one which is directly attached to not more than one other carbon atom, and a secondary carbon atom is one which is directly attached to two others while those linked to three and four others are called respectively tertiary and quaternary. In the formula of propane the carbon atoms at the end of the chain are primary, the one in the middle is secondary. Turning to the formulæ of the iodine substitution products, it will be seen that in (1) the iodine is attached to a primary, in (2) to a secondary carbon atom. This accounts for the names primary and secondary propyl iodide.

As was pointed out above, the two compounds are also distinguished as normal propyl iodide and isopropyl iodide. In Organic Chemistry, the word 'normal' indicates that the formula of a compound can be written in such a manner that all its carbon atoms shall form parts of one straight chain without arms or branches. The prefix 'iso' is unfortunately less easy to define, because it has been applied rather indiscriminately to compounds of different types, to indicate a less important isomer. Among the simpler compounds of the aliphatic series, however, the prefix is quite uniformly employed to designate a substance whose formula has a secondary propyl group at the end of the chain. This is well seen, for example, in the formula of isobutane on page 45, and in that of isoamyl alcohol on page 69.

The student now has the names and formulæ of two more important radicles to remember. They are *normal propyl*,



$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-$, and *isopropyl*,



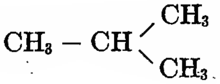
$-CH\begin{matrix}\diagup C\begin{matrix}\diagup H\\ -H\\ \diagdown H\end{matrix}\\ \diagdown C\begin{matrix}\diagup H\\ -H\\ \diagdown H\end{matrix}\end{matrix}$

All that has thus far been said serves only to distinguish between the *formulæ* of two possible compounds, C_3H_7I. No answer has thus far been given to the more important question of which formula belongs to each of the two actual compounds. This has been satisfactorily decided, but the answer must be postponed until the corresponding alcohols have been taken up. In studying the next hydrocarbons of the series, the butanes, we shall meet with an instance of isomerism in which it will be possible to apply the formulæ theoretically derived to the actual compounds at once.

Before leaving the halogen derivatives of propane, it should be stated that propane is the highest member of the marsh-gas series in which all the hydrogens can be directly substituted by chlorine without causing a break in the carbon chain. When butane and its higher homologues are exhaustively chlorinated, the result is a mixture of varying proportions of tetrachloromethane, CCl_4, and hexachloroethane, C_2Cl_6.

The Butanes. It has just been shown that one halogen atom can be substituted for hydrogen in the formula of propane in two different ways. The same holds true for substitution by the methyl group. This leads to the two following formulæ:

(1) $CH_3-CH_2-CH_2-CH_3$. (2)



$CH_3-CH\begin{matrix}\diagup CH_3\\ \diagdown CH_3\end{matrix}$

It is obvious that formula (1) is that of normal butane. The other, containing the forked chain, is that of isobutane. Further inspection of this formula shows it is that of a methane in which three of the hydrogens have been substituted by methyl groups. This leads to the name *trimethylmethane.* This latter method of naming hydrocarbons should be carefully noted, for it is frequently used when dealing with complicated formulæ.

Turning now from the formulæ to the compounds themselves, it is found that there exist two hydrocarbons which have the molecular formula C_4H_{10}. Both are gases which can readily be condensed. In one case the liquid thus formed boils at 1°, in the other at −17°. The two liquids have different specific gravities. It is necessary to decide which of the formulæ discussed above applies to each of the hydrocarbons. This has been determined in the following way. If ethyl iodide is treated with zinc, zinc iodide is formed and that butane which boils at 1°. Now the only butane which can be formed by the reaction is the normal compound, as will be seen by inspection of the following equation:

$$CH_3 \cdot CH_2I + Zn + ICH_2 \cdot CH_3 = \\ ZnI_2 + CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_3.$$

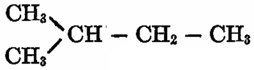
It follows that the butane which boils at 1° is the normal compound, while that which boils at −17° must have the structure of trimethylmethane. The latter formula is also supported by positive evidence, the details of which it would not be profitable to introduce at this point.

The kind of argument just employed may be regarded as typical of the manner in which the constitution of organic compounds is established in practice. Since this is the first case of the kind which the student has met, it may be worth while to analyze the last equation a little more in detail. Ethyl iodide can only have the formula ascribed to it because whichever one of the hydrogens in ethane is substituted by halogen, only one compound can result, the hydrogens in ethane being all exactly equivalent. When the iodine atoms are removed by the action of the zinc, the free ethyl groups thus formed unite by those bonds which formerly held the iodine atoms. The two ethyl groups set free can unite with each other in no other way than to produce a compound with a normal chain of carbon atoms.

The Pentanes. The hydrocarbons of the methane series having the general formula C_5H_{12} are called pentanes. Three graphic formulæ are possible on the basis of the valence theory, and there are three hydrocarbons actually known. By processes of reasoning and experiment analogous to those employed in determining the constitution of the two butanes, the possible formulæ have been distributed among the pentanes as follows:

Normal pentane $CH_3 - CH_2 - CH_2 - CH_2 - CH_3$ boiling at 36°,

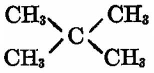
Dimethylethylmethane



$(CH_3)_2{>}CH - CH_2 - CH_3$

boiling at 30°,

Tetramethylmethane



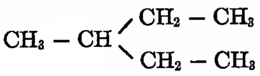
$(CH_3)_2{>}C{<}(CH_3)_2$

boiling at 9°.

The Hexanes. For the formula C_6H_{14} the theory accounts for the existence of five different compounds, and five hydrocarbons are known. These are distinguished as follows:

Normal hexane $CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$ boiling at 89°,

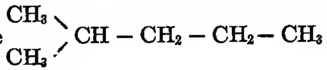
Methyldiethylmethane



$CH_3 - CH{<}(CH_2 - CH_3)_2$

boiling at 64°,

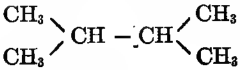
Dimethylpropylmethane



$(CH_3)_2{>}CH - CH_2 - CH_2 - CH_3$

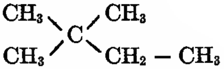
boiling at 62°,

Dimethylisopropylmethane



boiling at 58°,

Trimethylethylmethane



boiling at 49.6°.

This list is not given because of the intrinsic importance of the compounds themselves. They are, on the contrary, very unimportant, and the student could hardly make a worse use of his time than in memorizing these names and boiling-points. On the other hand, it would be an excellent exercise in the application of the valence theory for the student to write the graphic formulæ of all the possible heptanes, C_7H_{16}, and to construct rational names for each.

The value of the list is that it serves to illustrate several important properties of the methane series and of homologous series in general. As already indicated, it holds true for compounds of analogous constitution, — the normal hydrocarbons for example, — that the boiling-points rise as the molecular weight increases. Among isomers the normal compounds have the highest boiling-points, while those with the most forked chains, in general, have the lowest. Thus in the case of the hexanes, it will be noticed that the one with the lowest boiling-point contains a quaternary carbon atom, while the next lowest contains two tertiary carbons. It is generally true that those hydrocarbons which have the normal structure and those which contain quaternary carbon atoms are the most indifferent chemically, whereas the presence of a tertiary carbon atom seems to be associated with greater chemical reactivity. It will have been already noticed that the number of possible isomers increases rapidly with an increase in the number of carbon atoms. This is strikingly illustrated by the fact that for the general formula $C_{13}H_{28}$ there are no less than 802 isomers theoretically possible. Not to discourage the beginner, it should be stated at once that only one is at present known. It is the same with most of the higher formulæ. Chemists have not found it worth while to attempt the preparation of all these compounds, since their properties, as far as can be judged from analogy, would possess little individual interest. The methane series is not infinite in extent. The highest empirical formula belonging to the series which can boast an actual hydrocarbon to represent it is $C_{60}H_{122}$. The properties of this compound, however, show nothing to lead us to suppose that still higher members might not be prepared. This substance, which is called *hexacontane*, is supposed to have the normal structure, though the proof is not quite complete. At all events the idea of a molecule containing sixty carbon atoms in a single chain furnishes food for reflection, although speculations of this kind must be deferred for the present.

Turning now to the physical properties of the compounds actually known, it will be seen by the list of boiling-points already given that one of the pentanes and all members of the series containing less than five atoms of carbon are gases at ordinary temperature. Those which contain from five to seventeen carbon atoms are liquids, while the normal hydrocarbons with more than seventeen atoms of carbon — and in the higher series the normal hydrocarbons are practically the only ones known — are solids. All are colorless when pure. They are lighter than water, the specific gravity of the solid and liquid members ranging from 0.45 to 0.78, and increasing slightly with the molecular weight. All are insoluble in water and more or less soluble in alcohol and ether. The different members of the series are miscible with each other, the liquids dissolving both the gases and the solids. Ordinary paraffin is a mixture of the higher solid members of the series, and its chemical inertness has extended the use of this name to cover the whole class. In spite of the name, there have been discovered in recent years quite a number of reactions in which these hydrocarbons take part, but it still holds true that they belong to the less reactive organic substances. The student will have an entirely adequate idea of their chemical behavior if he will recall that they are, for the most part, quite indifferent toward all reagents except chlorine and bromine.

The names of the hydrocarbons of this series deserve a word of comment. After the first four members the names are derived from the Greek numerals. Thus there are hexane, heptane, octane, and so forth. The lower members of the series have names more or less arbitrary, which were originally given them to indicate relationships which would now be considered rather remote. The student should, however, fix these names carefully in mind, because these, or such as are closely associated with them, are of constant occurrence. Thus there is associated with each of the hydrocarbons at least one univalent radicle which stands in the same relation to the hydrocarbon that methyl does to methane. The names of this homologous series of radicles follow those of the hydrocarbons. The lower members are methyl, CH_3; ethyl, C_2H_5; propyl, C_3H_7; butyl, C_4H_9; amyl, C_5H_{11}; hexyl, C_6H_{13}, etc. The members of this series are spoken of collectively as the *alkyl* radicles. The general formula of the alkyl radicles is C_nH_{2n+1}. It is especially important that the student have a perfectly clear idea of what is meant by the terms methyl, ethyl, propyl, and isopropyl.

Occurrence. The petroleum found in Pennsylvania consists almost entirely of a mixture of the hydrocarbons of the methane series. These are also present in most other petroleums, but the Russian and Texas products contain, as well, hydrocarbons belonging to other series. Many pure hydrocarbons have been isolated from petroleum, but on account of the mutual solubility of the various constituents, and the well-known fact that many mixtures distill at a constant temperature, it is an extremely difficult operation to secure material of which we can be sure that it represents a true chemical individual. For this reason, together with the general chemical indifference of the members of the methane series, petroleum has scarcely served at all as a starting point for the preparation of chemical compounds. Instead, its components have been employed almost exclusively for purposes of heating and lighting, or as lubricants. For these uses the crude petroleum is distilled and the various products washed with sulphuric acid and dilute alkali in order to remove basic and acid impurities respectively.

The various distillates have received different names according to their boiling-points and specific gravities. It should be understood, however, at the outset, that these names do not indicate chemical individuals, but are commercial designations which are not even consistently applied. In general, the material boiling between 40° and 70°, consisting mostly of pentanes and hexanes, is usually called petroleum ether, and that which boils between 70° and 90° is known as gasolene. The fraction which distills between 80° and 110° is naphtha while that between 80° and 120° is also known as ligroin. The portion boiling between 150° and 300° is called kerosene, and this used to be industrially the most important product. Above 300° come various oils used as lubricants. By cooling these heavy oils paraffin may be made to crystallize out. The latter is used extensively in the preparation of candles. Paraffin is also obtained from the distillation of various other materials such as the boghead coals and the oil-bearing shales. When the heavier oils are heated to a temperature somewhat above their boiling-point a peculiar action takes place which is technically known as 'cracking.' Chemically this consists of a decomposition in which hydrocarbons of higher and lower molecular weight are simultaneously produced. By the application of this principle the oil-refiner is sometimes enabled to modify advantageously the nature of his product.

Many theories have been advanced by scientists in order to account for the formation of petroleum in the earth. Those of the most importance are, first, that which ascribes the formation of petroleum to the distillation of vegetable material; second, that which ascribes it to the distillation of animal tissues, — probably of marine origin, — and, finally, what may be called the inorganic chemical theory, in accordance with which petroleum is formed by the action of water upon various metallic carbides. Some interesting arguments have been brought forward to support each of these theories, but as the question is by no means settled to universal satisfaction, any discussion of the details would be out of place here.

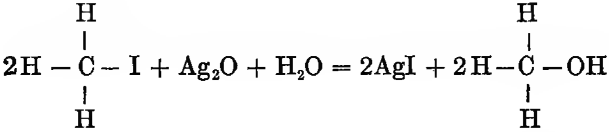
Constants which are considered of importance in dealing with oils are their specific gravity and flash-point. The latter is especially important in the case of illuminating oils, as it is essential that an oil should not be sold which is dangerous for use in lamps. The flash-point may be defined as the temperature at which the vapor of an oil forms an inflammable mixture with air. As determined in practice, this is not to be considered as an accurate physical constant in the scientific sense, since the apparatus used for the purpose is prescribed by law in the various states, and the method of making the determination is also prescribed. For this reason the flash-points determined in accordance with the differing specifications can hardly be expected to give concordant numerical results. The flash-point of an oil should, therefore, always be accompanied by a statement of the method by which it has been determined.

In Massachusetts the apparatus employed consists of a glass cup set in a water bath of metal. In the oil cup hangs a thermometer. The cup is filled with oil to within $\frac{3}{32}$ of an inch from its top, and the bath is heated by a flame $\frac{3}{4}$ of an inch long at such a rate that the oil rises $2\frac{1}{2}$° per minute until 97° F. is reached. After this, as often as the thermometer rises one degree, a small flame is passed across the rim of the cup. The temperature at which this operation first causes a transitory 'flash' is taken as the flash-point of the oil. In Massachusetts, the law prescribes that an oil shall not be sold for illuminating purposes whose flash-point as determined by this method is lower than 100° F.

CHAPTER III.

ALCOHOLS AND THEIR DERIVATIVES.

If an alkyl halide such as methyl iodide is treated with moist silver oxide, a reaction takes place in the sense of the following equation:



$$2\mathrm{H}-\overset{\overset{\displaystyle\mathrm{H}}{|}}{\underset{\underset{\displaystyle\mathrm{H}}{|}}{\mathrm{C}}}-\mathrm{I} + \mathrm{Ag_2O} + \mathrm{H_2O} = 2\mathrm{AgI} + 2\mathrm{H}-\overset{\overset{\displaystyle\mathrm{H}}{|}}{\underset{\underset{\displaystyle\mathrm{H}}{|}}{\mathrm{C}}}-\mathrm{OH}$$

The product may be looked upon as a binary compound of an alkyl radicle with the hydroxyl group, or as a hydrocarbon in which one of the hydrogens has been replaced by hydroxyl. Such substances are called alcohols. They form a homologous series of which the simplest member is methyl alcohol, whose formula has just been given. This alcohol, and incidentally the methyl group as well, derives its name from the Greek words, μέθυ, wine, and ὕλη, wood. It received this name (which finds an equivalent in our expression 'wood-spirit') from the fact that technically it is prepared by the distillation of wood. Several other important organic compounds are formed at the same time, and any description of the details of the process and the purification of the methyl alcohol will be postponed until the chemistry of these substances has received attention.

Methyl Alcohol is a colorless liquid which is odorless when pure, but as ordinarily prepared it possesses a raw odor somewhat resembling that of ordinary alcohol, and a sharp burning taste. Under the influence of intense cold, it forms a solid which melts at $-97°$. Methyl alcohol boils at 64.5° and has a specific gravity of 0.812 at 0°. It burns with a blue smokeless flame and is miscible in all proportions with water. When such a mixture is saturated with solid potassium carbonate, the latter dissolves in the water while the methyl alcohol separates out as a layer upon the surface of the aqueous solution. In this way the alcohol may be separated from the water. The same thing may be effected with a considerable expenditure of time by fractional distillation. In the arts methyl alcohol is used to a considerable extent as a solvent for gums, resins, and the like, as well as for fuel. In these ways it serves as a substitute for ordinary alcohol, and is also employed for denaturing the latter. (See page 62.) The two are similar in their physiological effect upon the organism, but methyl alcohol is much more poisonous.

The chemical properties of this substance deserve careful study as they are typical of the behavior of a large and important class of substances.

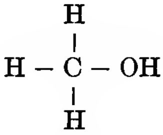
If methyl alcohol is treated with sodium, hydrogen is evolved and a substance is produced having the formula CH_3ONa. This is methyl alcohol in which one hydrogen atom has been replaced by sodium. It is called sodium methylate. If more sodium is employed than is called for by the equation $2\,CH_3OH + Na_2 = H_2 + 2\,CH_3ONa$, no other product is formed. From this it may be concluded that methyl alcohol contains one, and only one, hydrogen which is replaceable by a metal.

If methyl alcohol is treated with one of the halogen compounds of phosphorus, the pentachloride for example, the following reaction takes place:

$$CH_3OH + PCl_5 = HCl + POCl_3 + CH_3Cl.$$

The organic product is methyl chloride, with which the student is already familiar as one of the products of the action of chlorine upon methane (page 37). The net result, then, of the action of phosphorus pentachloride upon methyl alcohol is the replacement of oxygen and hydrogen by a chlorine atom.

We are now ready to discuss the constitution of methyl alcohol. In the first place, in accordance with the valence theory, if we accept the valence of four for carbon, two for oxygen, and one for hydrogen, no other formula than



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

is possible for a substance of the composition of CH_4O. It is, however, desirable to have some more positive argument, because the same reasoning could not be applied to the higher homologues of methyl alcohol. Fortunately such arguments are not lacking. It has already been shown that of the four hydrogen atoms, one can be replaced by sodium. From this it follows that one atom of hydrogen is combined differently from the other three. The formula given accounts for this fact by representing three of the hydrogen atoms as connected to carbon directly, while the fourth is connected to carbon through oxygen. When an alcohol is treated with phosphorus chloride, one oxygen and one hydrogen are eliminated and replaced by one atom of chlorine. This fact, that the oxygen and hydrogen go out together, may also be looked upon as entirely consistent with the assumption that the two are directly united in the molecule of methyl alcohol. This leads us to look upon this compound as made up of a methyl group combined with a hydroxyl group. In some of its reactions, this hydroxyl group shows some analogy with that of the inorganic bases. If methyl alcohol is treated with an acid, a reaction takes place which results in the elimination of water and the formation of a compound in which the methyl group is combined with the acid radicle. Such substances are called esters and their formation suggests the reaction of acids and bases to form salts:

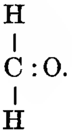
$$CH_3OH + HNO_3 = CH_3NO_3 + H_2O.$$
$$KOH + HNO_3 = KNO_3 + H_2O.$$

The analogy is, however, almost entirely formal, for whereas acids and bases unite instantaneously and completely, the alcohols react with acids only slowly and incompletely. Furthermore, the products are not salts at all but, for the most part, volatile substances insoluble in water and not electrolytes. Now the fact that their aqueous solutions conduct the electric current is one of the most characteristic things about salts. The student will therefore have a clearer idea of the chemical character of esters if he remembers the differences between them and salts rather than their points of resemblance. Because the alcohols react with acids in the manner just indicated it must by no means be concluded that they are bases, any more than, on the other hand, one would be justified in concluding that they were acids because they possess one hydrogen which may be replaced by a metal. Acids are electrolytes which yield hydrogen ions in aqueous solution, and the presence of these may be readily detected by their action upon indicators like litmus. Bases, in the same way, furnish hydroxyl ions which may be tested for in a similar manner. Alcohols, on the other hand, are neutral toward litmus and other indicators, and the reactions just learned are to be looked upon as characteristic of the hydroxyl group and not of the hydroxyl ion.

These reactions are so important that they may be profitably recapitulated. Alcohols have a hydrogen atom which may be replaced by metals like sodium and potassium. By the action of phosphorus halides the hydroxyl is replaced by halogen, and by the action of acids it is replaced by acid radicles. The student should associate this behavior with the presence in a compound of a hydroxyl group combined with an alkyl radicle.

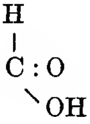
The behavior of methyl alcohol when treated with oxidizing agents is also extremely important because a large class of alcohols, though not all, yield analogous products.

If vapors of methyl alcohol mixed with air are passed over freshly heated platinum, oxidation takes place upon the surface of the latter with such velocity that it is kept glowing by the heat generated in the reaction. The chief product is a substance called formaldehyde, which has the formula,



$$\begin{array}{l} \mathrm{H} \\ | \\ \mathrm{C:O.} \\ | \\ \mathrm{H} \end{array}$$

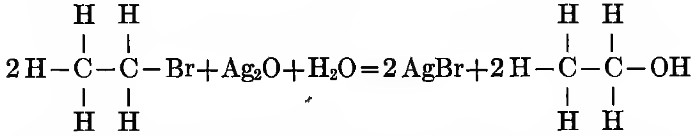
This aldehyde, on further oxidation, yields a strong acid, formic acid,



$$\begin{array}{l} \mathrm{H} \\ | \\ \mathrm{C:O} \\ \quad\diagdown \mathrm{OH} \end{array}$$

The properties and constitutions of these substances will be treated in detail later. Here we are concerned only with the fact that methyl alcohol when treated with oxidizing agents yields first an aldehyde and then an acid, and that both the aldehyde and the acid contain the same number of carbon atoms as the original alcohol.

Ethyl Alcohol, better known simply as 'alcohol,' is the next member of this homologous series. It is industrially by far the most important member of the entire group. It closely resembles methyl alcohol in all its physical properties and chemical relationship. Thus it can be prepared from ethyl bromide by the action of moist silver oxide:



$$2\,H-\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}-\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}-Br+Ag_2O+H_2O=2\,AgBr+2\,H-\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}-\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}-OH$$

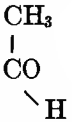
Like methyl alcohol, it contains a hydrogen atom which can be replaced by sodium to form sodium ethylate:

$$2\,C_2H_5OH + 2\,Na = H_2 + 2\,C_2H_5ONa.$$

The hydroxyl, too, may be replaced by halogen on treatment with one of the halogen compounds of phosphorus,

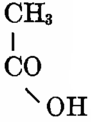
$$3\,C_2H_5OH + PI_3 = 3\,C_2H_5I + P(OH)_3.$$

Finally, when it is oxidized, it yields an aldehyde, acetaldehyde, of the formula,



$$\begin{array}{l} CH_3 \\ | \\ CO \\ \;\diagdown H \end{array}$$

and finally an acid, acetic acid.



$$\begin{array}{l} CH_3 \\ | \\ CO \\ \;\diagdown OH \end{array}$$

both aldehyde and acid having the same number of carbon atoms as the original alcohol.

Ethyl alcohol freezes at −117°, and boils at 78°. It is a colorless liquid of characteristic odor and burning taste. It is miscible in all proportions with water, and from such solutions it may be 'salted out' by means of potassium carbonate. A comparison of the above with what has been said of the properties of methyl alcohol (page 55) may serve to give the student a good idea of the didactic advantages to be derived from homologous series.

Unlike methyl alcohol, the ethyl compound cannot be separated completely from an aqueous solution by fractional distillation. The two form a mixture of minimum constant boiling-point which, at ordinary atmospheric pressure, contains about 95% of alcohol. To remove the water from this mixture and obtain the so-called 'absolute alcohol,' it is necessary to employ dehydrating agents. For this purpose, lime is most frequently used. The alcohol is boiled for some time with the lime, and finally distilled over it. If extremely dry alcohol is required, the product is finally distilled over small quantities of metallic sodium, or, perhaps better, over metallic calcium, which is now to be had quite cheaply in the market, and has the advantage over sodium that it does not so readily react with the alcohol. To test for the presence of water in alcohol, anhydrous copper sulphate is commonly added. After standing for some time this turns blue if the alcohol contains water. Another test consists in the addition of calcium carbide, which evolves acetylene — easily recognized by its odor — when any water is present, but does not react with the alcohol.

In mixtures of alcohol and water, such as distilled spirits, the proportion of the former is usually determined in practice by taking the specific gravity of the liquid. Inasmuch, however, as alcohol and water unite with contraction of volume, tables are necessary in order to obtain the alcohol content from the specific gravity. Special forms of hydrometers have been constructed with a stem so graduated that when immersed in a mixture of alcohol and water, the depth to which the apparatus sinks shows directly the percentage of alcohol. Such instruments are called alcoholometers. If it is required to determine the alcohol in a mixture which, in addition to water, contains other substances that might affect the specific gravity, enough of the liquid is distilled to bring over into the distillate all of the alcohol. Water is then added to the distillate until its volume is equal to that of the liquid originally distilled. In this mixture, which should now contain only alcohol and water, the percentage of the former may be determined by the specific gravity method. The alcohol content of a wine or beer is found in this way. It is obvious that if the mixture contains an appreciable quantity of other volatile constituents, the method cannot be employed.

Industrial Preparation. Since prehistoric times alcoholic beverages have been prepared by the fermentation of sugars, and this method is still the only technical one for the production of alcohol. It is now known that this fermentation process is brought about by the presence in a dilute sugar solution of a substance called 'zymase.' Nothing is known of the constitution of this substance and very little about its chemical character. What is known is that it exists in yeast and some other organisms, and that its presence causes sugar to break up into alcohol and carbon dioxide in the sense of the following equation:

$$C_6H_{12}O_6 = 2\,C_2H_5OH + 2\,CO_2.$$

Organic substances of this kind, which like zymase promote fermentation, are called *enzymes*. In practice, the source of the sugar used for these purposes is either the juice of fruits like the grape, or else the starch of grains or of the potato. In the latter case the starch is changed over to grape sugar by other enzymes before alcoholic fermentation takes place. All this will be more intelligible when the chemistry of the sugars and starches has been studied. Here it is sufficient to note that when grape sugar is fermented by yeast, there results a mixture consisting chiefly of ethyl alcohol, but containing also a number of the higher alcohols. These are collectively known as 'fusel-oil,' and recent investigations have made it highly probable that they owe their formation to the action of zymase upon the protein material present rather than to any decomposition of the sugar. The purification of crude alcohol is a process of fractional distillation which is carried on with very complicated apparatus and on the largest scale. By this means there is obtained the alcohol of commerce. This is the mixture of alcohol and water of constant boiling-point which has already been alluded to. It contains about 95% of alcohol.

Aside from the enormous consumption of alcohol in beverages, large amounts are employed in the arts. It is used to some extent as fuel (in explosion-engines, for example) but perhaps chiefly as a solvent, particularly in the chemical industries and in compounding medical preparations. It is the practice of all nations to levy a tax upon alcoholic beverages. Alcohol intended to be used in the arts may, however, be exempt from this tax if it has been rendered unfit for drinking by the addition of poisonous or distasteful materials. Such a mixture is called denatured alcohol.*

It is of interest to note that ethyl alcohol is of much wider occurrence in nature than is commonly supposed. It has been shown to be present in small but recognizable quantities in the leaves of plants, in rain water, and in snow.

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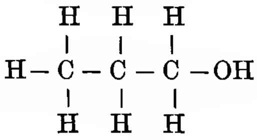
* The United States regulations prescribe two general methods by which alcohol may be denatured. According to the first, 100 parts of alcohol are mixed with 10 parts of wood alcohol and 1 or 2 parts of benzine. According to the second, 100 parts of alcohol are mixed with 2 parts of wood alcohol and 1 or 2 parts of pyridine bases. Manufacturers to whom the use of these substances would be an especial hardship are permitted to substitute other denaturants subject to the approval of the Commissioner of Internal Revenue.

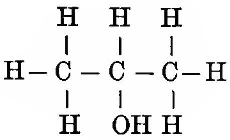
Propyl Alcohols. In the formula of propane, a hydrogen may be substituted by hydroxyl in either of two ways forming, respectively,

(1)



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

and (2)

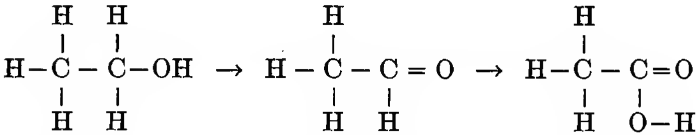


$$\begin{array}{ccccccc} & & H & & H & & H \\ & & | & & | & & | \\ H & - & C & - & C & - & C-H \\ & & | & & | & & | \\ & & H & & OH & & H \end{array}$$

In formula (1) the hydroxyl is attached directly to a primary carbon atom, that is, to one which is itself attached to but one other carbon atom. In (2), however, the hydroxyl is connected to a secondary carbon atom. The two formulæ are therefore distinguished as those belonging to primary and to secondary propyl alcohols. Now two alcohols of the composition C_3H_8O are known. One of them is formed in small quantities during alcoholic fermentation; the other is a laboratory product. The one found in fusel-oil boils at 97° and has the specific gravity 0.804, while the other boils at 81° and has the specific gravity 0.789. Both of these substances show the reactions which have just been described with sodium, with the chlorides of phosphorus, and with acids. This shows that they are both alcohols, that is, that they both contain the hydroxyl group. Since they are not identical, their differences must arise from a different position of the hydroxyl group. Such a difference of position is shown in the two formulæ derived above. To determine, however, which formula belongs to which alcohol, it is necessary to study the oxidation products of each. The propyl alcohol found in fusel-oil, when oxidized with such a reagent as chromic acid, behaves in the manner already described as characteristic of methyl and ethyl alcohols, that is, it yields first an aldehyde and then an acid, both of which contain the same number of carbon atoms as the original alcohol. The alcohol boiling at 81°, on the other hand, yields under similar circumstances a substance called acetone. When this is oxidized a mixture of acetic and carbonic acids is produced. Now since methyl and ethyl alcohols are typical primary alcohols, it follows that the propyl alcohol from fusel-oil has the constitution of a primary alcohol (1); while the other, which behaves differently on oxidation, must be secondary propyl alcohol and have the formula (2). These distinctions are so important, and the conclusions involved are so far-reaching, that it will repay us to enumerate the various products of oxidation at this time, despite the fact that it will be necessary to assume the validity of certain constitutional formulæ for which complete proof can only be given later.

Turning first to ethyl alcohol, its relation to the compounds which are formed from it by oxidation is shown by the following scheme:

−3 −1

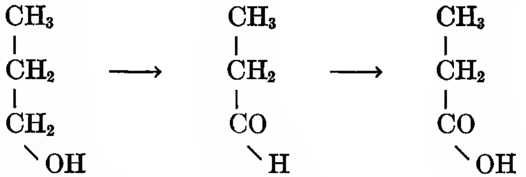


$$\mathrm{H{-}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}{-}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}{-}OH} \rightarrow \mathrm{H{-}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}{-}\underset{\underset{H}{|}}{C}{=}O} \rightarrow \mathrm{H{-}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}{-}\underset{\underset{O-H}{|}}{C}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

Ethyl alcohol　　Acetaldehyde　　Acetic acid.

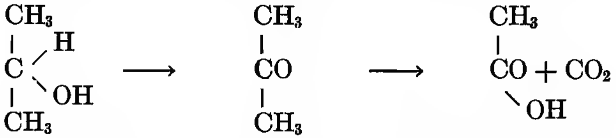
This may be expressed in the following form: Under the influence of oxidizing agents like chromic acid, the hydroxyl group, OH, is changed to the *carbonyl* group $\underset{|}{\overset{|}{\mathrm{C}}}\mathrm{O}$, and this, in turn, to the *carboxyl* group, $\overset{|}{\mathrm{C}}\mathrm{=O}\diagdown\mathrm{OH}$

Of these the former is characteristic of aldehydes and ketones, the latter of acids. It will be noticed that, taking these groups as a whole, carbonyl has a valence of two and carboxyl a valence of one. For this reason the latter group can stand only at the end of a carbon chain. When we turn to the oxidation products of the propyl alcohols, we find that the primary compound is perfectly analogous in its behavior to ethyl alcohol. This is shown by the following scheme:



Primary propyl alcohol Propionic aldehyde Propionic acid.

It has already been stated that secondary propyl alcohol acts differently. Its behavior may be shown as follows:



Secondary propyl alcohol Acetone Acetic acid and carbon dioxide.

It will be noticed here that the first product of oxidation is a substance which is isomeric with propionic aldehyde. It differs from that compound, however, by the position of its carbonyl group, for whereas in the aldehyde this is connected on one side to an alkyl radicle and on the other to hydrogen, in this compound the carbonyl group is attached to two alkyls. Such substances are called ketones. They may be distinguished from aldehydes by their behavior on oxidation. It has been shown that aldehydes yield acids containing the same number of carbon atoms as the aldehydes themselves. Ketones, on the contrary, yield mixtures of acids containing fewer carbon atoms than the ketones. This behavior finds complete expression in the graphic formula, for since a carboxyl group can exist only at the end of a chain, it is clear that a carbonyl group between two alkyls cannot be oxidized to carboxyl, unless its connection with one of the alkyls is broken. The latter itself then undergoes oxidation.

As these two alcohols are types of important classes, it is worth while to recapitulate the distinctions between them in general terms.

A *primary* alcohol, as defined according to its behavior, is one which, on oxidation, yields first an aldehyde and then an acid, both of which have the same number of carbon atoms as the original alcohol. This behavior finds expression in a formula which represents a hydroxyl group attached to a primary carbon atom, that is, to one which is itself attached to not more than one other atom of carbon. It is clear that such an atom must stand at the end of a carbon chain.

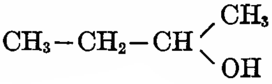
A *secondary* alcohol is one which, on oxidation, yields first a ketone having the same number of carbon atoms as the alcohol, but this, on further oxidation, yields a mixture of acids each of which contains fewer carbon atoms than the ketone. Defined according to its formula, it is an alcohol whose hydroxyl is attached to a secondary carbon atom, that is, to one which is itself connected to two others.

Neither of the propyl alcohols is of sufficient intrinsic importance to justify further description here. Before leaving the subject, however, the proof should be given for the constitution of the two propyl iodides which was postponed when these two substances were first mentioned on page 43. It is now obvious that the propyl iodide which can be prepared by the action of phosphorus and iodine upon primary propyl alcohol is the normal compound, while the substance which is formed by the same reaction from secondary propyl alcohol is isopropyl iodide.

Butyl Alcohols. For the general formula $C_4H_{10}O$, the valence theory contemplates the possibility of the existence of four isomeric alcohols. All are known. They are distinguished as follows:

(1) Normal primary butyl alcohol $CH_3-CH_2-CH_2-CH_2OH$ boiling at 117°.

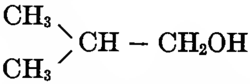
(2) Normal secondary butyl alcohol



$CH_3-CH_2-CH\begin{matrix}\diagup CH_3\\ \diagdown OH\end{matrix}$

boiling at 100°.

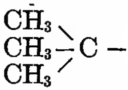
(3) Isobutyl alcohol



$\begin{matrix}CH_3\diagdown\\ CH_3\diagup\end{matrix}CH-CH_2OH$

boiling at 107°.

(4) Tertiary butyl alcohol



$\begin{matrix}CH_3\diagdown\\ CH_3-\\ CH_3\diagup\end{matrix}C-OH$

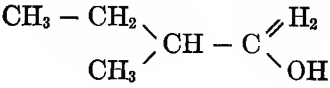
boiling at 83°.

The first three suggest nothing with which the student is not already familiar, and he should be able from the formulæ to predict with a good deal of certainty much of their chemical behavior, including the formulæ of all the oxidation products of each. The fourth formula suggests something new. The hydroxyl of this alcohol is connected to a carbon atom which is in turn united to three other carbons. Such a compound is called a *tertiary* alcohol, and can be distinguished from the others by its behavior on oxidation. Inspection of the formula shows that the hydroxyl group of this alcohol cannot be oxidized to the bivalent carbonyl radicle $\overset{|}{\underset{|}{CO}}$, unless at the same time at least one of the bonds which unite the carbon atoms be broken. As a matter of fact, it is found that tertiary alcohols when vigorously oxidized yield a mixture of products, usually acids and ketones, all of which contain fewer carbon atoms than the original alcohol. In the case immediately under consideration, tertiary butyl alcohol yields acetone and carbon dioxide. The oxidation products of acetone have already been mentioned (page 65).

Before leaving the discussion of the three classes of alcohols it is worth while to point out that the primary alcohols are characterized by the grouping $-C\begin{matrix}\diagup H_2 \\ \diagdown OH\end{matrix}$, the secondary by $\begin{matrix}\diagdown \\ \diagup\end{matrix}C\begin{matrix}\diagup H \\ \diagdown OH\end{matrix}$, and the tertiary by $\begin{matrix}\diagdown \\ -C-OH. \\ \diagup\end{matrix}$

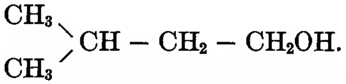
The butyl alcohols are of little practical importance. Their formulæ may, however, serve as material for illustrating a method of nomenclature which has been found extremely convenient in the case of the more complicated alcohols. It has already been shown that hydrocarbons which possess very complicated formulæ can be appropriately named by considering them as derivatives of methane. In the same way, alcohols may be looked upon as substitution products of methyl alcohol. For reasons of euphony, methyl alcohol then receives the name *carbinol.* Ethyl alcohol, when named in this way, would be called methyl carbinol. Similarly, the four butyl alcohols whose formulæ have been given above would receive respectively the following names: (1), normal propyl carbinol; (2), methyl ethyl carbinol; (3), isopropyl carbinol; (4), trimethyl carbinol.

Amyl Alcohols. For the formula $C_5H_{12}O$, eight alcohols are theoretically possible, and all of these are known. The names and formulæ should be written by the student as an exercise. In the case of the amyl alcohols, a further diversity is introduced by the fact that secondary-butyl carbinol of the formula,



$$\begin{matrix}CH_3-CH_2\diagdown \\ CH_3\diagup\end{matrix}CH-C\begin{matrix}\diagup H_2 \\ \diagdown OH\end{matrix}$$

exists in two different forms which are alike in most of their properties, but differ in their action upon the plane of polarized light. One of them rotates this to the right, the other an equal amount to the left. The fundamental principles underlying this particular kind of isomerism will be discussed later, when we come to study lactic acid. For the present it is sufficient to note that the one which rotates the plane of polarized light to the left is one of the more important components of fusel-oil. On account of this action upon polarized light, it is commonly referred to as 'active' amyl alcohol. In fusel-oil it is accompanied by a still larger proportion of isoamyl alcohol (isobutyl carbinol) of the formula,



$$\begin{matrix} CH_3 \searrow \\ CH_3 \nearrow \end{matrix} CH - CH_2 - CH_2OH.$$

A new interest attaches to the latter compound because it has recently been suggested as a starting-point in the technical preparation of synthetic rubber (page 310). A mixture of these two alcohols constitutes the ordinary 'amyl alcohol' of commerce. This is an oily liquid boiling at about 130°. It has a characteristic odor which in high dilution is not disagreeable, but when the vapors are inhaled in considerable quantity, they have a very irritating effect upon the mucous membrane. This amyl alcohol is used to a certain extent as a solvent for gums and resins and for gelatinizing nitrocellulose. It is also used somewhat in the preparation of esters and other chemical derivatives. It should be borne in mind that since the original amyl alcohol is a mixture, the same holds true of its chemical derivatives.

We are now in a position to survey the homologous series of alcohols as a whole. In the first place the series has the general formula $C_nH_{2n+1}OH$. So far as the relationship is concerned which exists between structure and molecular weight on the one hand, and physical and chemical properties on the other, much which was said concerning the methane series of hydrocarbons might be repeated unchanged here. The student will have already noticed, for example, that with increasing molecular weight the boiling-points become higher, and also, that, among isomers, the alcohols of normal constitution have the highest boiling-points. It is rather curious that the tertiary alcohols, which as a rule have the lowest boiling-points, generally have the highest melting-points. Thus tertiary butyl alcohol is solid at room temperature while all its isomers are liquids. The solubility in water decreases as we ascend the scale; thus normal propyl alcohol is miscible in all proportions with water, while twelve parts of the latter are required to dissolve normal butyl alcohol. A saturated aqueous solution of commercial amyl alcohol contains only about 3% of the alcohol. The chemical activity decreases as the molecular weight increases. The reason for this may be that as the carbon chains increase in length, the hydroxyl group becomes a more and more insignificant fraction of the whole molecule. Hence, in the higher members of the series, the hydrocarbon character comes to predominate. The same thing expresses itself in the physical properties. The highest members of the group are wax-like solids somewhat resembling paraffin. As the molecular weight increases, the number of isomers theoretically possible also increases enormously, but among the compounds of high molecular weight hardly any except the normal alcohols are known. These are chiefly found as esters of the fatty acids in the natural waxes. It is an interesting fact, which applies not only to the alcohols but also to most of the various series of aliphatic compounds, that, in the higher series, those compounds with normal structure are the ones found in nature.

Alkyl Halides.

While discussing the hydrocarbons and alcohols, we have frequently had occasion to refer to the alkyl halides, and at different points the student has already had opportunity to become acquainted with most of the methods of preparation and chemical reactions of these substances. Those already mentioned may profitably be recapitulated at this point.

When the hydrocarbons of the methane series are treated directly with chlorine or bromine, substitution takes place with the formation of an alkyl halide:

$$C_2H_6 + Cl_2 = HCl + C_2H_5Cl.$$

It is characteristic of alcohols that they react with the halogen compounds of phosphorus in the sense of the following equation:

$$3\,C_2H_5OH + PCl_3 = P(OH)_3 + 3\,C_2H_5Cl.$$

Finally, it has been shown that the alcohols unite with acids to form products called esters, water being eliminated. This reaction holds true also of the halogen acids:

$$C_2H_5OH + HCl = C_2H_5Cl + H_2O.$$

Some of the reactions of the alkyl halides are also familiar. Thus the student has already learned that the alcohols may be prepared from the alkyl halides by the action of moist silver oxide:

$$2\,C_2H_5I + Ag_2O + H_2O = 2\,C_2H_5OH + 2\,AgI,$$

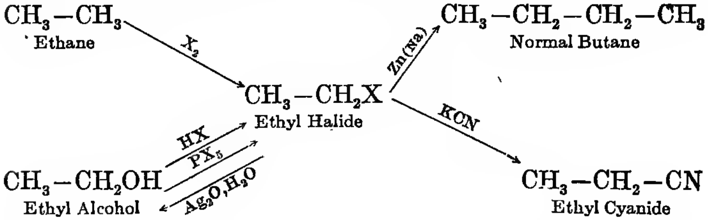
and when these compounds are treated with metals like zinc or sodium, the halogen is removed by the metal and a synthesis takes place:

$$2\,C_2H_5I + Zn = ZnI_2 + C_4H_{10}.$$

Furthermore the alkyl halides take part in many metathetical reactions in which they usually serve to combine an alkyl group with some other organic radicle. Most of these reactions will best be considered separately as they arise, but one of the more important which may serve as a type is the following:

$$C_2H_5Br + KCN = KBr + C_2H_5CN.$$

The way in which the alkyl halides are related to other classes of organic compounds is well indicated by the following scheme, in which the ethyl compound is taken as an example, and the halogen atom is represented by the symbol X:



The student is strongly advised to prepare charts of this kind for himself in dealing with the various classes of compounds which he will have occasion to study. They are of great assistance in keeping in mind the genetic relationships which exist between the different classes of substances.

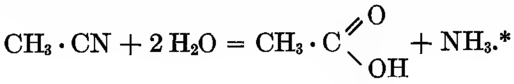
The number of halogen compounds known is very large. Including the fluorine compounds, they comprise four homologous series having the general formula $C_nH_{2n+1}X$. In theory there would be as many compounds possible in each series as in the case of the alcohols. There is no occasion for describing any considerable number of these substances in this place. Those which are most familiar because of their frequent use as reagents are ethyl bromide, the iodides of methyl and ethyl, and those of the two propyls.

These are volatile liquids, colorless when pure, of ethereal odor and heavier than water, the specific gravity being roughly proportional to the amount of halogen which they contain. In laboratory practice the bromides are usually prepared from the alcohols by the action of potassium bromide and sulphuric acid. The iodides are prepared from the same source by treatment with phosphorus and iodine. Ethyl bromide boils at 38°, methyl iodide at 45°, and ethyl iodide at 72°. The specific gravities of these substances are 1.468, 2.293, and 1.949, respectively.

An important difference has to be noted between the alkyl halides on the one hand, and the inorganic compounds of analogous formula such as sodium or potassium chloride on the other. These last two chlorides are soluble in water and are electrolytes. So far as the halogen is concerned, almost all soluble inorganic chlorides act alike in aqueous solution, because under these circumstances they all furnish the common halogen ion. For example, they all give with silver nitrate a precipitate of silver chloride. With the alkyl halides it is different. These are sparingly soluble in water, their solutions are not conductors, and their behavior with such reagents as silver nitrate is not uniform but varies from compound to compound. Ethyl iodide reacts with this reagent almost instantly, the bromide after standing for some time, and the chloride not at all, even after continued heating.

The Cyanides. The radicle cyanogen is closely allied to the halogens in many of its reactions, and this makes it appropriate to take up at this time the study of the important organic compounds which may be looked upon as alkyl derivatives of hydrocyanic acid. The cyanogen group can be combined with methyl for example, in one of two ways, to form compounds of the formulæ $CH_3 \cdot CN$ and $CH_3 \cdot NC$ respectively. As a matter of fact, two compounds of this composition are known. One of these is formed when methyl iodide is allowed to react with potassium cyanide, the other when the same reagent is treated with silver cyanide. The two substances differ widely in their properties, and notably in their behavior upon hydrolysis. Under these circumstances the substance formed by the action of methyl iodide upon potassium cyanide reacts in the sense of the following equation:

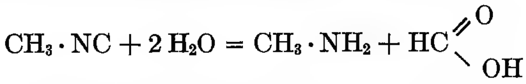
(1)



$$CH_3 \cdot CN + 2\,H_2O = CH_3 \cdot C{\begin{matrix} /\!\!/ O \\ \diagdown OH \end{matrix}} + NH_3.^*$$

The other product, however, reacts as follows:

(2)



$$CH_3 \cdot NC + 2\,H_2O = CH_3 \cdot NH_2 + HC{\begin{matrix} /\!\!/ O \\ \diagdown OH \end{matrix}}$$

It is not intended to take up the study of the products of these reactions at this point. Attention is simply called to one fact which is apparent from the equations them-

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* In practice such a hydrolysis is usually carried out in one of three ways:

(1) By superheated water in a sealed tube. In this case the ammonia adds directly to the acid to form a salt:

$$CH_3 \cdot CN + 2\,H_2O = CH_3 \cdot CO \cdot ONH_4.$$

(2) By boiling with alkali. In this case the products are the same as those which would be obtained by decomposing the above ammonium salt with alkali:

$$CH_3 \cdot CN + KOH + H_2O = CH_3 \cdot CO \cdot OK + NH_3.$$

(3) By boiling with acids:

$$CH_3 \cdot CN + 4\,H_2O + H_2SO_4 = CH_3 \cdot CO \cdot OH + (NH_4)_2SO_4.$$

The reaction as it is written in the text is a convention employed by organic chemists to cover all three cases, and analogous expressions will be used throughout the book in this sense except when a special method of hydrolysis is referred to.

selves. In (1) the organic product on the right-hand side has the same number of carbon atoms as the original cyanogen compound; that is, the carbon atoms have remained together. In equation (2) they have been separated. This is regarded as evidence that the cyanogen derivative in the first equation has its two carbon atoms directly united, while in the second case the carbons must have been connected by means of the nitrogen. This constitutes proof for the formulæ assigned to the two compounds in the equations as written.

Those substances of which CH_3NC is a type have hardly enough importance to warrant further attention here. Methyl cyanide CH_3CN and its homologues are, on the other hand, extremely important. As is shown by equation (1) itself, these compounds are closely related to the acids. On treatment with hydrolyzing agents, they yield acids containing the same number of carbon atoms as the cyanides themselves; that is, the cyanogen group is changed to carboxyl. In synthetic organic work this is one of the more common ways of preparing acids. This accounts for another name frequently given these substances. They are called acid nitriles, and the individual members are named from the acid which is formed by hydrolysis. Methyl cyanide, for example, is also called acetonitrile. These substances will again be referred to when the study of the acids and their derivatives is taken up in detail. Here it is sufficient to add that in physical properties they are quite comparable to the alkyl halides and esters. Methyl cyanide is a colorless liquid boiling at 81° and having the specific gravity 0.805. Ethyl cyanide boils at 98° and has the specific gravity 0.801. The solubility of these substances in water resembles that of the alcohols. The lower members of the series dissolve, but can be salted out by means of potassium carbonate. The higher members are insoluble.

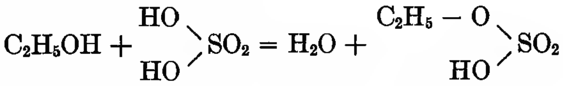
Esters of Inorganic Acids.

It has already been shown that the alkyl halides are formed when the corresponding alcohols are treated with the halogen acids:

$$C_2H_5OH + HBr \rightleftarrows C_2H_5Br + H_2O.$$

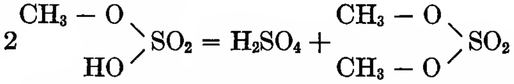
This means that these compounds may be considered as esters of such acids. Now since some of the other esters of the inorganic acids have an importance as reagents scarcely inferior to that of the halides, a few of them will be mentioned at this time, although the esters of the organic acids will not be taken up until the acids themselves have been discussed. Esters may be defined as those substances which are formed by the union of alcohols and acids with elimination of water. The process is called *esterification.* The products are, for the most part, volatile substances of ethereal odor, soluble with difficulty in water, and non-conductors of the electric current. The most characteristic thing in their behavior is the fact that by heating with water under pressure, or more readily in the presence of alkalies and acids, they are again decomposed into the acids and alcohols from which they are formed. This process is called *saponification.* It follows from what has been said that the equation written above represents a typical reversible reaction, and consequently, in actual practice, will rarely go to completion in either direction. Instead an equilibrium is reached when the velocities of esterification and saponification are equal. This is an extremely interesting application of the law of chemical mass-action. The conditions which obtain will be considered more fully when we come to take up the preparation of ethyl acetate, a reaction which has been thoroughly studied quantitatively. Here it is sufficient to note that, in practice, when it is desired to prepare an ester by this method, it is necessary, in order to obtain a maximum yield, to remove the water formed in the reaction, so as to reduce to a minimum the splitting action of the water upon the ester formed. This is usually accomplished by the addition of dehydrating agents such as concentrated sulphuric acid. On the other hand, when the object is to decompose an ester (saponification), it is customary to work in alkaline solution, in order that the acid formed may be neutralized, and hence removed from the reaction as soon as it is formed. The word 'saponification' deserves a word of explanation. It literally means 'the making of soap.' As a matter of fact that technical operation is a chemical process of just this kind, and hence the word has gradually come to cover the whole class of chemical reactions of this type, so that it is often used in Organic Chemistry practically as a synonym of *hydrolysis*.

One of the more important esters of this class is ethyl sulphuric acid. It is formed when concentrated sulphuric acid is warmed with ethyl alcohol:



$$C_2H_5OH + \begin{matrix} HO \diagdown \\ HO \diagup \end{matrix} SO_2 = H_2O + \begin{matrix} C_2H_5 - O \diagdown \\ HO \diagup \end{matrix} SO_2$$

The resulting mixture contains the organic product mixed with a large excess of sulphuric acid. For purposes of separation, the mixture is diluted and treated with solid calcium carbonate. This forms insoluble calcium sulphate and leaves in solution the soluble calcium salt of ethyl sulphuric acid. When the filtered solution is evaporated, this calcium salt crystallizes out, and may be dried and weighed. It is again put into solution, and decomposed with the calculated quantity of sulphuric acid. This precipitates calcium sulphate and leaves ethyl sulphuric acid in the solution. It may now be isolated by evaporation of the solvent at moderate temperature. The product is a syrupy liquid soluble in water. Esters of this type break up on heating into sulphuric acid and the neutral ester. Thus with methyl sulphuric acid:



$$2\begin{matrix}CH_3-O\diagdown\\ HO\diagup\end{matrix}SO_2 = H_2SO_4 + \begin{matrix}CH_3-O\diagdown\\ CH_3-O\diagup\end{matrix}SO_2$$

Neutral methyl sulphate can be prepared in this way. It is employed as a reagent for introducing the methyl group. For this purpose it is almost as useful as methyl iodide and has the practical advantage of being much cheaper.

Among other esters of the inorganic acids which possess some practical importance may be mentioned ethyl nitrite and amyl nitrite, which both find some use in medicine. The former is commonly known as 'sweet spirits of niter.' The latter has a peculiar physiological action. Inhalation of its vapors produces sudden dilation of the blood vessels. It is also used to some extent as a reagent.

Ethers.

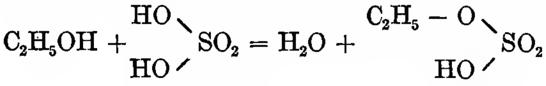
If methyl iodide is treated with sodium methylate, a metathesis takes place in the sense of the equation:

$$CH_3I + Na\cdot O\cdot CH_3 = NaI + CH_3\cdot O\cdot CH_3.$$

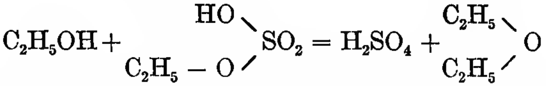
The product is called dimethyl ether. Its constitution is sufficiently fixed by the method of preparation just given. It will be noticed that it is an isomer of ethyl alcohol, both substances having the empirical formula C_2H_6O. This compound, however, shows none of the characteristic reactions of the alcohols. It is the simplest representative of the class of substances called ethers. These may be looked upon as oxides of the alkyl radicles, of which the alcohols may be considered hydroxides; or they may be regarded as water in which both of the hydrogen atoms have been substituted by alkyls, just as an alcohol is water in which one of the hydrogens has been so replaced.

Although acted upon by some reagents, it still holds as a general rule that the ethers are quite indifferent chemically. This finds an adequate expression in the graphic formula, for the hydrogen atoms are all connected directly to carbon just as is the case with the indifferent hydrocarbons, while the oxygen is between the carbon atoms and therefore is protected from disturbing influences. The ethers, then, are to be thought of as but slightly more reactive than the hydrocarbons, and therefore well adapted to serve as solvents in many chemical reactions.

The most important member of the series, and the only one which can receive detailed consideration here, is the ordinary 'ether' of commerce, or diethyl ether. This may be formed by the action of ethyl iodide upon sodium ethylate. It is, however, commercially prepared in a different way. It has just been shown that when ethyl alcohol is treated with concentrated sulphuric acid, an acid ester called ethyl sulphuric acid is formed. When this ester is heated with an excess of alcohol, sulphuric acid is regenerated and ether distills off:



$$(1)\qquad C_2H_5OH + \begin{array}{l}HO\diagdown\\ \qquad\quad SO_2\\ HO\diagup\end{array} = H_2O + \begin{array}{l}C_2H_5-O\diagdown\\ \qquad\qquad\quad SO_2\\ \qquad\quad HO\diagup\end{array}$$



$$(2)\qquad C_2H_5OH + \begin{array}{l}\qquad\quad HO\diagdown\\ \qquad\qquad\qquad SO_2\\ C_2H_5-O\diagup\end{array} = H_2SO_4 + \begin{array}{l}C_2H_5\diagdown\\ \qquad\quad O\\ C_2H_5\diagup\end{array}$$

Advantage is taken of these two reactions in the commercial preparation of ether. To a mixture of sulphuric acid and alcohol kept at a constant temperature near 140°, alcohol is allowed to flow. As the ether formed in the second reaction distills off, the sulphuric acid, which is at the same time regenerated, reacts with more alcohol as indicated by equation (1). In theory, then, a given quantity of sulphuric acid should serve to change an unlimited quantity of alcohol into ether. Such an operation is called a 'continuous process' and those engaged in chemical manufacture find it economical to make as many as possible of the processes which they employ proceed in this way. In the case just cited, in practical work some charring takes place, and the spent mixture occasionally has to be removed and the reaction again begun. Ether was prepared from alcohol by the action of sulphuric acid long before the theory of the process had been worked out, and hence the product received the name 'sulphuric ether.' This name is still in use commercially, and serves to remind us of the time when the substance was supposed to contain sulphur.

Ether is a light volatile oil boiling at 35°. It is employed constantly as a solvent in chemical laboratories, and is useful as an anæsthetic in surgery, having been employed in this way for the first time at Boston in 1846. For purposes of this kind it is now generally preferred to chloroform because it does not exert so depressing an effect upon the action of the heart; though physicians differ on this point.

The other ethers need not be described here. It will be noticed that they are isomeric with those alcohols having the same number of carbon atoms.

It should be added that it is possible to prepare "mixed" ethers, which contain different alkyl radicles attached to one atom of oxygen. Thus, if methyl iodide be treated with sodium ethylate, methyl ethyl ether is obtained.

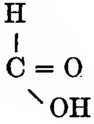
$$CH_3I + Na \cdot O \cdot CH_2CH_3 = NaI + CH_3 \cdot O \cdot CH_2CH_3.$$

CHAPTER IV.

ACIDS AND THEIR DERIVATIVES.

At the present time those substances are considered as acids which, in aqueous solution, undergo electrolytic dissociation yielding hydrogen ions. The latter are perhaps most easily recognized by their action upon indicators; thus a blue litmus solution is changed to red by their action. There are several classes of organic compounds which possess acidic properties to a greater or less degree. By far the most important of these comprises those substances whose formulæ contain a carboxyl group. It is of these compounds that one usually thinks when the term 'organic acid' is employed, and it is to these alone that attention will be called in the pages immediately following.

The student is already sufficiently familiar with some of the methods of preparing the acids to permit a discussion of their constitution at this point. This discussion practically limits itself to the proof of the presence of a carboxyl group. For the acid of the lowest molecular weight, formic acid, this is very simple, since no formula is possible for a monobasic acid of the composition CH_2O_2 except

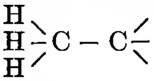


In the case of the higher members of the series, this particular form of reasoning cannot be used, though the fact that these show similarity to formic acid in their behavior might well be considered an argument for analogous constitution. Beyond this, however, it is fortunately possible to furnish direct proof in these cases also. Acetic acid may be taken as an example. Attention is first called to the two following equations:

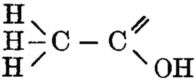
$$(1) \qquad CH_3I + KCN = KI + CH_3 \cdot CN.$$

$$(2) \qquad CH_3 \cdot CN + 2\,H_2O = NH_3 + CH_3 \cdot COOH.$$

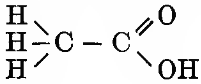
In the first place, methyl iodide can have no other formula than that here assigned to it. It follows that both methyl cyanide and acetic acid contain a methyl group. On page 74 equation (2) has already been used to prove that methyl cyanide has its two carbons directly connected. Putting these together the following skeleton formula is obtained:



From this the further conclusion may be drawn that both of the oxygens in acetic acid are connected to one carbon atom. Now it has already been stated that the acids have one hydrogen which may be replaced by a metal, and it is also true that under the influence of phosphorus chloride an oxygen and a hydrogen may be substituted by a single chlorine atom. When studying the alcohols (page 55), it was shown that these reactions are characteristic of the hydroxyl group. Adding this to the part of the formula already established, the result is



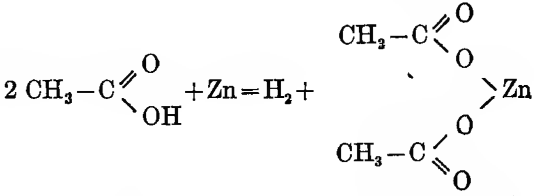
This leaves two bonds as yet unaccounted for, and this is just sufficient to unite with the two bonds of the remaining oxygen. It follows that the constitution of acetic acid is appropriately represented by the symbol,



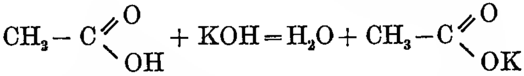
This is commonly abbreviated to the form, $CH_3 \cdot CO \cdot OH$. Similar reasoning, the details of which need not be repeated here, serves to establish the formulæ of the higher members of the series. Before leaving the subject of the constitution of the acids, a word should be said concerning the specific influence of that oxygen atom which is united to carbon by two bonds. The presence of this carbonyl group constitutes the difference between an acid and an alcohol, and this consists chiefly in a greater reactivity of the hydroxyl group and in particular of its hydrogen. This is more easily replaced than in the alcohols, and it is ionized in aqueous solution, which, as has already been pointed out, is not the case with the alcohols. This effect of the carbonyl group is frequently spoken of as making the substance in which it occurs more 'negative,' a term which is not exactly easy to define. The words positive and negative are, however, frequently employed in Organic Chemistry to express a very useful but somewhat intangible idea of this sort.

The principal general methods for the preparation of the acids have been already touched upon. They may be prepared by the hydrolysis of the corresponding nitriles and by various oxidation processes. The fact that they are formed by the oxidation of aldehydes having the same number of carbon atoms, and also from ketones having a larger number, has already been mentioned. Other methods involving oxidation will be met with later.

Among the chemical reactions which are common to the acids, probably the most important and characteristic is their action upon metals and bases which results in the formation of salts:

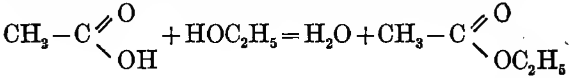
(1) 

$$2\,CH_3-C\begin{array}{l}/\!\!/O\\ \diagdown OH\end{array}+Zn=H_2+\begin{array}{l}CH_3-C\begin{array}{l}/\!\!/O\\ \diagdown O\diagdown\end{array}\\ \qquad\qquad\qquad\quad Zn\\ CH_3-C\begin{array}{l}\diagup O\diagup\\ \diagdown\!\!\diagdown O\end{array}\end{array}$$

(2) 

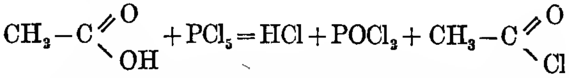
$$CH_3-C\begin{array}{l}/\!\!/O\\ \diagdown OH\end{array}+KOH=H_2O+CH_3-C\begin{array}{l}/\!\!/O\\ \diagdown OK\end{array}$$

It has been shown that they react with alcohols to form esters. This is facilitated by the addition of condensing agents which remove the water formed in the reaction:

(3) 

$$CH_3-C\begin{array}{l}/\!\!/O\\ \diagdown OH\end{array}+HOC_2H_5=H_2O+CH_3-C\begin{array}{l}/\!\!/O\\ \diagdown OC_2H_5\end{array}$$

Reference has also already been made to the fact that the hydroxyl group of the acids, like that of the alcohols, may be substituted by halogens on treatment with the halides of phosphorus, for example:

(4) 

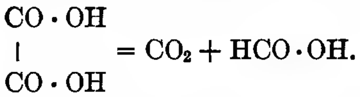
$$CH_3-C\begin{array}{l}/\!\!/O\\ \diagdown OH\end{array}+PCl_5=HCl+POCl_3+CH_3-C\begin{array}{l}/\!\!/O\\ \diagdown Cl\end{array}$$

The product of this reaction is called an acid chloride. The properties and behavior of such compounds will be dealt with later, along with those of the other acid derivatives.

Another familiar reaction is that which was applied in the preparation of methane (page 35). The salts of the acids when distilled with the alkalies or with lime yield hydrocarbons containing one less atom of carbon than the original acid.

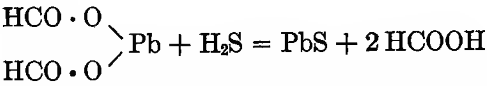
(5) $CH_3CH_2COONa + NaOH = Na_2CO_3 + CH_3CH_3.$

Formic Acid. (Latin, *formica,* an ant.) This acid, as its name implies, occurs in the bodies of ants as well as in the nettle, and it was obtained by early chemists from such sources. The general methods of preparation already cited are applicable to the formation of this acid; thus it is produced by the oxidation of formaldehyde, and by the hydrolysis of hydrocyanic acid, which may be regarded as its nitrile. Neither of these methods, however, is of practical importance. The most common laboratory method for its preparation consists in heating oxalic acid with glycerol. Under these circumstances the former substance breaks up into carbon dioxide and formic acid:



$$\begin{array}{c} CO\cdot OH \\ | \\ CO\cdot OH \end{array} = CO_2 + HCO\cdot OH.$$

According to its formula, CO, carbon monoxide might be regarded as the anhydride of formic acid. Now though carbon monoxide does not unite with water to form the acid under ordinary conditions, yet under the influence of the silent electrical discharge, this reaction does take place to an appreciable extent; and if the gas is passed over moist caustic soda at a temperature just below 220° under pressure, sodium formate is produced with good yield. This process is now in use technically for manufacturing the acid. The product yielded by any of these methods contains water, from which it cannot be separated by distillation, since the two liquids form a mixture which distills at constant temperature. One of the methods of obtaining the anhydrous acid is to prepare the lead salt by the action of lead oxide upon the aqueous acid. This is soluble with difficulty and is beautifully crystalline. At 100°, it may be decomposed by dry hydrogen sulphide, forming lead sulphide and anhydrous formic acid.



$$\left.\begin{matrix}HCO\cdot O\\ HCO\cdot O\end{matrix}\right>Pb + H_2S = PbS + 2\,HCOOH$$

Another method of dehydration is to mix the strong aqueous acid with its sodium salt, and distill with concentrated sulphuric acid avoiding excess. Pure formic acid is a colorless liquid of sharp irritating odor. Its specific gravity is 1.2187 at 20°. It boils at 101°, and freezes at 8°. It is miscible in all proportions with water. The anhydrous acid produces extremely disagreeable effects upon animal tissue, a drop falling upon the skin often causing a painful wound.

Formic acid finds some technical use as a substitute for acetic acid, which in the past few years has been increasing in price. It is also used for some operations in dyeing and tanning, where a combination of acid and reducing properties is required.

Although a weak acid when compared with the mineral acids like hydrochloric, formic acid is by far the strongest member of its series, being about twelve times as strong as acetic acid. The latter is not, however, appreciably stronger than the acids of higher molecular weight. This sudden falling off in the strength of the acids after the first member has been passed is an illustration of one of the peculiarities often noticed in homologous series. It is frequently the case that the first member of such a series, especially when it contains but one atom of carbon, shows less resemblance to the next member than this exhibits to those which follow. This is not surprising when it is considered that such substances as formic acid, formaldehyde, and the like contain no alkyl radicle, whereas all their homologues do. This peculiarity of the lowest members of homologous series has an interesting analogy in Inorganic Chemistry. The student will already be familiar with the fact that something similar holds true of the elements with lowest atomic weight in each group of the Periodic System. Fluorine, for example, is much less similar to chlorine than the latter is to bromine and iodine; while beryllium differs as widely from barium, strontium, and calcium.

Acetic Acid. The constitution and the laboratory methods of preparation for this acid have been already considered (page 82). It may be formed by the oxidation of the aldehyde or by the saponification of the nitrile, — methyl cyanide.

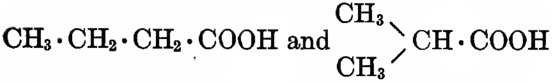
Two technical methods of preparation have to be added. One of these is suitable for the production of a concentrated, the other of a dilute acid.

When hard woods like birch or beech are distilled, tar is obtained, and also an aqueous distillate commonly known as 'pyroligneous acid.' This last contains, besides water and numerous impurities, three important organic compounds of which it furnishes the chief technical source. These are methyl alcohol, acetone, and acetic acid. The first two are more volatile than acetic acid, and can be removed from it by distillation. The residue is then neutralized by lime forming a crude acetate. This is usually roasted at a moderate heat to remove certain organic impurities and is then distilled with hydrochloric acid, avoiding an excess. The distillate is a crude acetic acid which can be further purified by fractional distillation. Acetic acid has a sour taste and characteristic sharp odor. It has the specific gravity 1.050, melts at 16° and boils at 118°. Since its melting point is so high, the pure acid is a crystalline solid on cool days, and this has given it the name 'glacial acetic acid.' It finds employment in the laboratory both as a solvent and as a reagent, as well as to some extent technically; the dilute solution is particularly useful where a weak acid is required. The sodium and lead salts are familiar reagents, while the salts of iron, aluminium, and chromium find extensive use as mordants in dyeing. The theoretical considerations underlying this process will be taken up in connection with a study of the dyes themselves.

A dilute solution of acetic acid is the principal constituent of vinegar (Latin, *acetum*). This was originally prepared by the 'souring' of wine or cider under the influence of certain micro-organisms, collectively known as 'mother of vinegar.' Vinegar is now largely manufactured by what is known as the 'rapid vinegar process.' This is carried out as follows: Casks supplied with holes for the admission of air are loosely filled with beech shavings. Over these is first poured old vinegar in order to distribute upon the surface of the shavings sufficient micro-organisms to start the fermentation. A dilute solution containing about 10% of alcohol is allowed to trickle over these. Fermentation sets in, the temperature rises, and a 4% to 6% solution of acetic acid runs off. The original product thus formed is colorless, but coloring and flavoring materials are usually added before it is brought upon the market.

Propionic Acid. $CH_3 \cdot CH_2 \cdot COOH$ (Greek, πρῶτος, first and πίων, fat). This acid derives its name from the fact that it was formerly regarded as the first of the fatty acids. This original significance has, however, been practically lost since the term 'fatty acids' has come to include the whole series from formic acid up. The substance is a colorless liquid of a sharp, somewhat rancid odor. It is soluble in water, but may be separated from such solutions by the addition of calcium chloride. It is of little practical importance.

Butyric Acids. Two acids are theoretically possible having the formula $C_4H_8O_2$, and both are known,



$$CH_3\cdot CH_2\cdot CH_2\cdot COOH \text{ and } \left.\begin{matrix}CH_3\\ CH_3\end{matrix}\right\rangle CH\cdot COOH$$

The normal acid occurs as an ester of glycerol in butter, and from this source it has received its name. The free acid occurs also in the fæces and in perspiration, so that its odor has come to have many disagreeable associations. Butyric acid is most conveniently prepared from sugar by a fermentation process, under the influence of certain micro-organisms found in decaying cheese. Lactic acid is then formed as an intermediate product. The isomeric acid, commonly known as isobutyric acid, is also formed in certain fermentation processes and occurs to a limited extent in nature. It much resembles the normal acid in physical and chemical properties, and has little specific importance. In this respect these acids may serve as types of most of the members of the series containing from four to ten atoms of carbon. It is unfortunate that these acids do not, like the alcohols and alkyl radicles, possess names based upon the Greek numerals. Instead, they all have special names. None of those between butyric and palmitic acids have, however, so much importance that the student need burden his memory with their names or properties. Attention should be called to the interesting fact that, among the higher members of the series it is almost exclusively the normal members, containing an even number of carbon atoms, which are found in nature. Those with an odd number are either not met with or are extremely rare.

The acids of this series containing twelve or more atoms of carbon are solids which no longer possess the disagreeable odor of butyric acid and its neighboring homologues. On the contrary, they resemble the fats, in which they also occur. By far the most important are palmitic and stearic acids which as esters of glycerol make up a large proportion of the natural fats. These acids are the normal compounds containing sixteen and eighteen carbon atoms respectively. Their alkali salts along with those of oleic acid, a member of another series, form the soaps. All these matters will again be taken up in connection with the technology of the fats.

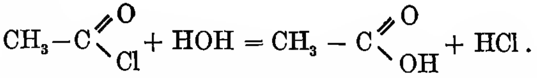
The Acid Derivatives.

Under this head belong certain substances which are closely associated with the acids. There are several classes. Those which will be considered here are the acid chlorides, anhydrides, esters, and amides.

Acid Chlorides. It is characteristic of the hydroxyl group that when substances which contain it are treated with the halogen compounds of phosphorus, the hydroxyl group is replaced by halogen; thus, as has already been shown, acetic acid reacts as follows:

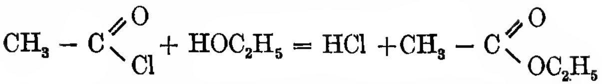
$$CH_3\cdot CO\cdot OH + PCl_5 = HCl + POCl_3 + CH_3\cdot CO\cdot Cl,$$

forming hydrochloric acid, phosphorus oxychloride, and acetyl chloride. The last is a colorless liquid boiling at 51°, and having the specific gravity 1.05 at 20°. It possesses a sharp, intolerable odor, and its vapors violently attack the mucous membrane of the eyes and nasal passages. It fumes in moist air on account of the vigorous reaction into which it enters with water. The two substances unite with almost explosive violence. The products formed are acetic acid and hydrochloric acid:



$$CH_3-C\begin{matrix}\nearrow O\\ \searrow Cl\end{matrix} + HOH = CH_3 - C\begin{matrix}\nearrow O\\ \searrow OH\end{matrix} + HCl\,.$$

Another very important reaction of this substance is that with the alcohols. Here hydrochloric acid is produced and an acetate of the alcohol:



$$CH_3-C\begin{smallmatrix}\nearrow O\\ \searrow Cl\end{smallmatrix}+HOC_2H_5=HCl+CH_3-C\begin{smallmatrix}\nearrow O\\ \searrow OC_2H_5\end{smallmatrix}$$

This reaction, it will be noticed, is analogous to the preceding, and justifies the conception of the alcohols as water in which hydrogen has been replaced by an alkyl.

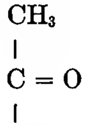
This is one of the reactions which make acetyl chloride so valuable as a reagent, for, by its aid, it is possible to determine how many of the oxygens in an unfamiliar compound are of alcoholic character. It is generally true that when acetyl chloride reacts with substances containing several hydroxyl groups, each of these is substituted by the acetic acid radicle.

Acetyl chloride shows many other important reactions which it would be impracticable to enumerate at this time. Suffice it to say that the carbonyl group, by its negative character, makes the halogen atom to which it is directly attached even more reactive than that in the alkyl halides. This halogen takes part in the most diverse metathetical reactions. Some of these will be considered later when the products formed come up for discussion.

The higher homologues of acetyl chloride resemble it closely in physical and chemical properties. They show only such variations as are familiar to the student from the study of other homologous series. Most of the individual compounds of this series are, however, rarely met with in practice.

No chloride of formic acid is known. Reactions which might be expected to form this compound yield instead a mixture of carbon monoxide and hydrochloric acid. It is an interesting fact that under certain conditions a mixture of these gases reacts as if a chloride of formic acid were present.

The nomenclature of the series of acid chlorides is important because it introduces another series of radicles whose names will be frequently encountered. The name 'acetyl chloride' implies that the substance is a binary compound of chlorine with the univalent radicle, *acetyl*, which has the formula,



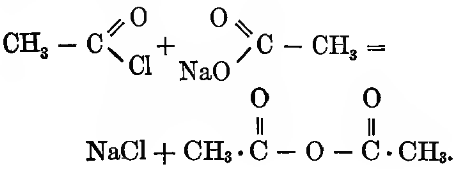
$$\begin{array}{c} CH_3 \\ | \\ C=O \\ | \end{array}$$

For every acid there must exist a similar radicle, the formula of which may be obtained by taking the hydroxyl group away from the formula of the acid. Thus there may be derived:

from acetic acid, $CH_3 \cdot CO -$, *acetyl;*
from propionic acid, $CH_3 \cdot CH_2 \cdot CO -$, *propionyl;*
from butyric acid, $CH_3 \cdot CH_2 \cdot CH_2 \cdot CO -$, *butyryl,* etc.

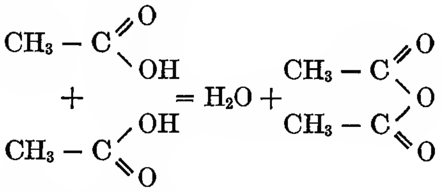
Collectively these are known as the *acyl* radicles, and the manner of naming the individual members is sufficiently obvious from the examples just given. The essential thing to be remembered about the acid chlorides is that they are chlorides of the acyl radicles, and their chemical significance lies chiefly in the fact that they serve to introduce the acyl group into other organic compounds.

The Acid Anhydrides. When acetyl chloride is heated with sodium acetate, sodium chloride is formed and acetic anhydride distills off:

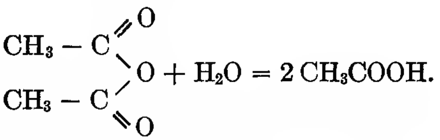


It is a colorless liquid having a sharp odor somewhat resembling that of the free acid, but more penetrating. It boils at 136°, and has the specific gravity 1.078 at 21°. This substance is a type of the large class of compounds known as acid anhydrides.

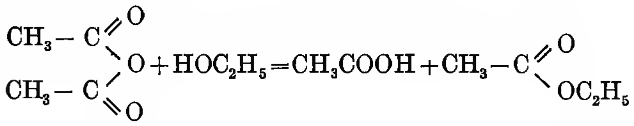
As indicated by their formulæ, these substances may be regarded as the product formed by removing one molecule of water from two molecules of a fatty acid:



Some of the acid anhydrides may, as a matter of fact, be prepared by treating the acids with dehydrating agents as the above equation suggests. There is considerable variety in the behavior of the acids in this respect. Some require the use of the most vigorous dehydrating agents in order to remove the water, while others lose water when distilled. Some of the anhydrides of the higher acids may even be heated with water for some time without noticeable regeneration of the acid. Acetic anhydride, however, and its neighboring homologues, while they do not react quite as vigorously with water as do the acid chlorides, yet are rapidly decomposed by it in the manner indicated by the following equation:



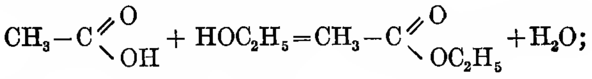
With alcohols and many other substances, the anhydrides behave quite similarly to the chlorides. Thus with the alcohols they substitute the hydrogen of the hydroxyl group by an acyl radicle forming esters. In this way acetic anhydride reacts with ethyl alcohol forming ethyl acetate:



$$\left.\begin{array}{l}CH_3-C{=}O\\ CH_3-C{=}O\end{array}\right\rangle O + HOC_2H_5 = CH_3COOH + CH_3-C\left\langle\begin{array}{l}O\\ OC_2H_5\end{array}\right.$$

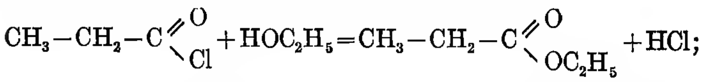
Acetic anhydride boils higher than acetic acid, while the chloride boils materially lower. It follows that when a high temperature is required, the anhydride is preferred to the chloride as an acylating agent.

Esters. Esters may be defined as acids in which the hydrogen of the carboxyl group has been replaced by an alkyl radicle. A good deal has already been said concerning this important class of substances, and the esters of the inorganic acids have been dealt with in some detail. Three general methods of preparation have been mentioned: the direct action of an acid upon an alcohol:



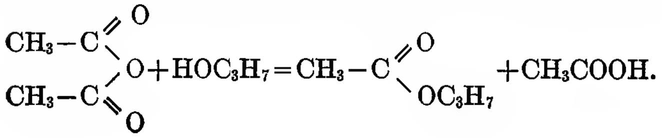
$$CH_3-C\left\langle\begin{array}{l}O\\ OH\end{array}\right. + HOC_2H_5 = CH_3-C\left\langle\begin{array}{l}O\\ OC_2H_5\end{array}\right. + H_2O;$$

the action of an acid chloride upon an alcohol:



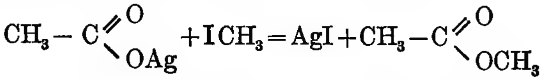
$$CH_3-CH_2-C\left\langle\begin{array}{l}O\\ Cl\end{array}\right. + HOC_2H_5 = CH_3-CH_2-C\left\langle\begin{array}{l}O\\ OC_2H_5\end{array}\right. + HCl;$$

and the action of the anhydride of the acid upon the alcohol:



$$\left.\begin{array}{l}CH_3-C{=}O\\ CH_3-C{=}O\end{array}\right\rangle O + HOC_3H_7 = CH_3-C\left\langle\begin{array}{l}O\\ OC_3H_7\end{array}\right. + CH_3COOH.$$

A fourth method consists in treating the salt of an acid with an alkyl halide; thus methyl acetate may be prepared by treating silver acetate with methyl iodide:

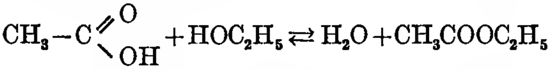


$$CH_3-C\begin{matrix}/\!\!/O\\ \diagdown OAg\end{matrix}+ICH_3=AgI+CH_3-C\begin{matrix}/\!\!/O\\ \diagdown OCH_3\end{matrix}$$

Of these methods, by far the most important is the first mentioned, which consists in the action of the acid upon the alcohol. This reaction is a reversible one, that is, by the action of water the ester is again decomposed into alcohol and acid.

It will be profitable to study the relations which obtain here with a good deal of care, because the process of ester-formation was, historically, one of the earlier reactions studied in the establishment of the mass-action law, and it still serves as an especially good illustration of that important generalization.

If an acid is mixed with an alcohol the reaction typified by the following equation,



$$CH_3-C\begin{matrix}/\!\!/O\\ \diagdown OH\end{matrix}+HOC_2H_5\rightleftarrows H_2O+CH_3COOC_2H_5$$

will begin to proceed from left to right at a certain rate. As soon as any ester and water have been formed, however, these will begin to react in the sense of the same equation when read from right to left. The net result of this will be to cut down the quantities of ester and water formed in a given time. A point is finally reached where the velocity of saponification is equal to that of esterification. This is a chemical equilibrium; that is, beyond this point analysis will show no further change in the proportions of alcohol, acid, ester, and water present in the reacting mixture.

If instead of a mixture of acid and alcohol, a similar mixture of the ester and water had been taken, something entirely analogous would have occurred. Then saponification would have taken place until equilibrium was reached, and at this point the relative concentrations of the four reacting components would have been the same as it was in the first case. That is to say, in any reversible reaction, the same equilibrium is reached from whichever direction it is approached.

The fundamental relationship expressed by the mass-action law is the fact that the velocity with which a reaction takes place is directly proportional to the products of the molecular concentrations of the reacting components. Translated into the terms of the present case, this means that the velocity of esterification, for example, is proportional to the number of molecules of acid present in unit volume multiplied by the number of molecules of alcohol. A perfectly similar statement can be made concerning the velocity of saponification. This is proportional to the product of the molecular concentrations of ester and water.

Now when equilibrium has been reached, the velocities of esterification and saponification are equal. Hence, at this point, the product of the concentrations of acid and alcohol must stand in a fixed relation to the product of the concentrations of ester and water. This relation may be conveniently expressed mathematically as follows:

$$\frac{\text{mol. conc. of acid} \times \text{mol. conc. of alcohol}}{\text{mol. conc. of ester} \times \text{mol. conc. of water}} = \text{constant.}$$

For a given reaction it is not difficult to determine the numerical value of this constant. Experiment has shown that when acetic acid and ethyl alcohol are mixed in equimolecular quantities, that is, in the proportion of 46 grams alcohol to 60 grams acetic acid, equilibrium is established when two-thirds of a mol of both ester and water have been formed. The condition in the reacting mixture at this point finds expression in the following equation: *

$$\frac{\frac{1}{3} \cdot \frac{1}{3}}{\frac{2}{3} \cdot \frac{2}{3}} = K = \frac{1}{4},$$

or $\frac{1}{4}$ is the constant of this particular reaction.

Verification of the law is found in the fact that when the proportions of acid and alcohol originally taken are varied most widely, the reaction always proceeds in such a way that when equilibrium has been reached, and the molecular concentrations found present in the reacting mixture are substituted in the above equation, the same constant, $\frac{1}{4}$, is always obtained.

The applications of the mass-action law are extremely important and far-reaching. Only one will be considered at this point. In chemical work, questions like the following are of frequent occurrence: From a given amount of acid (or alcohol) how may the maximum quantity of ester be obtained? The mass-action law suggests two ways by which the yield of ester may be improved. One is the elimination of water from the reaction. Since at equilibrium the products of the concentrations of ester and water must have a certain value, decrease in the quantity of water must increase the amount of ester formed. It is, of course, impossible to remove all the water from the reacting mixture, but the addition of dehydrating agents is a general practice in carrying out esterification processes.

The yield may be further influenced in another way. It follows from the law that the product of the concentrations of ester and water at equilibrium will be increased if the

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* It will be noticed that the terms in the equation are quantities, — not concentrations; but since the volume of the reacting mixture is constant in any given case, the two values are proportional.

product of the concentrations of alcohol and acid are also increased, and since, by the terms of the problem, the quantity of one of these substances — the acid for example — is limited, the end can be attained by increasing the quantity of the other constituent, — in this case the alcohol. What can be accomplished in this way is best indicated by calculating the yield in a specific case.

Let it be supposed that one mol of acetic acid has been treated with four mols of ethyl alcohol, and that, at equilibrium, x mols of ethyl acetate have been formed. Then it is evident from the equation,

$$CH_3COOH + HOC_2H_5 \rightleftarrows H_2O + CH_3COOC_2H_5,$$

that for every mol of ester, one mol of water is also formed; consequently the water present may also be represented by x. Similarly, for each mol of ester formed, one mol of acid and one of alcohol are used up, hence the quantities of these substances present in the reacting mixture at equilibrium may be represented by $1 - x$ and $4 - x$ respectively. Making these substitutions in our fundamental equation (page 96), we obtain the following:

$$\frac{(1 - x)(4 - x)}{x^2} = \frac{1}{4}.$$

The solution of this equation yields the result, $x = 0.93$. This means that when one mol of acetic acid is treated with four mols of ethyl alcohol, 0.93 mol of ester is formed, whereas it has already been shown on page 97, that when the acid and alcohol are employed in equimolar quantities, but 0.66 mol of ester is produced.

The relation of the mass-action law to esterification processes has been considered here in so much detail because it is applicable to all reversible reactions, and recent investigations have shown that many reactions which had formerly not been considered reversible in reality are so. Indeed many assert that all chemical reactions are reversible, but that, in certain cases, at equilibrium, the concentration of one or more components is so small as to escape observation with any means at our command. Without going so far as this somewhat dogmatic statement might imply, it is certainly true that many of the most important chemical reactions are reversible, that reversible reactions predominate in the organic field, and, consequently, that the reactions of organic compounds are best understood when they are looked upon as steps leading to a chemical equilibrium.

Turning back to the chemistry of the esters themselves, it is obvious that since any alcohol may unite with any acid to form an ester, the number of these compounds theoretically possible defies computation. Esters are usually prepared in the laboratory by heating together the alcohol and acid in the presence of some condensing agent, usually either concentrated sulphuric or gaseous hydrochloric acid.

Ethyl acetate may serve as a type of the esters formed by the action of the lower fatty acids upon the lower alcohols. It is a colorless liquid boiling at 77°, and has the specific gravity 0.924 at 0°. It has an agreeable, sweetish odor, usually described as 'fruity.' An odor of similar character is possessed by most compounds of this type. They are used somewhat as perfumes and in producing the 'bouquet' of artificial wines. Ethyl acetate itself is manufactured in considerable quantity as an intermediate product in the preparation of 'antipyrine,' a popular fever remedy.

The esters of the higher fatty acids with the higher alcohols constitute the chief ingredients of the natural waxes, of which beeswax is a familiar example. Spermaceti, a wax occurring in the head of the sperm whale and used to a certain extent for making candles, contains as principal ingredient, cetyl palmate, having the formula $C_{15}H_{31}\cdot COOC_{16}H_{33}$.

The esters which occur most widely in nature, as well as those of the highest technical utility, include compounds of alcohols and acids belonging to other series. The student will therefore not be in a position to realize the full importance of this class of substances until somewhat later.

The most important and characteristic reaction of the esters has been already noted. It is the splitting action which hydrolytic agents have upon them, producing alcohol and acid. In laboratory practice, this is carried out by boiling the ester with alkalies or dilute acids. The action of alkalies is easily understood. They unite with the acid as rapidly as it is formed, and so eliminate it as a factor in the reversible reaction, so that saponification can now go to completion. The equation now assumes the form:

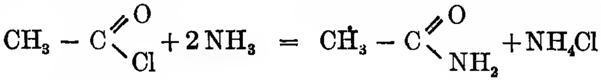
$$CH_3CO \cdot OC_2H_5 + KOH = CH_3CO \cdot OK + C_2H_5OH,$$

and it is obvious that one mol of ethyl acetate will require one mol of potassium hydroxide to saponify it. Use is made of this principle in oil-analysis, when it is customary to define the 'saponification-equivalent' as that weight of an ester which can be saponified by one equivalent of alkali. It is clear that this number will always stand in a simple ratio to the molecular weight of the ester concerned, and that it may serve to distinguish the latter from any other ester not isomeric with it.

When saponification is effected by acids, the action of the latter is catalytic, that is to say, they promote saponification without being themselves used up by the reaction. This catalytic action of the acids has proved an important support of the theory of electrolytic dissociation, for the hydrolyzing action of the acid has been shown to belong to the hydrogen ion. All acids show the property in some degree, and the velocity of saponification caused by different acids is proportional to their respective degrees of dissociation as determined by measurements of electric conductivity.

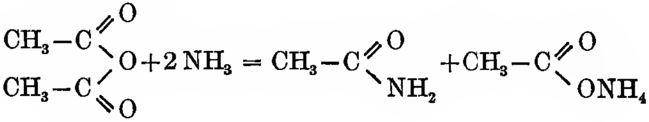
The Amides. These compounds are closely associated with the acids, and furnish a convenient means of identifying the latter, since they are, for the most part, crystalline solids of sharp and characteristic melting-point. They also appear as intermediate products in important reactions. The acid amides may be prepared by the action of ammonia upon the acid chlorides, the anhydrides, and the esters, in accordance with the following equations:

(1)



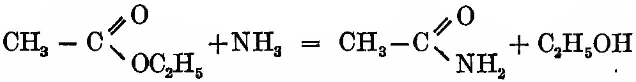
$$CH_3-C\begin{array}{l}/\!\!/O\\ \backslash Cl\end{array}+2NH_3 = CH_3-C\begin{array}{l}/\!\!/O\\ \backslash NH_2\end{array}+NH_4Cl$$

(2)



$$\begin{array}{l}CH_3-C\begin{array}{l}/\!\!/O\\ \backslash\end{array}\\ \qquad\qquad\;\; O\\ CH_3-C\begin{array}{l}/\\ \backslash\!\!\backslash O\end{array}\end{array}+2NH_3 = CH_3-C\begin{array}{l}/\!\!/O\\ \backslash NH_2\end{array}+CH_3-C\begin{array}{l}/\!\!/O\\ \backslash ONH_4\end{array}$$

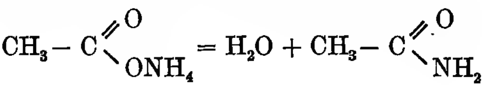
(3)



$$CH_3-C\begin{array}{l}/\!\!/O\\ \backslash OC_2H_5\end{array}+NH_3 = CH_3-C\begin{array}{l}/\!\!/O\\ \backslash NH_2\end{array}+C_2H_5OH$$

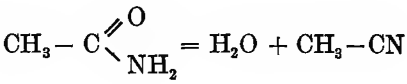
When the ammonium salts of the acids are heated, they readily lose water and go over to amides:

(4)



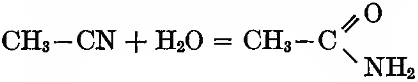
$$CH_3-C\begin{array}{l}/\!\!/O\\ \backslash ONH_4\end{array}= H_2O + CH_3-C\begin{array}{l}/\!\!/O\\ \backslash NH_2\end{array}$$

The amides themselves, on treatment with a dehydrating agent, such as phosphorus pentoxide, yield the nitriles of the acids:

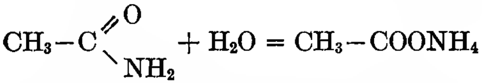


$$CH_3-C\begin{array}{l}/\!\!/O\\ \backslash NH_2\end{array}= H_2O + CH_3-CN$$

These reactions place the amides as intermediate products between the nitriles and the acids in the saponification of the latter:



$$CH_3-CN + H_2O = CH_3-C\genfrac{}{}{0pt}{}{/\!\!/ O}{\backslash NH_2}$$

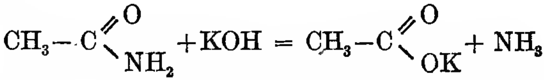


$$CH_3-C\genfrac{}{}{0pt}{}{/\!\!/ O}{\backslash NH_2} + H_2O = CH_3-COONH_4$$

(see page 74) and they can sometimes be obtained thus by careful regulation of the experimental conditions.

The methods of preparation furnish the experimental evidence for the formula given. This represents the amides as acids in which hydroxyl has been substituted by NH_2, the amino-group. It is also possible to regard these substances as ammonia in which one hydrogen has been substituted by an acyl radicle.

So far as chemical behavior is concerned, one of their most important reactions has been mentioned already. This is the fact that they may be hydrolyzed to form acids. In practice this is usually accomplished by boiling with alkalies, when the alkali salt of the acid is formed, and ammonia is evolved:



$$CH_3-C\genfrac{}{}{0pt}{}{/\!\!/ O}{\backslash NH_2} + KOH = CH_3-C\genfrac{}{}{0pt}{}{/\!\!/ O}{\backslash OK} + NH_3$$

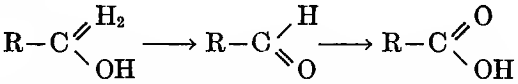
The amides show certain other important reactions, consideration of which must be postponed until the study of some of the other classes of nitrogen compounds has been taken up.

Acetamide is a hygroscopic, crystalline solid. As usually prepared, it contains some impurity, having an odor suggestive of mice. The pure amide is, however, odorless. It melts at 82°. The other amides of this series do not have sufficient individual importance to make it worth while to enumerate their physical properties. The student will observe later, however, that there are a great many more complicated substances of the utmost importance whose structure is analogous to that of the amides. It is therefore necessary to fix the chemical relations of the group carefully in mind.

CHAPTER V.

ALDEHYDES, KETONES, AND AMINES.

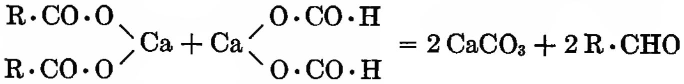
It has already been shown (page 63) that when the primary alcohols are oxidized to acids, the aldehydes appear as intermediate products. This relationship may be indicated by the following scheme in which R represents any alkyl radicle:



$$R-C\overset{H_2}{\underset{OH}{\lessgtr}} \longrightarrow R-C\overset{H}{\underset{O}{\lessgtr}} \longrightarrow R-C\overset{O}{\underset{OH}{\lessgtr}}$$

The formulæ for acids and the alcohols having been already established, that of the aldehydes can scarcely be in doubt. The formula of an aldehyde, then, is characterized by the possession of the carbonyl group $\overset{|}{\underset{|}{\mathrm{C}}}\mathrm{O}$, united on one side to an alkyl radicle and on the other to hydrogen.

Though the aldehydes can be obtained by the oxidation of the alcohols, they cannot be prepared conveniently by the direct reduction of the corresponding acids. The most common way of passing from an acid to the corresponding aldehyde is to distill the calcium salt of the acid with calcium formate:



$$\begin{matrix} R\cdot CO\cdot O \\ R\cdot CO\cdot O \end{matrix}\!\!>\!Ca + Ca\!<\!\!\begin{matrix} O\cdot CO\cdot H \\ O\cdot CO\cdot H \end{matrix} = 2\,CaCO_3 + 2\,R\cdot CHO$$

This is an extremely important and general reaction for the preparation of compounds containing the carbonyl group. The names of the aldehydes (except in those cases where special names are employed) are derived from those of the corresponding acids; thus we have the names formaldehyde, acetaldehyde, and the like. By convention it is customary in abbreviated formulæ to write the aldehyde group CHO in order to avoid confusion with the alcohols.

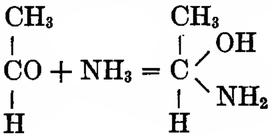
As a rule, the aldehydes boil lower than either the acids or alcohols having the same number of carbon atoms. The lower members of the series have a peculiar penetrating odor. In general it may be said that the odors of the aldehydes are strongly marked, and in the majority of cases agreeable.

Chemically the aldehydes are extremely reactive. One of the most characteristic items in their behavior is the ease with which they are oxidized to form the acids having the same number of carbon atoms. On account of this peculiarity they serve as reducing agents. They reduce, for example, metallic silver from ammoniacal solutions of its salts:

$$\begin{aligned} &2\,AgNO_3 + CH_3CHO + 3\,NH_4OH \\ &\qquad = CH_3COONH_4 + 2\,NH_4NO_3 + 2\,H_2O + Ag_2, \end{aligned}$$

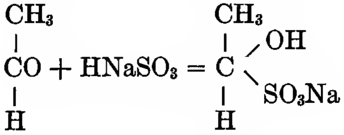
and they reduce alkaline solutions of cupric salts with the formation of cuprous oxide. A typical solution of this kind is that commonly known as 'Fehling's solution.' It is prepared by mixing solutions of copper sulphate, potassium hydroxide, and sodium potassium tartrate in such proportions that cupric hydroxide shall not be precipitated by the alkali.

Aldehydes show numerous and important addition reactions, thus ammonia is added in accordance with the equation,

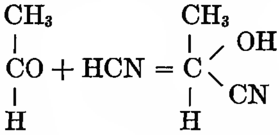


$$\begin{array}{c} CH_3 \\ | \\ CO \\ | \\ H \end{array} + NH_3 = \begin{array}{c} CH_3 \\ | \\ C \\ | \\ H \end{array}\!\!\begin{array}{l} \diagup OH \\ \\ \diagdown NH_2 \end{array}$$

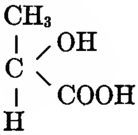
With sodium bisulphite, also, addition products are formed:



These compounds are crystalline and particularly useful for the separation and purification of the aldehydes, since they can easily be decomposed again by treatment with acids or alkaline carbonates, the aldehydes being regenerated. A reaction more important than either of the above is that which takes place with hydrocyanic acid:



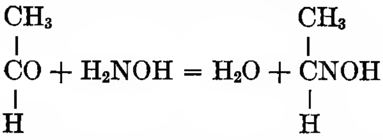
The resulting product is the nitrile of a hydroxy-acid:



This illustrates a general method for the preparation of those acids which have a hydroxyl group attached to that carbon atom which is next to the carboxyl. This is termed the *alpha* carbon atom.

Another peculiarity of the aldehydes which may be mentioned among the addition reactions is their tendency to polymerize; that is, several molecules of aldehyde combine to form a complex of the same percentage composition as the original aldehyde but of higher molecular weight. Such polymerizations take place in several different ways, forming diverse classes of products. Some of these will be described when the individual aldehydes are studied.

Still another class of reactions shown by aldehydes includes those involving condensation. This term is usually applied to those reactions where two compounds unite with elimination of water or some other simple inorganic compound.* When aldehydes take part in such reactions the oxygen of the carbonyl group usually unites with two hydrogen atoms of the other compound, and the remaining portions of the two molecules unite. Though aldehydes show many reactions of this type, but one will be mentioned here as an example. Hydroxylamine condenses with aldehydes in accordance with the following equation:



$$\begin{array}{l}CH_3\\ |\\ CO\\ |\\ H\end{array} + H_2NOH = H_2O + \begin{array}{l}CH_3\\ |\\ CNOH\\ |\\ H\end{array}$$

The products are called oximes and they are characteristic derivatives of the aldehydes and ketones.

One other reaction should be mentioned, since it serves to distinguish aldehydic from hydroxyl oxygen. It will be remembered that, upon the latter, phosphorus pentachloride

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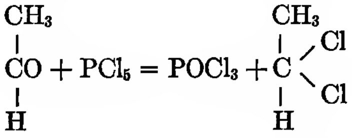
* The term *condensation* is also used by most organic chemists in such a way as to include reactions involving only addition, as in the expressions 'aldol condensation,' 'benzoin condensation,' and the like. Now it must be conceded that this use of the word has a logical foundation, for when addition takes place between two gas-molecules there is an actual condensation, that is, decrease in volume. In common with some other chemists, however, the author prefers to restrict the use of the word to that class of reactions referred to in the text, because no other general term is equally available for these, while for reactions of the other type the terms 'addition' and 'polymerization' are both at our disposal. (See also Lassar-Cohn: 'Arbeitsmethoden,' page 578 [1903].)

reacts in such a way that the hydroxyl group is replaced by chlorine:

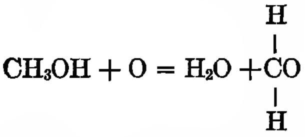
$$C_2H_5OH + PCl_5 = HCl + POCl_3 + C_2H_5Cl.$$

With aldehydes, oxygen alone is replaced by two atoms of chlorine.



This reaction is of frequent application for the preparation of compounds having two halogen atoms attached to the same carbon atom.

Formaldehyde. When the vapors of methyl alcohol mixed with air are passed over a warm metallic surface (platinum or copper may be employed), oxidation takes place upon the surface of the metal and formaldehyde is produced:



$$CH_3OH + O = H_2O + \overset{\displaystyle H}{\overset{|}{\underset{\underset{\displaystyle H}{|}}{C}}}O$$

The heat generated by the reaction is usually sufficient to keep the metal glowing. This method is carried out on a large scale for producing this substance for technical purposes. The quantities manufactured are very large, Germany alone producing annually about a half million kilograms. Formaldehyde is a gas of a peculiar sharp choking odor. It is quite soluble in water, and a 40% solution is brought upon the market under the name of 'formalin.' This is largely used as a preservative, formaldehyde being an efficient germicide. The hardening action of this material upon substances of protein character makes it useful in many branches of industry. The gas itself is used for disinfecting purposes, advantage being frequently taken of the method of preparation outlined above. Methyl alcohol is burned in a specially constructed lamp which permits only incomplete combustion, with consequent formation of the aldehyde. The gas may be condensed to a liquid by low temperatures. This liquid boils at −21°. The polymerization of formaldehyde yields several products whose molecular weight is uncertain. When a solution of formalin is evaporated, an amorphous white solid known as paraformaldehyde is precipitated. This substance has the odor of the gas, and is soluble in water, such solutions differing in no respect from those formed when formaldehyde itself is dissolved in water. If formalin solution is treated with small amounts of concentrated sulphuric acid, a mixture of products is obtained, all of which are solid. These are known as polyoxymethylenes and are not well characterized. The aqueous solution of formaldehyde doubtless represents an equilibrium between the monomolecular compound and several of the polymers. From formaldehyde vapor, under certain conditions, may be formed still another substance, — α-oxytrimethylene, — which, unlike those just mentioned, does not smell of formaldehyde, and gives none of the aldehyde reactions. This substance has three times the molecular weight of the simple compound.

Especial interest attaches to formaldehyde on account of a theory originally suggested by Baeyer to the effect that this substance is the first reduction product of carbon dioxide in the leaves of the green plant, and that the plant produces carbohydrates by the polymerization of formaldehyde. This theory, which has been under discussion for many years without having been found susceptible of definite proof, has much speculative interest. As will be seen when the study of the carbohydrates is taken up, it has been found possible to build up substances of this class from formaldehyde under certain conditions. On the other hand, only traces of formaldehyde have ever been found in plants, and even at low concentrations it is an active poison for the plant cell. It is, however, a part of the theory that the formaldehyde is further polymerized as soon as it is formed.

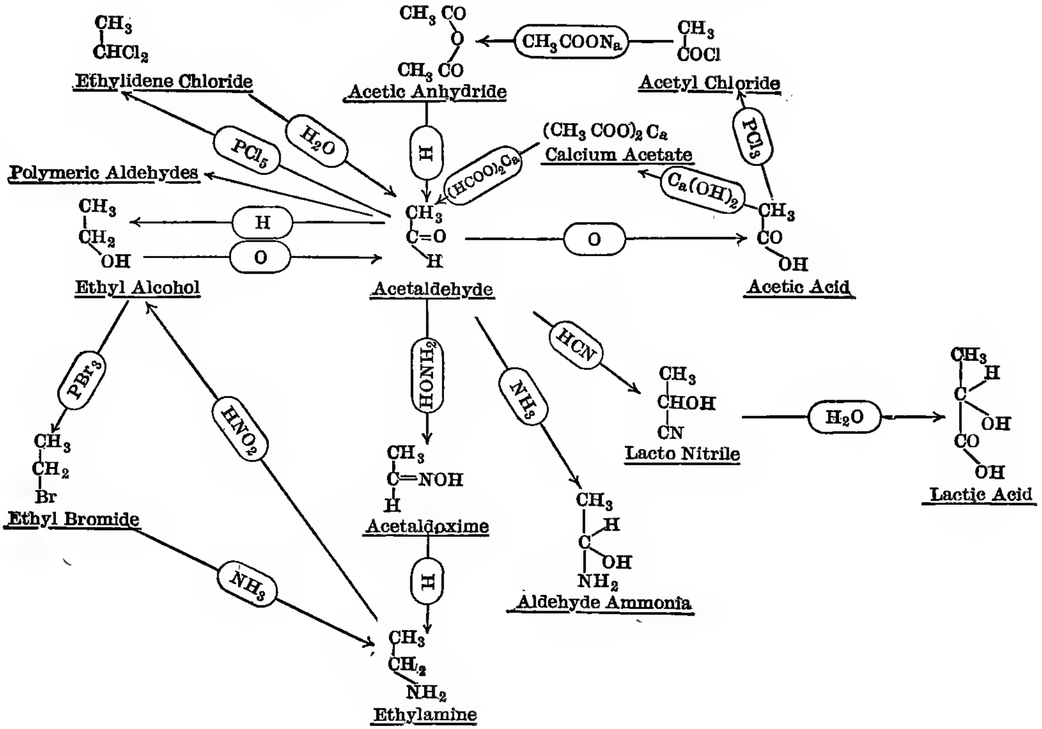
Acetaldehyde. This substance is usually prepared by the oxidation of ethyl alcohol by means of potassium bichromate and sulphuric acid:

$$3\,CH_3CH_2OH + K_2Cr_2O_7 + 4\,H_2SO_4 =$$
$$3\,CH_3CHO + K_2SO_4 + Cr_2(SO_4)_3 + 7\,H_2O.$$

It is an extremely volatile liquid boiling at 21°. It has a peculiar odor which, in strong dilution, is refreshing and agreeable. On the other hand, when the vapors are inhaled in concentrated form a peculiar cramp in the chest is produced, which temporarily takes away the power of breathing. Acetaldehyde shows all the typical aldehyde reactions. It reduces ammoniacal silver nitrate solution in the cold; when treated with ammonia gas in ethereal solution a crystalline addition product called aldehyde-ammonia is precipitated; it adds sodium bisulphite, etc.

When acetaldehyde is treated with a very small quantity of concentrated sulphuric acid, polymerization takes place with almost explosive violence. The product is called paraldehyde. It is a liquid which boils at 124°, and shows none of the ordinary aldehyde reactions. Its vapor density indicates that three molecules of the original aldehyde have united. When distilled with dilute sulphuric acid it is again depolymerized. If acetaldehyde is treated in the cold with hydrochloric, sulphuric, or sulphurous acid, there is formed in addition to paraldehyde a solid product called metaldehyde. This substance also has a molecular weight

GENETIC RELATIONS OF THE ALDEHYDES.



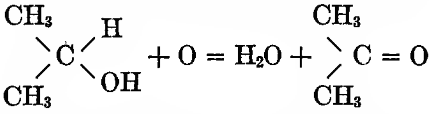
three times as great as the simple aldehyde. Its vapors dissociate again to the ordinary variety.

A substance of different character is formed when aldehyde is boiled with alkalies. This is a yellow gummy material known as aldehyde resin. It is formed from aldehyde by loss of water. It has an aromatic odor, and a study of its decomposition products goes to show that it is probably a derivative of benzene. Acetaldehyde is almost always present in commercial alcohol, and betrays its presence by the yellow color which a solution of caustic soda or potash in such alcohol assumes. The color is due to the formation of a small quantity of aldehyde resin.

The higher aldehydes of this series are not very important, but some of them find use as perfumes. The odor is a less noticeable property of those members of the series containing more than fourteen atoms of carbon.

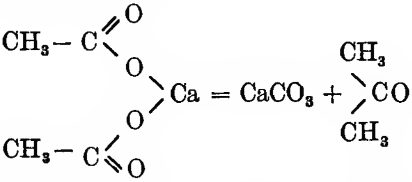
Ketones.

The ketones are closely related to the aldehydes. Both contain the carbonyl group, but whereas in the aldehydes this is connected on one side to an alkyl radicle and on the other to hydrogen, in the ketones it is connected on both sides to alkyl radicles. As might be expected, the two classes of substances show many analogies in their methods of preparation and behavior: thus, while the aldehydes are formed by the oxidation of primary alcohols, ketones are formed by the oxidation of secondary alcohols:

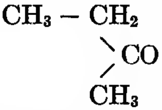


$$\begin{matrix} CH_3 & & H \\ & \diagdown C \diagup & \\ & \diagup \quad \diagdown & \\ CH_3 & & OH \end{matrix} + O = H_2O + \begin{matrix} CH_3 & \\ \diagdown & \\ & C = O \\ \diagup & \\ CH_3 & \end{matrix}$$

One of the most important methods for the preparation of ketones depends upon another reaction closely analogous to one employed for the preparation of aldehydes. It will be recalled that when calcium acetate is distilled with calcium formate, acetaldehyde is produced. Similarly, when calcium acetate is distilled alone, calcium carbonate is formed and the simplest ketone, acetone, distills over:

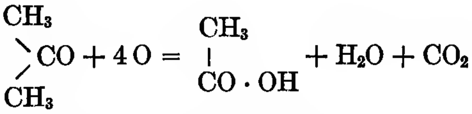


The same reaction may also be applied to the preparation of what are called mixed ketones, that is, substances in which two dissimilar alkyl radicles are attached to the carbonyl group. If a mixture of calcium acetate and calcium propionate is subjected to dry distillation, ethyl methyl ketone,



is formed, along with some acetone and some diethyl ketone.

In chemical behavior, the ketones strongly resemble the aldehydes. Reduction yields secondary alcohols, while oxidation takes place with much more difficulty than with the aldehydes, because here oxidation involves a rupture of the carbon chain:



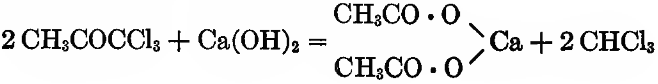
This makes it plain why ketones do not act as reducing agents.

The ketones enter into addition and condensation reactions which are similar to those shown by the aldehydes, but since they have no hydrogen atom attached to the carbonyl group, they do not readily polymerize.

Acetone or dimethyl ketone is the simplest and best known member of the series. It is found in pyroligneous acid, and may be obtained thence after the acetic acid has been removed by treatment with lime, and the methyl alcohol has been combined with calcium chloride or oxalic acid. Much of the crude calcium acetate formed in the same process is also distilled with superheated steam for the preparation of acetone. The yield by this method is good, but the product contains some of the higher homologues, notably ethyl methyl ketone.

Acetone is a colorless liquid of a peculiar, not disagreeable odor and burning taste. It boils at 57°, and is miscible in all proportions with water as well as with alcohol and ether. Like alcohol, it can be separated from its aqueous solution by means of potassium carbonate. It finds extensive use as a solvent, as well as in the preparation of chloroform, iodoform, and sulphonal. It is also used for gelatinizing nitro-cellulose in the preparation of smokeless powder and allied products.

In the preparation of chloroform, acetone is treated with a mixture of bleaching powder and water, and the mixture is distilled. The chloroform settles out as a heavy oily liquid at the bottom of the distillate. The mechanism of the reaction is regarded as consisting in a chlorination of the acetone to form trichloroacetone, CH_3COCCl_3, which then splits under the action of the lime in the bleaching powder, yielding chloroform and calcium acetate:

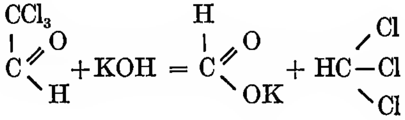


$$2\,CH_3COCCl_3 + Ca(OH)_2 = \begin{matrix} CH_3CO \cdot O \\ CH_3CO \cdot O \end{matrix}\!\!>\!Ca + 2\,CHCl_3$$

Ethyl alcohol may also be used as a starting point in the preparation of chloroform. In this case trichloroacetaldehyde, more commonly known as 'chloral,'

$$\begin{array}{c} CCl_3 \\ | \\ CHO \end{array}$$

is an intermediate product. When it is desired to isolate this compound, chlorine gas is led directly into ethyl alcohol. If water is present, chloral unites with it to form a crystalline addition product known as 'chloral hydrate.' This is used in medicine as a hypnotic. When boiled with alkalies, chloral yields chloroform and an alkaline formate:



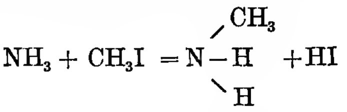
Chloroform is a heavy, colorless liquid of a rather sweetish, agreeable odor. It boils at 61°, and has the specific gravity 1.5. Owing to its high chlorine content, it is not inflammable. The use of chloroform as an anæsthetic is well known. It was first employed in surgery for this purpose by Simpson in Edinburgh in 1847.

The preparation of iodoform depends upon a series of reactions entirely similar to those which take place when chloroform is prepared from alcohol or acetone. Ethyl alcohol is treated with iodine and caustic potash, and the mixture gently warmed. The product is a yellow, crystalline solid. It has a characteristic odor and melts at 120°. It is used in dressing wounds. The formation of iodoform by the method above outlined makes a delicate and convenient test for the presence of ethyl alcohol or of acetone. Some other substances, however, show the reaction.

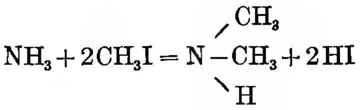
The Amines.

There are several distinct classes of organic compounds which contain nitrogen. Of these, the nitriles, the amides and the ammonium salts have already received some attention. Another important class is that of the amines or substituted ammonias. Those of technical importance belong to the aromatic members of the group, but several things of interest can be learned by a study of the aliphatic representatives.

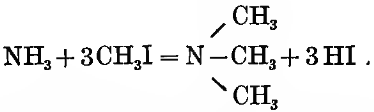
If ammonia is treated with an alkyl halide, such as methyl iodide, one, two or three of the hydrogens of ammonia may be substituted by an alkyl group: [*]



$$NH_3 + CH_3I = N\begin{array}{l}\diagup CH_3\\ -H\\ \diagdown H\end{array} + HI$$



$$NH_3 + 2CH_3I = N\begin{array}{l}\diagup CH_3\\ -CH_3\\ \diagdown H\end{array} + 2HI$$



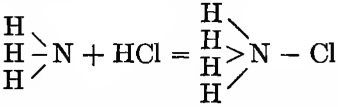
$$NH_3 + 3CH_3I = N\begin{array}{l}\diagup CH_3\\ -CH_3\\ \diagdown CH_3\end{array} + 3HI\,.$$

The products are called respectively primary, secondary, and tertiary amines. The first class is characterized by the grouping $R-NH_2$, the second by $\begin{array}{l}R\diagdown\\ \quad\;>NH\\ R\diagup\end{array}$ and the third by $\begin{array}{l}R\diagdown\\ R-N\\ R\diagup\end{array}$

---

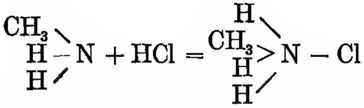
[*] The equations are written in this form in order to emphasize the fundamental fact of substitution. In practice, of course, the hydriodic acid forms addition-products with the ammonia and also with the amines as indicated on the following pages. The methyl iodide behaves similarly, and the result is a complex mixture of salts.

The amines of lower molecular weight are gases at ordinary temperature. They have the odor of ammonia, and closely resemble that substance in physical and chemical properties. This is particularly well illustrated in the matter of salt-formation. If the gases, hydrochloric acid and ammonia, come together in the atmosphere, addition takes place and solid ammonium chloride is formed:



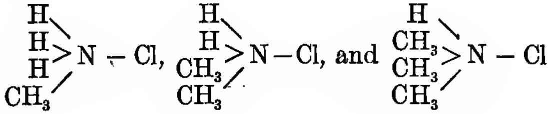
$$\begin{matrix}H\\H\\H\end{matrix}\!>N + HCl = \begin{matrix}H\\H\\H\\H\end{matrix}\!>N - Cl$$

The amines act in precisely the same way. They also add acids:



$$\begin{matrix}CH_3\\H\\H\end{matrix}\!>N + HCl = \begin{matrix}H\\CH_3\\H\\H\end{matrix}\!>N - Cl$$

and the salts formed are substituted ammonium salts, having properties closely resembling those of the latter; thus they are crystalline solids, soluble in water, and their solutions conduct the electric current. It is therefore appropriate that the compounds whose formulæ follow:



$$\begin{matrix}H\\H\\H\\CH_3\end{matrix}\!>N - Cl,\quad \begin{matrix}H\\H\\CH_3\\CH_3\end{matrix}\!>N - Cl, \text{ and } \begin{matrix}H\\CH_3\\CH_3\\CH_3\end{matrix}\!>N - Cl$$

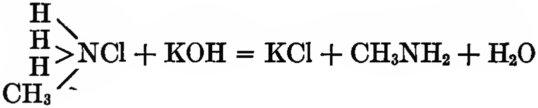
should be named methyl ammonium chloride, dimethyl ammonium chloride, and trimethyl ammonium chloride respectively. Before the valence theory was perfected these substances were formulated as double compounds, thus: CH_3NH_2,HCl; $(CH_3)_2NH,HCl$; and $(CH_3)_3N,HCl$; and given the names, methylamine hydrochloride, dimethylamine hydrochloride, and trimethylamine hydrochloride respectively.

The latter names will still be met with in many books. We meet in these compounds the first representatives of the organic salts, while the amines themselves are the most typical organic bases.

The salts resemble ammonium chloride in the manner of their decomposition as well as in their formation. When ammonium chloride is heated with alkalies, the ammonium hydroxide first formed is at once decomposed into ammonia gas and water:

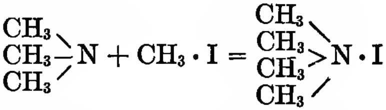
$$NH_4Cl + KOH = KCl + NH_4OH = KCl + NH_3 + H_2O.$$

Similarly, if methylamine hydrochloride is heated with alkali, decomposition takes place into water and methylamine:



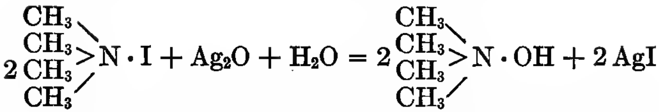
$$\left.\begin{array}{r}H\\H\\H\\CH_3\end{array}\right\rangle NCl + KOH = KCl + CH_3NH_2 + H_2O$$

The amines not only have the capacity for adding acids, but they also add the alkyl halides; thus trimethylamine can add methyl iodide as indicated by the following equation:



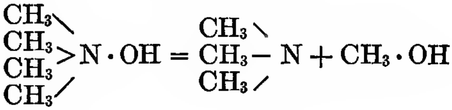
$$\left.\begin{array}{r}CH_3\\CH_3\\CH_3\end{array}\right\rangle N + CH_3\cdot I = \left.\begin{array}{r}CH_3\\CH_3\\CH_3\\CH_3\end{array}\right\rangle N\cdot I$$

The product bears the appropriate name, tetramethyl ammonium iodide. This substance differs slightly in its chemical behavior from the salts just mentioned, but it shows only those differences which might be expected from its formula. Its salts are not readily decomposed by aqueous alkalies, but if they are treated with moist silver oxide, insoluble silver iodide is precipitated, and the solution contains the free base, tetramethyl ammonium hydroxide:



$$2\left.\begin{matrix}CH_3\diagdown\\CH_3\\CH_3\\CH_3\diagup\end{matrix}\right> N\cdot I + Ag_2O + H_2O = 2\left.\begin{matrix}CH_3\diagdown\\CH_3\\CH_3\\CH_3\diagup\end{matrix}\right> N\cdot OH + 2\,AgI$$

It is obvious that this base cannot decompose as ammonium hydroxide does, because there is, in this case, no hydrogen attached directly to the nitrogen which might split off to form water. It accordingly remains undecomposed in solution. If heated for itself, however, the base does decompose into trimethylamine and methyl alcohol:



$$\left.\begin{matrix}CH_3\diagdown\\CH_3\\CH_3\\CH_3\diagup\end{matrix}\right> N\cdot OH = \begin{matrix}CH_3\diagdown\\CH_3-\\CH_3\diagup\end{matrix} N + CH_3\cdot OH$$

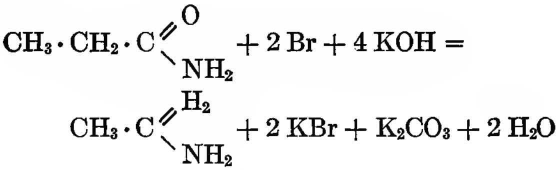
This is the closest analogy to the behavior of ammonium hydroxide which its structure permits. Substances of this type, or quaternary bases as they are called, are comparable in strength to the hydroxides of the alkali metals. Other points of resemblance are the caustic action which they exert upon the skin, and the readiness with which they absorb carbon dioxide from the air to form carbonates.

The reaction between ammonia and the alkyl halides leads to the formation of all three kinds of amines as well as the ammonium bases just mentioned, and the isolation of each component in such a mixture is a chemical operation of no little difficulty. As the primary amines are rather more important for us than any of the other classes, it is fortunate that there are several methods which lead to the formation of this class unmixed with representatives of the other types.

One of these methods consists in the reduction of the nitriles. When these substances are treated with zinc and hydrochloric acid, or better with sodium and alcohol, primary amines are formed in accordance with the following equation,

$$CH_3\cdot CH_2\cdot C \vdots N + H_4 = CH_3\cdot CH_2\cdot CH_2\cdot NH_2.$$

Another method of preparation is important on several grounds. This starts from the amides of those acids which contain one more atom of carbon than the amines in question. When the amides are treated with bromine and caustic potash, a complicated series of reactions takes place. The net result is the elimination of the carbonyl group from the amide, and the operation can be summed up in the following equation:



$$CH_3\cdot CH_2\cdot C\begin{matrix}\nearrow\!\!\!\!\nearrow O\\ \searrow NH_2\end{matrix} + 2\,Br + 4\,KOH =$$

$$CH_3\cdot C\begin{matrix}\nearrow\!\!\!\!\nearrow H_2\\ \searrow NH_2\end{matrix} + 2\,KBr + K_2CO_3 + 2\,H_2O$$

This reaction is particularly important as a step in passing from one acid of the fatty series to another having one less carbon atom. In the case of those acids containing more than five atoms of carbon, the reaction results in the formation of the lower nitrile instead of the amine. This makes an even more convenient method for preparing an acid from the next higher:

$$(1)\quad R\cdot CH_2\cdot CO\cdot NH_2 + 6\,Br + 8\,KOH = R\cdot CN + 6\,KBr + K_2CO_3 + 6\,H_2O,$$

$$(2)\quad RCN + 2\,H_2O = RCOOH + 2\,NH_3.$$

Among the reactions of the amines, that of salt-formation has been already mentioned. There is another reaction which is not only important in its application to primary amines, but by its aid it is possible to distinguish the several classes from each other. This reaction is the one with nitrous acid. It will be recalled that ammonium nitrite is not a very stable compound, and that even upon boiling its aqueous solution, it breaks up into nitrogen and water;

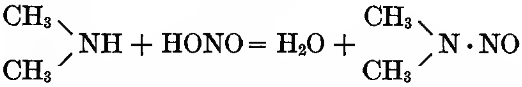
in fact this is a convenient laboratory method for the preparation of nitrogen:

$$NH_4NO_2 = 2\,H_2O + N_2.$$

Primary amines, when treated with nitrous acid, behave in an analogous manner. Nitrogen gas is formed and one molecule of water, but instead of the second molecule, a substituted water, that is, an alcohol, is produced:

$$C_2H_5NH_2 + HNO_2 = H_2O + N_2 + C_2H_5OH.$$

This replacement of the amino-group, NH_2, by hydroxyl is closely associated with some other chemical reactions of great theoretical as well as technical importance which will be studied later. Here it should be added that secondary amines do not react in a similar way with nitrous acid. Instead, substances called nitrosamines are formed in accordance with the following equation:



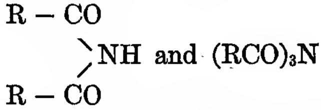
$$\begin{matrix}CH_3\diagdown \\ CH_3\diagup\end{matrix}NH + HONO = H_2O + \begin{matrix}CH_3\diagdown \\ CH_3\diagup\end{matrix}N\cdot NO$$

Finally, the tertiary amines have no hydrogen which is directly connected to nitrogen, and, apparently in consequence of this fact, do not react with nitrous acid.

Individual Amines. Methylamine, dimethylamine, and trimethylamine are all gases at ordinary temperature. They resemble ammonia in their odor and their solubility in water. What has been said of their odor refers to the odor of the gases or highly concentrated solutions. In high dilution, the odor of ammonia becomes associated with an odor of decaying fish, and in such material several substances of this class occur. The methylamines differ from ammonia in the fact that they are combustible. The ethylamines are volatile liquids of similar properties.

The Acid Amides.

These substances have already received brief consideration in connection with the other acid derivatives. Here it is desired only to point out the analogies which exist between them and the amines. They differ from the latter in having the hydrogen of ammonia replaced by an acyl (page 92) instead of an alkyl radicle. The negative character of the acyl group may be regarded as compensating the basic nature of ammonia, and, as a result, the amides are practically neutral substances. Secondary and tertiary amides having such formulæ as



$$\begin{matrix} R-CO & & \\ & \rangle NH & \text{and } (RCO)_3N \\ R-CO & & \end{matrix}$$

are known, but are rare and unimportant as compared with the primary compounds. The latter show the same reaction with nitrous acid as the primary amines, and this affords an additional means of passing from the amides to the corresponding acids:

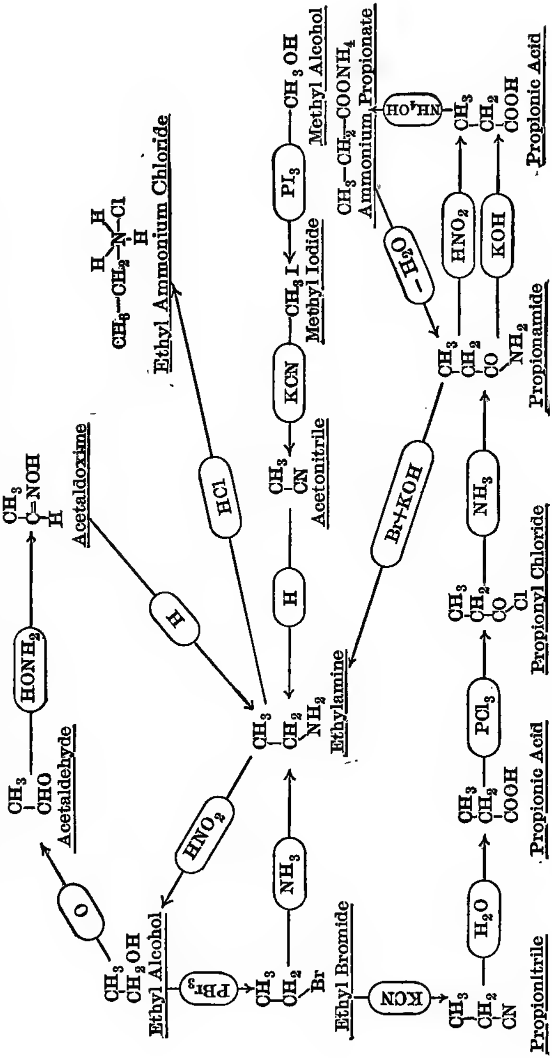
(1) $CH_3CONH_2 + KOH = CH_3COOK + NH_3$.

(2) $CH_3CONH_2 + HNO_2 = H_2O + N_2 + CH_3COOH$.

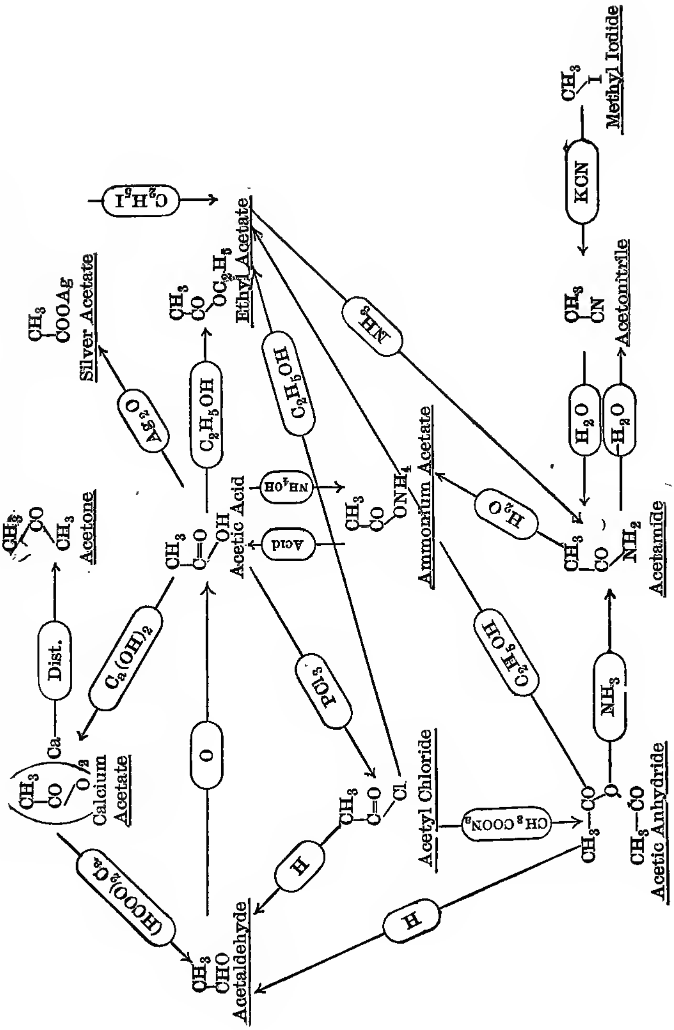
Relations between the Fatty Acids and Their Derivatives. Upon page 125 will be found a scheme representing, among other things, methods of passing from acetic acid to propionic acid and back again. It indicates most of the more important genetic relationships which obtain between the various classes of substances hitherto studied, and the operations referred to are, for the most part, of general application, coördinating a good deal of valuable information.

It should be added that the constitution of substances belonging to the higher series is usually established by connecting them, through some of the reactions here indicated, with other compounds of known constitution.

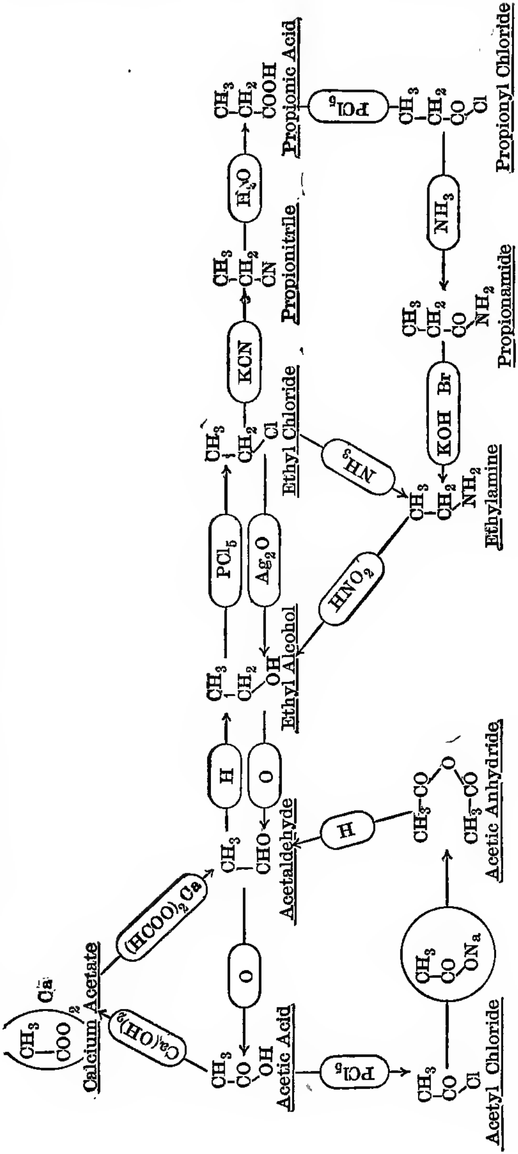
GENETIC RELATIONS OF THE AMINES AND AMIDES.



GENETIC RELATIONS OF THE ACID DERIVATIVES.



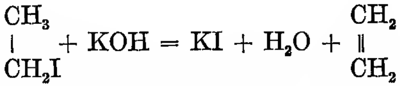
GENETIC RELATIONSHIPS CONNECTING ACETIC AND PROPIONIC ACIDS.



CHAPTER VI.

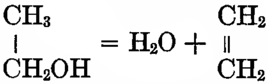
UNSATURATED COMPOUNDS.

Ethylene. When ethyl iodide is treated with potassium hydroxide in alcoholic solution, the following reaction takes place:



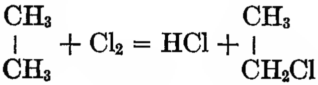
$$\begin{array}{c}CH_3\\ |\\ CH_2I\end{array} + KOH = KI + H_2O + \begin{array}{c}CH_2\\ \|\\ CH_2\end{array}$$

The product, whose constitution will be discussed later, is called ethylene. It is a colorless gas of a sweetish odor which burns with a flame more luminous than that of methane. Ethylene makes up about 2% of ordinary coal gas, and the latter owes much of its luminosity to the presence of this constituent. Ethylene is usually prepared in the laboratory by the action of sulphuric acid on alcohol, the sulphuric acid being kept in excess. The reaction is essentially a dehydration of ethyl alcohol:



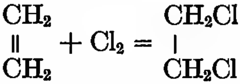
$$\begin{array}{c}CH_3\\ |\\ CH_2OH\end{array} = H_2O + \begin{array}{c}CH_2\\ \|\\ CH_2\end{array}$$

In its chemical properties, this gas differs in an important respect from the hydrocarbons previously studied. When ethane, for example, is treated with chlorine, the following familiar reaction occurs:



$$\begin{array}{c}CH_3\\ |\\ CH_3\end{array} + Cl_2 = HCl + \begin{array}{c}CH_3\\ |\\ CH_2Cl\end{array}$$

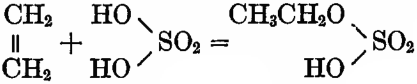
In the case of ethylene, however, substitution does not occur but addition:



$$\begin{array}{c}CH_2\\ \| \\ CH_2\end{array} + Cl_2 = \begin{array}{c}CH_2Cl\\ | \\ CH_2Cl\end{array}$$

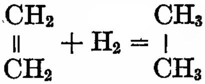
Ethylene chloride, the product of this reaction, is a heavy oil, and the chemists who first studied this reaction were so much impressed by the formation of an oil by the union of two gases, that they gave to ethylene the name 'olefiant' or oil-forming gas. The term olefine is still retained as a class-designation for ethylene and its homologues.

Chlorine is not the only substance added by ethylene. It also unites directly with quite a number of others. Here will be mentioned only its union with bromine to form ethylene bromide, with hydrobromic acid to form ethyl bromide, and with sulphuric acid to form ethyl sulphuric acid. The last reaction is most rapid at about 150°.



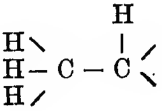
$$\begin{array}{c}CH_2\\ \| \\ CH_2\end{array} + \left.\begin{array}{r}HO\\ HO\end{array}\right\rangle SO_2 = \left.\begin{array}{r}CH_3CH_2O\\ HO\end{array}\right\rangle SO_2$$

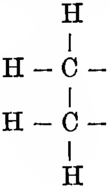
By reduction in hydrogen, ethane may be obtained:



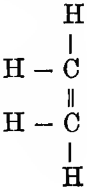
$$\begin{array}{c}CH_2\\ \| \\ CH_2\end{array} + H_2 = \begin{array}{c}CH_3\\ | \\ CH_3\end{array}$$

Since ethylene adds so many substances directly, it is evident that its carbon atoms cannot be utilizing their full combining capacity, that is, they are unsaturated. This might find expression in one of the three following graphic formulæ:

I. 

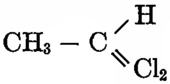
II. 

$$\begin{array}{c}H\\ | \\ H-C-\\ | \\ H-C-\\ | \\ H\end{array}$$

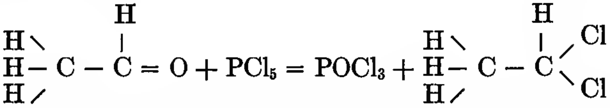
III. 

$$\begin{array}{c}H\\ | \\ H-C\\ \| \\ H-C\\ | \\ H\end{array}$$

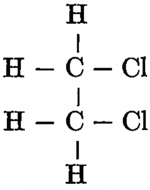
Formula I can be excluded by the following reasoning: A hydrocarbon of that formula, when treated with chlorine, should yield a chloride of the formula,



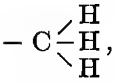
Now a substance having this formula is known, and its constitution is rendered certain by the fact that it can be prepared from acetaldehyde by the action of phosphorus pentachloride:



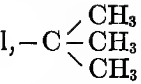
while it yields acetaldehyde again when it is treated with hydrolytic agents. This compound, however, is not identical with that which is formed by the addition of chlorine to ethylene. The latter must then have the only other formula possible, namely,



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

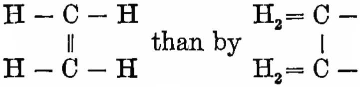
and this is in harmony with either formula II or III for ethylene. It is not quite so easy to reach a decision between these two, but III is universally preferred to II for the following reasons: If carbon valencies could exist free in the sense of II, there would seem to be no good reason why they might not exist alone. It might be expected that such compounds as methyl, 

$$-C\begin{matrix}\diagup H\\ -H\\ \diagdown H\end{matrix},$$

or tertiary butyl, 

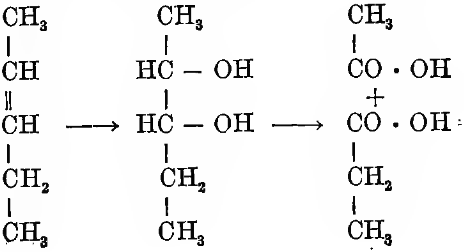
$$-C\begin{matrix}\diagup CH_3\\ -CH_3\\ \diagdown CH_3\end{matrix}$$

might be frequently met with. Such compounds are, however, most exceptional. Instead, the molecules of unsaturated compounds like ethylene add an even number of atoms of other substances, and study of the products reveals the fact that addition, except in a few cases otherwise well accounted for, takes place upon two adjacent carbon atoms. The quality of unsaturation manifested by ethylene is then a relationship existing between adjacent carbon atoms, and hence this relation is better expressed by the formula,



$$\begin{matrix}H-C-H\\ \Vert\\ H-C-H\end{matrix}\quad \text{than by}\quad \begin{matrix}H_2=C-\\ \quad\;\, |\\ H_2=C-\end{matrix}$$

An important reaction of ethylene and other substances possessing a double bond is their behavior upon oxidation. This also may be looked upon as addition. The aqueous solution of an oxidizing agent may be thought of as containing free hydroxyl groups. If an olefine is present, these react with it in such a way that a hydroxyl group is added to each carbon atom adjacent to the double bond. Further oxidation then leads to rupture of the carbon chain, usually resulting in the formation of acids. These operations are indicated in the following scheme:



$$\begin{matrix}CH_3\\ |\\ CH\\ \Vert\\ CH\\ |\\ CH_2\\ |\\ CH_3\end{matrix}\longrightarrow\begin{matrix}CH_3\\ |\\ HC-OH\\ |\\ HC-OH\\ |\\ CH_2\\ |\\ CH_3\end{matrix}\longrightarrow\begin{matrix}CH_3\\ |\\ CO\cdot OH\\ +\\ CO\cdot OH\\ |\\ CH_2\\ |\\ CH_3\end{matrix}$$

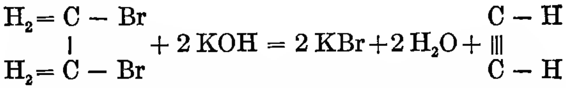
It will be noted that the chain is broken at the point originally occupied by the double bond, and in practice it is by oxidation that the position of the double bond in an unsaturated compound of unknown constitution is usually determined.

The homologues of ethylene can be most conveniently named as alkyl derivatives of ethylene itself thus:

$CH_3 \cdot CH = CH_2$ methyl ethylene
$CH_3 \cdot CH_2 \cdot CH = CH_2$ ethyl ethylene
$CH_3 \cdot CH = CH \cdot CH_2CH_3$ methyl ethyl ethylene, etc.

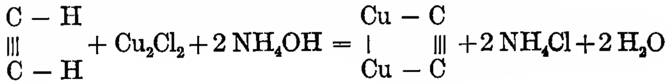
Other names are also in use which are formed by adding the syllable 'ene' to the name of the saturated alkyl radicle having the same number of carbon atoms. For the compounds just mentioned, this method gives the names propylene, butylene, and amylene.

Acetylene. If ethylene bromide be treated with alcoholic potash, two molecules of hydrobromic acid are removed, and acetylene is produced:



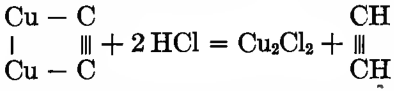
$$\begin{array}{l} H_2 = C - Br \\ \qquad \; | \\ H_2 = C - Br \end{array} + 2\,KOH = 2\,KBr + 2\,H_2O + \begin{array}{l} C - H \\ \,||| \\ C - H \end{array}$$

The triple bond in the formula indicates that it possesses another pair of unsatisfied valencies; indeed acetylene is twice as unsaturated as ethylene. It unites directly, for example, with four atoms of chlorine or bromine instead of two. It has just been shown that upon oxidation the carbon chain of an olefine is broken at the double bond. This also holds true of the compounds of the acetylene series, and in addition, the triple bond seems to be the cause of general instability. Acetylene itself is not indeed explosive under ordinary conditions, but it becomes so when subjected to high pressure, and it has many explosive derivatives. The triple bond has another peculiarity. Hydrogen connected to carbon atoms united by such a bond may be replaced by heavy metals such as silver or copper, and the compounds thus formed are explosive. Such a product is precipitated when acetylene, for example, is passed through an ammoniacal solution of cuprous chloride:



$$\begin{array}{l}\mathrm{C-H}\\ \,|||\\ \mathrm{C-H}\end{array} + \mathrm{Cu_2Cl_2} + 2\,\mathrm{NH_4OH} = \begin{array}{lcr}\mathrm{Cu} & - & \mathrm{C}\\ | & & |||\\ \mathrm{Cu} & - & \mathrm{C}\end{array} + 2\,\mathrm{NH_4Cl} + 2\,\mathrm{H_2O}$$

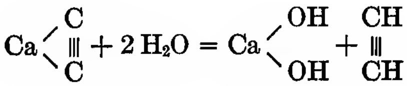
Such compounds are readily decomposed by dilute acids, the hydrocarbons being regenerated:



$$\begin{array}{lcr}\mathrm{Cu} & - & \mathrm{C}\\ | & & |||\\ \mathrm{Cu} & - & \mathrm{C}\end{array} + 2\,\mathrm{HCl} = \mathrm{Cu_2Cl_2} + \begin{array}{l}\mathrm{CH}\\ |||\\ \mathrm{CH}\end{array}$$

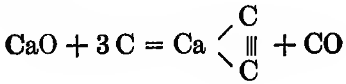
The formation of these explosive metallic compounds is characteristic of substances containing a triple bond, and furnishes a convenient means of distinguishing them from the isomeric compounds containing two double bonds.

Acetylene itself is usually prepared in practice by the action of water upon calcium carbide:



$$\mathrm{Ca}\begin{array}{l}\diagup\\ \diagdown\end{array}\!\!\begin{array}{c}\mathrm{C}\\ |||\\ \mathrm{C}\end{array} + 2\,\mathrm{H_2O} = \mathrm{Ca}\begin{array}{l}\diagup\,\mathrm{OH}\\ \diagdown\,\mathrm{OH}\end{array} + \begin{array}{c}\mathrm{CH}\\ |||\\ \mathrm{CH}\end{array}$$

The latter compound, which was considered a chemical curiosity a few years ago, is now manufactured upon a large scale by heating coke and lime to the high temperature of the electric furnace:



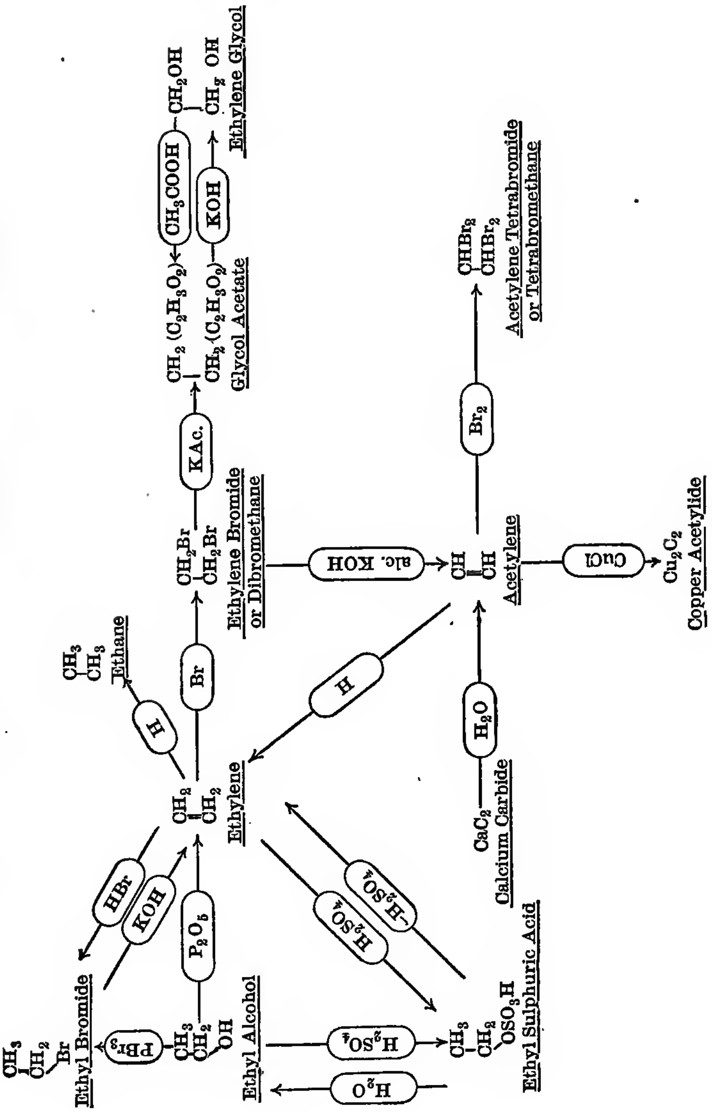
$$\mathrm{CaO} + 3\,\mathrm{C} = \mathrm{Ca}\begin{array}{l}\diagup\\ \diagdown\end{array}\!\!\begin{array}{c}\mathrm{C}\\ |||\\ \mathrm{C}\end{array} + \mathrm{CO}$$

When pure, calcium carbide is a hard, colorless, crystalline solid, but the commercial product is dark in color owing to the presence of many impurities. On this account the gas evolved from it usually contains hydrogen sulphide, ammonia, some phosphine, and some organic sulphur and phosphorus compounds. From these it can be largely freed by passing through lime and some oxidizing material, such as bleaching powder or one of the chromates. When an especially pure gas is desired, it can be prepared by passing the acetylene through an ammoniacal solution of cuprous chloride, and then decomposing the resulting copper compound by means of dilute acids or potassium cyanide.

Acetylene is produced to some extent in the flame of a 'struck back' Bunsen burner. Its presence in the gases issuing from such a flame may be shown by conducting them through an ammoniacal copper solution. Still another method of formation is of scientific interest. When the electric arc passes between carbon terminals in an atmosphere of hydrogen, the carbon and hydrogen react until equilibrium is reached. At this point the gases present are in the following proportions: hydrogen 90–91%, acetylene 7–8%, methane 1.25%, ethane 0.75%.

Acetylene is a colorless gas of a characteristic odor. When ignited in the air, it burns with a heavy deposition of soot owing to the extremely high percentage of carbon which it contains. By means of a specially constructed jet-piece, however, it is possible to obtain the brilliant illuminating effect familiar in the acetylene searchlight. Acetylene can hardly be considered an altogether safe illuminant, as, aside from its becoming less stable under pressure, it has two other disagreeable properties. One is its capacity for forming explosive metallic compounds, and the other is the fact that mixtures of it with oxygen or air are explosive throughout a wide range of percentage composition. For purposes

GENETIC RELATIONSHIPS OF ETHYLENE AND ACETYLENE.



of transportation acetylene may be conveniently and safely dissolved in acetone under pressure. Numerous homologues of acetylene are known.

The property of unsaturation is by no means confined to hydrocarbons. All classes of organic compounds may exhibit it. There are unsaturated alcohols like allyl alcohol, $CH_2 = CH \cdot CH_2OH$, unsaturated aldehydes like acrolein, $CH_2 = CH \cdot CHO$, and numerous unsaturated acids. One of these, oleic acid, should be mentioned at this time. It is important because of its occurrence as an ester in the natural fats. Oleic acid is an oily liquid insoluble in water. Under ordinary pressure, it does not distill without decomposition. It has the same number of carbon atoms as stearic acid, into which it is readily transformed on reduction. It therefore differs from the latter only in the possession of a double bond. The position of the double bond was for a long time in doubt, but recent investigation makes it certain that this is found just in the middle of the chain. The structural formula of oleic acid is, therefore, the following:

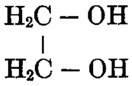
$$CH_3-(CH_2)_7-CH=CH-(CH_2)_7-COOH.$$

CHAPTER VII.

THE POLYATOMIC ALCOHOLS AND THEIR DERIVATIVES.

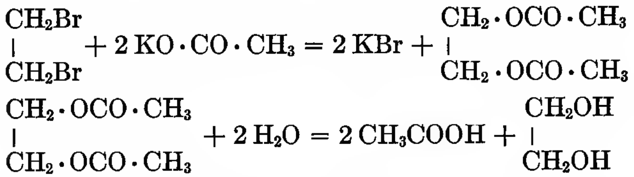
It has been shown in the preceding pages that each of the important groups of organic compounds is characterized by the possession of some particular group or radicle to which it owes its especial properties. The alcohols are characterized by the hydroxyl group, the aldehydes by carbonyl, the acids by carboxyl, and so forth. Now it is true of almost all of the compounds hitherto studied that they contain the characteristic group or radicle but once. The alcohols thus far met with were those containing but one hydroxyl group, the acids were those having but one carboxyl. Now there is, of course, no limitation of this sort in nature. On the contrary, many alcohols exist containing several hydroxyl groups (polyatomic alcohols), acids with several carboxyl groups (polybasic acids) and the same is true of other classes of compounds. Further, it is possible for one and the same substance to contain several different radicles, and compounds may exist which are, for example, amines, alcohols, and acids all at the same time. Fortunately, the study of such compounds does not involve much which is new in principle, since the different radicles each contribute their properties to the compound in a manner which is roughly additive. Nevertheless, the specific properties of particular groups are not infrequently a good deal modified by the simultaneous presence of others.

It is convenient to begin our study of these more complex substances with the polyatomic alcohols. Since it is seldom possible for two hydroxyl groups to remain attached to the same carbon atom, the simplest possible diatomic alcohol is the substance known as *glycol,* having the formula,



$$\begin{array}{c}H_2C - OH\\ |\\ H_2C - OH\end{array}$$

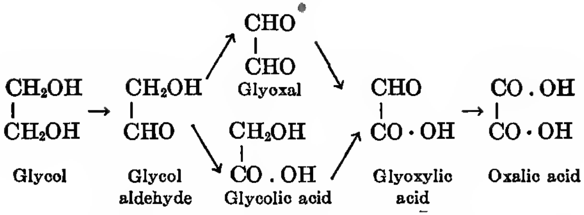
The constitution is obvious from the reactions by which it may be prepared from ethylene bromide. When that substance is treated with potassium acetate for some time, the bromine atoms are both replaced by acetic acid radicles, and when this acetate is then saponified, glycol is produced:



$$\begin{array}{l}CH_2Br\\ |\\ CH_2Br\end{array} + 2\,KO\cdot CO\cdot CH_3 = 2\,KBr + \begin{array}{l}CH_2\cdot OCO\cdot CH_3\\ |\\ CH_2\cdot OCO\cdot CH_3\end{array}$$

$$\begin{array}{l}CH_2\cdot OCO\cdot CH_3\\ |\\ CH_2\cdot OCO\cdot CH_3\end{array} + 2\,H_2O = 2\,CH_3COOH + \begin{array}{l}CH_2OH\\ |\\ CH_2OH\end{array}$$

It is a colorless liquid which is miscible with water in all proportions. High solubility in water and a sweet taste, from which glycol derives its name (Greek γλυκύς, sweet), are the rule among the polyatomic alcohols. The more important chemical properties of glycol can be derived directly from the formula. This shows the substance to be twice a primary alcohol. Hence it is possible to predict that either one or two of its hydrogen atoms may be substituted by sodium, that one or both hydroxyl groups may be substituted by chlorine or bromine, and that the substance may unite with one or two molecules of acids to form esters. Under the influence of oxidizing agents, it is clear that a considerable number of different compounds might be produced according to whether one or both of the hydroxyl groups undergoes oxidation. These possibilities are indicated in the following scheme:



All the above compounds are known, though most of them have little practical importance. An exception is the final product, oxalic acid. This substance is of especial importance, not only on its own account, but also because it is a typical representative of the dibasic acids. Two methods of preparation deserve mention for their scientific interest. One consists in the series of operations indicated above; the other involves the hydrolysis of cyanogen:

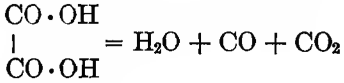
$$\begin{array}{l} CN \\ | \\ CN \end{array} + 4\,H_2O = \begin{array}{l} CO \cdot ONH_4 \\ | \\ CO \cdot ONH_4 \end{array}$$

This reaction exhibits cyanogen as the nitrile of oxalic acid. The acid derives its name from the sorrel (*oxalis acetosella*), in which it occurs in nature, as well as in rhubarb and some other plants. In practice, it may be prepared by the oxidation of numerous organic substances. One of the most convenient methods of laboratory preparation upon the small scale is the vigorous oxidation of cane sugar by means of nitric acid. For technical purposes, the salts may be obtained by heating the formates to about 450° with exclusion of air:

$$2\,HCO \cdot ONa = H_2 + \begin{array}{l} CO \cdot ONa \\ | \\ CO \cdot ONa \end{array}$$

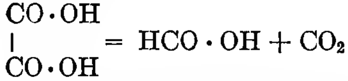
The more usual method of technical production consists in the fusion of sawdust with a mixture of sodium and potassium hydroxides at a temperature of about 220°. Hydrogen gas is evolved during the operation. The melt is first leached out with water, the solution containing a mixture of sodium and potassium oxalates along with other soluble impurities. From this solution, the addition of lime precipitates insoluble calcium oxalate, which may then be purified and decomposed with the calculated quantity of dilute sulphuric acid. Insoluble calcium sulphate is produced, while oxalic acid remains dissolved. Upon evaporation, this crystallizes from the solution with two molecules of water. By careful heating, the water of crystallization can be removed without decomposing the compound. The anhydrous acid may then be sublimed at about 150°, but on rapid heating it decomposes, partly into carbon monoxide, carbon dioxide, and water, and partly into carbon dioxide and formic acid:

(1)



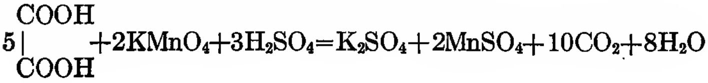
$$\begin{array}{l}CO\cdot OH\\ |\\ CO\cdot OH\end{array} = H_2O + CO + CO_2$$

(2)



$$\begin{array}{l}CO\cdot OH\\ |\\ CO\cdot OH\end{array} = HCO\cdot OH + CO_2$$

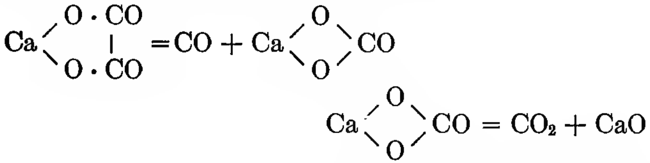
Heating with concentrated sulphuric acid favors the decomposition indicated by the first equation, and this is one of the most convenient laboratory methods for the preparation of carbon monoxide. Heating the crystalline acid with pure glycerol causes decomposition in the sense of the second equation. Formic acid is usually prepared in the laboratory by this method. Oxalic acid and its salts, when treated with permanganates in acid solution, are smoothly oxidized to water and carbon dioxide:



$$5\begin{array}{l}COOH\\ |\\ COOH\end{array} + 2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

Extensive use is made of this reaction in volumetric analysis.

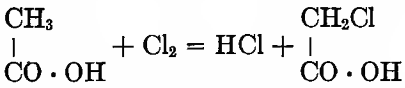
On ignition, most oxalates lose carbon monoxide with formation of the corresponding carbonate, which may then lose carbon dioxide forming the oxide. This decomposition is so smooth that practically no charring takes place. It may be conveniently observed in the case of the calcium salt:



The insolubility of this compound makes it useful for the gravimetric determination of both calcium and oxalic acid.

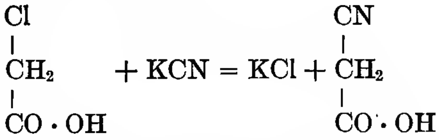
As already pointed out, oxalic acid may be considered as a type of the dibasic acids in general. Two other members of the series will, however, be mentioned.

Malonic Acid. When acetic acid is treated with chlorine, a hydrogen atom in the methyl group is substituted by the halogen, forming, in this case, chloroacetic acid:



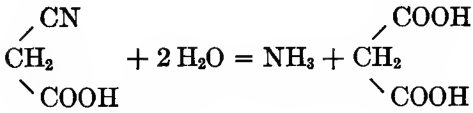
$$\begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{CO\cdot OH} \end{array} + \mathrm{Cl_2} = \mathrm{HCl} + \begin{array}{l} \mathrm{CH_2Cl} \\ | \\ \mathrm{CO\cdot OH} \end{array}$$

When the latter is treated with potassium cyanide, the following reaction takes place:

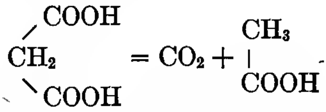


$$\begin{array}{l} \mathrm{Cl} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{CO\cdot OH} \end{array} + \mathrm{KCN} = \mathrm{KCl} + \begin{array}{l} \mathrm{CN} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{CO\cdot OH} \end{array}$$

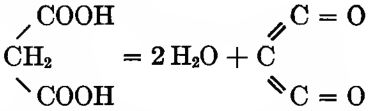
the product being the nitrile of malonic acid. From this, the acid itself may be formed by hydrolysis:



Malonic acid is a crystalline solid. When heated above its melting-point, it decomposes into carbon dioxide and acetic acid:

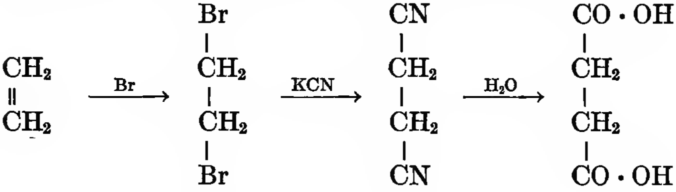


Behavior of this kind is common to substances containing two carboxyl groups attached to the same carbon atom. The ethyl ester of malonic acid is frequently employed in many syntheses which are very important for the professional worker in Organic Chemistry. This matter will not, however, be discussed here. One reaction of general interest does deserve mention, as it leads to the formation of the recently discovered third oxide of carbon. When malonic acid is heated with phosphorus pentoxide, water is removed, and among other less well-defined products, a gas is evolved which probably has the constitution indicated in the reaction which follows:



To this substance its discoverers have given the name *carbon suboxide.* It is a gas which may be readily condensed to a liquid boiling at 7°. It has an intolerable odor suggestive of the acid anhydrides. Indeed it may be considered as belonging to this class of substances, for with water it reacts readily, regenerating malonic acid.

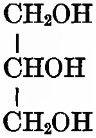
Succinic Acid. This acid has some important derivatives which will be taken up later. It is a crystalline solid, soluble in water, and is technically prepared by the distillation of amber, a source suggested by its name (Latin, *succinum*, amber). The constitution of the acid is made obvious by the synthesis indicated in the following scheme:



$$\begin{array}{c}\mathrm{CH_2}\\ \|\\ \mathrm{CH_2}\end{array} \xrightarrow{\mathrm{Br}} \begin{array}{c}\mathrm{Br}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{Br}\end{array} \xrightarrow{\mathrm{KCN}} \begin{array}{c}\mathrm{CN}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{CN}\end{array} \xrightarrow{\mathrm{H_2O}} \begin{array}{c}\mathrm{CO\cdot OH}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{CO\cdot OH}\end{array}$$

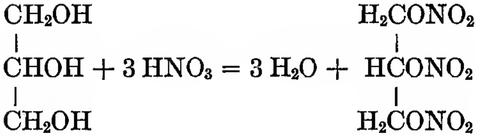
Triatomic Alcohols. Glycerol.

The simplest of the triatomic alcohols is glycerol. It is a syrupy, hygroscopic liquid of sweet taste, which crystallizes at low temperature, and can be distilled at ordinary pressure without decomposition only when extremely pure. As its formula,



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

indicates, it is twice a primary and once a secondary alcohol. Glycerol is widely distributed in nature since most animal fats and vegetable oils are esters of this alcohol with the higher homologues of acetic acid. Before taking up the study of these, however, it is convenient to turn to one of the simpler esters, the trinitrate. This substance, commonly known as 'nitroglycerin,' is an important explosive. It is prepared by intimately mixing glycerol with nitric acid in the presence of sulphuric acid as a dehydrating agent:

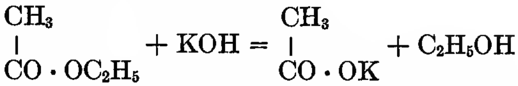


$$\begin{array}{l}\mathrm{CH_2OH}\\ |\\ \mathrm{CHOH}\\ |\\ \mathrm{CH_2OH}\end{array} + 3\,\mathrm{HNO_3} = 3\,\mathrm{H_2O} + \begin{array}{l}\mathrm{H_2CONO_2}\\ |\\ \mathrm{HCONO_2}\\ |\\ \mathrm{H_2CONO_2}\end{array}$$

When action has ceased, the nitrating mixture is run off into a large quantity of cold water. The glycerol nitrate then separates as a heavy oil, which is thoroughly washed with water and finally dried. The product has a characteristic heavy odor and burning taste. Administered in extremely small doses, it has found some use in medicine. The pure liquid has proved somewhat unreliable as an explosive, and its use in this form has now practically ceased. It has been found that when the oil is absorbed in porous material like infusorial earth, a dry-feeling mixture results which is not sensitive to slight changes of temperature or to shock, but may be brought to explosion with certainty when 'detonated' by a cap containing mercury fulminate. Under the name of 'dynamite,' such a mixture has come to be used extensively as a blasting material and is considered adequately safe.

Industries Involving the Natural Fats and Oils.

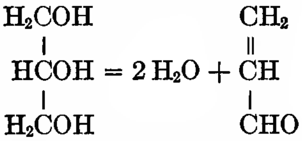
It has been pointed out above that the animal fats are the glycerol esters of acids of the acetic acid series. Those most commonly found in the animal organism are the esters of stearic, palmitic, and oleic acids. They are named stearin, palmitin, and olein, respectively. Like the free acids, stearin and palmitin are solids at ordinary temperature, while olein is a liquid. Olein predominates in a fat like lard, stearin, in mutton tallow. From the earliest times, soaps have been prepared from the fats by treatment with caustic alkali. When these are boiled together the esters undergo hydrolysis. The reaction which occurs is entirely analogous to that which takes place when a simple ester like ethyl acetate is treated with alkali:



$$\begin{array}{l}CH_3\\ |\\ CO\cdot OC_2H_5\end{array} + KOH = \begin{array}{l}CH_3\\ |\\ CO\cdot OK\end{array} + C_2H_5OH$$

The analogy between these two relations has led to the adoption of the word 'saponification' to cover the whole class of reactions of this kind. In actual soap-making, the products are glycerol and the sodium salts of palmitic, stearic, and oleic acids. When the reaction is complete, salt is added to the solution and the soaps rise to the top, while the glycerol with the excess of alkali forms a lower layer. From this the glycerol may be obtained by evaporation and subsequent distillation. It need hardly be pointed out that, in early times, when the constitution of the fats was unknown, the glycerol, on account of its solubility in water, was overlooked entirely, and allowed to go to waste with the spent alkaline liquors.

Another industry involving the saponification of the fats is the manufacture of stearin candles. These do not consist (as their name might imply) of true stearin, that is, glycerol stearate, but, instead, of the solid free fatty acids, mostly stearic and palmitic. The superiority of the stearin candle to the tallow candle has a chemical reason. When glycerol is heated, especially if in the presence of dehydrating agents, an unsaturated aldehyde is formed named acrolein:



$$\begin{array}{c}H_2COH\\ |\\ HCOH\\ |\\ H_2COH\end{array} = 2\,H_2O + \begin{array}{c}CH_2\\ \|\\ CH\\ |\\ CHO\end{array}$$

This substance attacks vigorously the mucous membrane of the nose and eyes, and its presence in small quantities is responsible for the disagreeable odor produced when fat is burned. The acids of which the stearin candle is composed are free from glycerol, and consequently do not produce the same disagreeable results. Technically the material for making these candles is usually obtained by heating the fats with a small amount of lime under pressure. The lime acts chiefly as a catalyzer, and the chief products of the reaction are glycerol and the free fatty acids along with a small amount of a calcium soap. The latter is then decomposed with sulphuric acid. The fatty acids now float upon the top of the aqueous glycerol solution. This upper layer is run off and allowed to cool, when the stearic and palmitic acids mostly crystallize out. These are freed from the liquid oleic acid by means of mechanical pressure and the solid material is molded into candles.

It should be added that the above is by no means the only source from which candles are obtained. Perhaps most of the candles in use are made from paraffin, while others are prepared from many of the natural waxes, such as beeswax, and from spermaceti, which is found in the head of the sperm whale.

The Drying Oils.

Allied to the fats in chemical composition is a class of substances known as drying oils. Of these, linseed oil, the oil found in the seeds of the flax, is the most conspicuous example. It is well known that this oil is the chief constituent of most paints and varnishes, and it is of interest to see how its chemical properties fit it for this use. Paint or varnish is applied to a wood or other surface chiefly to preserve the material from the action of the atmosphere. The object to be attained is a waterproof coating which shall be sufficiently elastic not to crack when dry. This may be realized in two ways. One of these, which may be called the mechanical method, is to dissolve a suitable gum or resin in a volatile solvent like alcohol or ether. When such a solution is spread upon a surface, the solvent evaporates, leaving a thin coat of the original gum or resin. A familiar example of this type is ordinary shellac. The other method is to employ a drying oil like linseed oil. When such an oil 'dries,' the drying is not due to the evaporation of any portion of it, but to oxidation. Linseed oil has the property of taking up oxygen from the air, and the product is an adhering solid material suitable for the protection of surfaces from the weather. This power of absorbing oxygen as exhibited by linseed oil is doubtless closely associated with the unsaturated character of its components. These are glycerol esters of oleic, linoleic, linolinic, and isolinolinic acids. Oleic acid has been already discussed (page 134). The other acids, like oleic, have the same carbon skeleton as stearic acid, but differ from this by their high degree of unsaturation. The free acids have only recently been prepared in a pure state, but, from a study of their derivatives, it is quite certain that linoleic acid contains two double bonds, while the two linolinic acids each contain three.

All who have had to do with paints are familiar with the terms 'raw' and 'boiled' linseed oil. The latter term is applied to an oil which has been boiled for some time, usually with oxides of lead or manganese. Some of these bases are taken up by the oil, which becomes a good deal darker in color. It has also acquired the power of drying more rapidly. This has usually been ascribed to the catalytic action of the bases absorbed by the oil, but recent investigations seem to indicate that it is largely due to the partial oxidation effected during the process of boiling. The oxidation of linseed oil is an autocatalytic process, that is to say, the reaction is hastened by the presence in the oil of some of the oxidized product. An application of this principle has made it possible to use an oil which, instead of being boiled, has been partially oxidized at ordinary temperatures by agencies which do not affect the color. A light, very transparent varnish is the result. A word remains to be said concerning the function of turpentine in paints and varnishes. The theory is that pinene, the chief constituent of oil of turpentine, absorbs oxygen from the air, forming a substance of peroxide character, which acts as a particularly energetic oxidizing agent upon any oxidizable material which may be present, in this case the linseed oil. Other materials used as 'driers' play a similar rôle.

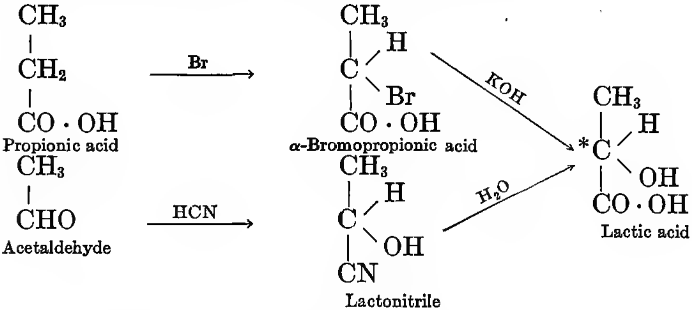
Before leaving the fats, it should be mentioned that they are used to a certain extent as a substitute for butter under the name of 'oleomargarine.' Butter itself is an allied substance. It is a complicated mixture containing not only the substances common to most fats but also the glycerol esters of several of the lower homologues of acetic acid. Prominent among the latter are the glycerides of butyric, caproic, caprylic and capric acids.

CHAPTER VIII.

HYDROXY-ACIDS. OPTICAL ISOMERISM.

Lactic Acid.

In the souring of milk, and in the fermentation of sugar under the influence of certain bacteria, lactic acid is produced. The product obtained in this way is a syrupy liquid which retains a little water with great tenacity. The pure acid is, however, a crystalline solid melting at 18°. A practically identical product can be obtained synthetically either by the action of alkalies upon α-bromopropionic acid or by the hydrolysis of the addition product formed by the action of hydrocyanic acid upon acetaldehyde:



These syntheses would seem to put the constitution of the compound beyond question, but the substance has twice the molecular weight indicated by the formula, for it has been found possible, by methods which will be described later, to split it into two other acids very similar to itself.

Both of these acids seem to have the graphic formula just suggested, for they differ among themselves in respect to practically but one property. One of them, in solution, rotates the plane of polarized light to the right; the other, in the same concentration, rotates it an equal amount to the left.

This property is well known among minerals. Here it is closely associated with unsymmetrical crystalline form. Quartz, for example, shows the peculiarity in a marked degree. There are two kinds of quartz crystals, one of which rotates the plane of polarized light to the right and the other to the left. If we examine the form of these crystals (Fig. 10) we shall see that neither is perfectly symmetrical on account of the plane *x*. They are not equal since they cannot be superimposed upon each other, nor are they symmetrical for no plane can be passed through either so as to divide it into halves which are mirror-images of each other. Nevertheless, the two crystals considered together are symmetrical, that is, a plane of symmetry can be passed between them. One is the mirror image of the other, or, to use a more homely comparison, they resemble each other as the right and left

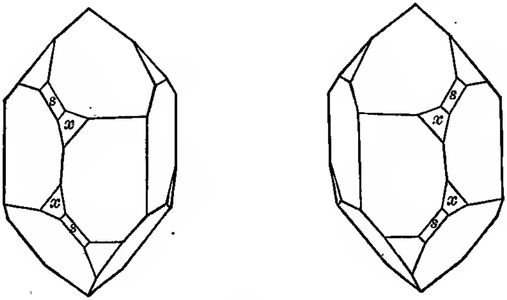


Fig. 10.

hands. Mineralogists are accustomed to speak of this relationship as *enantiomorphism.*

Pasteur in reflecting upon the optical activity of organic substances came to the conclusion that this property must here also be associated with asymmetry; but since organic compounds show the property both in solution and also in the gaseous state, the asymmetry must here belong to the molecules themselves. If we could show that the molecule as it exists in space has an unsymmetrical structure we should be able to account for the two forms of lactic acid, so like in all their other properties but different in their action upon polarized light.

Let us see what data we have to help us in studying the spacial arrangement of the atoms in an organic molecule. What we know about the carbon compounds leads directly to the conclusion that all the four bonds of carbon are equivalent. This chemical fact would find geometrical expression in the statement that the points of affinity divide the surface of the atom equally among themselves; or, what is essentially the same thing, that the valencies extend outward from the center of the carbon sphere in such a way that the solid angles included between the bonds are all equal. These conditions are realized when the carbon atom is thought of as placed in the center of a regular tetrahedron toward the apexes of which the bonds are extended (Fig. 11). Now a tetrahedron is highly symmetrical, but if each separate apex be *differently* marked then no plane of symmetry can be passed through the resulting figure. From this we may draw the chemical conclusion that if a tetrahedron adequately symbolizes the arrangement of the carbon valencies

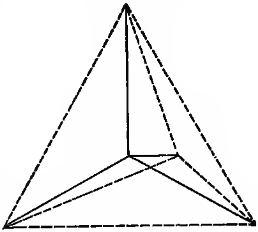


Fig. 11.

in space, then any molecule will be unsymmetrical when it contains even a single carbon atom whose bonds are satisfied by four *different* elements or groups. In consequence of this, just as in the case of quartz crystals, two different optically active forms would be possible, one of which might rotate the plane of polarized light to the right and the other an equal amount to the left. It will be seen that these conditions are fulfilled in the case of lactic acid. We shall soon learn that they are also fulfilled in all the numerous natural compounds which show optical activity. For the study of such relationships, it is convenient to employ models consisting of a central sphere to represent the carbon atom and rods to represent the bonds. Then balls of different colors can be used to represent the various substituting elements or groups.* When all four bonds are attached to spheres of different colors, no plane of symmetry can be passed through the resulting figure. This justifies the use of the word 'asymmetric' as applied to a carbon atom whose four bonds are satisfied by four different atoms or atomic groups.

It will be noticed that the relationship existing between the models (Fig. 13) is admirably adapted to illustrate that which exists between the lactic acids. The two models are

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* The student can easily verify these relations for himself by making a tetrahedron of pasteboard in the manner indicated below and marking differently the four corners. To construct the tetrahedron, draw an equilateral triangle, bisect each of the three sides, and connect the three middle points thus found. Finally cut out the large triangle and fold up the corners along the lines of the smaller inscribed one. Join the points at the top by a piece of fine wire or paste over with paper. With such models the simpler relations of space isomerism can be studied almost as well as with the more expensive ones described above.

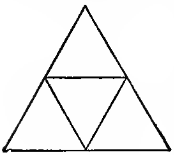


Fig. 12.

made up of the same components similarly arranged but differing only in what may be termed the direction of arrangement. This point may be brought out by the fact that if, in model I, it is desired to pass from *a* to *b* to *c*, it is necessary to go in the direction followed by the hands of a watch, whereas the same requirement can only be fulfilled in model II by proceeding in the opposite direction. In the lactic acids, also, the closest similarity exists in all chemical and physical properties, with the important difference that the two acids rotate the plane of polarized light equally in *opposite* directions. Isomerism of this type is of common occurrence, and because it can be so well illustrated by the structure of the molecule as represented in three dimensions it has received the name of *space-* or *stereo-isomerism* (Greek, στερεός, cubic). The term, optical isomerism is also applied to the special kind of space isomerism we are now studying, as the more general term also includes certain types of compounds not optically active.

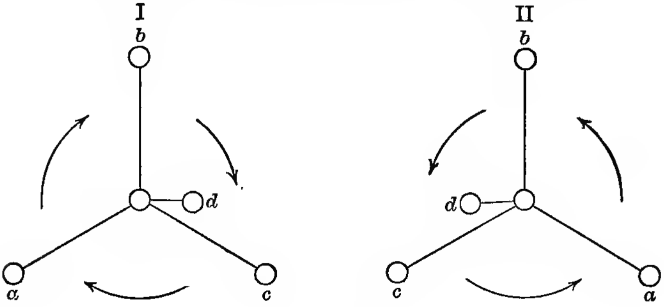
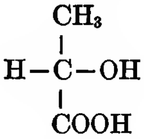


Fig. 13.

Substances like the lactic acids whose differences are to be explained by the presence of asymmetric carbon atoms are said to possess the same constitution but different 'configurations.' In the case of lactic acid, it is customary to distinguish that acid which rotates the plane of polarized light to the right by the prefix *d*- (dextrorotatory) and its optical opposite by the prefix *l*- (lævorotatory). It should be stated at the outset that the prefixes *d*- and *l*- are not now used to indicate the direction in which a specific compound rotates the plane of polarized light. Instead, a prominent dextrorotatory compound in a given group is selected as a standard and all other members of the group which stand in a genetic relationship to this substance receive the prefix *d*- while to the optical opposites of these compounds is given the prefix *l*-. The convenience of such an arbitrary standard will be more apparent as we proceed. The principle involved can, however, be made clear from the following simple case. Let it be supposed that a given acid rotates the plane of polarized light to the right, while its ethyl ester (as might well be the case) rotates to the left. It is obvious that it is more important that the nomenclature employed should show the relationship of the acid to its ester than that it should record the specific action of either upon the plane of polarized light.

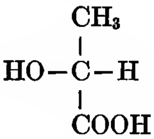
At this point the question naturally arises: Which of the models referred to on page 151 is to be considered as representing *d*- and which *l*-lactic acid? Since the relations between all the components are the same in both except in the matter of direction, it is impossible to answer this question in the form stated. It can only be said that if one is arbitrarily selected to represent the first form, then the other represents the second. It is the same with representations made upon the plane of the paper. Such are necessary for convenience of discussion, and for this purpose a purely arbitrary system is employed. The model is held in such a position that the longest possible chain of carbon atoms shall be projected upon the paper as a vertical line. Then the other elements or groups are projected directly as side arms or branches. For the lactic acids, formulæ like the following are thus obtained. Such projection reproduces somewhat inadequately the geometrical relationship between the models.

I.



$$\begin{array}{c} \mathrm{CH_3} \\ | \\ \mathrm{H-C-OH} \\ | \\ \mathrm{COOH} \end{array}$$

II.



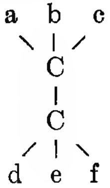
$$\begin{array}{c} \mathrm{CH_3} \\ | \\ \mathrm{HO-C-H} \\ | \\ \mathrm{COOH} \end{array}$$

When *d*- and *l*-lactic acids are mixed in equal quantities, an optically inactive compound results which has double the molecular magnitude of the components. Its name is written *dl*-lactic acid. Compounds of this type are usually formed when two optical opposites are mixed, and they are designated as *racemic* compounds. The name comes from racemic acid, the first substance of this type to be studied. It is closely allied to tartaric acid.

When the attempt is made to synthesize in the laboratory substances containing asymmetric carbon atoms, inactive products are always first obtained, and it is necessary to 'split' these in order to obtain the optically active substances. The latter are usually formed directly by the plant or animal organism. That the racemic form should be the first product of artificial synthesis is entirely in line with what might be expected of isomers of this type, for since the kind and arrangement of the atoms are the same in the molecules of both isomers, both must have the same energy content, and as the chances of formation of each form are equal, both will be formed by any synthesis in equal quantities. Why it is that the syntheses going on in plant and animal organisms proceed unsymmetrically is one of the fascinating unsolved problems of Physiological Chemistry.

From what has been said, it will be seen that the 'splitting' of racemic compounds is an important laboratory operation, but before the subject can be adequately discussed, it will be necessary to consider the number and character of the isomers which are possible among the compounds containing two asymmetric carbon atoms. In such a case it is customary to assume that the rotating power which the compound exercises upon the plane of polarized light represents the algebraic sum of the rotatory powers belonging to each asymmetric atom separately. This is usually spoken of as the principle of *optical superposition,* and with its aid it is easy to derive the number and character of the isomers corresponding to a given constitutional formula.

The most general formula for a substance containing two asymmetric carbon atoms is



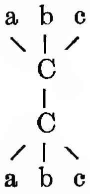
Here it will be convenient to designate the rotation produced by that carbon atom attached to a, b, and c by X, and that of the other carbon atom by Y. It is then clear that one of the possible isomers will be one in which both carbon atoms tend to rotate the plane of polarized light to the right. Let this be called +X, +Y. Another compound will be possible in which both atoms cause rotation to the left. This may be called −X, −Y. The rotatory powers of these two compounds will be equal and opposite and, like the two lactic acids, they will resemble each other closely in physical and chemical properties, and when mixed they will unite to form an inactive racemic compound.

In addition to the above, there must be two compounds in which the rotatory powers of the two asymmetric atoms are exerted in *opposite* directions. These may be designated by the symbols +X, −Y and −X, +Y, and, like the other pair, they will show the usual similarities, and be capable of uniting to form another inactive racemic substance.

In this connection, it is particularly important to bear in mind that such compounds as +X, +Y and +X, −Y are *not* optical opposites, *do not* as a rule unite to form bimolecular racemic compounds, and *do* show very material differences in such properties as melting-point, crystalline form, solubility, and the like. Upon this fact depends one of the most important methods employed for splitting racemic compounds.

We have seen in the foregoing that the maximum number of isomers for compounds containing two asymmetric carbon atoms is two pairs of optically active compounds and the two racemic inactive products formed by the union of these pairs. In an analogous manner it may be demonstrated that for a substance containing n asymmetric carbon atoms the maximum number of optically active isomers is 2^n, that is, eight for three such carbon atoms, sixteen for four, etc.

The number of possible isomers is reduced when the two asymmetric carbon atoms are each united to the same elements or groups. The most general formula for such a compound is

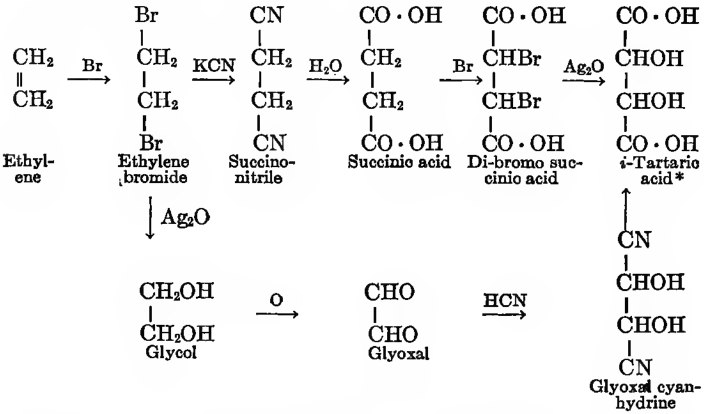


$$\mathrm{(abc)C{-}C(abc)}$$

This differs from the one previously given in that X = Y. It follows that as before there must exist two optically active compounds, +2 X and −2 X, and that these will form an inactive racemic compound. When, however, the two atoms exert their rotatory power in opposite directions, it is clear that the result must be zero, and we shall have another kind of optically inactive substance which is said to be 'inactive by internal compensation.' Substances of this type may be distinguished experimentally from racemic compounds by the fact that they cannot, like the latter, be split into optically active components.

The Tartaric Acids.

The relations just described are admirably illustrated by a group of well-known substances, — the tartaric acids. These all have the general constitutional formula indicated by the following syntheses of the inactive acids.



There exist, in full confirmation of the theory, a dextrorotatory and a lævorotatory acid and also two inactive ones. Of these, one can and the other cannot be split into the active components. The first of these inactive acids is

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* The inactive product is a mixture of the racemic and meso forms.

called *racemic acid* (*racemus*, a bunch of grapes) and the second *meso-tartaric acid.* The dextrorotatory compound is the ordinary tartaric acid of commerce, while *l*-tartaric acid is a laboratory product. The configurations generally adopted for the different acids are represented below, both as the models would appear and also in the abbreviated or 'projected' form.

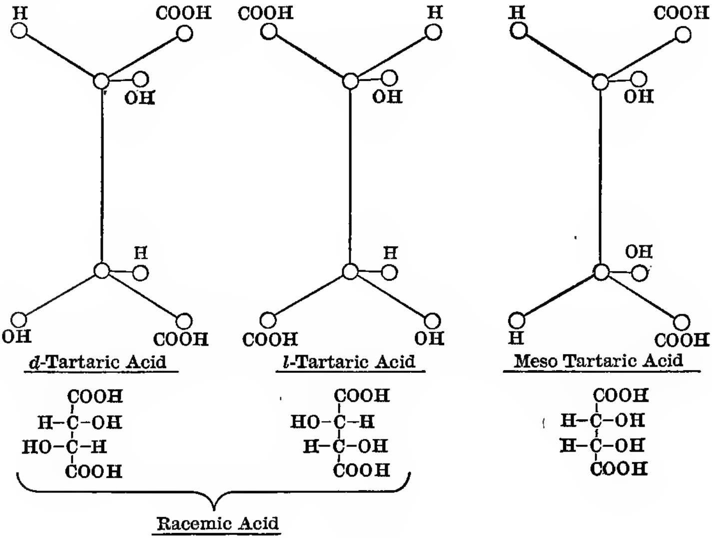


Fig. 14.

The splitting of racemic acid into its optically active components was historically the first operation of the kind ever carried out. It may be accomplished in three ways, each of which represents a general method applicable to cases of the same kind.

If a solution of the double sodium ammonium salt of racemic acid is allowed to evaporate at a temperature below 28°, the salts of right and left tartaric acids separate from the solution in distinct crystals. If these are sufficiently large and well developed they can be separated mechanically, for while both crystallize in the same system, the crystals differ from each other in the same way as the models described on page 151: they are enantiomorphous. The crystals of the dextrorotatory salt show upon one side certain unsymmetrical hemihedral faces which occur in the crystals of the lævorotatory salt upon the opposite side. The forms usually exhibited by these crystals are shown in the figure.

Fig. 15.

The method just described is not very frequently employed in practice, especially where large quantities are involved, on account of the various mechanical difficulties which it presents. It is, however, extremely important because, by its aid, optically active compounds may be prepared without the agency of any living organism.

A second method depends upon the action of microorganisms. It is a remarkable fact that although optical opposites are so much alike in most of their properties, bacteria and similar organisms distinguish sharply between them. Thus if *penicillium glaucum* is introduced into a solution containing racemic acid, it grows at the expense of the dextrorotatory compound and finally the solution rotates to the left. It will be observed that this method always sacrifices one of the active forms.

A third method consists in the formation of the cinchonine salts. This alkaloid is itself dextrorotatory. Its addition to a solution of racemic acid must therefore result in the formation of two salts which contain at least one more asymmetric carbon atom than the original acids. Applying the principle of optical superposition already referred to on page 154, and representing the optical activity of cinchonine by $+C$, the two resulting salts may be distinguished by the formulæ, $+X, +X, +C$ and $-X, -X, +C$. This means that the salts are *not* optical opposites. They may therefore be expected to differ in solubility and other properties, and to permit separation by fractional crystallization. From the salts, the acids may then be set free by the action of a stronger acid. This last method of splitting racemic compounds is of the widest application. Acids, as in the case just cited, may be separated by combining them with optically active bases, or with optically active alcohols forming esters, while for the separation of racemic bases, an optically active acid like lactic or one of the tartaric acids may be employed.

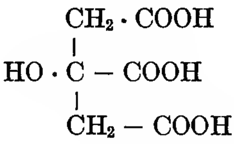
d-Tartaric acid is an important natural product. It occurs in the juices of many fruits, and is technically obtained from argol, a material which deposits when wine is fermented. This can be purified by crystallization, and the product is then commercially known as 'cream of tartar.' It is the acid potassium salt of tartaric acid. It is extensively used in the manufacture of baking powders. The latter also contain sodium acid carbonate. While both substances are dry no reaction takes place between them, but when mixed with moist dough they react in the sense of the following equation:

$$KHC_4H_4O_6 + NaHCO_3 = KNaC_4H_4O_6 + H_2O + CO_2.$$

The carbon dioxide evolved serves to 'raise' the dough. The neutral compound formed in the reaction is technically known as 'Rochelle salt.' Another well-known salt of this acid is 'tartar-emetic.' It finds some use in medicine, and has the following formula: $C_4H_4O_6KSbO, \frac{1}{2} H_2O$. Free tartaric acid crystallizes in large plates. It is readily soluble in water and finds extensive use in dyeing. Analytically it is usually recognized either by the difficult solubility of the acid potassium salt or by the characteristic fact that its calcium salt dissolves in cold dilute sodium hydroxide, but is again precipitated on boiling.

Citric Acid.

Another well-known hydroxy-acid is citric acid. This is the substance which gives the familiar sour taste to the juice of the lemon and similar fruits. It is a solid which crystallizes from water in large rhombic prisms containing a molecule of water. This water is readily lost on heating. The anhydrous acid melts at 153° and shows the interesting peculiarity that it can be recrystallized from water without again taking up any of the solvent. The calcium salt of citric acid is more difficultly soluble in hot than in cold water, and advantage is taken of this fact in the isolation of citric acid from lemon juice. It has recently been found that citric acid can be prepared economically from glucose by the action of a micro-organism (*citromycetes*). The graphic formula of citric acid which appears below has been adequately proved by a somewhat complicated synthesis from glycerol.



$$\begin{array}{rl} & CH_2 \cdot COOH \\ & | \\ HO \cdot & C - COOH \\ & | \\ & CH_2 - COOH \end{array}$$

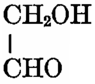
CHAPTER IX.

THE CARBOHYDRATES.

There is no class of substances wherein the principles of stereoisomerism have proved more signally useful than in the case of the carbohydrates. This group includes the sugars, starches, gums, and cellulose. In most of these substances, hydrogen and oxygen are present in the same proportion as in water. Further, when they are treated with strong dehydrating agents like concentrated sulphuric acid, extensive decomposition takes place, accompanied by separation of carbon. In the earlier days of the science, these facts caused the whole group to be regarded as compounds of carbon and water, and this is the historic origin of the name. It is retained because the substances to which the term had been applied form a natural group with characteristic peculiarities of structure and behavior. Chemically this group may be said to comprise the simple sugars (monosaccharides) and substances which may be regarded as anhydride-like condensation products of these. According to the number of such molecules which have entered into combination, the latter are classified as disaccharides, trisaccharides or polysaccharides.

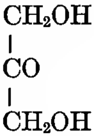
The Monosaccharides.

The simple sugars may also be defined as substances which combine the chemical properties of alcohols with those of an aldehyde or ketone. There is usually but one carbonyl group in a monosaccharide, but almost always there are several hydroxyl groups. Those sugars which are at the same time alcohol and aldehyde are called aldoses; those which combine the character of alcohol and ketone are known as ketoses. The simplest possible aldose would therefore be



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

while the constitution of a simple ketose is represented by

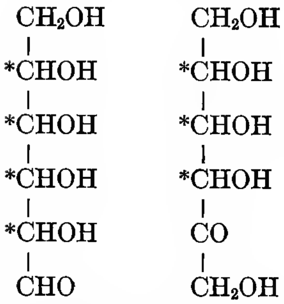


$$\begin{array}{l} CH_2OH \\ | \\ CO \\ | \\ CH_2OH \end{array}$$

The carbon chain is usually normal, and the number of carbon atoms is equal to the number of oxygens. According to the number of the latter which are present, the monosaccharides are classified as tetroses, pentoses, hexoses, etc.

In physical properties the student will not go far astray if he associates them with those of ordinary cane-sugar, which, however, does not belong to this class. They are crystalline solids, usually very soluble in water and but slightly soluble in most organic solvents. They have a sweet or insipid taste, and when heated above their melting-points or treated with dehydrating agents they readily char.

The monosaccharides which are most commonly met with, and the only ones which will receive individual consideration here, are the hexoses. As suggested above, these fall naturally into two classes, the aldohexoses and the ketohexoses. The constitution assigned to these two classes of compounds is shown in the following formulæ:



$$\text{Aldohexose}\quad \begin{array}{c} CH_2OH \\ | \\ {}^*CHOH \\ | \\ {}^*CHOH \\ | \\ {}^*CHOH \\ | \\ {}^*CHOH \\ | \\ CHO \end{array} \qquad \begin{array}{c} CH_2OH \\ | \\ {}^*CHOH \\ | \\ {}^*CHOH \\ | \\ {}^*CHOH \\ | \\ CO \\ | \\ CH_2OH \end{array}\quad \text{Ketohexose}$$

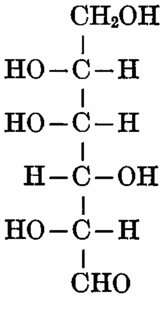
The experimental evidence upon which these formulæ are based rests, among other things, upon the following facts. Reduction leads to the formation of hexatomic alcohols, which in turn yield the normal secondary hexyl iodides:

$$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CHI \cdot CH_3$$

and $$CH_3 \cdot CH_2 \cdot CH_2 \cdot CHI \cdot CH_2 \cdot CH_3$$

This proves the presence of a normal carbon chain. Acetic anhydride forms pentacetates, showing the presence of five hydroxyl groups. The distribution of the latter is determined by the well-known empirical rule that two or more hydroxyl groups usually cannot remain attached to the same carbon atom. Finally the distinction between the aldoses and ketoses rests upon the difference of behavior upon oxidation. The former yield acids containing the same number of carbon atoms. The ketoses, however, yield products containing less than six carbon atoms. The location of the carbonyl group follows from the constitution of the oxidation products. These fundamental proofs are supplemented by a large number of genetic relationships which exist between the different isomers, and which are in harmony with the constitution outlined. This leads to a discussion of the possibilities of stereoisomerism involved. An examination of the formulæ just given reveals the fact that the aldohexoses contain four asymmetric carbon atoms, while the ketohexoses contain three. According to the rule that the number of optically active isomers is 2^n, where n is the number of asymmetric carbon atoms, it follows that for an aldohexose of the formula given eight pairs of optical opposites are possible, in addition to eight racemic compounds formed by the mixture of these two. Of the ketoses there will be considerably less, viz.: four optically active pairs and four racemic compounds. Most of these isomers are actually known, and the configurations of each have been determined with considerable certainty. The methods of proof which are employed in each case need not be entered into here. It is sufficient to say that they rest upon the same kind of reasoning as that employed in determining the configurations of the tartaric acids. Some of these compounds are extremely important both in nature and technically.

d-Glucose, also known as *grape-sugar* and as *dextrose,* is found in the juices of most sweet fruits. It is a colorless, crystalline solid of a sweetish taste, which, however, is much less marked than that of cane-sugar. Crystals containing water appear in several modifications. From methyl alcohol, *d*-glucose crystallizes without water, and then melts at 146°. It rotates the plane of polarized light to the right, and reduces alkaline silver and copper solutions (Fehling's solution). Either of these properties can be utilized for its quantitative determination. Its accepted configuration is

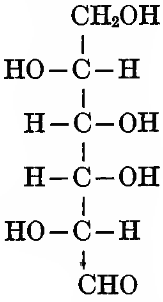


$$\begin{array}{c} CH_2OH \\ | \\ HO-C-H \\ | \\ HO-C-H \\ | \\ H-C-OH \\ | \\ HO-C-H \\ | \\ CHO \end{array}$$

It is extremely widely distributed in nature, occurring free in the juices of many fruits, but more often combined with other sugars in the form of bi-, tri-, or polysaccharides, as well as with other classes of compounds in the substances known as glucosides. These various classes will be mentioned again later on. *d*-Glucose also plays a very important rôle in animal nutrition, and in certain pathological conditions (*diabetes mellitus*) it is a constituent of the urine.

Commercial glucose is a product obtained on the large scale by the hydrolysis of starch. It is not pure *d*-glucose, though it contains a large percentage of this substance. It finds extensive use as a sweetening material in the manufacture of preserves and confectionery. It has also been employed as an adulterant of honey. Both the product and the process of formation will again be touched upon when we take up the study of starch.

d-Galactose is another aldohexose. It is obtained by the hydrolysis of milk sugar and crystallizes in fine needles which melt at 166°. Its configuration is

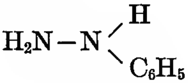


$$\begin{array}{rcl} & CH_2OH & \\ & | & \\ HO- & C & -H \\ & | & \\ H- & C & -OH \\ & | & \\ H- & C & -OH \\ & | & \\ HO- & C & -H \\ & | & \\ & CHO & \end{array}$$

Of the ketohexoses only one need be mentioned, *d*-fructose. This substance is also known as *fruit-sugar* and *levulose.* It occurs in fruit juices and in honey along with *d*-glucose. It forms hard rhombic crystals which melt at 95°.

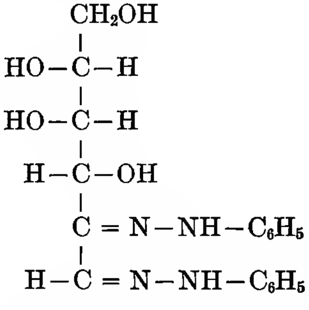
Solutions of *d*-fructose rotate the plane of polarized light to the left.

This last fact suggests the query: Why should the substance be called *d*-fructose if it rotates to the left? In accordance with the principles of nomenclature set forth on page 152 the letters *d*- and *l*-, when prefixed to the names of the carbohydrates or related substances, do not indicate the direction of rotation of the specific compound, but rather whether it is genetically related to *d*- or *l*-glucose. In the present case, the relation to *d*-glucose is traced in the following manner. There is an aromatic compound called phenyl hydrazine whose formula is



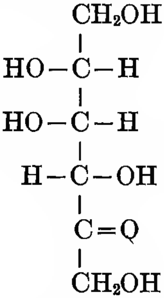
$$H_2N-N\begin{matrix}\diagup H\\ \diagdown C_6H_5\end{matrix}$$

This substance reacts with *d*-glucose to form a compound called *d*-glucosazone which has the constitution indicated by the following formula:



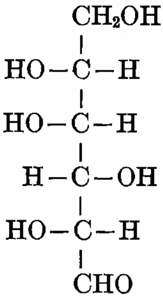
$$\begin{array}{rcl} & CH_2OH & \\ & | & \\ HO- & C & -H \\ & | & \\ HO- & C & -H \\ & | & \\ H- & C & -OH \\ & | & \\ & C & =N-NH-C_6H_5 \\ & | & \\ H- & C & =N-NH-C_6H_5 \end{array}$$

Exactly the same compound is produced when phenyl hydrazine reacts with fruit-sugar. Now it will be noted that the formula of the glucosazone contains but three asymmetric carbon atoms, and since this compound is formed from both grape- and fruit-sugars, it follows that three of the asymmetric carbon atoms of *d*-glucose have the same arrangement in the molecule as the three of fruit-sugar. From this it follows that the constitution of the latter must be correctly represented by the following formula:



$$\begin{array}{c} CH_2OH \\ | \\ HO-C-H \\ | \\ HO-C-H \\ | \\ H-C-OH \\ | \\ C=O \\ | \\ CH_2OH \end{array}$$

d-glucose being



$$\begin{array}{c} CH_2OH \\ | \\ HO-C-H \\ | \\ HO-C-H \\ | \\ H-C-OH \\ | \\ HO-C-H \\ | \\ CHO \end{array}$$

Consequently it is properly named *d*-fructose. It should be added that *l*-glucose and *l*-fructose are also well known, but have no practical importance. They show scarcely any difference from the corresponding *d*-compounds except in their action upon the plane of polarized light.

Fermentation.

Since the earliest times it has been known that when dilute sugar solutions are left standing exposed to the air, gas is evolved and alcohol accumulates in the solution. The production of alcoholic beverages rested upon this fact. An early improvement in the process consisted in bringing into the solution some material like yeast, instead of trusting to the chance inoculation of the air. In later times it was found that if grape-sugar were the material fermented, the reaction was nearly quantitative in the sense of the following equation:

$$C_6H_{12}O_6 = 2\,C_2H_5OH + 2\,CO_2.$$

The nature of the processes involved in fermentation has been differently interpreted at different times. It was the idea of Liebig that the atoms of a substance like sugar were in a constant state of vibration which was, however, under ordinary circumstances, restricted within certain limits. In the presence of rapidly decomposing substances, however, this vibratory motion was so far stimulated that it exceeded the bounds of chemical affinity and the compound broke up. This purely chemical view was contested by Pasteur, who was able to show that when micro-organisms were excluded, no fermentation took place; and further, that different fermentations were induced by different micro-organisms. Thus while grape-sugar with yeast yields alcohol, with another organism (*bacillus acidi lactici*) it yields lactic acid. These facts caused fermentation to be looked upon as in some obscure way related to the vital processes of the micro-organisms employed, and until recently this has been the dominant view, in spite of the fact that, in course of time, products had been discovered which contained no living cells, and yet by their presence caused or rather catalyzed certain chemical reactions. It thus became necessary to draw a distinction between materials like yeast which were called 'formed ferments,' and these other substances, which were now called 'unformed ferments' or *enzymes*. Of the nature of the latter or of their chemical action we really have no knowledge. As a matter of fact, no pure enzyme has probably ever been isolated, and we know the active principle only by its action. An illustration may be found in the case of the gastric juice. It is known that in the stomach our food 'digests.' This action, as we shall see later, is essentially a hydrolysis which is accelerated by the action of the secretions of the walls of the stomach. From these juices there can be isolated a white amorphous powder which appears to belong to the class of substances known as proteins. This powder, when added to materials like the foods, outside the stomach, induces hydrolytic action. We say, therefore, that the powder contains the active enzyme 'pepsin' which causes gastric digestion. It is to be noted that we should say the powder *contains* rather than *is* pepsin, for, in the first place, the properties of substances of this kind offer no guaranty of purity or homogeneity, and, secondly, different samples of otherwise similar appearance show different efficiency. From these facts, we are assured that we do not know the enzymes as such, but only their effects.

The distinction between formed and unformed ferments has now lost practically all significance, since the recent discovery that it is possible to induce alcoholic fermentation in a sugar solution by adding to it the extract from crushed yeast cells. Biological tests have shown that this material contains no living cells, and yet it causes the same fermentation as the living yeast. The conclusion seems unavoidable that the fermentation produced by the yeast itself has little to do with its vital processes, but rather is due to an enzyme which it contains. This particular ferment has received the name 'zymase.' It is probably true that the fermentations produced by other micro-organisms are due to similar causes. How the enzyme produces the fermentation is, of course, as little understood as ever. It simply holds true that this catalysis takes place.

A word may not be out of place here upon the subject of catalysis in general. A catalyzer is now defined as a substance whose presence modifies the velocity of a chemical reaction without itself being used up by the reaction. Catalyzers which accelerate chemical reactions have therefore been appropriately compared to the oil which lubricates machinery, thus causing it to go faster without itself contributing any energy. A single simple chemical illustration will suffice. Hydrogen peroxide is a somewhat unstable compound which, even in quite dilute aqueous solution, decomposes slowly into oxygen and water. If there be introduced into such a solution a little powdered manganese dioxide, the evolution of oxygen becomes brisk, and decomposition is complete in a short time. The same effect will be produced if there is brought into the solution a little blood. The blood contains a ferment whose presence accelerates the decomposition of the hydrogen peroxide. How it is that these two so different substances should produce so similar an effect is entirely unknown to us. In some reactions of this type, it has been shown that the catalyzer first enters into combination with one of the reacting substances, and then in a second reaction is again regenerated. Whether this holds true in either of the present instances we do not know, nor do we know whether there is any real analogy between the mechanisms of the two reactions. We only know that the same end-products are formed in each case, and we call both actions catalytic.

In the case of the enzymes or organic catalyzers, one fact must be especially emphasized. Their action is in high degree specific. This applies both to the material acted upon and to the reaction induced. Thus yeast ferments *d*-fructose with ease, while it acts but slowly upon *l*-fructose. So, too, yeast causes *d*-glucose to decompose into alcohol and carbon dioxide, while other enzymes may produce lactic or butyric acid, or other products. Emil Fischer has well compared the relation which exists between enzyme and fermenting substance to that between lock and key. Probably there is no more striking example of this than the fact that the enzymes act so differently upon optical opposites, substances which are so exactly alike in most other particulars.

The Disaccharides.

This name has been given to a class of substances which may be considered as derived from two like or unlike molecules of monosaccharides by the elimination of one molecule of water. Their physical properties are in general quite similar to those of the former class. When disaccharides are treated with hydrolyzing agents, monosaccharides are again regenerated in accordance with the equation,

$$C_{12}H_{22}O_{11} + H_2O = 2\,C_6H_{12}O_6.$$

There are a great many disaccharides, as might be expected when it is recalled how many hydroxyl groups the monosaccharides contain, and consequently in how many different ways water might be eliminated. This also makes it difficult to determine the constitution of the former. A few important ones will receive individual consideration.

Sucrose, or cane-sugar, is a most important article of food. It occurs in the juices of many plants, notably of the sugar-cane, the beet, the sugar-maple, sorghum, etc. It is a colorless solid which may be crystallized from water, in which it is extremely soluble. It melts at 160°, and its solutions rotate the plane of polarized light to the right. This property is the one usually made use of in the quantitative determination of sugar. Since the angle of rotation is directly proportional to the concentration of the solution, the former serves as a direct measure of the latter when no other optically active substance is present. When cane-sugar is heated above its melting-point, a brown ill-characterized product called caramel is formed. This is extensively used to impart a dark color to certain food products or beverages. When the caramel is further heated, extensive decomposition takes place, accompanied by carbonization. Cane-sugar does not reduce ammoniacal silver solutions or Fehling's solution. It is therefore not an aldehyde, and it may be inferred that in its formation the aldehyde oxygen of the *d*-glucose was the oxygen atom lost in the condensation. Several constitutional formulæ have been proposed for cane-sugar, but none of them can as yet be regarded as definitely established. By hydrolytic agents it is smoothly decomposed. The products are one molecule of *d*-glucose and one of *d*-fructose for each molecule of sucrose hydrolyzed. Since *d*-fructose rotates the plane of polarized light to the left more strongly (for equivalent concentrations) than *d*-glucose rotates it to the right, such a molecular mixture of the two monosaccharides is lævorotatory. As cane-sugar itself is dextrorotatory, it follows that when its solutions are hydrolyzed, a reversal of the direction of rotation is observed. On this account the hydrolysis of cane-sugar has received the specific name *inversion,* and the molecular mixture of *d*-glucose and *d*-fructose which constitutes the product is called *invert-sugar.* Cane-sugar is not directly fermented by zymase. When it is treated with yeast, fermentation cannot take place until hydrolysis has been effected by another enzyme also present which is called *invertase* on account of this action. It is an interesting fact that invert-sugar is occasionally met with in nature. Honey is one of the most marked examples.

Lactose, or milk-sugar, as its name indicates, is the substance to which milk is indebted for its sweet taste. In order to prepare it from skimmed milk, the casein of the latter is first coagulated and precipitated by acids; then the albumin and globulin are removed by boiling, and finally the solution is evaporated. Milk-sugar is by no means as sweet as cane-sugar. It is a reducing agent, and hence in contradistinction to cane-sugar it probably contains an aldehyde group. Upon hydrolysis it yields one molecule of *d*-glucose and one of *d*-galactose. This accounts for the name of the latter compound.

Maltose, or malt sugar, is a most important intermediate product in the technical production of alcohol. It is best prepared by the hydrolysis of starch under the influence of a ferment called *diastase.* Maltose itself undergoes alcoholic fermentation when treated with yeast. When hydrolyzed by acids, it yields two molecules of *d*-glucose.

Little of importance has been done toward the synthesis of the important natural disaccharides. When monosaccharides are condensed in the laboratory products are usually obtained which are not identical with those found in nature. When *d*-glucose, for example, is treated with concentrated hydrochloric acid under certain conditions, a disaccharide is formed which resembles maltose but is not identical with it. This substance has received the name iso-maltose. It is not very well characterized.

The trisaccharides have no representatives which possess such general interest as the carbohydrates just mentioned. They are substances not unlike the latter which, on hydrolysis, yield three molecules of monosaccharide instead of two.

The Glucosides. These substances may be considered as condensation products of a sugar with one or more substances which do not belong to this class. They are readily split by hydrolytic agents into the components mentioned. The variety of organic compounds which are found combined with the sugars in this way is very considerable. Some of the glucosides are interesting on account of their physiological action. The non-carbohydrate components of most of the important ones belong to the aromatic series; benzaldehyde, alizarin, and indigo, for example, form complexes of this kind.

The Polysaccharides.

The carbohydrates thus far considered all possess properties such as are commonly associated with sugar. This resemblance is much less marked in the polysaccharides. The latter are, for the most part, tasteless and hardly soluble in water, though some of them swell in that medium and form colloidal solutions.* This difference in properties corresponds to a difference in composition. The formation of the polysaccharides may be attributed to a combination of *two* molecules of monosaccharide accompanied by the elimination of *two* molecules of water, and this followed by a polymerization of the organic product. For the compounds to be discussed here this leads to the general empirical formula $(C_{12}H_{20}O_{10})_x$. Since it has hitherto proved impossible to determine the molecular weight of these substances, the numerical value of x is unknown. It may safely be assumed to be large. The hydrolysis proceeds in several stages, and by suitably selecting the conditions a variety of intermediate products can often be obtained. When the action is carried to completion it results in the formation of monosaccharides in accordance with the following equation:

$$(C_{12}H_{20}O_{10})_x + 2\,x\,H_2O = 2\,x\,C_6H_{12}O_6.$$

Two polysaccharides have an importance in nature not exceeded by any organic compound. They are starch and cellulose.

Starch is found in the carbohydrate stores of all plants and is readily obtained from corn, rice, and the potato. The food value of these products depends chiefly upon their starch content. Starch always occurs in nature in the form of grains of concentric structure. The shape of the grains

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* The fundamental distinction between 'true' and colloidal solutions may be stated somewhat as follows: In a true solution the individual molecules (or ions) of the dissolved substance move freely in the solvent. In colloidal solutions the average free particle is of considerably greater magnitude. Colloidal solutions possess some extremely interesting properties. The opalescent solutions of starch are sufficiently typical.

differs somewhat with the kind of plant. One of the most sensitive and characteristic chemical reactions of starch is the formation of a blue addition product when treated with iodine. The combination here is of a very loose character. If water which has been colored distinctly blue by starch iodide is heated to boiling, it is completely decolorized. The color returns on cooling. When starch is heated with water, it swells up, forming a paste, and this gives an opalescent colloidal solution with water. Starch may be hydrolyzed either by ferments or by dilute acids. The first products formed are of high molecular weight and closely allied to starch. They bear a variety of names, — 'soluble starch,' 'amylodextrin,' 'dextrin,' etc. These names, however, can hardly be held to stand for distinct chemical individuals, but rather for complexes of starch molecules in various degrees of disintegration.* The first well-defined product of hydrolysis is maltose. This is produced under the influence of diastase, and we know that upon further hydrolysis, it yields *d*-glucose. It follows that the starch molecule, however complicated its constitution, is essentially an anhydride-like union of molecules of *d*-glucose.

The hydrolysis of starch is carried out industrially with two objects in view. The first is the preparation of ethyl alcohol from grain. After the grain has been well soaked, malt is added in order that the diastase which it contains may hydrolyze the starch of the grain, forming maltose. Yeast is then allowed to act upon the maltose, forming alcohol.

The second, which consists in the hydrolysis of starch by acids, yields commercial glucose and dextrin. The latter is the chief impurity in commercial glucose. The properties and uses of glucose have already been mentioned. Dextrin, which is a gummy, amorphous material, finds extensive employment as a cheap and efficient adhesive, suitable for

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* Crystalline dextrins have recently been prepared.

use upon the flaps of envelopes, the backs of postage stamps, and the like.

The Gums. These are natural products usually occurring as exudations from trees. Their composition is not very uniform nor their properties well characterized. In general, most of them are to be considered as polysaccharides or dextrin-like derivatives of the latter. Many of them upon hydrolysis yield pentoses.

The so-called 'pectic substances' constitute another class of ill-characterized carbohydrates. They occur in the juices of many fruits and have the property of gelatinizing with water. This makes possible the preparation of fruit jellies.

Cellulose.

In cellulose the resemblance to the sugars in physical properties has disappeared. The sweet taste and solubility in water which are characteristic of most of the carbohydrates are here entirely lacking, and the substance is very inert toward almost all reagents. These properties fit it admirably for its important place in nature. It forms an essential part of the cell walls of plants and is an important component of woody fiber. Hence it is probably the most widely distributed substance in the vegetable world. The most convenient source for the production of pure cellulose is the cotton fiber, and 'absorbent cotton' (cotton from which the fatty materials have been removed by extraction) is nearly pure cellulose. The so-called 'Swedish' filter paper (paper from which the mineral contents have been removed by treatment with hydrochloric and hydrofluoric acids) is perhaps a still purer form.

The propriety of classifying cellulose with the carbohydrates is seen in its behavior upon hydrolysis. If filter paper is covered with cold concentrated sulphuric acid, it soon goes into solution without charring. If this solution is now diluted and boiled, it is found to contain *d*-glucose. It has been observed very recently that cellulose is smoothly dissolved by extremely concentrated aqueous hydrochloric acid and that such solutions after standing several hours also contain *d*-glucose. It is obvious that the product obtained from either of these sources might be fermented for the production of alcohol, so that under favorable market conditions the latter product might be obtained advantageously from wood. One of the intermediate products in the hydrolysis of cellulose is a disaccharide called cellose. This is supposed to stand in the same relation to cellulose which maltose does to starch. Like the latter, cellulose must be a polymerized condensation product of *d*-glucose, but whether its molecular weight is greater or less than that of starch is only a matter of conjecture.

If paper is treated with slightly diluted sulphuric acid for a short time it becomes partly gelatinized, and the product when washed out and dried is a tough hard material which makes a good substitute for parchment.

Potassium and sodium hydroxides in moderately concentrated solutions also have a peculiar effect upon cotton. They cause a twisting and shrinking which strengthen the fiber, and if the latter is thus treated while under tension, it acquires luster. This gives to the product a certain resemblance to silk, and cotton goods treated in this way have enjoyed considerable popularity. The process is known as 'mercerization,' from the name of its inventor.

Certain rather unusual reagents dissolve cellulose quite readily with little apparent chemical change. One such medium is a mixture of zinc chloride and hydrochloric acid. Another is a solution of cupric hydroxide in ammonia. If the hydroxide is prepared by precipitation all salts should be washed out before dissolving in ammonia. Another excellent method is to allow metallic copper to stand in aqueous ammonia while a current of air or oxygen is passed through. When cellulose is covered with this solvent it first gelatinizes, and then becomes gradually distributed throughout the liquid. The solution is typically colloidal. From it the cellulose may be precipitated again as an amorphous powder, either by treatment with acids or by dilution with water or alcohol. In any case, the product contains a little water which is perhaps chemically combined.

By the action of acids and acid anhydrides upon cellulose, esters are formed and some of these are of great technical importance. From the extent to which esterification takes place, the conclusion is justified that cellulose contains six hydroxyl groups for each twelve atoms of carbon. Its empirical formula $[C_{12}H_{20}O_{10}]_x$ may therefore be expanded to $[C_{12}H_{14}O_4(OH)_6]_x$.

Cellulose Nitrates. If cellulose is treated with nitric acid in the presence of strong dehydrating agents, it is possible to replace all six hydroxyls by nitric acid radicles forming a compound $C_{12}H_{14}O_4(NO_3)_6$. Commercially a mixture of concentrated nitric and sulphuric acids is employed, and the product contains somewhat less nitrogen than the above formula requires. It is known as gun-cotton or pyroxylin, and in physical properties it closely resembles cellulose. The fibers are a little more harsh to the touch, but otherwise little is noticed which would distinguish it from the original cotton. It is, however, extremely combustible, and when detonated by mercury fulminate it explodes with great violence. As an explosive, it has several advantages; when wet it is practically non-combustible, but wet gun-cotton will explode like the dry if ignited by some of the latter. This makes it practicable to store, transport, and use the explosive in the wet condition, keeping only enough of the dry on hand to serve as priming.

If the acids used in the nitrating mixture are more dilute than above described, esters are obtained which contain fewer nitric acid groups, usually four or five. In appearance there is not much to distinguish these various nitrates, but the lower ones are, as a rule, more soluble in organic liquids, particularly in a mixture of alcohol and ether. It should be distinctly understood in this connection that solubility in organic solvents is not to be regarded as an infallible clue to the degree of nitration of a nitrocellulose. Tetranitrates have sometimes proved as insoluble in these media as the hexanitrate itself. The properties of the nitrate seem in general to depend fully as much upon the conditions of nitration as upon the percentage composition of the product. It is doubtful whether these lower nitrates of cellulose should in any case be considered as distinct chemical individuals.

A solution of cellulose nitrate in alcohol and ether is commonly known as collodion. On evaporation of the solvent, the cellulose nitrates are deposited as a coherent, elastic, transparent film. This makes collodion a convenient thing with which to paint scratches or abrasions of the skin in order to protect them from the irritating action of the air. Collodion is also frequently used as a varnish where a perfectly colorless coating is desired, as for example for photographic negatives. Here any color would retard printing.

When lower nitrates of cellulose or 'collodion cotton' are mixed with camphor, either in solution or mechanically, a product is formed which is not explosive and whose properties fit it for a great number of applications. This is *celluloid,* whose use in films and as a cheap substitute for bone and ivory is so well known. It is unfortunately very combustible, and this is a serious objection to its use especially in the manufacture of objects of large size.

Smokeless Powder. When gun-cotton or a slightly lower nitrate of cellulose is treated with certain organic solvents

— usually mixtures containing a good deal of acetone — it gelatinizes, forming a non-fibrous mass which can be pressed into any shape. After evaporation of the acetone there is left a hard yellow substance somewhat like tortoise shell. This is the material from which 'smokeless powder' is made. It is brought upon the market in grains and cylinders of various forms and sizes. It is faster burning than black powder, cleaner in the gun, and for military purposes has the advantage of not obscuring the view by clouds of smoke. When nitro-glycerin is absorbed by cellulose nitrates, a material called 'blasting gelatin' is produced.

Cellulose Acetates. When cellulose is treated with acetic anhydride in the presence of small amounts of sulphuric acid or of zinc chloride, six hydroxyls are esterified. The product is generally known technically as the 'triacetate.' This term involves an inconsistency in nomenclature which requires a word of explanation. Since the molecular weight of cellulose is unknown, there is no objection so far as cellulose itself is concerned to writing its formula $[C_6H_7O_2(OH)_3]_x$ instead of $[C_{12}H_{14}O_4(OH)_6]_x$, tacitly giving to x in the first case twice the value it has in the second. Nitrates of cellulose, however, appear to exist which contain three and five nitric acid groups respectively for each twelve atoms of carbon in cellulose. For them no formula can be written upon a six-carbon-atom basis which does not involve the use of fractional molecules or groups. Consequently the twelve-carbon formula for cellulose is practically always used when speaking of the nitrates. With the acetates the case is somewhat different. Of these, three are known, the one just mentioned, and two others containing respectively one-third and two-thirds as many acetyl groups. When acetates alone are considered, therefore, it involves no inconsistency to call these products mono-, di-, and triacetates of cellulose, and to assign to the most highly acylated product the formula $[C_6H_7O_2(C_2H_3O_2)_3]_x$. To put this into a form which should bring out its relation to the corresponding nitrate, it should be written $[C_{12}H_{14}O_4(C_2H_3O_2)_6]_x$ and called a hexacetate. Unfortunately this has not been done in practice, and consequently the student must bear in mind that the product commonly called cellulose 'triacetate' represents a degree of esterification of the cellulose molecule corresponding to that designated by the term 'hexanitrate.'

This acetate, whatever name be given it, much resembles the nitrates in physical properties. It is soluble in a variety of organic solvents, notably in chloroform. From such solutions it is deposited as a tough transparent film, which has the practical advantage over that formed by the nitrate that it is not explosive, and no more combustible than the original cellulose in a similar state of subdivision. Cellulose acetate has also been used as an insulating material for fine copper wire like that used for winding the small electromagnets of telegraph and telephone instruments. For most purposes its relatively high cost of production has prevented its extensive employment.

Artificial Silk. Various attempts have been made to prepare from cellulose some cheap substitute for silk. The earliest methods involved the use of collodion. Solutions of cellulose nitrate were forced through fine apertures under water, and in this way there was formed a fine thread which could be dried, spun, and woven like any other fabric. Such a product has a luster rather superior to that of natural silk. It also can be easily dyed and so is well fitted to replace the latter for ornamental purposes, though where wearing qualities are required it cannot be used to advantage on account of its low tensile strength. The product just described has all the further disadvantages associated with the combustibility of the cellulose nitrate, and is no longer brought on the market in its original form. By passing the fibers through calcium sulphide solution a 'denitrification' is effected. This is a saponification by which cellulose is regenerated. The action does not seem to sensibly affect the physical properties of the fiber. Cellulose acetate, the solution of cellulose in ammoniacal cupric oxide, and other cellulose products have also been used for the manufacture of artificial silk. Fine effects can be obtained by all processes, but none has thus far produced a fiber equal in strength and durability to natural silk. A word on the distinction of artificial from natural silk may not be out of place. Natural silk being albuminous gives when burning the odor commonly associated with burned feathers. No cellulose product does this when pure. When observed under the microscope the fibers of artificial silk are round, while those of the natural product have a cross-section like the figure 8.

CHAPTER X.

DERIVATIVES OF CYANOGEN AND CARBONIC ACID.

Cyanogen and Its Derivatives.

AMONG the compounds related to cyanogen, the nitriles have already been touched upon (page 75), and the behavior of the simpler cyanides is doubtless already familiar to the student from his work in Inorganic and Analytical Chemistry. Nevertheless a brief recapitulation will not be out of place at this point.

The first industrial source of cyanogen compounds was animal refuse like horns and hoofs. When these are heated with potash and metallic iron, complicated reactions take place, and the resulting melt when leached out with water yields potassium ferrocyanide, $K_4Fe(CN)_6$, which crystallizes in large yellow aggregates. This substance is known commercially as 'yellow prussiate of potash.' When treated with oxidizing agents such as chlorine water, it is changed to the ferricyanide, commonly known as 'red prussiate of potash':

$$2\,K_4Fe(CN)_6 + Cl_2 = 2\,KCl + 2\,K_3Fe(CN)_6.$$

These compounds are not to be looked upon as double cyanides of iron and potassium but rather as potassium salts of the acids $H_4Fe(CN)_6$ and $H_3Fe(CN)_6$. As such they undergo various metathetic reactions with salts of various metals, for example with iron. When potassium ferrocyanide is treated with the solution of a ferric salt, a dark blue precipitate is produced:

$$4\,FeCl_3 + 3\,K_4Fe(CN)_6 = 12\,KCl + Fe_4[Fe(CN)_6]_3.$$

As the above equation indicates, this product is usually regarded as a ferric ferrocyanide. It is much used as a pigment and is commonly called 'Prussian blue.' An altogether similar precipitate is formed when a soluble ferricyanide is treated with a ferrous salt. The product in this case is usually spoken of as 'Turnbull's blue,' but recent investigations have made it not improbable that the two pigments are identical.

In recent times it has proved possible to obtain potassium ferrocyanide as a by-product in the gas-works. It will be recalled that in order to free illuminating gas from sulphur it is passed through purifiers usually filled with a mixture of oxides of iron, lime and sawdust. This material gradually absorbs nitrogenous material from the gas and when exhausted contains large amounts of a very impure Prussian blue. By heating the latter with lime it can be changed to a calcium ferrocyanide, and this in its turn, by precipitation with potassium carbonate, yields the potassium salt.

The Cyanides.

If potassium ferrocyanide is heated to fusion, decomposition takes place which results in the formation of nitrogen, iron carbide, and potassium cyanide:

$$K_4Fe(CN)_6 = N_2 + FeC_2 + 4\,KCN.$$

The last is a colorless salt extremely soluble in water and very poisonous.

Both potassium and sodium cyanides now have a very considerable industrial importance, and more economical methods of production than the one just described have been worked out. One of the most important consists in the interaction of carbon, sodium and ammonia at a high temperature. Several steps can be distinguished in the reaction, but the total effect may be summarized by the equation:

$$2\,NH_3 + 2\,Na + 2\,C = 3\,H_2 + 2\,NaCN.$$

It is estimated that the process just mentioned furnishes about two-thirds of the cyanide now brought upon the market. The remainder is prepared mostly from the last residues of beet-sugar molasses from which no more sugar can be made to crystallize. This exhausted molasses contains much nitrogenous material and when destructively distilled it yields large quantities of trimethylamine. Strong heating of the latter compound splits it into methane and hydrocyanic acid in the sense of the following equation:

$$N(CH_3)_3 = 2\,CH_4 + HCN.$$

Cyanides can, of course, be obtained by neutralizing the hydrocyanic acid formed.

The cyanides find extensive use in the extraction of low-grade gold ores on account of the remarkable properties they possess of dissolving metallic gold. The formation of such solutions is usually interpreted in the sense of the following equation:

$$2\,Au + 4\,KCN + 2\,H_2O + O_2 = 2\,KAu(CN)_2 + 2\,KOH + H_2O_2;$$
$$2\,Au + 4\,KCN + H_2O_2 = 2\,KAu(CN)_2 + 2\,KOH.$$

From these solutions the gold may be recovered either by the action of metallic zinc or by electrolysis.

Another technical application for the cyanides consists in preparing electroplating baths, particularly for silver and gold solutions. Here, as in numerous other cases, use is made of the general tendency on the part of cyanides to form complex ions with salts of the various metals. The solubility of the halogen compounds of silver in potassium cyanide is attributed to this cause, and the tendency is further illustrated by the existence of the complex iron compounds already described. The ferrocyanides are readily formed when a ferrous salt is digested in alkaline solution with a soluble cyanide:

$$FeSO_4 + 6\,KCN = K_4Fe(CN)_6 + K_2SO_4,$$

and it is probable that the production of potassium ferrocyanide in the decomposition of animal refuse above described is really due to a similar reaction when the melt is leached out with water, for the temperature at which the melt is made is high enough to decompose any ferrocyanide which might have been formed by the fusion.

Hydrocyanic Acid. If potassium cyanide is treated with dilute acids, it is decomposed with liberation of hydrocyanic acid:

$$KCN + HCl = KCl + HCN.$$

This decomposition is even effected to a certain extent by the carbon dioxide of the air. The free acid, commonly called 'prussic acid,' is usually obtained in the laboratory by the distillation of potassium ferrocyanide with *dilute** sulphuric acid:

$$2\,K_4Fe(CN)_6 + 3H_2SO_4 = 3K_2SO_4 + K_2Fe_2(CN)_6 + 6\,HCN.$$

The product is first passed through calcium chloride in order to remove any water and then condensed. It is a volatile liquid boiling at 26° and freezing at −15°. It has a characteristic odor suggestive of bitter almonds which, however, some persons are unable to perceive. It is extremely poisonous. The anhydrous liquid is stable, but with small amounts of water decomposition gradually takes place, resulting in the formation of the ammonium salts of formic and oxalic acids. As its formula indicates, prussic acid may be regarded as the nitrile of the former:

$$HCN + 2\,H_2O = NH_3 + HCOOH.$$

On reduction, methyl amine is formed:

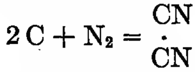
$$HCN + 2\,H_2 = CH_3NH_2,$$

---

* Concentrated sulphuric acid yields carbon monoxide instead of hydrocyanic acid. This may be interpreted as a partial hydrolysis to formamide $HCO \cdot NH_2$ and removal of ammonia from the latter.

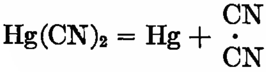
and this is in entire accord with the behavior of the organic nitriles.

Cyanogen. When the sparks of an induction coil pass between carbon electrodes in an atmosphere of nitrogen the spectroscope reveals the presence of cyanogen:



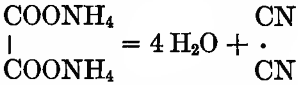
$$2\,C + N_2 = \begin{array}{c} CN \\ \cdot \\ CN \end{array}$$

The same gas can be obtained by heating mercuric cyanide:



$$Hg(CN)_2 = Hg + \begin{array}{c} CN \\ \cdot \\ CN \end{array}$$

Cyanogen is a gas with an odor suggestive of bitter almonds, and like hydrocyanic acid, it is extremely poisonous. It can be condensed to a liquid at −25°, and burns with a characteristic purple-bordered flame. It may be regarded as the nitrile of oxalic acid. In this connection, it is interesting to note that it may be prepared by the dehydrating action of phosphorus pentoxide upon ammonium oxalate:



$$\begin{array}{l} COONH_4 \\ | \\ COONH_4 \end{array} = 4\,H_2O + \begin{array}{c} CN \\ \cdot \\ CN \end{array}$$

Cyanamid, H_2NCN, would hardly have interest for us but for the fact that the two hydrogens of the amino-group are replaceable by metals, and the calcium salt has acquired considerable importance as a fertilizer. It is readily prepared by the action of nitrogen gas on calcium carbide at a temperature of about 1000°:

$$CaC_2 + N_2 = CaNCN + C.$$

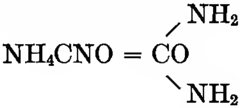
This reaction takes place with considerable evolution of heat, and may be catalyzed to a certain extent by the addition of calcium chloride. The product comes upon the market under the name of 'lime-nitrogen' or 'cyanamide' neither of which names is appropriate. Its production represents one of the important modern methods for the fixation of atmospheric nitrogen. Under the influence of micro-organisms in the soil calcium cyanamide is supposed to yield successively urea, ammonium carbonate, ammonium nitrite and finally ammonium nitrate. When heated with water ammonia is formed:

$$CaNCN + 3\,H_2O = CaCO_3 + 2\,NH_3.$$

Cyanates. If potassium cyanide be oxidized, the cyanate is formed:

$$KCN + O = KCNO.$$

The corresponding ammonium salt is of interest on account of its spontaneous transformation into urea:



$$NH_4CNO = CO\begin{matrix} \diagup NH_2 \\ \diagdown NH_2 \end{matrix}$$

Fulminates. When a solution of mercury in nitric acid is treated with ethyl alcohol, an extremely violent reaction sets in, explosive vapors are evolved, and finally a heavy white or gray precipitate settles out. This product is mercuric fulminate, commonly spoken of as fulminating mercury. It is a valuable explosive easily ignited by the electric spark or by percussion, and it therefore finds use in caps, cartridges, etc., for detonating other explosives. The formula of the compound is $Hg(ONC)_2$, and the mechanism of its formation by the method described above cannot well be represented by any simple equation.

An entirely similar compound, AgONC, is known and it is still more explosive. Free fulminic acid has not yet been isolated in the pure state, but unstable solutions of it can be prepared. The odor and physiological action of the free acid are strikingly similar to those of hydrocyanic acid.

It will be observed that the salts are isomeric with the corresponding cyanates, and it is of historical interest that this was the first case of isomerism ever observed. The best evidence which we have concerning the structure of the fulminates is found in their behavior upon hydrolysis. Under these circumstances they yield a salt of formic acid and hydroxylamine:

$$HONC< + 2\,H_2O = HCOOH + HONH_2.$$

This tends to represent fulminic acid as the oxime of carbon monoxide. There is, of course, something fanciful in the thought of carbon monoxide as a ketone, but the formal analogy involved may prove an assistance to the memory. It will be noted that this formulation assumes the presence of bivalent carbon. This, however, must in any case be assumed in the case of carbon monoxide, and many chemists assume its presence in several other classes of compounds, notably in the isonitriles, $R \cdot NC<$.

Sulphocyanates. The sulphocyanates of the alkali metals are frequently employed in Analytical Chemistry. The student will doubtless recall the deep red color which they produce with ferric salts,

$$FeCl_3 + 3\,KSCN = Fe(SCN)_3 + 3\,KCl,$$

and their usefulness in the determination of copper and silver. The sulphocyanates are easily prepared by fusing the cyanides with sulphur or by digesting them with a polysulphide:

$$KCN + S = KSCN.$$

$$NH_4CN + (NH_4)_2S_x = NH_4SCN + (NH_4)_2S_{x-1}.$$

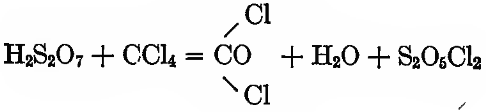
The technical source of these compounds is the ammonium sulphocyanate which accumulates in the purifiers of the gas works.

The mercury salt of sulphocyanic acid swells up and assumes the most grotesque forms when heated. The pellets commonly sold as playthings under the name 'Pharaoh's serpents' consist of this material. It is doubtful whether their unrestricted use is entirely safe, both on account of the poisonous character of mercury salts, and because of the gases liable to be evolved when the material is ignited.

Carbonic Acid Derivatives.

On account of the common occurrence of the carbonates as minerals (calcite, dolomite, etc.), carbonic acid is usually regarded as belonging to Inorganic Chemistry. It is allied, however, to a great number of organic substances and it is, strictly speaking, the simplest member of the series of dibasic organic acids. An intimate acquaintance with the chemistry of the organic derivatives of carbonic acid is hardly necessary for any save the professional organic chemist, but a few of them deserve some mention here. In general, it may be said that the properties and methods of preparation of these substances do not differ widely from those of analogous compounds in other series; thus the esters are formed, for example, by the action of the alkyl halides upon silver carbonate, or by the action of the chloride of carbonic acid upon the alcohols, and their properties are much the same as those of other esters.

Phosgen. The symmetrical chloride of carbonic acid is an interesting substance. It is prepared industrially on the large scale by the action of chlorine upon carbon monoxide under the influence of light. This reaction was historically one of the first 'photo-chemical reactions' to be observed, and from this method of formation the substance itself received the name *phosgen* (Greek, φῶς, light). A method of preparation which is more convenient for laboratory purposes consists in the action of fuming sulphuric acid upon carbon tetrachloride. This rather peculiar reaction proceeds in accordance with the following equation:

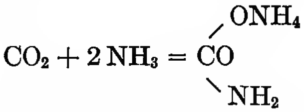


$$\mathrm{H_2S_2O_7 + CCl_4 = CO}\begin{matrix}\diagup \mathrm{Cl} \\ \diagdown \mathrm{Cl}\end{matrix} \mathrm{+ H_2O + S_2O_5Cl_2}$$

The last product is called pyrosulphuryl chloride.

Phosgen is a colorless gas which, however, is easily condensed by a freezing mixture. It dissolves readily in toluene and such a solution is usually employed for keeping and transporting it. It possesses the usual physical and chemical properties of the acid chlorides including an intolerable odor. As might be expected, it acts upon alcohols forming esters, with ammonia to form amides, and, in a variety of other ways, proves a valuable reagent. Large quantities of it are used technically in the preparation of certain dyes.

Amides: Urea. Since carbonic acid is dibasic, two amides are possible. The first, commonly known as carbamic acid, is incapable of existence in the free state but its ammonium salt is formed when carbon dioxide reacts directly with ammonia gas:

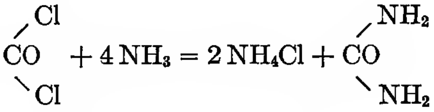


$$\mathrm{CO_2 + 2\,NH_3 = CO}\begin{matrix}\diagup \mathrm{ONH_4} \\ \diagdown \mathrm{NH_2}\end{matrix}$$

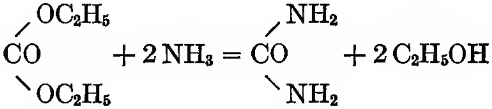
and hence is always present to some extent in commercial ammonium carbonate.

A compound of far greater interest is the symmetrical amide named carbamide, or more commonly, *urea*. This substance is of great interest to the physiologist, since in mammals it is in the form of urea that practically all the nitrogen which originally enters the organism in the food is finally eliminated from it. The amount of urea secreted is regarded as a measure of the protein material decomposed by the body. The average amount of this substance which is produced daily by an adult man may be roughly estimated at about thirty grams. The quantity varies a good deal according to the diet and the state of health, so that a determination of the quantity produced in a given time is often a valuable aid in diagnosis.

In the laboratory, urea may be formed by the customary methods for preparing acid amides, such as the action of ammonia upon phosgen or upon the esters:

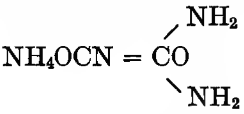


$$\mathrm{CO}\begin{matrix}\diagup \mathrm{Cl}\\ \diagdown \mathrm{Cl}\end{matrix} + 4\,\mathrm{NH_3} = 2\,\mathrm{NH_4Cl} + \mathrm{CO}\begin{matrix}\diagup \mathrm{NH_2}\\ \diagdown \mathrm{NH_2}\end{matrix}$$



$$\mathrm{CO}\begin{matrix}\diagup \mathrm{OC_2H_5}\\ \diagdown \mathrm{OC_2H_5}\end{matrix} + 2\,\mathrm{NH_3} = \mathrm{CO}\begin{matrix}\diagup \mathrm{NH_2}\\ \diagdown \mathrm{NH_2}\end{matrix} + 2\,\mathrm{C_2H_5OH}$$

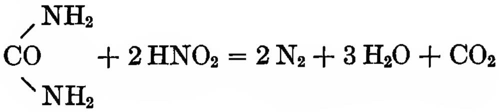
A more interesting method, as well as one which is more convenient in practice, depends upon the molecular rearrangement by which urea is formed from ammonium cyanate:



$$\mathrm{NH_4OCN} = \mathrm{CO}\begin{matrix}\diagup \mathrm{NH_2}\\ \diagdown \mathrm{NH_2}\end{matrix}$$

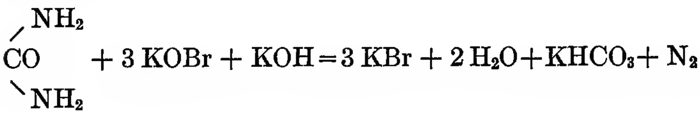
This takes place upon merely evaporating the aqueous solution of the salt. The reaction was first observed by Wöhler in 1828 and had great historical significance. At the time this discovery was made, those substances were classed as 'organic' which were produced directly or indirectly from the animal or vegetable organism. It was believed that such substances could come into existence only in this way, and that while inorganic compounds were held together by chemical affinity — then supposed to be electrical in character — the organic ones owed their formation and preservation to the action of the 'vital force.' The formation of urea, a typical product of the animal organism, from ammonium cyanate, which was then regarded as an inorganic compound, showed that, in the production of this substance at least, no vital force was necessary, and this hypothetical agency soon after disappeared from the theories of the science. Shortly after Wöhler's discovery, cyanic acid was itself prepared from the elements, and thus the synthesis of urea was made complete.

Urea is a colorless, crystalline solid of cooling taste. It is very soluble in water, and shows the reactions of the acid amides. As it contains two amino-groups, it is perhaps a little more basic than most substances of this class, and forms salts with acids. The nitrate is soluble only with considerable difficulty in water, and it is customary to take advantage of this fact for the purpose of isolating urea from urine. With nitrous acid, urea reacts as might be expected, forming carbon dioxide, water, and nitrogen:



$$\mathrm{CO}\left\langle\begin{matrix}\mathrm{NH_2}\\ \mathrm{NH_2}\end{matrix}\right. + 2\,\mathrm{HNO_2} = 2\,\mathrm{N_2} + 3\,\mathrm{H_2O} + \mathrm{CO_2}$$

With the hypobromites of the alkali metals it reacts in the sense of the following equation:



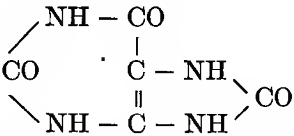
$$\mathrm{CO}\left\langle\begin{matrix}\mathrm{NH_2}\\ \mathrm{NH_2}\end{matrix}\right. + 3\,\mathrm{KOBr} + \mathrm{KOH} = 3\,\mathrm{KBr} + 2\,\mathrm{H_2O} + \mathrm{KHCO_3} + \mathrm{N_2}$$

This reaction furnishes a convenient method for its quantitative determination, the volume of nitrogen gas evolved serving as a measure of the urea present.

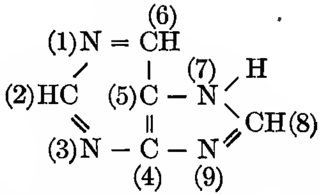
Uric Acid and Its Derivatives.

A complicated substance which may be considered as a derivative of urea, and which has perhaps as much importance to the physiologist as the latter, is uric acid. This substance seems to play the same rôle in the organism of birds and reptiles that urea does in that of mammals. The half-solid excreta of the former are largely made up of uric acid. It is also present normally to a slight extent in the urine of mammals, and in pathological conditions its formation throughout the organism may be very much increased. It is a white solid, soluble with great difficulty in water. It frequently appears in renal calculi, and it is the essential ingredient of the concretions deposited in the joints in the disease of gout. Rheumatism is generally attributed to an excessive quantity of uric acid in the system, and consequently solvents of uric acid, such as lithium salts or piperazine derivatives, are frequently prescribed as remedies in the treatment of this disease.

The constitution of uric acid is expressed by the following formula:

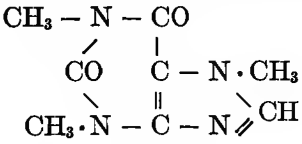


which has been satisfactorily established by several syntheses. There is a large number of substances of considerable physiological importance which have analogous constitutions. These may all be regarded as derivatives of a substance called purine,

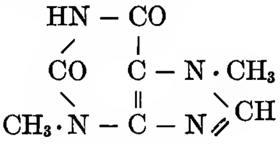


and the scientific nomenclature of the group is fixed with this relationship in mind. Uric acid itself is called 2.6.8 trioxypurine. The numbers designate the position of the oxygen atoms in the molecule as referred to the carbons and nitrogens in purine. It is customary to assign to these various atoms the numbers indicated in parentheses in the above formula. A discussion of the ways in which the position of the substituting groups is determined would take us far beyond the limits of a work of this kind. We shall have opportunity to become acquainted with somewhat similar methods of reasoning later on.

Only two other purine derivatives will be considered here. They are 1.3.7 trimethyl-2.6 dioxypurine or *caffeine,* and 3.7 dimethyl-2.6 dioxypurine or *theobromine:*



Caffeine



Theobromine

The former is the stimulating principle found in tea and coffee. The latter is found in cocoa. Its physiological action is much like that of caffeine.

Carbon Bisulphide.

Carbon bisulphide may be considered as an analogon of carbon dioxide, and this is borne out by much of its chemical behavior. It is usually prepared by the action of sulphur upon hot coals. The product is a colorless oil, heavier than water, which boils at 47°. It has a high refractive index as well as high dispersive power, and in consequence it is sometimes used to fill prisms designed to show a much elongated spectrum. Technically it is much employed as a solvent. Among other things it readily dissolves phosphorus and sulphur, and it is used in the vulcanization of rubber. The vapors of carbon bisulphide when in contact with warm air undergo oxidation at such a rate that the temperature may rise to the point of ignition. There is therefore real danger of fire when carbon bisulphide vapors come in contact with hot steam-pipes. This fact should be borne in mind by those who have occasion to work with this substance, especially in evaporating any quantity of it. It should further be remembered that a carbon bisulphide fire is a particularly difficult one to fight, as the sulphur dioxide formed by the combustion makes the respiration of the surrounding air intolerable.

Chemically this substance is quite reactive. The products formed may, for the most part, be regarded as derivatives of carbonic acid in which more or less of the oxygen has been replaced by sulphur. Most of these compounds are not, however, of much interest to the non-professional student. One reaction which is, perhaps, as well worth mentioning as any, is the formation of ammonium sulphocyanate from carbon bisulphide and an alcoholic solution of ammonia:

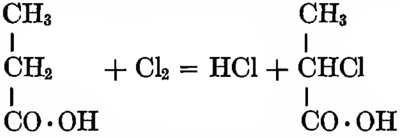
$$4\,NH_3 + CS_2 = NH_4SCN + (NH_4)_2S.$$

CHAPTER XI.

THE AMINO-ACIDS AND PROTEINS.

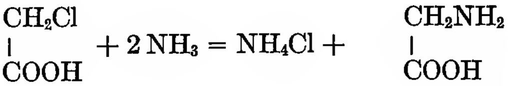
The Amino-acids.

When chlorine or bromine acts upon a fatty acid, the direct substitution of one hydrogen by the halogen is effected. With practical uniformity, the hydrogen atom substituted is one connected to that carbon atom which stands next to the carboxyl group. This is called the *alpha* carbon atom. What happens is shown graphically in the following equation:



$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CO\cdot OH \end{array} + Cl_2 = HCl + \begin{array}{l} CH_3 \\ | \\ CHCl \\ | \\ CO\cdot OH \end{array}$$

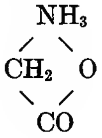
and the product in this particular case is called α-chloropropionic acid. If such a chlorinated acid be now treated with ammonia, a reaction takes place entirely analogous to that which occurs when an alkyl halide is treated with the same reagent. The halogen is now in its turn substituted by the amino-group:



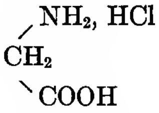
$$\begin{array}{l} CH_2Cl \\ | \\ COOH \end{array} + 2\,NH_3 = NH_4Cl + \begin{array}{l} CH_2NH_2 \\ | \\ COOH \end{array}$$

The product of the reaction just written, aminoacetic acid, has properties which are typical of a large class of similarly constituted substances and, on that account, deserves more than passing notice. As will be shown a little later, those important constituents of animal tissue, the proteins, stand in a close chemical relationship to the amino-acids, and this gives tō the latter an especial significance.

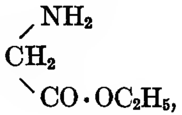
Aminoacetic acid is a colorless, crystalline solid very soluble in water. For a substance called an acid, it has the unusual property of a sweet taste, and to this it is indebted for two other names, glycine and glycocoll. The acid can be obtained by the action of hydrolytic agents upon glue. The acid properties of glycine are not very marked, although it forms salts, among others a beautiful copper compound which is frequently made use of in purifying the mother substance. The formula of glycine gives rise to some interesting considerations. Obviously it is at once an acid and a primary amine, and since compounds of the latter class are strongly basic, the neutral character of glycine may be accounted for by the mutual neutralization of its constituent radicles. This might perhaps be still more clearly expressed by ascribing to glycine the structure of an internal salt. For this reason the formula,



is preferred by some chemists. From either formula it is easy to predict certain points of chemical behavior which are found verified by experience. When the amino-group is neutralized by an acid, the nature of the carboxyl group makes itself felt, and the salt,



is a true acid. On the other hand, when the acidic tendencies of the carboxyl group are negated by esterification, the resulting compound,



$$\begin{array}{l} \quad / NH_2 \\ CH_2 \\ \quad \backslash CO\cdot OC_2H_5, \end{array}$$

is a strong base.

The properties of glycine which have just been mentioned are typical for the group. The other more important amino-acids will be mentioned when their relationship to the proteins have been discussed.

The Proteins.

The proteins are the extremely important substances which make up the principal portion of the animal tissues, such, for example, as the skin, hair, nerves, muscles, and the bulk of the internal organs. Among those which may reasonably be concluded to represent true chemical individuals are the material of the white of egg, casein from milk, keratin from horn, fibroin from silk, gelatin from cartilage. As will be seen at once, these substances show wide differences in physical properties. It is therefore at first sight rather surprising to find that they exhibit so narrow a range of percentage composition. This is shown in the accompanying table.

Elements in the proteins	Lower limit, per cent	Upper limit, per cent
Carbon	50.0	55.0
Hydrogen	6.9	7.3
Oxygen	19.0	24.0
Nitrogen	18.0	19.0
Sulphur	0.3	2.4

Very few of these substances can be obtained in a crystalline form, and the usual criteria of purity are lacking in most of them. Further, they usually form only colloidal solutions, and are easily affected or totally altered in physical properties by changes of temperature. The white of an egg, and the way in which it is affected by heat, will serve as a familiar illustration. Properties like this naturally make it a difficult matter to determine the molecular weights of these substances, and no thoroughly reliable measurements have been made. Some idea of their molecular magnitude can be obtained from reasoning like the following: Almost all substances of this class contain sulphur. This is usually present in small quantities of which it would probably be fair to call one per cent a fair average. Now upon the assumption that a molecule of a protein containing one per cent of sulphur contains one atom of that element, a minimum value for its molecular weight would be arrived at by the proportion,

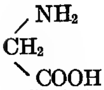
$$1 : 100 :: 32 : 3{,}200.$$

Similarly, there is an important substance in the blood called hæmoglobin. It contains iron, which is certainly not an impurity, though it makes up but 0.40% of the compound. A similar proportion gives

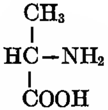
$$0.4 : 100 :: 56 : 14{,}000,$$

and this is in fair agreement with such direct determinations as have been attempted. It will be seen that, in any case, the molecular weight must be very high, and this is in line with what might be expected from properties of the substances concerned.

The key to the chemical character of the proteins is furnished by their behavior upon hydrolysis. By such energetic means as protracted boiling with dilute acids, they may be decomposed almost quantitatively into a mixture of about twenty amino-acids. Almost all of these acids are produced by the hydrolysis of every protein, but the proportions of each which are formed vary widely in different cases. Thus, fibroin from silk yields 36% glycine, whereas keratin from horn gives only a trace. If ferments are used instead of acids, the reaction proceeds in stages, and more or less well-marked intermediate products can be obtained. These have received various names, such for instance as *albumoses*, *peptones*, and the like, but it is now very doubtful whether these represent true chemical individuals. It is rather probable that they are analogous to the dextrins which appear as intermediate products in the hydrolysis of starch. In their turn, the albumoses and peptones, whatever their chemical nature, yield amino-acids on further hydrolysis. The names and formulæ of the amino-acids usually met with as components of proteins will be found in the accompanying table.

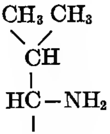


Glycine]

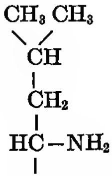


$$\begin{array}{c} CH_3 \\ | \\ HC-NH_2 \\ | \\ COOH \end{array}$$

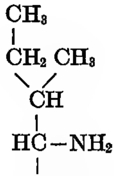
Alanine



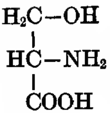
Valine



Leucine

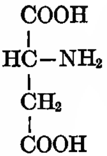


Isoleucine



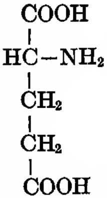
$$\begin{array}{c} H_2C-OH \\ | \\ HC-NH_2 \\ | \\ COOH \end{array}$$

Serine



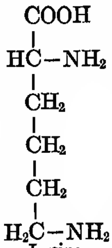
$$\begin{array}{c} COOH \\ | \\ HC-NH_2 \\ | \\ CH_2 \\ | \\ COOH \end{array}$$

Aspartic acid



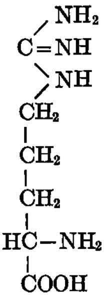
$$\begin{array}{c} COOH \\ | \\ HC-NH_2 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ COOH \end{array}$$

Glutamic acid



$$\begin{array}{c} COOH \\ | \\ HC-NH_2 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ H_2C-NH_2 \end{array}$$

Lysine

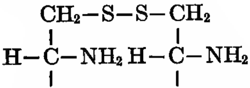


Arginine

Diamino-trihydroxy-dodecylic acid*

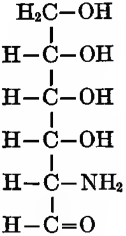
* Constitution not yet determined.

Some of the following compounds contain aromatic radicles, but as we are not now concerned further with their specific properties, their introduction at this point need cause no confusion.



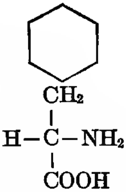
$$\begin{array}{ccc} CH_2-S-S-CH_2 & & \\ | \qquad\qquad | & & \\ H-C-NH_2\;H-C-NH_2 & & \\ | \qquad\qquad | & & \\ COOH \qquad COOH & & \end{array}$$

Cystine

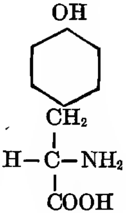


$$\begin{array}{c} H_2C-OH \\ | \\ H-C-OH \\ | \\ H-C-OH \\ | \\ H-C-OH \\ | \\ H-C-NH_2 \\ | \\ H-C{=}O \end{array}$$

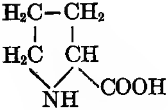
Glucosamine



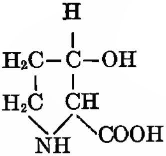
Phenylalanine



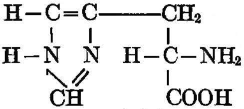
Tyrosine



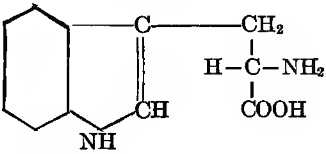
Proline



Hydroxy-proline



Histidine



Tryptophane

A question which naturally suggests itself at this point is how the amino-acids are linked together in the protein molecule. Thanks to the recent synthetic studies of Emil Fischer and his students it is now possible to answer this question with considerable certainty.

It seems evident that the linking is of the type familiar in the acid amides. In these substances it will be recalled that the hydroxyl of the carboxyl group is replaced by a simple or substituted amino-group. Now since amino-acids contain both carboxyl and amino-groups, it ought to be possible to link several molecules together in an analogous manner. Several ways have been discovered for doing this experimentally, and one of the more simple ones will be stated here as an illustration. If chloroacetyl chloride is treated with glycine the following reaction takes place:

$$\begin{aligned} &\mathrm{Cl \cdot CH_2 \cdot COCl + H_2N \cdot CH_2 \cdot COOH} \\ &\qquad = \mathrm{HCl + Cl \cdot CH_2 \cdot CO \cdot NH \cdot CH_2 \cdot COOH.} \end{aligned}$$

When the chlorine in the product has been replaced by an amino-group, the resulting compound

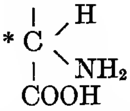
$$\mathrm{H_2N \cdot CH_2 \cdot CO \cdot NH \cdot CH_2 \cdot COOH}$$

is a glycine

$$\mathrm{H_2N \cdot CH_2 \cdot COOH}$$

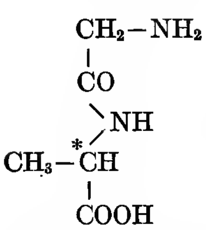
in which one hydrogen of the amino-group has been substituted by a second glycine radicle. In consequence, the compound is named glycyl-glycine. The complex substances thus formed need not necessarily consist of a single amino-acid as in the case just cited. On the contrary, products containing quite a large number and variety of components have been synthesized. The system of nomenclature applied to such products and the number of isomers possible can best be made clear by a few illustrations.

The next higher homologue of glycine, aminopropionic acid, is commonly called alanine:

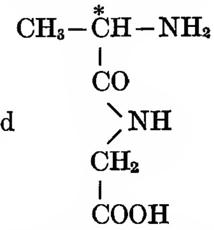


$$\begin{array}{c} \mathrm{CH_3} \\ | \\ {}^{*}\mathrm{C}\!\begin{array}{l} \diagup \mathrm{H} \\ \diagdown \mathrm{NH_2} \end{array} \\ | \\ \mathrm{COOH} \end{array}$$

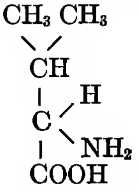
It is obvious that this substance can be combined with glycine in such ways as to form two different products:



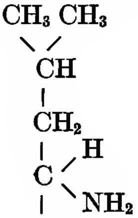
and



These are called respectively glycyl-alanine and alanyl-glycine. It must further be borne in mind that alanine contains an asymmetric carbon atom (indicated in the formula by an asterisk). It follows from this that each of the two above formulæ must represent two optically active forms which are to be distinguished in the first case as glycyl-*d*-alanine and glycyl-*l*-alanine, and in the second as *d*-alanyl-glycine and *l*-alanyl-glycine. As a further example, a more complicated case may be cited. Aminoisovalerianic acid is known as valine and aminoisocaproic acid as leucine:

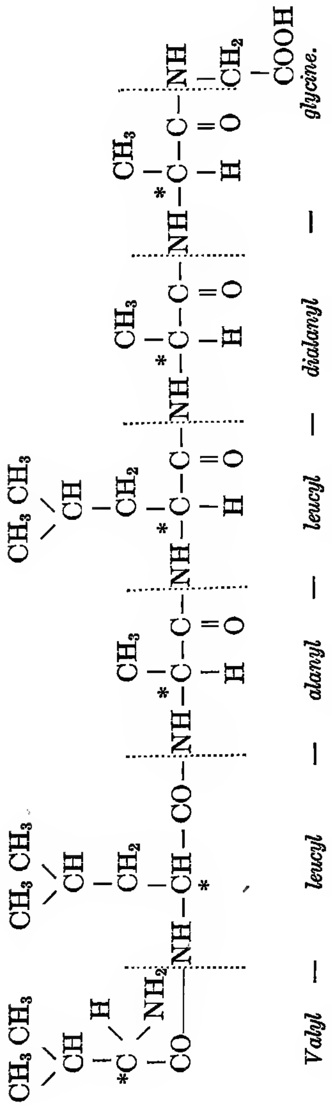


Valine



Leucine

Now let it be supposed that several molecules of the four amino-acids just mentioned are combined into a complex having the formula indicated on the following page. In this formula the asterisks indicate the asymmetric carbon atoms, and the dotted lines mark off the portions of the compound originally belonging to each amino-acid. The name of this compound would be *valyl-leucyl-alanyl-leucyl-dialanyl-glycine.* The number of possible isomers which


Valyl
leucyl
alanyl
leucyl
dialanyl
glycine.

might exist when we consider all the asymmetric carbon atoms as well as all the possible permutations in the order of the different amino-acids might be an attractive problem if the exact numerical result had any real interest for us. As it is, the question is raised only to arrest the attention and convince the student that the number is extremely large. Another important fact concerning the complex substances of this type is that they all, when treated with energetic hydrolytic agents, are split again into the same amino-acids from which they were originally built up. In the case of the compound cited, molecules of water would be added in such a way as to cause splitting at the points indicated in the formula by the dotted lines, and the products in this case would be two molecules of leucine, one of valine, one of glycine, and three of alanine. This particular compound is imaginary, but the formation of such structures should not be considered as at all beyond the limitations of practical synthesis. Indeed Emil Fischer, the pioneer in this field, has already been able to build up compounds of this type which on hydrolysis yielded no less than eighteen molecules of amino-acids. He calls all such complexes polypeptides.

The value of all this synthetic work may be seen from the fact that when proteins are subjected to especially cautious hydrolysis by the means of ferments, it has been found possible to isolate from the reaction mixture certain products which are *identical* with synthetic polypeptides. Conversely, it has been found in the synthesis of the latter compounds that as the molecular weight and complexity increased, the physical and chemical properties observed became more and more like those of the natural peptones. This not only serves to show the appropriateness of the name 'polypeptides,' but it furnishes substantial evidence that the proteins themselves are essentially polypeptides of great complexity and high molecular weight.

Until a natural protein has been synthesized, such evidence still falls short of absolute proof, but it is obvious that it must be some time before such a synthesis can be effected. The great practical difficulties which lie in the way will be partially realized from a study of the number of possible isomers suggested by the formula of the imaginary (yet in comparison with the natural proteins extremely simple) polypeptide shown on page 205. For the present, the general chemical character of the proteins may be regarded as qualitatively well established.

Proteins of Industrial Importance.

The chief use of the natural proteins is for food, and the chemical questions involved will receive some attention in the next chapter. The textile industries also deal with large quantities of wool and silk but the processes employed hardly involve any chemical changes in the protein molecule.

Casein has recently become an article of commerce, and has found use in a variety of ways; as a sizing for paper, as a constituent of adhesives and cements, as a waterproofing material, in substitutes for celluloid, etc. The source of casein is milk. It may be precipitated from this solution by the addition of a little dilute acid. Precipitation may also be brought about by the ferment of the rennet; thus, as its name indicates, casein is the chief constituent of cheese. It may be purified by re-solution in dilute alkalies and precipitation with acid. Thus prepared, casein is a white amorphous powder which on hydrolysis yields about 10% each of leucine and glutamic acid, with smaller quantities of the other amino-acids.

Other industries which deserve mention here are those which produce leather and glue. Animal hides (from which hair and other adhering material has been removed) consist essentially of a protein called collagen. This substance if boiled with water absorbs the solvent and goes over into soluble gelatin. It is this reaction which is made use of in the manufacture of glue from hides and similar materials.

For the manufacture of leather the cleaned hides are treated with some substance which renders them insoluble in water and more or less impervious to it. There are several distinct methods of tanning, but only two representative ones need be mentioned here. In the older process the hides are soaked for long periods in so-called tanning extracts. These are obtained from a variety of vegetable sources, mostly the bark and leaves of plants. Oak, hemlock, sumac and mimosa barks, nutgalls and catechu are representative materials but there are many others. The active principles of practically all these mixtures are compounds of complex structure which, on hydrolysis, usually yield sugars and hydroxy-acids of the aromatic series. Their chemistry will again receive attention when substances of the latter class are taken up.

A more recent innovation in the industry is the process of 'chrome tanning.' In this operation the hides are soaked in a chromate solution until they have been thoroughly impregnated. They are then treated with reducing agents which serve to precipitate the chromium as hydroxide. This method of tanning is more rapid than the old and yields a leather which is exceptionally impervious to water.

Just what happens when a hide is tanned is still by no means clear. Whether the tanning material forms a compound with the hide, or whether it is 'adsorbed' or held in solid solution, or, finally, whether mechanical influences come chiefly into play are questions which are as yet by no means decided. The relationship is analogous to that between dye and fiber, and presents similar difficulties of interpretation. The tanning operation, however, now offers to the trained specialist many attractive problems in Physics, Chemistry and Bacteriology.

CHAPTER XII.

ORGANIC CHEMISTRY OF CERTAIN VITAL PROCESSES.

It has already been shown that organic compounds need not owe either their formation or preservation to any mysterious forces connected with the living cell, but that their syntheses and reactions depend upon the play of the same physical and chemical influences which are active in the inorganic field. This should not blind us, however, to something else which is equally true. Though it has proved possible, for example, by all the resources of a well-equipped laboratory, to prepare a small amount of grape-sugar from the elements by the action of numerous reagents and much complicated apparatus, nevertheless this achievement has done surprisingly little toward revealing the method by which nature accomplishes similar results. Having no material to work with except water, the gases of the atmosphere, and dilute salt solutions obtained from the moist soil, the plant is able at ordinary temperatures to produce, often in surprisingly large quantities, such complicated substances as cane-sugar, starch, cellulose, chlorophyll, and the vegetable alkaloids, — substances which still stand beyond the reach of laboratory synthesis. How these results are attained is still practically unknown, although it has been possible to get glimpses of the mechanism of certain processes here and there. The importance of making an attempt to get an answer to such questions lies in the fact that life itself, at least upon the vegetative and mechanical sides, is essentially a chemical process. The digestion of the food, the contraction of the muscles, even the action of the brain cells, are all doubtless accompanied by chemical changes, and depend for the energy required in their execution upon chemical reactions. As these reactions take place largely between organic substances, the problems involved have a proper and natural interest for organic chemists, although hitherto the latter have largely contented themselves with studying the products in the laboratory, instead of attempting to discover what goes on within the organism. The latter subject has developed into a special branch of the science called Physiological Chemistry. It is the aim of this department of science to trace the transformations undergone by the chemical elements from the time when they are first assimilated into a living organism until they are again eliminated from it. This involves as an ultimate goal the discovery of all the changes which go on in every kind of living cell, the character of the products, and the ways in which the activity of the cell is affected by all the chemical influences which can be brought to bear upon it. It is needless to say that only the first steps have been taken toward carrying out so ambitious a program. Much interesting work has, however, been done, and many important generalizations are under discussion. Nevertheless the inherent difficulties of animal experimentation are so great, and the whole subject really so new, that there still exists wide divergence of opinion among the experts even concerning fundamentals. This state of things makes it clear enough why no very full presentation of the subject can be attempted here. What is included will only be a few points having mainly to do with nutrition. These are discussed partly on account of their general interest, and partly to direct the attention of the student of Biology to the numerous and increasing points of contact between that science and Organic Chemistry. It will be necessary to abandon any attempt at a critical presentation of the material, and to content ourselves with simple and perhaps seemingly dogmatic statements of what the author understands to represent the concensus of expert opinion at the present time.

With the exception of certain parasitic and so-called carnivorous species, plants depend entirely upon inorganic material for their nourishment. They absorb carbon dioxide from the air, and dilute salt solutions through their roots from the soil. Perhaps the most important constituents of this solution are the nitrates and nitrites, from which the plant must get practically its whole supply of nitrogen. A few other inorganic salts in small quantities seem to be necessary to the life of the plant. Phosphates, potassium and calcium salts should be mentioned as perhaps the most important of these. The organic compounds which the plant builds up fall, for the most part, into three classes: the carbohydrates (sugars, starch, and cellulose); the fats, (materials like cotton oil, palm oil, linseed oil, and the like); and certain protein materials, found mostly in nuts and seeds. It will be understood that the plant also produces many substances belonging to other classes, such as the acids in fruits, the terpenes in coniferous trees, and the alkaloids in various poisonous plants. The three classes first mentioned are, however, entitled to be considered as most important, partly because their production is most general, and partly because they serve the animal organism as foods.

The synthesis of these organic compounds from carbon dioxide is a reduction process. When organic material, wood (cellulose) for example, is burned, heat is evolved. This means that if cellulose is, in its turn, to be prepared from carbon dioxide, energy must be furnished. This energy comes from the sun. Plants, as a rule, flourish only when they receive a certain amount of sunlight, and under these conditions they absorb carbon dioxide through the leaves and give off oxygen. For the animal, on the other hand, carbohydrates, fats, and proteins constitute the nourishment, and these are oxidized by the organism, forming, in the case of mammals, carbon dioxide, water, and urea. The solar energy which the plant had stored up is now set at liberty, partly as animal heat, and partly in the form of mechanical work, using this term to include not only the muscular activity and locomotion of the animal, but also the work done in carrying out the vital functions within the organism. This brings out the curious unconscious partnership existing between plant and animal life taken as a whole, — the animal absorbing oxygen and evolving carbon dioxide, while the plant exercises the reciprocal functions. A similar mutual relationship exists in what is often spoken of as the 'nitrogen cycle.'

Neither plant nor animal can, as a general rule, make direct use of the nitrogen of the atmosphere. Plants derive practically all their supply from the nitrites and nitrates in the soil. Herbivorous animals get theirs from the proteins of the plant; carnivora from the herbivora which they devour. The nitrogenous excreta of animals, after leaving the body, usually go over rapidly into ammonia, and, in this form, the nitrogen is not available for the plant. By the aid of certain bacteria, however, oxidation to nitrite or nitrate can be brought about and the nitrogen becomes available. In the course of this oxidation a good deal of the valuable material is lost as gaseous nitrogen. In compensation, there exist, among other agencies, upon leguminous plants, certain symbiotic organisms which are able to so utilize the nitrogen of the air that a soil which has been planted with this kind of vegetation becomes richer in nitrogen.

When we come to trace the organic side of vegetable processes in a little more detail, we encounter at the outset the difficulty that the metabolism (internal chemical change) of the plant is even less clearly understood than that of the animal, and the very first step made by the plant in building up its carbon compounds is perhaps the darkest chapter in the whole series. The absorption of carbon dioxide in the leaves is carried on through the agency of chlorophyll, an exceedingly complicated substance to which the leaf also owes its green color. The mechanism of the action of chlorophyll is not understood, nor is there any certainty as to what the first product formed by the reduction of the carbon dioxide may be. It is, however, generally agreed that carbohydrates are formed at an early stage. In fact, the carbohydrates seem to play the most important rôle in the plant's economy: cellulose is the chief constituent of its tissues, sugars circulate in its sap and are found in its fruits, while its reserve supplies are mostly stored up in the form of starch.

A number of years ago, Baeyer proposed a theory which is very attractive chemically, but which, in spite of the long time which it has been under discussion, can by no means lay claim to being proved. This theory assumes that, under the catalytic influence of chlorophyll, the first reaction to take place produces formaldehyde:

$$CO_2 + H_2O = HCHO + O_2.$$

As was stated when the properties of this substance were discussed, only slight traces of formaldehyde have ever been found in plants, — in fact this substance acts as a vigorous poison upon vegetable organisms. It is therefore necessary to make the further assumption that the formaldehyde first produced is immediately utilized in the synthesis of more complex products. Certainly carbohydrates are soon formed, and it is known from laboratory investigations that sugars can be prepared by the polymerization of formaldehyde. Once the monosaccharides have been reached, the problem begins to look a little simpler. It is easily credible that these should further condense and polymerize to form such compounds as cane sugar, starch, and cellulose. It is true that hardly a beginning has been made toward carrying out such syntheses in the laboratory, but that the organism does synthesize the higher carbohydrates from the lower admits of no doubt. It is entirely safe to conclude that the starch and cellulose of the plant are formed from the monosaccharides. Concerning the formation of the vegetable fats and proteins little is known. Whether these are to be considered as built up directly from formaldehyde, — admitting this to be the primary organic substance produced by the plant, — or whether they owe their formation to secondary reactions of the carbohydrates, is a question to which at present no definite answer can be given. It may be noted that stearic and oleic acids each contain eighteen atoms of carbon, whereas glycerol contains three, and some of the more important and common amino-acids which go to make up the proteins contain three or six carbon atoms. This might suggest that such components of the fats and proteins were formed by the combining and splitting of the common hexoses. This is, however, little better than idle speculation. Well-established intermediate steps are wanting.

At this point the student may well ask how it is that it is ever possible to affirm that the cell performs this or that chemical reaction, for which on the basis of ordinary laboratory experience the necessary conditions seem to be wanting, or where the reaction (as for example the synthesis of cellulose) cannot be carried out in the laboratory at all. The answer is that in some cases the question can be approached by direct experiment. Thus, if blood containing both benzoic acid and glycine is circulated through the kidneys of a freshly killed animal, hippuric acid is formed. This is very satisfactory evidence that the synthetic reaction,

$$C_6H_5COOH + H_2NCH_2COOH = H_2O + C_6H_5CONHCH_2COOH,$$

which cannot be carried out in the laboratory at ordinary temperature, is effected in some way by the cells of the kidney. Perhaps more frequently the evidence is not as good as this. The well-known fact, however, that many reactions take place in the laboratory when the assistance of certain enzymes is available, which would not go on outside the organism without such assistance, leads us to believe that the cell produces one compound from another if certain conditions are fulfilled. Thus the presence of both in the organism should be assured, the constitutions of the two should stand in such relation that the reaction itself looks reasonable, and, in general, it should be shown that the quantity of one substance grows as the other decreases. Of course it must be admitted at the outset that evidence of this kind only leads to more or less temporary conclusions, and that the physiological chemist is under obligation not to be content with this, but to verify it by experiments bringing to light the greatest possible number of intermediate steps, either in the laboratory or in the organism.

When we turn to the subject of animal nutrition, the relations are somewhat better studied and therefore a little more clearly traced. Of the three classes of foods utilized by the animal, the carbohydrates are perhaps the best to begin with. Most carbohydrate nourishment is taken in the form of starch. Following starch, then, in its course through the digestive tract, we find that in the mouth it first becomes mixed with the saliva. This secretion contains a ferment called *ptyalin*, which has the power of beginning a hydrolytic action resulting in the formation of dextrins and a little maltose. These, together with the unhydrolyzed portions of the starch, pass, mixed with the saliva, into the stomach. Whatever hydrolysis takes place here is due to the continued action of the saliva, for the secretions of the walls of the stomach do not act upon starch. In the duodenum, however, the dextrins are acted upon by diastatic ferments secreted by the pancreas. These further hydrolyze them into the component monosaccharides. These, absorbed by the intestinal wall, pass by the way of the portal vein and the liver into the blood. Now the liver, in addition to several other important functions, acts as a regulator for the carbohydrate nourishment of the body. The way in which it does this has been an object of much study and is extremely interesting. It is well known that the livers of those animals used as food have a sweet taste. This is due to the presence of *d*-glucose. Nevertheless if the animal is killed, and the liver at once removed and examined, it will be found to contain no glucose, but a substance resembling starch. This is *glycogen*, sometimes called 'animal starch.' It gives a brownish red instead of a blue color with iodine, but upon hydrolysis, like the vegetable product, it yields *d*-glucose. The fact that this hydrolysis takes place spontaneously soon after the death of the animal shows that a suitable hydrolytic ferment must be present in the liver cells themselves. Many experiments have conclusively shown that the organism depends normally in large measure upon its carbohydrate nourishment for the performance of muscular work. Further it is known that the muscles contain some glycogen as well as the liver, and that the sugar content of the blood is small but extremely constant even under wide variations of diet and exercise. These facts taken together furnish data for a consistent theory of carbohydrate metabolism. This may be outlined in general terms as follows: *d*-Glucose is the form in which carbohydrate nourishment is transported and glycogen the form in which it is stored. The liver takes up monosaccharides produced by the digestion of starch and other carbohydrates, and from them forms glycogen, except for a certain minimum of *d*-glucose which circulates in the blood. When a muscle contracts, the nerve stimulus doubtless releases at the same time a ferment which hydrolyzes some of that muscle's glycogen, the *d*-glucose formed being oxidized to furnish the energy required for the contraction. The muscle then recoups itself by taking up glucose from the blood, and the sugar concentration of the latter is in turn kept constant by the action of the liver, which hydrolyzes enough of its own store of glycogen to replace the deficit. An interesting confirmation of these views is found in the fact that the livers of animals which have been kept a long time without food contain no glycogen.

If the organism receives a larger quantity of carbohydrate than it requires, it seems to have the power of transforming this into fat, but the chemical stages by which this is accomplished can, for the present, only be guessed at.

The fats represent that portion of the nutriment which is most valuable for the maintenance of the temperature of the body, since the combustion of fat furnishes, per unit of weight, more heat than the oxidation of either carbohydrate or protein. The fats are not appreciably acted upon by the saliva or by the gastric juices. In the duodenum, however, they come under the influence of a ferment called lipase. Here the fat becomes very finely divided and a part of it at least is hydrolyzed into fatty acids and glycerol. The fact that during the digestion of fat the chyle becomes milky with fat globules has led to some controversy as to whether the larger part of the fat is saponified by the process of digestion, then absorbed, and finally recombined, or whether in a fine emulsion it passes without hydrolysis through the intestinal wall. This controversy need concern us little here since it is well known that some hydrolysis does take place, and also that the organism does have the power of synthesizing fat. Experimental evidence on this point is to be found in the fact that animals deficient in fat increase their supply when they are fed upon fatty acids. In this case the organism must itself furnish the necessary glycerol, but from what source this is derived is not known.

An interesting side-light is thrown on the assimilation of the fats by the experiment described below. It is a familiar fact that the fat deposits of the various animals consist of varying, but for a given species characteristic, proportions of the oleate, palmitate, and stearate of glycerol. Olein being liquid at ordinary temperatures, while stearin and palmitin are solids, the melting point of a given fat becomes a characteristic constant for the animal species from which it is derived. Now a dog (whose fat melts at about 20°) was starved until his fat deposits were nearly exhausted, and then fed freely with fatty acids formed by saponifying mutton fat. This melts at about 40°. It was found by post-mortem examination that the animal experimented upon had acquired fat melting at 40°. This seems to indicate that the organism was in such extreme need of fat that it used the acids provided without chemical transformation.

Such an experiment shows what the organism is capable of doing under certain, for the animal involved, desperate conditions. It is always doubtful how much light such experiments throw upon what the organism normally does under healthy conditions. For this reason, conclusions drawn from experiments upon living animals should always be received with caution, especially where the animal experimented upon is subjected to operations involving great nervous shock or extensive derangement of its vital processes.

We now come to the consideration of the proteins contained in our food. It has already been pointed out that these probably represent long chains of amino-acids condensed somewhat in the manner suggested upon page 205. In the acid digestion of the stomach, the proteins are broken down into albumoses and peptones. These we are again to consider as polypeptides of uncertain but, for the most part, high molecular weight. In the small intestine the food is subjected to the action of alkaline ferments. Predominant among these is *trypsin,* contained in the secretion of the pancreas. Here the hydrolysis is completed and the products absorbed. Amino-acids are certainly formed. Whether other partially hydrolyzed fragments like the polypeptides are absorbed without complete hydrolysis has not been settled with certainty. The evidence seems to indicate that the organism can at least make use of certain larger fragments.

The organism transforms so rapidly the proteins which it absorbs, that it has hitherto been found impossible to trace any steps in the process. Upon the other side of the intestinal tract there can be found neither albumoses, peptones, nor amino-acids. Instead, the intestinal wall has already synthesized the material which it has absorbed into proteins characteristic of the organism itself and not of the foods. The blood thus comes to contain its own proteins, which are characteristic of the animal species and do not depend qualitatively upon those administered in the food. This gives to the tissues an essentially constant and uniform source of nutrition. From the blood-stream the cells apparently take up such proteins as they require, split them under the action of specific ferments to a certain extent, and build them up again into that form of protein required by the particular cell. These processes must be very complex, and their mechanism is little understood. How far-reaching the changes must be is suggested, for example, by contrasting the physical properties of the hair and nails with the globulin of the blood.

In comparing the three chief classes of organic foods, it should be pointed out that it is possible to sustain life solely upon protein material. Further, it is impossible to maintain life without a certain minimum of this class of nourishment. One reason of this appears when it is considered that the organs are chiefly made up of proteins, and the wear and tear upon them can be made good in no other way. A certain amount of protein can, however, be profitably substituted by fats and carbohydrates, and it is for the advantage of the organism to employ a mixed diet where this is practicable. It is an interesting fact that while, if the diet contains an excess of fat, this is stored up, and the same holds true to a limited extent of carbohydrates, this is not the case with protein. Here the rule is that in a healthy individual, the nitrogen excreted in a given time is equal to the amount present in the nourishment. When this is true, the animal is said to be 'in nitrogen equilibrium.' In mammals almost all of the nitrogen is excreted in the form of urea. This accounts, of course, for but one carbon atom in the molecule of each amino-acid. What becomes of the rest of the chain is not known. It may be oxidized directly, or it may be used for the synthesis of fats and carbohydrates. When an animal is existing upon an exclusively protein diet, the latter would seem more probable. Perhaps the material is available in a variety of ways, according to the temporary needs of the organism.

In addition to the foods previously considered, the organism also requires large quantities of oxygen, of water, and much smaller but essential minima of certain inorganic salts, notably sodium chloride. The functions of the salts are not perfectly understood, although it is known how important for the vital processes are certain osmotic effects in the walls of various organs. The rôle which salt solutions play in stimulating and maintaining the pulsations of the heart, as well as in certain cases of parthenogenesis would be fascinating topics, but these are contributions made to Physiological by Physical rather than by Organic Chemistry.

The Blood.

It is by means of the blood that almost all transportation of material takes place between the various organs. It brings to the cells the carbohydrates, proteins, and fats in such form that they can be appropriated by the cells as needed. By means of its corpuscles, it brings oxygen from the lungs to the cells, where it may be employed for the oxidation of the food material or the tissues themselves; and it receives from the cells the products of oxidation, taking carbon dioxide back to the lungs whence it is expelled in the breath, and the urea to the kidneys whence it is discharged in the urine. The various kinds of material circulating in the blood, and the functions of each, furnish an attractive study, but must for the most part be passed over here. A word should perhaps be said concerning the important but doubtless familiar subject of oxygen transportation. It has already been pointed out (page 200) that the blood contains a material called *hæmoglobin* which is an extremely complicated substance and contains a small but essential quantity of iron. Within the lungs, this substance has the power of adding directly a certain quantity of oxygen, forming oxyhæmoglobin. This in its turn gives up its oxygen to the tissues as it is needed for oxidation, returning again to the lungs for a renewed supply, Hæmoglobin is of a dark purplish color, while oxyhæmoglobin is a brilliant red, and this accounts for the well-known difference in color between venous and arterial blood. Recent investigations go to show that there is a certain analogy in constitution between hæmoglobin on the one side, and chlorophyll on the other. This is extremely interesting, since the two substances perform functions which are in one sense analogous and in another sense reciprocal. In connection with the iron content of hæmoglobin may also be mentioned the interesting fact that in the blood of certain mollusks and crustacea, the substance which performs the functions of an oxygen carrier contains copper, and the arterial blood of such animals is normally blue while the venous is colorless.

It would be interesting to continue these discussions to include the functions of each organ and every secretion, but for such topics the student must be referred to special treatises upon Physiological Chemistry.

CHAPTER XIII.

BENZENE AND ITS HOMOLOGUES.

The Aromatic Compounds.

THE original meanings of the terms aliphatic and aromatic have already been discussed. As now used, the latter adjective suggests only certain chemical characteristics. Probably the most important of these is the presence in the compounds of this group of an especially stable nucleus. In the case of the most important group of aromatic compounds, the benzene derivatives, this nucleus consists of six carbon atoms, and the general rule holds that to whatever chemical treatment these substances are subjected — short of complete disintegration or combustion — a compound containing at least six carbon atoms is one of the products.

In addition to this peculiarity, aromatic substances almost always contain several hydrogen atoms which show a capacity for substitution different from that exhibited by hydrogens of the aliphatic compounds. This will be illustrated more fully in the description of benzene itself. Finally it holds true in a general way that the various classes of aromatic compounds — the halides, the acids, the aldehydes, the amines, etc. — show in their chemical character and behavior certain well-marked points of difference from the corresponding compounds of the fatty series. It would, of course, be premature to attempt to point out these differences until the separate classes are taken up individually.

Benzene.

The simplest and most thoroughly studied of the aromatic compounds is the hydrocarbon benzene. This is a colorless liquid of a characteristic aromatic odor which freezes at 6° and boils at 80°. Analysis and molecular weight determinations lead to the empirical formula C_6H_6. The commercial source of benzene is the lower boiling portion of the coal-tar distillate. A method of preparation which is very interesting scientifically consists in the polymerization of acetylene. When that gas is passed through red-hot tubes, some benzene is formed:

$$3\ C_2H_2 = C_6H_6.$$

Transitions of this kind between the aliphatic and aromatic series are the reverse of common, and this is one of the most important. Further, since acetylene itself can be prepared without difficulty from the elements (page 132), this reaction completes the synthesis of benzene, and, in consequence, that of all the extremely numerous aromatic compounds which can be prepared from it.

When benzene is treated with chlorine or bromine in the presence of certain catalytic agents, all the hydrogen atoms may be successively substituted by the halogen:

$$\begin{gathered} C_6H_6 + Cl_2 = HCl + C_6H_5Cl, \\ C_6H_5Cl + Cl_2 = HCl + C_6H_4Cl_2, \qquad \text{etc.} \end{gathered}$$

This is something like an analogous property of methane and its homologues. Here, however, the reaction is much more easy to control, so that it is not difficult to isolate the several products.

When benzene is treated with fuming sulphuric acid, the following reaction takes place:

$$C_6H_6 + H_2SO_4 = H_2O + C_6H_5 \cdot SO_3H.$$

The hydrogen of benzene is replaced by the group SO_3H. This is called the sulpho-group, and the substances produced are known as sulphonic acids. Their properties will be dealt with later. By the continued action of highly concentrated acid more than one hydrogen may be replaced in a similar way.

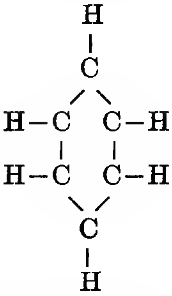
If benzene is treated with fuming nitric acid, or with a mixture of nitric and sulphuric acids, one or more hydrogens are substituted by the nitro-group:

$$C_6H_6 + HNO_3 = H_2O + C_6H_5 \cdot NO_2.$$

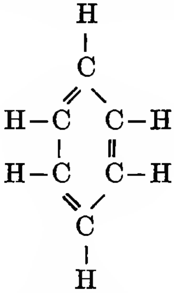
The product of this reaction is called nitrobenzene. Its properties are typical of a large and important class of compounds.

Of these four reactions, chlorination, bromination, nitration, and sulphonation, the last two are especially characteristic of the aromatic compounds in general. While it is true that these reactions may, by special modifications, be applied with analogous results to some aliphatic compounds, the ease and smoothness with which the reactions take place in the aromatic series is so striking in comparison, that it furnishes a well-marked and useful line of distinction.

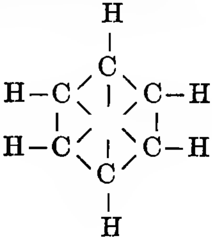
In attempting to fix a suitable graphic formula for benzene, perhaps the most decisive single fact is that but one mono-substitution product is ever obtained by any of the above reactions. There exists but one monochloro-, monobromo-, or mononitrobenzene. This indicates that all the hydrogens in benzene are chemically equivalent, and this conclusion has been confirmed by many elaborate investigations, the details of which cannot be given here. This equivalence finds expression in the formula,



which represents the six carbon atoms connected in a ring, and one hydrogen attached to each. It will be noted that this formula makes use of but three of the valencies of carbon, and many suggestions have been made which attempt to fix the position of the additional bond. The original theory of Kekulé (to whom we are indebted for the ring formula) represents the carbon atoms connected by alternate single and double bonds:

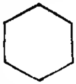


A theory supported by Baeyer represents the additional bonds as all tending toward the center of the ring:

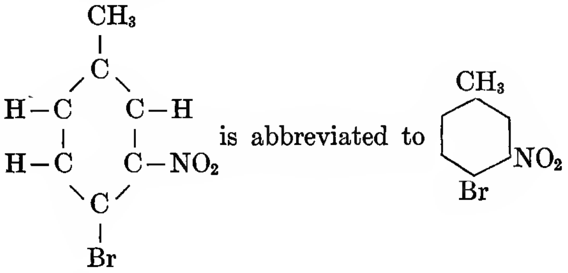


Various other formulæ have been suggested, but none have found so general acceptance as these two, the relative merits of which will be discussed very briefly later.

Far more important than the disposition of the fourth valency is the confirmation of the propriety of using a ring formula for benzene, and to this point our attention must next be turned. Before beginning the discussion, however, a word should be said concerning a system of abbreviation universally employed in practice for the formulation of benzene derivatives. This consists in representing benzene itself by a simple hexagon, concerning which it is conventionally understood that each corner represents one carbon atom *and the hydrogen attached.*

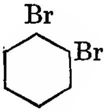


In reading the formula of a substitution product, it is to be understood that when a substituting group is attached to any corner of the hexagon, that hydrogen has been replaced. On the other hand, those corners where no substituting groups appear continue to stand for carbon atoms *with* their accompanying hydrogen. This will be made entirely clear by a single example:

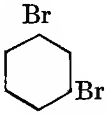


The testing of the ring formula for benzene has been the subject of countless investigations, and a whole literature has grown up upon the subject. The one argument which will be presented here is perhaps the simplest and is sufficiently convincing. It is also the easiest to retain, because the essentials of it can always be derived at will from the geometrical properties of the hexagon. The argument consists first in enumerating the number of compounds which can be formed when one element (bromine for example) successively substitutes the various hydrogens in a compound of the formula given; second, in tracing the necessary genetic relations between such isomers; and finally in comparing the results thus obtained with the observed facts.

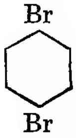
Since the formula represents all the hydrogen atoms as equivalent, it can make no difference in the character of the product which of them is substituted by a single atom of bromine. In other words, but one mono-substitution product should be possible, and it has already been stated that this is the fact. Turning now to the di-substitution products, a brief inspection shows that three dibromobenzenes should exist as represented by the following formulæ:



ortho



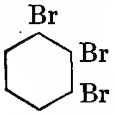
meta

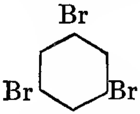


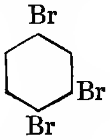
para

The relative positions occupied by the two bromine atoms in the above formulæ are known respectively as the *ortho*, the *meta*, and the *para* positions. The student should fix these terms and their significance very carefully in mind, as the words are of constant use in all discussions concerning benzene derivatives. When an individual compound is referred to, it is customary to abbreviate the words to their initial letters and prefix these to the name of the compound. For example, the name of the substance corresponding to the first of the above formulæ is written *o*-dibromobenzene, etc.

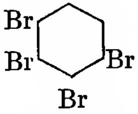
Of the tribromobenzenes, there should be three:

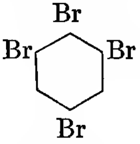

vicinal

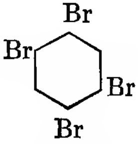

symmetrical


asymmetric

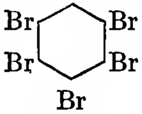
These are called the vicinal, the symmetrical, and the asymmetric. There should also be three tetrabromobenzenes, and it will be seen at once that the only three possible are those which have the unsubstituted hydrogens in the ortho, meta, and para positions respectively:

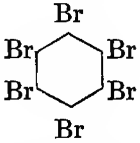

in ortho


in meta


in para

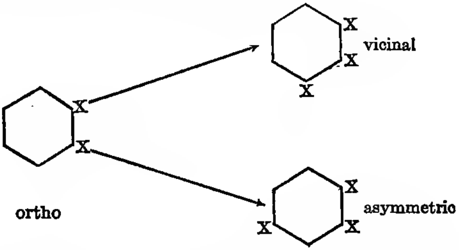
Finally it is clear that only one pentabromo- and one hexabromobenzene should be possible:



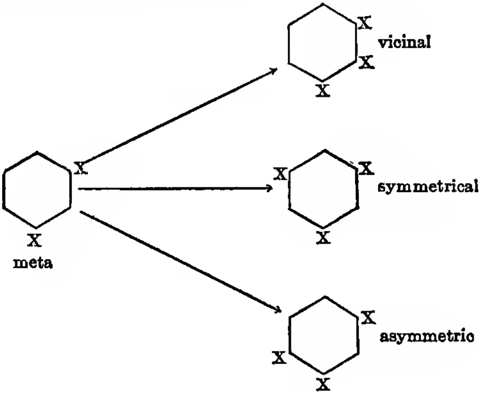


Now all the above bromobenzenes are known, and it has not proved possible to find others, despite the important bearing which such a discovery would have upon our theoretical views. We can go much farther. The same rule holds not only for the bromine derivatives but for every case where the hydrogens of benzene are substituted by a single element or group, so far as the various products involved are known. It is not surprising that it should not thus far have proved possible to prepare every compound whose formula is suggested by the theory. Gaps, however, do nothing to vitiate the hypothesis, which only claims to state the maximum number of compounds possible. The theory gives us further information besides that which has been already derived from it. By its aid it is possible not only to predict the number of products, but also such genetic relations between them as fix with certainty the graphic formula belonging to each compound.

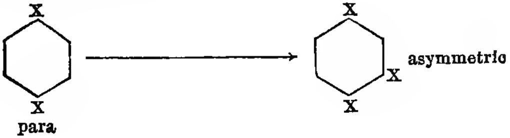
Let us consider, in the first place, the three di-substitution products. A study of the formula will convince the student that from the ortho compound it should be possible, by further substitution, to prepare two tri-substitution products, the vicinal and the asymmetric:



From the meta compound it should be possible to prepare all three tri-substitution products:

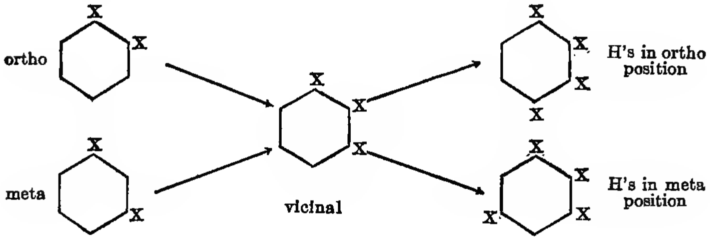


From the para only one tri-substitution product, the asymmetric can be obtained:

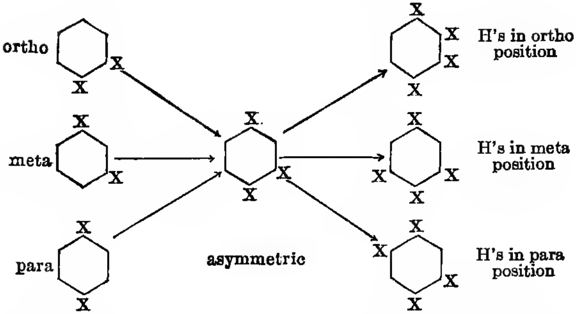


The above discussion gives the necessary data for fixing the identity of the three di-substitution products. That from which two tri-substitution products can be obtained is the ortho compound, that which yields three is the meta, that which gives but one, the para.

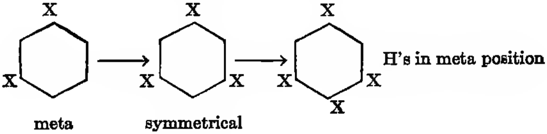
Similar reasoning fixes the identity of the tri-substitution products, and here additional evidence is furnished by the number of tetra-substitution products formed from each. Thus the vicinal compound, which is obtained from both ortho and meta di-substitution products, may yield in its turn two tetra-substitution products which have their unsubstituted hydrogens in the ortho and meta positions respectively:



The asymmetric, which can be obtained from all three di-substitution products, can yield, in its turn, all three tetra-compounds:



Finally the symmetrical compound can be obtained only from the meta, and it can yield only that tetra-substitution product whose hydrogens are in the meta position:



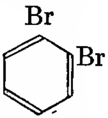
It will be noted that in the foregoing discussion only those compounds have received consideration which are produced by substituting the hydrogens of benzene by *one* other element. When the number of elements exceeds one, the number of possible isomers in the higher series is so much more complicated that we should not be repaid in following out all possibilities. Suffice it to say that here, also, facts contradicting the theory have not been established.

When it is realized that the ring formula for benzene was suggested more than forty years ago, and that since that time the benzene derivatives have increased until they number tens of thousands, it must be admitted that there are few scientific hypotheses which are supported by such a multitude of facts.

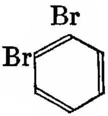
In practice the determination of the position occupied by a substituting group in a benzene ring consists in tracing out the genetic relations which connect that compound with certain other well-known ones, for which the positions have been fixed by exhaustive special investigations: with such, for example, as the bromine derivatives mentioned above.

At this point a brief discussion of the two methods proposed on page 226 for disposing of the additional carbon valency would not be out of place. Against the formula containing alternate single and double bonds, two experimental objections can be raised. The double bond is usually considered as a sign of unsaturation, and as a sign of weakness, especially toward oxidizing agents. Now benzene is exceptionally stable toward oxidizing agents, and it acts like a saturated compound. Although benzene derivatives can be made to add halogens, and although several other addition-reactions can be effected, these are generally accomplished with very considerable difficulty. Substitution usually takes place instead.

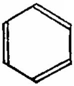
Another objection is found in the number of possible isomers. According to a strict interpretation of this formula, two ortho-substituted dibromobenzenes, for example, might be expected to exist. These would differ in the sense of the following formulæ:



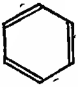
and



the bromine atoms being separated in one case by a single bond, in the other by a double one. Such isomers have not been observed with certainty. Kekulé, who originally suggested this formula, afterward modified it by the statement that it should not be regarded as representing a rigid structure, but rather the end-stages of an oscillation between the forms,



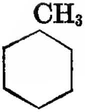
and



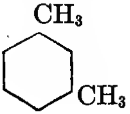
If a hypothesis of oscillation is to be accepted, most of the differences between the formula of Kekulé and that of Baeyer disappear, for one can be regarded as representing the oscillation arrested in one point and the other in another. The latter formula has the advantage that in combining all the residual affinities of carbon in the center of the ring, it gives an explanation for the extraordinary stability of that complex. On the other hand, it is true that most of the syntheses of benzene derivatives from aliphatic compounds lead naturally to the Kekulé formula. The whole question is, however, more of speculative than of practical interest, and the important reactions of the compounds involved can be satisfactorily interpreted with the aid of either formula.

The Homologues of Benzene.

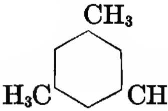
When one or more hydrogens in a benzene ring are substituted by alkyl radicles like methyl, ethyl, etc., there results a homologous series of hydrocarbons whose physical and chemical properties are analogous to those of benzene itself. Correct names for these compounds can be derived by prefixing to the word benzene the name or names of the substituting alkyl radicles. In this way such names as methylbenzene or isopropylbenzene are obtained. It so happens, however, that several of these hydrocarbons have such technical or scientific importance that they have obtained special names of their own. Below will be found a list of names and formulæ of those hydrocarbons of this series which are probably best worth keeping in mind:



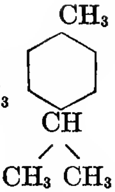
Toluene



meta-Xylene



Mesitylene

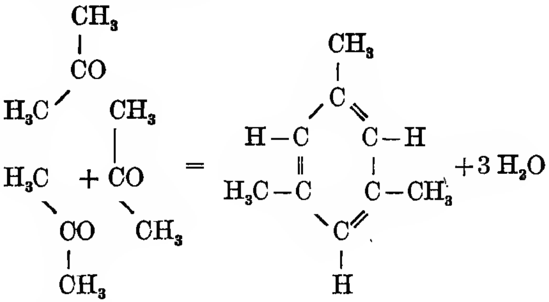


para-Cymene

Toluene like benzene is found in coal-tar and shares with benzene itself a great technical importance as the source from which many useful substances may be prepared. It is a colorless oil lighter than water. It has an odor resembling that of benzene, and boils at 110°.

m-Xylene, the most common of the xylenes, is also found in considerable quantities in coal-tar, and has properties very much like those mentioned. It boils at 139°.

Mesitylene, or symmetrical trimethylbenzene, is a liquid boiling at 164°. It is chiefly interesting because of its formation from acetone when that substance is condensed by the action of sulphuric acid:



This is one of the best-known transitions from the aliphatic to the aromatic series.

p-Cymene, or *para*-methylisopropylbenzene, is a constituent of several essential oils. It is mentioned here because it is allied in constitution with some of the natural terpenes. There will be occasion to revert to this fact when these important substances are taken up.

Many of the methods of preparation of the aromatic hydrocarbons are analogous to those employed for obtaining the hydrocarbons of the aliphatic series. If, for example, one of the aromatic acids or its calcium salt be heated with an excess of lime, carbon dioxide is removed by the latter and a hydrocarbon distills over:

$$C_6H_5COOH + CaO = CaCO_3 + C_6H_6.$$

When an aromatic halogen compound like bromobenzene is treated with an alkyl halide in the presence of sodium, sodium bromide is formed and the two organic radicles enter into combination:

$$C_6H_5Br + Na_2 + BrC_2H_5 = 2\,NaBr + C_6H_5{-}C_2H_5.$$

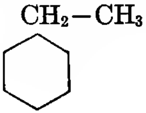
This reaction is especially important as a means of fixing the position of an alkyl group in a benzene ring. Rearrangements are seldom observed and it can generally be assumed that the alkyl group takes that place in the ring originally occupied by the halogen.

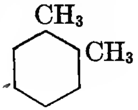
Another method for the preparation of the aromatic hydrocarbons should be mentioned which differs widely from any hitherto encountered. An alkyl chloride does not react with benzene when the two are mixed, but if a little anhydrous aluminium chloride be added, there is evolution of hydrochloric acid and a homologue of benzene is formed:

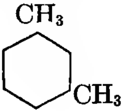
$$C_2H_5Cl + C_6H_6 = HCl + C_2H_5{-}C_6H_5.$$

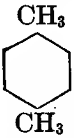
Ferric chloride and chromium chloride can sometimes be substituted for the aluminium chloride with good results. The mechanism of the reaction is not perfectly understood, although in some applications of it, well-characterized intermediate products containing aluminium have been isolated. The reaction is not always a pure catalysis, for in most cases these intermediate products do not regenerate aluminium chloride. An important condition for the success of the reaction is that the halide employed be aliphatic in character (see following section) and that the hydrogen which forms the other component of the hydrochloric acid evolved belong to a benzene ring. If these conditions are reversed, if, for example, hexane were treated with chlorobenzene, no reaction would result. The reaction is not of much use as a means of determining the constitution of the products, on account of frequent rearrangements and numerous side-reactions. It is, however, often extremely valuable for the laboratory preparation of many important compounds.

In discussing the chemical behavior of the aromatic hydrocarbons, a sharp line must be drawn between those atoms which belong to the benzene ring or nucleus, and those which form a part of the substituting alkyl groups. The latter are usually said to belong to a *side-chain*. The difference may be summed up concisely by saying that ring hydrogen is aromatic in character, while side-chain hydrogen is aliphatic. This means that those hydrogen atoms which are in the ring react readily, for example, with nitric and sulphuric acid, to form sulphonic acids and nitro-compounds (see reactions under benzene). The hydrogen of the side-chain, however, is more inert and resembles that of the hydrocarbons of the methane series. On the other hand, the side-chain is much more susceptible to the action of oxidizing agents, and so conspicuously is this the case that the following general rule holds good: When an aromatic hydrocarbon is subjected to the action of vigorous oxidizing agents, each side-chain which it contains is changed to a carboxyl group, and the latter occupies the same position as the original side-chain. This rule is of great value in determining the constitution of the aromatic hydrocarbons. A simple example will make this clear. It will be seen at a glance that the four compounds whose formulæ are written below are isomers, and that it will therefore not be possible to distinguish between them by analysis:

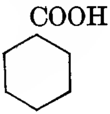


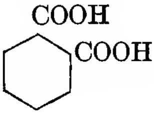


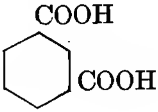


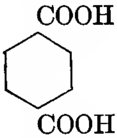


If they are oxidized, however, the resulting compounds must be the four following acids:









and since the constitutions of all the carboxyl-substituted benzenes have been thoroughly worked out, those of the three hydrocarbons are at once fixed by the reaction.

Halogen Compounds.

The halogen compounds of the aromatic series again serve to illustrate the differences in chemical character between the benzene ring and the side-chains. When aromatic hydrocarbons are treated with chlorine or bromine in the sunlight and at a boiling temperature, substitution of the hydrogens in the side-chain takes place. When, however, the reaction takes place in the cold, and not in the direct sunlight, substitution is effected in the ring. For carrying out the latter reaction, catalytic agents are usually employed. Prominent among these is metallic iron. This is one of those cases in which the mechanism of the catalysis is well understood, and on that account it deserves a word of notice. The iron and bromine first react to form ferric bromide:

$$Fe + Br_3 = FeBr_3.$$

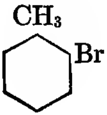
The latter reacts with benzene, for example, to form bromobenzene and hydrobromic acid:

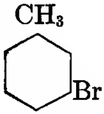
$$C_6H_6 + 2\,FeBr_3 = 2\,FeBr_2 + HBr + C_6H_5Br,$$

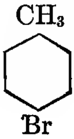
and ferrous bromide. Finally the ferrous bromide again takes up an atom of bromine:

$$FeBr_2 + Br = FeBr_3,$$

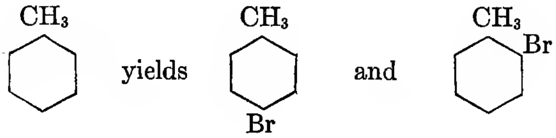
and the series of reactions is repeated. In cases of this sort the iron is said to act as a 'carrier.' The proof of the correctness of the above interpretation lies in the fact that each of the three reactions will take place separately. The product of the particular reaction cited may serve as a type of the other products of this class. It is a colorless liquid insoluble in water. It has the specific gravity 1.517, and boils at 155°. Another name for this compound is phenyl bromide, and the name *phenyl* for the group C_6H_5 is one which the student should fix carefully in mind. This radicle is fully as important as *methyl* or *ethyl*. When chlorine or bromine acts upon a hydrocarbon containing a single side-chain under the conditions just described, substitution still takes place in the ring; and from the theory it is clear that the formation of three isomeric products might be expected. Those which might be formed from toluene are indicated below:

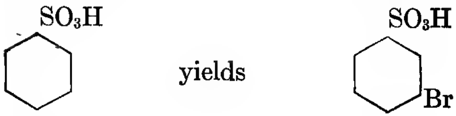


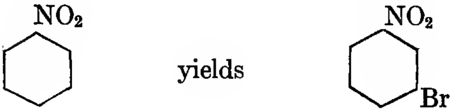




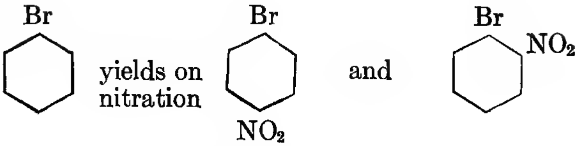
As a matter of fact, it is the para and ortho compounds which predominate as products of the reaction. Facts of this sort are difficult to remember, but fortunately there is an empirical rule by the aid of which it is usually possible to predict the constitution of the resulting compound when a mono-substituted benzene derivative receives a second substituent. The rule is that when the first substituent is one of the following five groups, viz.: NO_2, SO_3H, COOH, CHO, and CN, the second substituent may be expected to assume the meta position to that already occupied. If it is some group other than these five, substitution takes place in the para and ortho positions. It is generally true in this case that more para than ortho is formed. The five groups are not difficult to remember, for the first three suggest the important inorganic acids, nitric, sulphuric, and carbonic; while the aldehyde and nitrile groups are easily associated with carboxyl because they both easily go over into it, the first by oxidation and the second by saponification. It is not claimed that the rule is of universal application, but it covers a large number of cases, and indicates what may generally be expected. A few examples will serve to make clear the application of the rule. Under the influence of bromine,







whereas



When toluene is treated with chlorine in the sunlight and at boiling temperature, no substitution takes place in the ring, but the hydrogens of the side-chain are successively replaced by chlorine. The products are benzyl chloride, $C_6H_5CH_2Cl$; benzal chloride, $C_6H_5CHCl_2$; and benzotrichloride, $C_6H_5CCl_3$. These compounds are liquids having an extremely irritating effect upon the mucous membrane of the throat and eyes. The student should take pains to fix in mind the word *benzyl,* the name of the radicle $C_6H_5CH_2-$. It is of common occurrence.

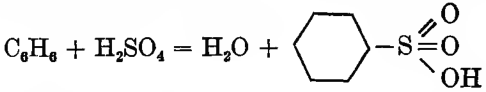
The chemical properties of the aromatic halides differ according to whether the halogen atoms are situated in the ring or in the side-chain. It will be remembered that the halides of the aliphatic series are very reactive substances, which freely exchange the halogen atom for other groups or radicles. This reactivity of the aliphatic halogen extends to the aliphatic portion of the derivatives of benzene, — that is, to the side-chain. Halogen there situated shows the same reactivity which characterizes the aliphatic halides, and it is interesting to note that it is also available for use in the aluminium chloride synthesis (page 236). Benzyl chloride, for example, when treated with benzene in the presence of aluminium chloride, smoothly yields diphenyl methane:

$$C_6H_5 \cdot CH_2 \cdot Cl + C_6H_6 = HCl + C_6H_5 \cdot CH_2 \cdot C_6H_5.$$

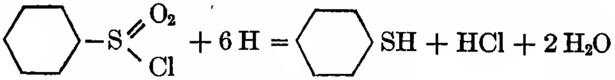
With halogen which is situated in the ring, the case is quite different. Here the halogen is held so firmly that it can be reacted upon by liquid reagents only with extreme difficulty. An example of this is the fact that bromobenzene yields no potassium bromide when treated with alcoholic potash, even after protracted boiling. Toward metals the aromatic halides are nearly as reactive as the aliphatic.

The Sulphonic Acids.

When benzene, or one of its homologues, is treated with concentrated, or better with fuming sulphuric acid, a sulphonic acid is formed:



The accepted constitution of such a compound is expressed in the formula given. Evidence that it is not an ester of sulphurous acid is found in the fact that it cannot be saponified by the usual agents. Further, when a chloride or anhydride of such a compound is subjected to the action of reducing agents the reaction proceeds as follows:



In the products of reduction, sulphur is directly connected to carbon, and the same holds true of the sulphonic acids, since no sulphur is split off in the operation.

The sulphonic acids are strong acids very soluble in water. They usually crystallize with one or more molecules of that solvent, and are not volatile without decomposition. The simpler compounds of this type have little importance of their own, but great practical importance attaches to the class, because the presence of a sulpho-group makes a compound more soluble in water without, in general, much affecting its other properties. This is of particular value in the manufacture of dyes. It is desirable that these should be soluble in water, and in consequence a large proportion of those upon the market are either sulphonic acids or salts of such acids. The coloring power of the dyes depends upon the presence of other groups.

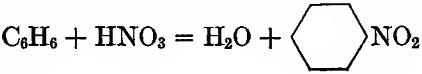
Sulphonic acids also possess importance as intermediate products in the preparation of phenols, but this reaction can well be postponed until that class of substances is taken up.

CHAPTER XIV.

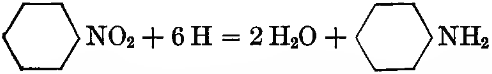
AROMATIC NITROGEN COMPOUNDS.

The Nitro-compounds.

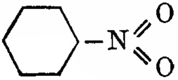
When benzene or one of its homologues is treated with fuming nitric acid, or more commonly with a mixture of concentrated nitric and sulphuric acids, the following reaction takes place:



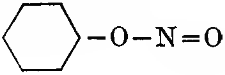
The product is one of the nitro-compounds. They are liquids or solids of strongly aromatic odor which on reduction in acid solution yield primary amines:



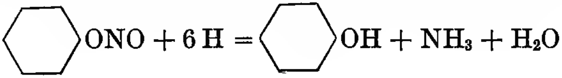
This reaction is interesting from two widely differing points of view. Its technical importance lies in the fact that the amines are valuable materials in the dyestuff industry, and they are, for the most part, prepared in this way. The reaction is theoretically important because it serves to fix the constitution of the nitro-compounds. For nitrobenzene, for example, either of the two following formulæ might, at first sight, appear reasonable:



or



It is clear, however, that only the first is consistent with the formation of a primary amine upon reduction, for a compound of the second formula must either yield a product containing both nitrogen and oxygen, or else the nitrogen would be completely split off as suggested in the following equation:



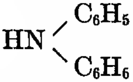
As intimated above, the nitro-compounds are chiefly important as intermediate products, rather than on account of any properties of their own. Consequently, only nitrobenzene, the simplest member of the class, will be described here. It is an oil heavier than water, and is colorless when pure, although the technical product is always yellow on account of an impurity which is difficult to remove. Nitrobenzene boils at 209° and is readily volatile with steam. It possesses an odor much like that of benzaldehyde, the characteristic ingredient of the oil of bitter almonds. In consequence it finds use as an adulterant and substitute for this more expensive material in confectionery and similar products. This is unfortunate, as nitrobenzene is quite poisonous.

Nitrobenzene is prepared technically in enormous quantities, and almost all of it is immediately reduced, in order to obtain the most important of the primary amines, aniline.

The Aromatic Amines.

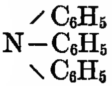
The primary amines of the aromatic series are prepared almost altogether by the reduction of the corresponding nitro-compounds. For laboratory purposes on the small scale, the reagents used are tin and concentrated hydrochloric acid. In technical work the cheaper iron and sulphuric acid are usually employed. The secondary and tertiary aromatic amines are generally obtained by processes of substitution in the primary compounds. As far as the methods used require description, they will be mentioned in connection with the individual products. The amines are oils or solids of a heavy odor which is sometimes designated as 'basic.' They are generally volatile with steam, and, in chemical properties, show a certain analogy to the amines of the aliphatic series. It will be remembered that in the latter compounds the resemblance to ammonia was strongly marked. Those aromatic amines, however, in which nitrogen is connected directly to a benzene ring no longer possess the odor of ammonia; they are insoluble in water, and are decidedly weaker bases than either ammonia or its aliphatic derivatives. It is customary to account for this fact by the statement that the phenyl group is more negative in character than the alkyl radicles, although the exact significance of this expression might prove a little difficult to determine. Nevertheless, to say that a given radicle is 'positive' or 'negative' is a constantly recurring expression in organic chemical discussion, and the student should early familiarize himself with the point of view involved. The present case is well adapted to serve as an example.

It is generally true that the aliphatic amines are stronger bases than ammonia. Accordingly, the alkyl radicles are said to be more positive or basic than hydrogen. Aniline, on the other hand, is a weaker base than ammonia, and the negative influence of the phenyl groups is still more clearly seen when more of the hydrogens of ammonia are substituted. Diphenylamine,



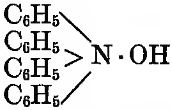
$$HN\begin{matrix} \diagup C_6H_5 \\ \diagdown C_6H_6 \end{matrix}$$

is a much weaker base than aniline, — so much so that its salts are decomposed by dilution with water. Triphenylamine,



$$N\begin{array}{l}\diagup C_6H_5\\ -C_6H_5\\ \diagdown C_6H_5\end{array}$$

has ceased to be a base at all and is not even soluble in acids. Finally pure aromatic bases of the type suggested by the following formula do not exist:



$$\begin{array}{l}C_6H_5\\ C_6H_5\\ C_6H_5\\ C_6H_5\end{array}\!\!>N\cdot OH$$

Inasmuch as radicles cannot be isolated either as such or in solution, it has not generally been possible to procure adequate numerical data by which the positive or negative character of a given group can be fixed quantitatively. This gives a certain vagueness to the whole underlying idea, and this vagueness is in no wise helped by the fact that when substituted in certain compounds a given group sometimes exerts an influence upon the character of the product quite out of harmony with what is known of it elsewhere. The phenyl group, for example, is an important and apparently essential constituent of certain very strong bases. Despite such inconsistencies, the idea of positive and negative radicles is essentially helpful, but the student should realize its limitations.

Another marked difference between the aliphatic and aromatic amines especially concerns the primary compounds. It will be recalled that the aliphatic representatives of this type react with nitrous acid in such a way that the amino-group is replaced by hydroxyl:

$$C_2H_5NH_2, HCl + HNO_2 = HCl + H_2O + N_2 + C_2H_5OH.$$

This result can also be obtained in the aromatic series, but here certain important intermediate products are formed which are extremely reactive:

$$C_6H_5NH_2, HCl + HNO_2 = 2\,H_2O + C_6H_5N_2Cl.$$

These are called diazonium salts, and the various transformations of which they are capable are so interesting and important that they will be treated a little later as a separate topic.

In addition to the differences already mentioned, the aromatic amines show the characteristic reactions belonging to the hydrogens of the benzene ring. They can, for example, be chlorinated, brominated, and sulphonated with even more readiness than the aromatic hydrocarbons themselves. Considering the amines as benzene derivatives, it may be said that the amino-group has a tendency to make especially reactive that hydrogen which stands in the para position to itself, and some of this reactivity extends to the ortho position as well. Amines are also more susceptible to the action of oxidizing agents than are most benzene derivatives, and many of the reactions involved are very complicated. They will receive attention only where the importance of the products makes it necessary.

Aniline, the simplest possible aromatic amine, is a compound of the highest technical importance, especially for the development of the dyestuff industry. So much is this the case that the term 'aniline dyes' has come, in popular usage, to stand for all synthetic coloring matters derived from coal-tar. Aniline is prepared technically by the action of iron and hydrochloric acid upon nitrobenzene. An interesting detail of the process is the small amount of acid required. It so happens that when, at the start, a little ferrous chloride has been formed, this acts catalytically in such a way that the reduction of the bulk of the nitrobenzene is effected by the metallic iron directly, so that only onefortieth as much hydrochloric acid is required as would be calculated from the equation:

$$C_6H_5NO_2 + 6\,HCl + Fe_2 = 2\,FeCl_3 + 2\,H_2O + C_6H_5NH_2.$$

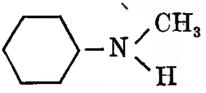
Aniline is an oil heavier than water, and soluble in that medium only to the extent of about 3%. It is colorless when pure, but on standing acquires first a reddish and finally a very dark color, probably due to oxidation. Aniline boils at 184° and is readily volatile with steam. This property is frequently made use of in isolating it from a reaction mixture in which it has been set free. As a base, aniline forms salts by direct union with acids. These are crystalline compounds more or less soluble in water. The sulphate is soluble only with considerable difficulty. The salts all hydrolyze to a certain extent in aqueous solution and react acid with the ordinary indicators.

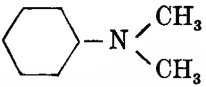
One of the most sensitive tests for aniline is a color reaction which it shows with hypochlorites. If a few drops of a solution of bleaching powder are added to an aqueous solution of aniline, a dark violet color appears on standing, even if the aniline solution is extremely dilute.

Homologues of aniline are of three kinds. These may be thought of as derived from aniline, (1) by the substitution of alkyl radicles for hydrogen in the benzene ring, (2) by the substitution of alkyl radicles in the amino-group, (3) by the transfer of the amino-group to the side-chain.

Typical members of the first class are the three toluidines, ortho, meta, and para. Of these the ortho and para compounds possess technical importance. For their preparation, the toluene from coal-tar is nitrated, and the mixture of *o*- and *p*-nitrotoluenes reduced without being separated. Finally, the mixed toluidines are distilled with a quantity of sulphuric acid insufficient to neutralize both. *o*-Toluidine then distills over, while the para compound remains behind as a sulphate. *o*-Toluidine is a liquid which boils at 197°, *p*-toluidine is a crystalline solid which melts at 45° and boils at 198°. The chemical properties of both are strictly analogous to those of aniline.

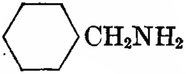
Prominent members of the second group are the technically important compounds, methylaniline and dimethylaniline:





As the formulæ indicate, one is a secondary and the other a tertiary amine. Since the hydrogens of ammonia are here substituted by both aliphatic and aromatic radicles, such bases are frequently referred to as 'mixed.' These compounds are commonly prepared by heating aniline with methyl alcohol and sulphuric acid. Both are liquids boiling at 192°, and are suggestive of aniline itself in their physical and chemical properties. They differ from that compound in not being primary amines.

Of the third type of homologue, only one need be mentioned, benzylamine,

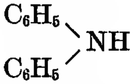


This compound is an isomer of the toluidines, but its amino-group is located in the side-chain. This constitution is sufficiently established by several methods of preparation, of which only one, that from benzyl chloride and ammonia, need be mentioned here:

$$C_6H_5CH_2Cl + 2\,NH_3 = NH_4Cl + C_6H_5CH_2NH_2.$$

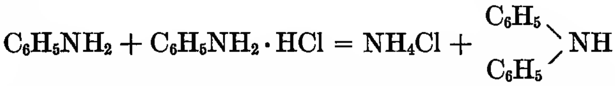
As might be expected, this substance more closely resembles the aliphatic amines than do any of the bases previously described. It is a liquid boiling at 187°. It is soluble in water and is a strong base which even absorbs carbon dioxide from the atmosphere.

Another aromatic amine should be mentioned in this connection, viz. diphenylamine:



$$\left.\begin{array}{l}C_6H_5\\C_6H_5\end{array}\right\rangle NH$$

As its formula indicates, this is a purely aromatic secondary amine. It is of considerable technical importance in the manufacture of certain dyes and is prepared technically by heating aniline with its hydrochloride to a temperature of 140°:

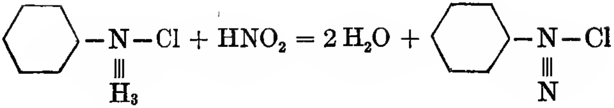


$$C_6H_5NH_2 + C_6H_5NH_2\cdot HCl = NH_4Cl + \left.\begin{array}{l}C_6H_5\\C_6H_5\end{array}\right\rangle NH$$

Diphenylamine is a crystalline solid which melts at 54° and boils without decomposition at 310°. Its slight basicity has already been referred to. In addition to its technical importance, diphenylamine is a familiar reagent. The deep blue color which it gives with even minute traces of nitric acid is one of the most delicate tests for the presence of that substance.

The Diazo-reaction.

Allusion has already been made to the fact that treatment of the primary aromatic amines with nitrous acid leads to the formation of diazonium salts. When it is desired to isolate the latter, it is usual to prepare the salts of the amines, dissolve these in alcohol, and add amyl nitrite and hydrochloric acid to the solution. These react, yielding nitrous acid, which then acts upon the salt of the amine in the manner indicated by the following equation:



The product being insoluble in alcohol is precipitated directly. The appropriateness of the graphic formula here given will be discussed a little later. The simpler diazonium salts are colorless crystalline substances soluble in water, but less so in other liquids. Such solutions are neutral toward indicators, and contain the salts in a highly ionized condition. In this respect, these substances resemble the ammonium salts, and the name, diazonium, is intended to recall this resemblance, as well as the fact that the compounds contain two atoms of nitrogen to one benzene ring. The compound whose formula has just been given is called phenyldiazonium chloride, and this sufficiently illustrates the system of nomenclature in use.

In the dry state, salts of this type are extremely explosive, and this property would render them unsafe to work with, were it not that most of their characteristic transformations can be effected in dilute aqueous solution. This makes it possible to obtain the final products without isolating the diazonium salts themselves at all. When this is desired, the method of preparation just outlined is not followed. Instead the amine is dissolved in dilute aqueous acid, and, while keeping the solution cold, the calculated quantity of a cold dilute solution of sodium nitrite is cautiously added:

$$C_6H_5NH_2, HCl + HNO_2 = 2\,H_2O + C_6H_5 \cdot N_2Cl.$$

The solution now contains the diazo-compound and is susceptible of a great number of transformations, of which some of the most important will be briefly mentioned:

(1) If the aqueous solution is simply heated to boiling, nitrogen escapes, hydrochloric acid is formed and hydroxyl takes the place in the benzene ring originally occupied by the amino-group:

$$C_6H_5N_2Cl + H_2O = HCl + N_2 + C_6H_5OH.$$

The product belongs to the class of compounds which will be studied later under the name of phenols.

(2) If the solution is reduced by means of alkaline stannous chloride, the diazo-group is eliminated completely and, in the particular case cited, benzene is formed:

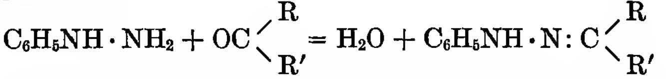
$$C_6H_5N_2Cl + 2\,H = HCl + N_2 + C_6H_6.$$

This is a general reaction, and serves in scientific work to discover the hydrocarbon from which a given unknown amine is derived.

(3) If the reduction is carried out in acid solution, the nitrogen is not evolved, and a hydrazine is formed:

$$C_6H_5N_2Cl + 4\,H = HCl + C_6H_5NH \cdot NH_2.$$

Phenylhydrazine, whose formula appears in the equation, is an important reagent for aldehydes and ketones. With such substances it reacts in the sense of the following equation:



$$C_6H_5NH \cdot NH_2 + OC\begin{matrix} \diagup R \\ \diagdown R' \end{matrix} = H_2O + C_6H_5NH \cdot N : C\begin{matrix} \diagup R \\ \diagdown R' \end{matrix}$$

The products formed are called hydrazones. Some mention was made of them in connection with the sugars, in the study of which they have proved of especial value.

(4) If a solution of a diazonium salt is treated with cuprous chloride, bromide, or cyanide, nitrogen is evolved, and chlorine, bromine, or cyanogen is substituted in the benzene ring:

$$2\,C_5H_5N_2Cl + Cu_2(CN)_2 = Cu_2Cl_2 + 2\,N_2 + 2\,C_6H_5CN.$$

The introduction of cyanogen is of particular importance because the products are nitriles of aromatic acids:

$$C_6H_5CN + 2\,H_2O = NH_3 + C_6H_5COOH.$$

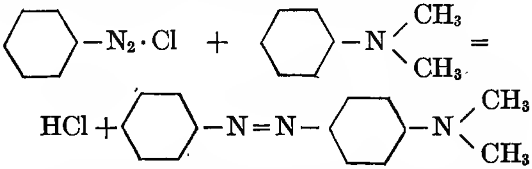
Hence the diazo-reaction furnishes an indirect means of replacing the amino-group by carboxyl.

(5) By the addition of potassium iodide to a diazo-solution, the nitrogen complex may be replaced by iodine without the use of copper salts:

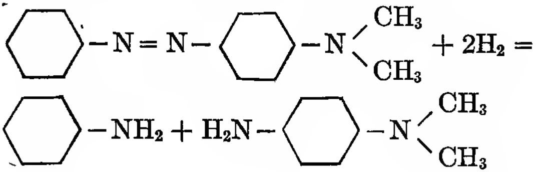
$$C_6H_5N_2Cl + KI = KCl + N_2 + C_6H_5I.$$

This is perhaps the most convenient method for introducing iodine into a benzene ring.

(6) Finally, there remains a reaction which leads to the formation of an extremely important group of dyes. If a diazonium salt be treated in a neutral or alkaline solution with a tertiary aromatic amine or with a phenol, a reaction takes place in the sense of the following equation:



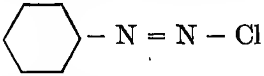
The acid component of the diazonium salt reacts with a ring hydrogen of the tertiary amine or phenol, and the remaining radicles become united in the manner denoted in the formula. In the example given the tertiary amine has a hydrogen atom in the para position to the amino-group. When this is the case, it is that atom which reacts with the diazo-compound. When the para position is otherwise substituted, the reaction usually takes place with a hydrogen in ortho position. In any case, the product belongs to the class of substances called azo-dyes. The chief evidence for the constitution of these compounds is to be found in their behavior upon reduction. In this particular case, treatment with tin and hydrochloric acid would lead to the formation of aniline and *p*-aminodimethylaniline:



These results show two things: first, that since the two nitrogens of the azo-group were separated by the reduction, one of them must have been connected with each benzene ring in the original dye. Secondly, the formation of *para*-aminodimethylaniline shows that the coupling of the dimethylaniline with the phenyldiazonium chloride took place in the para position. Both of these find expression in the formula given.

Constitution of the Diazonium Salts.

Since the dyes have the constitution just derived, it would at first seem natural to give the salts formulæ like



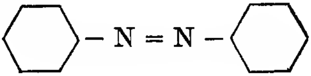
and as a matter of fact this was done until comparatively recently. Some of the reasons for the change of view are the following: It has already been pointed out that the aqueous solutions of the diazonium salts show similarity to those of the ammonium salts, and it has therefore seemed more rational to formulate these compounds with quinquivalent nitrogen. The formation of the azo-dyes need not be considered an argument against this formula, for these dyes are usually formed in alkaline or at least neutral solution, and it has been shown by a great mass of experimental evidence which need not be summed up here, that, under the influence of alkalies, the diazonium salts are changed to compounds whose constitution may be typified by the formula $C_6H_5-N=N-OK$. These and not the diazonium salts are therefore to be looked upon as most closely related to the dyes.

The Azo-dyes.

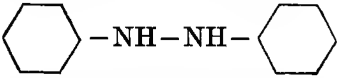
Since the azo-dyes are the first as well as one of the most important groups of such substances which we shall have to consider, this is an appropriate time to ask what is to be understood by the word *dye*, and what chemical character is to be associated with such compounds.

It is clear at the outset that not every colored substance is necessarily a dye. If a piece of wool is dipped in a solution of sodium chromate, it is colored brilliantly yellow, but a few minutes washing in running water will make it as white as before. A dye, then, must possess color and also a certain affinity to the fiber. It is generally recognized that these different properties depend upon the presence of certain specific groups in the dyestuff molecule. The following discussion will serve to give an idea of the kind of reasoning by which the functions of the different radicles are determined.

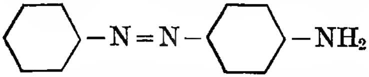
Benzene is a colorless substance, as are also most of its simpler derivatives, so that there is no occasion to regard the phenyl group as associated in any way with color. Azobenzene, however,



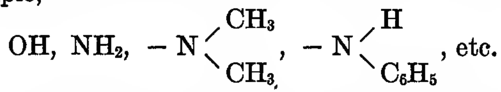
is dark red. It is therefore argued that the color is due to the grouping $-N=N-$. Further substantiation of this view is found in the fact that any modification of this complex influences the color; thus hydrazobenzene



is colorless. This azo-group then is called a *chromophore* or carrier of color. It is present in all the azo-dyes and gives its name to the class. Azobenzene itself, however, is not a dye, lacking affinity to the fiber. If an amino-group is introduced into it there is obtained the simplest possible azo-dye, commercially known as 'aniline yellow:'



This differs from azobenzene only by the presence of the amino-group. Hence to the latter is ascribed the power of giving affinity to the fiber. Such a group is called an *auxochrome* or helper of the color. It usually exerts also a marked influence upon the shade. The more common auxochromes, in this as well as in other classes of dyes, are the hydroxyl group and the free or substituted amino-group, for example,

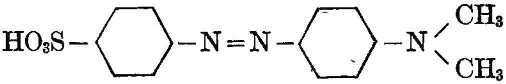


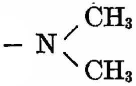
$$OH,\ NH_2,\ -N\begin{matrix}\diagup CH_3\\ \diagdown CH_3\end{matrix},\ -N\begin{matrix}\diagup H\\ \diagdown C_6H_5\end{matrix},\ \text{etc.}$$

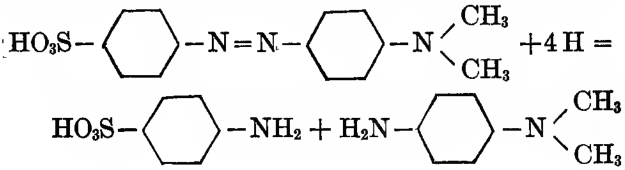
It is not equally practicable to give a list of the common chromophores, for while there is general agreement that most dyes possess a chromophore, there is, in many cases, the widest difference of opinion as to exactly what the real chromophore is in a given case. The whole subject of the relation of color to chemical constitution is at the present time in a most unsettled condition, and the nature of chromophores, the functions of auxochromes, and the influence of salt formation are all subjects of much controversy. Fortunately, there is less difference of opinion concerning the azo-dyes than almost any other group, and so this class is particularly well adapted for the exposition of the theory.

In addition to the possession of color and affinity to the fiber, it is desirable for practical reasons that a dye should be soluble in water. Since the presence of a sulpho-group can usually be depended upon to give this property without appreciable influence upon the color, such groups are introduced into most dyes intended for technical use.

The formula of the well-known indicator helianthin (whose sodium salt is also known as methyl orange),



offers a convenient example for illustrating and reviewing the points just mentioned. For its preparation, sulphanilic acid (formed by the action of concentrated sulphuric acid upon aniline) is diazotized and coupled in alkaline solution with dimethylaniline. The product possesses the chromophore $-N=N-$, the auxochrome  $-N\begin{matrix} CH_3 \\ CH_3 \end{matrix}$, and the sulpho-group $-SO_3H$, which insures solubility in water. Its constitution is fixed by the fact that upon reduction the products are *p*-aminodimethylaniline and sulphanilic acid:



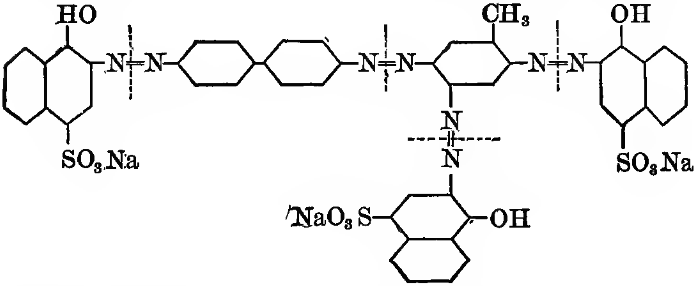
In the foregoing discussion, the question why the dye should adhere to the fiber at all has received no attention, nor is it possible to say much upon this subject at this time which is much better than a guess. Three theories at least have adherents and all are supported by more or less convincing experimental evidence: (1) the large molecules of the dye are enmeshed mechanically in the fiber, (2) the dye forms a solid solution in the fiber, (3) the dye forms a chemical compound with the fiber.

The truth probably is that all these influences are more or less at work in most practical cases. In the present state of the subject it would certainly be inappropriate to enter into discussion of their respective merits. One word may, perhaps, be ventured concerning the relation between the auxochrome groups and the chemical theory. Amino-groups are basic and aromatic hydroxyls are weakly acid. Further, it will be recalled that silks and wools are composed of protein material. Since compounds of the latter class probably have constitutions like the polypeptides, they contain both amino- and carboxyl-groups. This fits them for entering into salt-like combinations with either acidic or basic dyes.

It is also an interesting fact that while many dyes will impart their color to silks and wool, they cannot be dyed upon cotton without a mordant. By a mordant we understand something added to the cloth to make it hold the color. This is usually accomplished by the formation of some insoluble compound of dye and mordant in the pores of the fabric.

Those which require a mordant are known as 'adjective' dyes in contra-distinction to those which dye directly and are called 'substantive.' Another important classification of dyes is into 'acid' and 'basic.' In the former class, the auxochrome is usually a hydroxyl group, in the latter a simple or substituted amino-group. When a mordant is to be used this distinction is important. With acid dyes a metallic hydroxide (of iron, aluminium, or chromium) is usually employed. With basic dyes, tannin is more commonly used. The use of mordants in dyeing will receive more attention when we come to study the alizarins.

In point of numbers the azo-dyes exceed all the others. The reason for this appears when it is realized that any primary amine may be diazotized and then coupled with any secondary or tertiary amine, or with a phenol. In consequence, the number of azo-dyes theoretically possible defies calculation. In practice the number is limited by the cost of material, the fastness of the color, and the desirability of the shade from an æsthetic point of view. In color, the simpler members of this class vary from yellow through orange and reddish brown to red. Several methods are known, however, by which it is possible to multiply almost indefinitely the number of azo-groups in the product, and in this way all colors, even blues and purples, can be obtained. How complicated are the structures of some of these dyes is well illustrated by the accompanying formula:



This represents the constitution of a dye known to the trade as *Direct Heliotrope B.*

The determination of the constitution of such a compound is not so difficult a matter as the appearance of its formula would seem to indicate, for, in the first place, it usually can be predicted with a good deal of certainty from the nature of the materials coupled together in its preparation, and the order in which they were employed. These conclusions might be verified and extended by subjecting the product to the action of reducing agents. It might then be confidently expected that it would split in the manner indicated by the dotted lines in the formula, when the separation and identification of the amines found in the reaction mixture would give satisfactory evidence of the constitution of the original substance.

CHAPTER XV.

AROMATIC OXYGEN COMPOUNDS.

The Phenols.

The most important method for the preparation of the phenols has already been mentioned. It consists in boiling the diazonium salts with water:

$$C_6H_5N_2Cl + H_2O = C_6H_5OH + HCl + N_2.$$

Another method which is sometimes useful is the fusion of the sulphonic acids with caustic alkali:

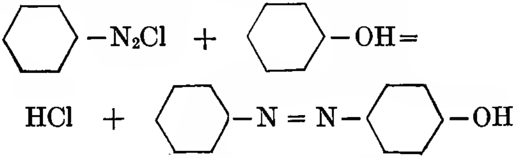
$$C_6H_5SO_3H + 3\,KOH = K_2SO_3 + 2\,H_2O + C_6H_5OK.$$

The formulæ of these substances suggest a resemblance to the alcohols, and this is borne out, to a certain extent, by their chemical behavior. They show, for example, several of the familiar hydroxyl reactions, forming ethers, esters, and the like. Nevertheless, the negative character of the phenyl group makes itself felt in the increased acidic properties of the phenols. They are weak acids, it is true, for the most part weaker than carbonic acid, but they dissolve readily in alkalies to form salts called phenolates. From such solutions they can usually be precipitated by the action of gaseous carbon dioxide:

$$C_6H_6OK + CO_2 + H_2O = KHCO_3 + C_6H_5OH,$$

and this reaction can frequently be used to advantage for isolating and purifying them.

Considered as benzene derivatives, the phenols share with the amines the increased reactivity of those hydrogens in the ortho and para positions to the hydroxyl group. Like these compounds, they couple with diazonium salts to form azo-dyes:



A genetic relationship which has not hitherto been mentioned also connects these two classes of compounds. When the phenols are treated with the addition product of zinc chloride and ammonia, amines are formed:

$$C_6H_5OH + NH_3 = H_2O + C_6H_5NH_2.$$

In some cases, this reaction is of importance for the preparation of primary amines.

Phenol, par excellence, commonly called 'carbolic acid,' has the formula C_6H_5OH. It is the simplest member of the group and its properties are quite typical. It may be prepared by either of the general methods already mentioned. It occurs in considerable quantities in coal-tar, where it is accompanied by several homologues. These can all be removed from the tar by shaking with alkali. Phenol is a crystalline solid which melts at 42° and boils at 182°. It is volatile with steam. When freshly prepared, it is colorless, but on standing exposed to the light it rapidly assumes a reddish tint. Phenol itself is a violent poison and exerts a destructive influence upon the skin or mucous membrane, at the same time producing a kind of local paralysis. It finds extensive use as a germicide and most phenols exert more or less action of this kind.

When phenols are heated with formalin, resinous amorphous substances of unknown constitution are produced, which are nevertheless of considerable technical importance.

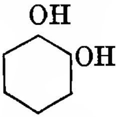
The physical properties of these substances are in a large measure dependent upon the proportions in which the components are taken, the nature of the phenols used, and the conditions of heating. Those which have been only moderately heated are soluble in organic solvents and are suitable for use as varnishes and lacquers. When these same substances are heated further under pressure insoluble substances are formed, and these may be used as insulating material, as substitutes for amber, etc. Most of the products of this sort now on the market are sold under the name of 'Bakelite.'

Picric Acid. When phenol is nitrated, three nitro-groups are easily introduced. These distribute themselves symmetrically, occupying the para and two ortho positions with reference to the hydroxyl group. Their influence is to increase the acidity of the compound. The product is called picric acid. It is a yellow crystalline solid which melts at 122°. By careful heating, it may be sublimed without decomposition, a remarkable fact when it is realized that the military explosive 'melinite' is made of this material. For vigorous explosive effects a suitable detonator must be employed. Picric acid is one of the first synthetic substances to be used as a dye. It colors woolen directly, but not cotton. If a mixed cotton and woolen fabric be dyed with picric acid and then washed out, the wool fibers will become yellow, while the cotton will not be affected. By means of a magnifier it is not difficult to count the number of yellow fibers in a given field and so ascertain roughly the proportion of wool in the fabric.

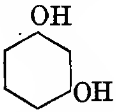
The salts of picric acid are more highly colored than the free acid. Like the latter, they are explosive.

The Cresols. Of the homologues of phenol, the three cresols or methyl phenols occur in coal-tar. It is, however, rather difficult to separate them from this mixture, and the pure compounds are usually prepared synthetically. They closely resemble phenol in their properties.

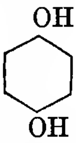
The Polyatomic Phenols. The diatomic phenols are crystalline solids which do not possess such irritating action upon the tissues as phenol and its lower homologues. The simplest ones are the dihydroxybenzenes, and all three are of interest.



Pyrocatechol



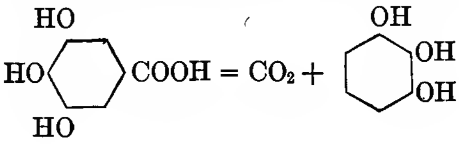
Resorcinol



Hydroquinone

They have special names which were applied before the benzene theory was worked out. The ortho compound is called pyrocatechol; the meta, resorcinol; and the para, hydroquinone. There will be occasion to speak of each more in detail later on. Hydroquinone is a reducing agent and finds extensive employment in photography as a developer. As the student is probably aware, the process of development consists in the application of a mild reducing agent to silver bromide which has been exposed to light in a camera. Those portions of silver bromide which have received most light are then reduced more rapidly and completely to metallic silver than the others. In this way a 'negative' image is obtained.

Of the trihydroxybenzenes only the vicinal compound will be mentioned. This is called pyrogallol. As the name indicates, it is usually prepared by the distillation of gallic acid:



Decomposition in the same sense may be obtained at a lower temperature by heating the acid with glycerol or aniline. Pyrogallol is a light, crystalline solid very soluble in water. Its alkaline solutions rapidly absorb oxygen from the atmosphere and this leads to its use in gas analysis for the determinations of free oxygen in gas mixtures. Pyrogallol is also much used as a developer.

The Aromatic Alcohols. From the phenols must be sharply distinguished those benzene derivatives which have hydroxyl groups in the side-chain. These compounds do not possess the acidic properties of the phenols. They are neutral substances resembling in their chemical behavior the aliphatic alcohols. The compounds of this class are of little practical importance. Benzyl alcohol may be mentioned as a type. The constitution of this substance is clear from its formation by the hydrolysis of benzyl chloride:

$$C_6H_5CH_2Cl + H_2O = HCl + C_6H_5CH_2OH.$$

It is a liquid which boils at 206°. It is soluble with difficulty in water. The oxidation of compounds of this type leads to the formation of aldehydes or ketones according to the position of the hydroxyl group, just as in the fatty series.

The Aromatic Acids.

The chief methods for the preparation of the aromatic acids are already familiar. They include (*a*) the oxidation of the aldehydes or alcohols, (*b*) the oxidation of aliphatic side-chains, (*c*) the saponification of the nitriles. The aromatic acids are solids and strong acids, the degree of acidity often showing a marked dependence upon the other substituents which may be present in the benzene ring. They form the familiar acid derivatives, salts, chlorides, amides, anhydrides, esters, etc. In chemical behavior, these derivatives show no marked differences from their aliphatic prototypes, except in matters which do not depend upon the carboxyl group.

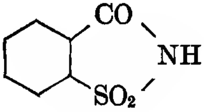
Benzoic Acid. Benzoic acid is the simplest member of the class. It may be considered as a benzene in which one hydrogen has been replaced by the carboxyl group. It receives its name from gum benzoin in which it occurs. The commercial product is, however, almost entirely obtained from toluene. When this hydrocarbon is chlorinated at high temperature in the sunlight the chlorine enters the side-chain until benzotrichloride is formed. The latter upon hydrolysis yields benzoic acid.

$$C_6H_5CCl_3 + 3\,H_2O = 3\,HCl + H_2O + C_6H_5 \cdot COOH.$$

Inasmuch as a little chlorine also enters the ring the commercial product is usually contaminated by a little *p*-chloro-benzoic acid.

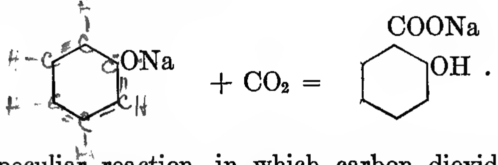
Benzoic acid is a crystalline solid which sublimes on heating. It possesses an extremely characteristic odor that is at once aromatic and suffocating. When benzoic acid is heated with an excess of lime, benzene is produced. This is entirely analogous to the formation of methane by heating sodium acetate with lime. As a benzene derivative, benzoic acid may be chlorinated, sulphonated, etc.

This may be an appropriate time to mention a derivative of *o*-sulphobenzoic acid. This is the imid, commonly known as 'saccharin':



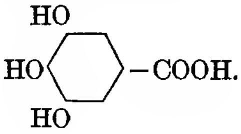
It is often prescribed in order to satisfy the craving for sweets experienced by sufferers from diabetes, who are not allowed sugar in their diet. The substance is said to be 500 times as sweet as cane sugar but has not the same physiological action as the latter, and, unlike it, is in no sense a food.

Salicylic Acid. Salicylic or *o*-hydroxybenzoic acid has obtained some importance in medicine as a remedy for rheumatism and also as an antiseptic. Its salts are not infrequently employed as food preservatives. The acid is best prepared by the action of carbon dioxide upon sodium phenolate under pressure:

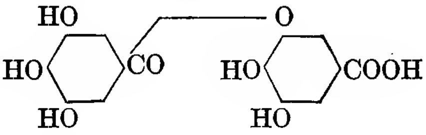


This peculiar reaction, in which carbon dioxide seems to force itself between a hydrogen atom and the ring, is of quite general application for the preparation of compounds of this type. The methyl ester of salicylic acid occurs in oil of wintergreen, and imparts the characteristic taste and odor to that substance.

Gallic Acid. This hydroxy acid occurs free in sumach and in China tea, and can be conveniently prepared by the hydrolysis of tannin. Its structure is



The fact that it easily loses carbon dioxide to form pyrogallol has already been referred to in connection with that substance. Gallic acid has the reducing properties of pyrogallol and forms some characteristic salts with metals. Under the action of dehydrating agents two molecules unite to form digallic acid of the formula



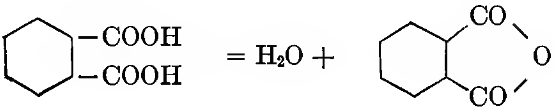
Tannin. This important substance occurs in many plants, but the most convenient source is furnished by the nutgalls of the oak. It is a colorless, amorphous substance readily soluble in water. It has an astringent taste and possesses the power of precipitating gelatin and other proteins from solution. It is much used as a mordant in dyeing, as well as in the manufacture of inks.

Until quite recently, most writing inks were prepared from tannin and ferrous sulphate. Ferrous tannate itself is nearly colorless but the ferric compound is a deep and fast black, and it is desirable that the oxidation from one form to the other shall take place upon the paper a few hours after writing. In addition to tannin and iron salts inks of this kind usually contain free acid to retard oxidation in the bottle, gum to prevent premature precipitation, an antiseptic to prevent decomposition of the gum, and some coloring matter, usually an organic dye, to make the writing temporarily visible while oxidation is going on. At the present time writing inks of this type are being replaced largely by mere solutions of coal tar dyes. India-ink is essentially a suspension of finely-divided carbon.

The structure of tannin has been a matter of much controversy, and the most valuable single fact which bears upon its constitution is found in the results of hydrolysis. This operation yields one molecule of *d*-glucose and ten of gallic acid. In the light of the best and most recent investigations, the simplest interpretation of this fact is to be found in the assumption that tannin is essentially a glucose in which each of the five hydroxyl groups has been esterified by digallic acid. Laboratory synthesis has, however, thus far failed to produce a substance identical with natural tannin.

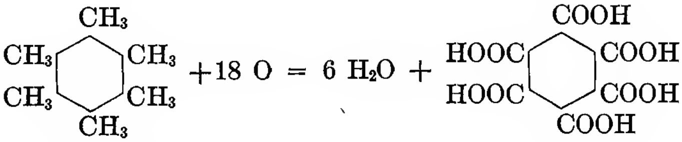
Tanning Substances. We have seen that tannin precipitates materials like gelatin, and it also possesses the property of changing hides into leather. It is, however, far too expensive a substance to be used in this latter way commercially. Instead crude extracts of various vegetable products, mostly bark and leaves of plants, are usually employed (page 208). The active principles of these substances are compounds whose structure is analogous to that of tannin. They have not, however, received any such thorough study as this substance, and their constitution is, therefore, more or less problematical. On hydrolysis they usually yield a sugar and certain hydroxy-acids of the aromatic series which have structures even more complex than that of gallic acid.

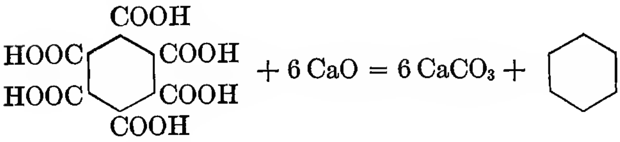
The Phthalic Acids. There are three acids which may be thought of as derived from benzene by substituting two hydrogens in that compound by carboxyl groups. These are known as the phthalic acids. They have all been of great importance in the development of chemical theory, and in fixing the constitution of aromatic substances. Here attention will be called only to the ortho compound which has some particularly interesting derivatives. When the word phthalic acid is used alone it is always this compound which is understood. It is produced on the large scale by the oxidation of naphthalene, and from this method of preparation derives its name. The reaction itself will be more clearly understood after naphthalene itself has been studied. When phthalic acid is heated above its melting-point, it loses water, forming an anhydride which sublimes in long, white needles:



This anhydride is manufactured technically in great quantities, since it is useful in the preparation of many important dyes, among them synthetic indigo.

Mellitic Acid. When charcoal or graphite are oxidized by nitric acid or by permanganates in alkaline solution, mellitic acid is formed. It also occurs as an aluminium salt in a natural mineral known as 'honey stone.' It can be prepared synthetically by the oxidation of hexamethyl benzene, and this method of formation, as well as the fact that it yields benzene when heated with lime, fixes its constitution as benzene hexacarboxylic acid:

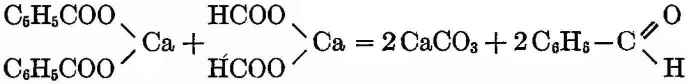




The preparation of this substance from amorphous carbon is interesting as an indication that the molecule of the latter contains at least twelve carbon atoms, and that it contains the benzene nucleus.

The Aldehydes.

The aldehydes of the aromatic series may be prepared by the oxidation of primary alcohols. More frequently they are formed by heating the calcium salts of the acids with calcium formate,



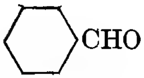
$$\left.\begin{matrix}C_6H_5COO\\C_6H_5COO\end{matrix}\right\rangle Ca + \left.\begin{matrix}HCOO\\HCOO\end{matrix}\right\rangle Ca = 2\,CaCO_3 + 2\,C_6H_5-C\begin{matrix}{/\!\!/}\,O\\ \diagdown\,H\end{matrix}$$

or by the saponification of those halides which have two halogen atoms united to a single carbon of the side-chain:

$$C_6H_5CHCl_2 + H_2O = 2\,HCl + C_6H_5CHO.$$

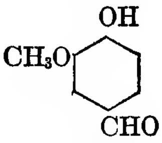
Not infrequently, also, aldehydes may be prepared by the cautious oxidation of certain hydrocarbons.

The chemical behavior of the aromatic aldehydes differs from that of the analogous aliphatic compounds in several minor particulars. These, however, hardly affect a general similarity. The aldehydes possess characteristic and, for the most part, agreeable odors. For this reason the CHO group is sometimes referred to as an 'odorophore.' Many of these substances occur in essential oils, and find use as perfumes or flavoring extracts. Benzaldehyde is found in bitter almonds, cinnamic aldehyde in cassia and cinnamon, vanillin in the vanilla bean:



Benzaldehyde

Cinnamic aldehyde



Vanillin

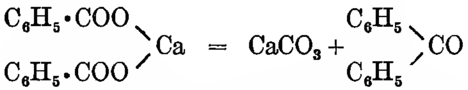
Benzaldehyde, the simplest member of the group, is technically prepared by boiling benzal chloride with lime water:

$$C_6H_5CHCl_2 + Ca(OH)_2 = CaCl_2 + H_2O + C_6H_5CHO.$$

It finds extensive employment in the dyestuff industry. It is a colorless liquid boiling at 179° and possessing the odor characteristic of bitter almonds. It readily absorbs oxygen from the air, forming benzoic acid. The occurrence of benzaldehyde in the bitter almond is of interest. Here it exists in the form of a glucoside called *amygdalin.* In the cells of the bitter almond there is also a ferment known as *emulsin.* When the almond is macerated with water, this ferment comes in contact with the amygdalin and, under its influence, the latter is hydrolyzed, forming benzaldehyde, glucose, and hydrocyanic acid.

The Ketones.

For the preparation of the aromatic ketones, three methods of preparation will be considered. The first is the familiar one consisting in the dry distillation of the calcium salts of the acids:

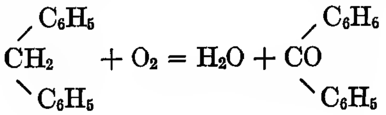


$$\left.\begin{matrix}C_6H_5\cdot COO\\C_6H_5\cdot COO\end{matrix}\right\rangle Ca = CaCO_3 + \left.\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\right\rangle CO$$

The second method is not available in the aliphatic series. It is essentially an adaptation of the aluminium chloride synthesis whose application to the preparation of hydrocarbons has already been discussed. In preparing ketones, acid chlorides are treated with aromatic hydrocarbons in the presence of aluminium chloride:

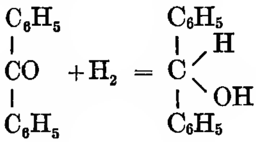
$$C_6H_6COCl + C_6H_6 = HCl + C_6H_5\cdot CO\cdot C_6H_5.$$

Finally ketones may be prepared by the oxidation of certain hydrocarbons:



$$CH_2\left\langle\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\right. + O_2 = H_2O + CO\left\langle\begin{matrix}C_6H_6\\C_6H_5\end{matrix}\right.$$

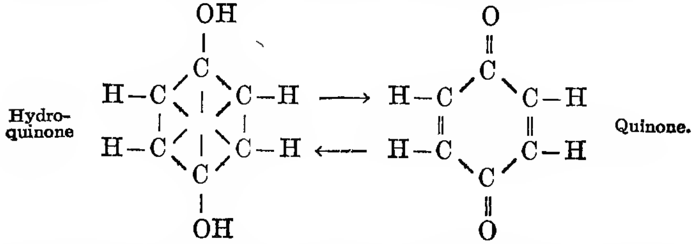
Only one of the individual compounds need be mentioned. This is benzophenone whose formula appears in the above equations. It is a crystalline solid of characteristic, faintly aromatic odor. It melts at 46° and boils without decomposition at 307°. It shows the characteristic ketone reactions and on reduction yields a secondary alcohol called benzhydrol:



The Quinones.

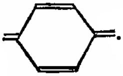
Allied to the ketones is an interesting class of substances called quinones. It is perhaps most convenient to begin the study of these substances with the description of a single representative. When hydroquinone is treated with certain oxidizing agents, such for example as ferric chloride or chromic acid, a product is formed which contains two hydrogens less than hydroquinone, and differs from it strikingly in many respects. This substance is *p*-benzoquinone often simply called quinone. It can be most economically prepared by the oxidation of aniline, but the reaction is complicated and the steps are even now but imperfectly understood.

While hydroquinone is colorless, odorless, and volatile with difficulty, quinone is bright yellow, has an odor suggestive of chlorine and sulphur dioxide, and sublimes with great readiness, being extremely volatile with steam and even with ether vapor. It blackens the skin and is a vigorous oxidizing agent, readily liberating iodine from solutions of the iodides. Gentle reducing reagents such as sulphurous acid change it back readily to hydroquinone. Quinone shows many of the properties of the ketones, but if it is to be formulated as such, it is obvious that certain far-reaching modifications in the benzene ring must be assumed at the same time. The consequences involved are perhaps made most easily intelligible when the centric formula of Baeyer is assumed for benzene. On this basis, the formulæ of quinone and hydroquinone would be written as follows:

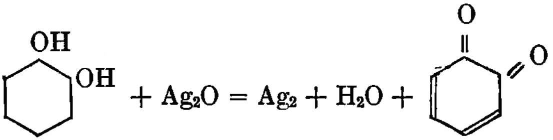


The formula ascribed to quinone requires the presence of two carbonyl groups whose carbon atoms form an integral part of a benzene ring. This can only be arranged by making use of two of the central bonds. The consequence of this, however, must be to destroy the symmetry of the combination, and the four remaining bonds no longer point to the center but go back to the periphery, forming two sets of ordinary double bonds. If now it be assumed, as the Baeyer formula tacitly does, that the aromatic character is due to the central grouping of the internal bonds, a substance of the formula given could hardly be expected to show the properties of an ordinary benzene derivative. Instead it would be apt to behave like an aliphatic compound with two double bonds. This is in large measure true of quinone. It not only differs from hydroquinone in all the properties already mentioned, but, when treated with halogens, it adds two or four atoms, whereas true benzene derivates behave, for the most part, as saturated compounds, and form addition products only with considerable difficulty.

The formula just discussed has an importance which far transcends that of the single compound itself. There are a great many colored substances, among them many important dyes, in which a similar 'quinoid' arrangement of a benzene ring is generally assumed. Almost all such substances stand in close relationship to some other compound which is colorless and which contains two atoms of hydrogen more than the colored one. They stand, in short, to the latter in the same relationship as quinone to hydroquinone. Such a colorless substance is frequently called a leuco-compound (Greek, λευκός, white).

The quinoid structure has to be referred to so frequently that it is convenient to have some abbreviation for it in our formulæ. That usually adopted is . On this basis benzoquinone itself would be written O  O.

It has been recently discovered that if pyrocatechol be shaken with silver oxide in perfectly dry benzene solution an entirely analogous *o*-benzoquinone is formed:



Resorcinol when subjected to similar treatment does not yield a quinone, and there has been some difference of opinion as to whether any substances of meta-quinoid character are capable of existence. A few compounds which have been recently prepared, however, can hardly have any other structure.

CHAPTER XVI.

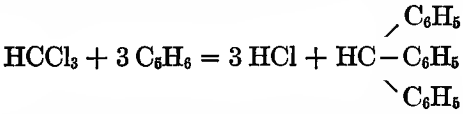
SOME IMPORTANT DYES.

The Triphenylmethane Dyes.

It is now possible to examine briefly a few of the important groups of dyes in which a quinoid chromophore is generally accepted.

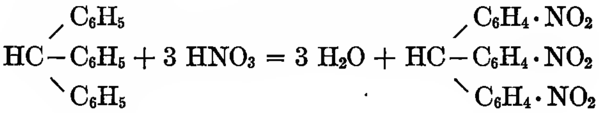
In the early days of the coal-tar-dye industry, it was found that when crude aniline oil was oxidized with arsenic acid a base was formed whose salts imparted to cloth a deep red color. These salts were brought on the market under the name of 'fuchsine' .or 'magenta' and soon had a large sale. To the base was given the name of rosaniline. Its constitution was then unknown, and any satisfactory explanation of its formation was for a long time wanting. It was soon learned, however, that the crude aniline oil was essentially a mixture of aniline with *o*- and *p*-toluidines. Later investigations revealed the fact that no one of these three compounds when oxidized alone gave any rosaniline, whereas a molecular mixture of the three yielded it in large quantities. It was also found that a similar base (pararosaniline) could be formed by oxidizing, in the same way, a mixture of one molecule *p*-toluidine and two molecules of aniline. The constitution of pararosaniline proved a little easier to fix than that of rosaniline itself, and its study furnished the key to the structure of the latter. When pararosaniline ($C_{19}H_{19}ON_3$) is reduced, it yields a substance free from oxygen which contains three amino-groups. By the diazo-reaction, it is possible to replace these by hydrogen (page 253). The product is triphenylmethane. From this point, the student will find no difficulty in forming a clear idea of the constitution of these substances by studying the steps of the following synthesis:

When chloroform and benzene react in the presence of aluminium chloride, triphenylmethane is formed in accordance with the following equation:



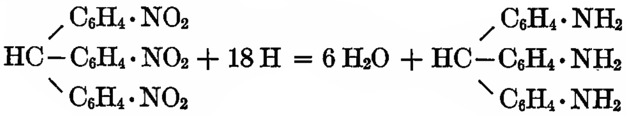
$$HCCl_3 + 3\,C_6H_6 = 3\,HCl + HC\begin{array}{l}\diagup C_6H_5\\ -C_6H_5\\ \diagdown C_6H_5\end{array}$$

Nitration of this compound introduces three nitro-groups in positions para to the methane carbon atom:



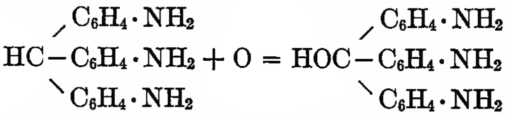
$$HC\begin{array}{l}\diagup C_6H_5\\ -C_6H_5\\ \diagdown C_6H_5\end{array} + 3\,HNO_3 = 3\,H_2O + HC\begin{array}{l}\diagup C_6H_4\cdot NO_2\\ -C_6H_4\cdot NO_2\\ \diagdown C_6H_4\cdot NO_2\end{array}$$

On reduction, the triamino-compound referred to above is formed. It is tri-*para*-triamino-triphenylmethane and is commonly known as paraleucaniline:



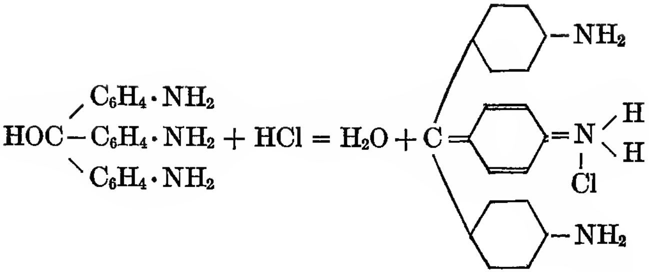
$$HC\begin{array}{l}\diagup C_6H_4\cdot NO_2\\ -C_6H_4\cdot NO_2\\ \diagdown C_6H_4\cdot NO_2\end{array} + 18\,H = 6\,H_2O + HC\begin{array}{l}\diagup C_6H_4\cdot NH_2\\ -C_6H_4\cdot NH_2\\ \diagdown C_6H_4\cdot NH_2\end{array}$$

On oxidation, this yields pararosaniline or tri-*para*-triamino-triphenyl-carbinol:

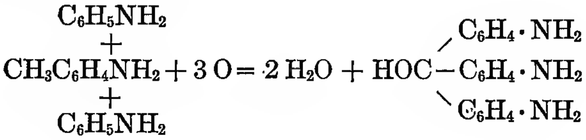


$$HC\begin{array}{l}\diagup C_6H_4\cdot NH_2\\ -C_6H_4\cdot NH_2\\ \diagdown C_6H_4\cdot NH_2\end{array} + O = HOC\begin{array}{l}\diagup C_6H_4\cdot NH_2\\ -C_6H_4\cdot NH_2\\ \diagdown C_6H_4\cdot NH_2\end{array}$$

The salt formed by treating this base (which is colorless) with one molecule of acid constitutes the dye parafuchsine:

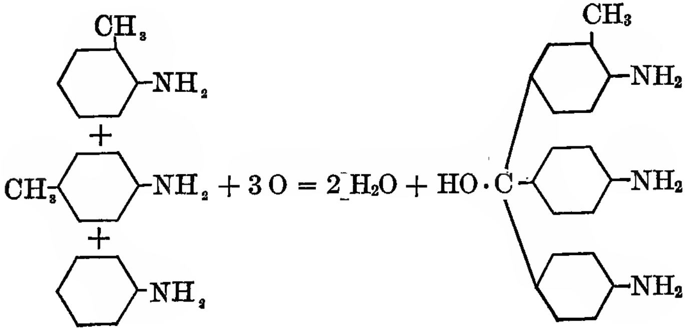


The formation of pararosaniline by the oxidation of aniline and *p*-toluidine is now sufficiently clear. The methyl group of the latter base must furnish the methane carbon atom for the final product:

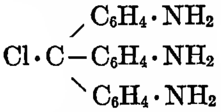


$$\begin{array}{c} C_6H_5NH_2 \\ + \\ CH_3C_6H_4NH_2 \\ + \\ C_6H_5NH_2 \end{array} + 3\,O = 2\,H_2O + HOC\begin{array}{l} \diagup C_6H_4\cdot NH_2 \\ -C_6H_4\cdot NH_2 \\ \diagdown C_6H_4\cdot NH_2 \end{array}$$

The constitution of rosaniline and its formation by the oxidation of aniline, *p*-toluidine and *o*-toluidine are, consequently, to be expressed by the following equation:

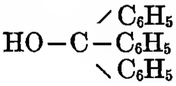


At this point, the student may wish to inquire why the complicated quinoid formula written above is assigned to the *salts* of pararosaniline and analogous compounds instead of the following apparently simpler one:



$$Cl\cdot C\begin{cases} C_6H_4\cdot NH_2 \\ C_6H_4\cdot NH_2 \\ C_6H_4\cdot NH_2 \end{cases}$$

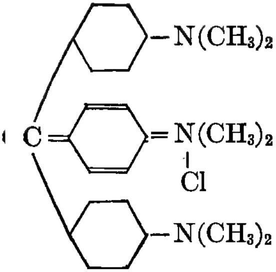
This has been the subject of a long and vigorous controversy, and it cannot be claimed that the last word has been said upon the subject. The consensus of opinion at the present time undoubtedly favors the quinoid formula. For this only one reason will be suggested here. The bright color of fuchsine certainly seems to call for a different constitution from that of the corresponding carbinol. This is colorless, and for it the constitution given is established by the fact that, by means of the diazo-reaction, it readily goes over into triphenylcarbinol:



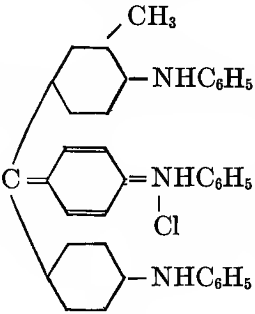
$$HO-C\begin{cases} C_6H_5 \\ C_6H_5 \\ C_6H_5 \end{cases}$$

Fuchsine itself is a crystalline solid of semimetallic luster and green reflex. In its technical preparation, it has been found possible in recent years to substitute nitrobenzene for the poisonous arsenic acid as an oxidizing agent.

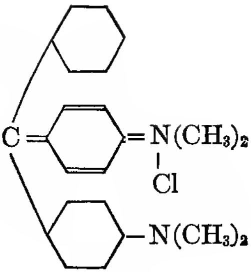
There are many important dyes allied to the fuchsines. Substitution of various radicles for hydrogen in the amino-groups leads to the formation of products whose color is more nearly blue. Elimination of one amino-group gives a green product. A few formulæ representing important dyes of this type follow:



Crystal violet

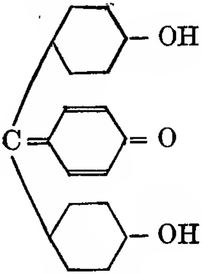


Aniline blue

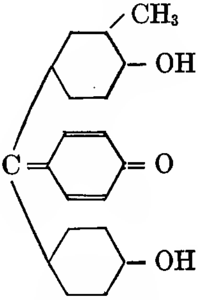


Malachite green

If rosaniline derivatives are treated with nitrous acid and the resulting diazo-compounds boiled with water, substances are produced which are known as aurins and rosolic acids. The analogy between these and the dyes just described is well brought out by the fact that they can be prepared by oxidizing phenol along with the cresols. The graphic formulæ given below make these relationships sufficiently clear:



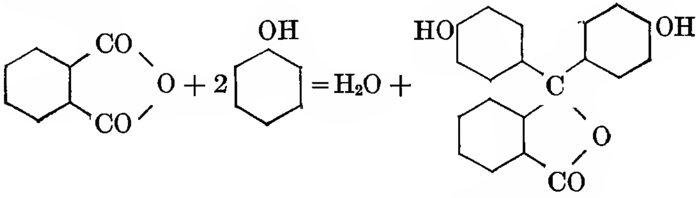
Aurin



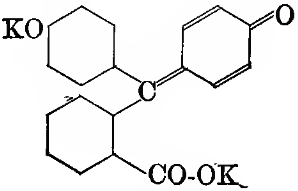
Rosolic acid

The Phthaleins.

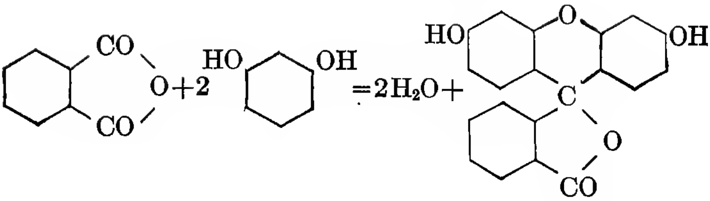
Another interesting group of colored compounds which are related to triphenylmethane can be prepared by the action of phthalic anhydride upon phenols. When these substances are heated together in the presence of some dehydrating agent, one of the carbonyl oxygens of the anhydride unites with the hydrogens of two phenol molecules to form water, and the remaining radicles are united. In the phenols that hydrogen atom usually reacts which stands in the para position to the hydroxyl group. These relations can be illustrated in the simplest case by the following equation:



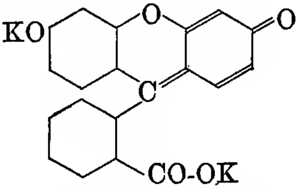
The product of this reaction is *phenolphthalein* whose use as an indicator is already familiar. It is a colorless substance which dissolves in alkalies to form a deep red salt containing two atoms of the alkali metal. To this there is generally ascribed the quinoid constitution:



Phenolphthalein is not itself a dye, but there are several important dyes which belong to the same class of compounds. If, for example, resorcinol is used instead of phenol, an analogous condensation occurs. In this case, however, an additional molecule of water is formed from two of the phenol hydroxyl groups as indicated in the equation below:



The product forms salts of the formula



The solutions of these salts fluoresce with great brilliancy and this has given the name of *fluorescein* to the original condensation product. The fluorescence is so intense that it is noticeable in extreme dilution, and this substance has been used for tracing the currents of subterranean water courses. The sodium salt of fluorescein is brought on the market under the name of *uranin.*

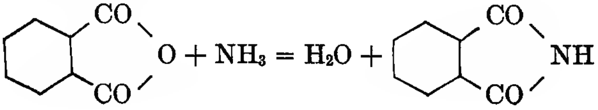
Fluorescein itself is now little used as a dye. A substitution product, however, tetrabromfluorescein, better known as *eosin,* finds use in a number of ways, particularly for the dyeing of silk.

Indigo.

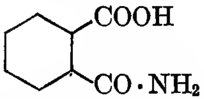
This important blue coloring matter has been an article of commerce from the earliest times. Until recently its principal source has been the plant *Indigofera tinctoria,* which grows chiefly in India. In the sap of this plant there exists a glucoside consisting of a reduction product of indigo coupled with *d*-glucose. When the plant is macerated with water and exposed to the air, hydrolysis takes place followed by oxidation and indigo blue is formed. The crude commercial product contains several coloring matters of different tints. The principal one, *indigotin*, is a dark blue powder insoluble in water, alcohol, dilute acids, and alkalies. On careful heating it sublimes, forming beautiful prisms of metallic luster. The vapor of indigo is sufficiently stable to permit the determination of its molecular weight.

For dyeing purposes, it is customary to treat indigo with such reducing agents as grape sugar or the hydrosulphites. The product is a colorless compound called indigo-white. It contains two hydrogen atoms more than indigotin. It is soluble in alkalies, and when cloth is dipped in such a solution and exposed to the air, oxidation takes place and indigo becomes fixed upon the fiber. The constitution of indigo was the subject of much study by some of the foremost investigators for many years, and several methods have been proposed for its synthetic preparation on the large scale. In recent years these have been so successful that the synthetic indigo has to a very large extent replaced the natural product in the markets of the world. No attempt will be made here to give even a fragmentary review of these interesting investigations, nor will any rigid proof for the constitution of indigotin itself be presented. Instead, one of the more recent commercially successful syntheses will be briefly outlined. From this the constitution of the product will be sufficiently apparent.

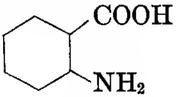
When phthalic anhydride is treated with ammonia gas phthalimid is formed:



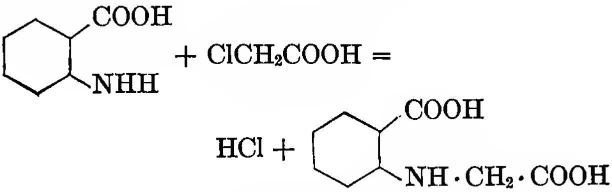
This substance may be regarded as an internal anhydride of the compound,



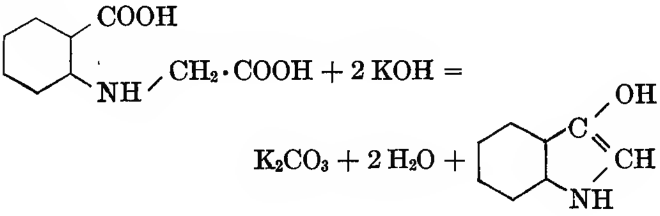
Now just as acetamide when treated with bromine and caustic potash goes over into methyl amine (page 120), so this substance under the influence of chlorine and caustic alkali loses a carbonyl group and yields *o*-aminobenzoic acid — commonly called anthranilic acid:



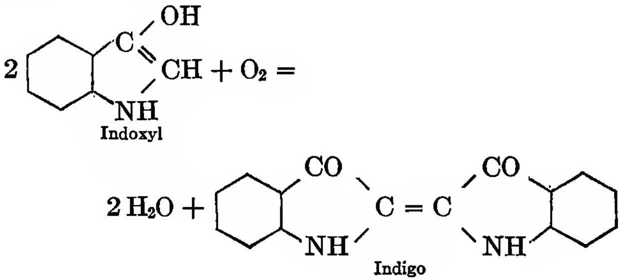
When the latter is treated with chloroacetic acid, hydrochloric acid is eliminated, and phenylglycine-*o*-carboxylic acid is formed in accordance with the following equation:



When this substance is fused with alkali, carbon dioxide and water are split off, and a compound called indoxyl is formed:



This substance is closely related to indigo, and readily goes over into it by the most gentle oxidation, — even by contact with the air:

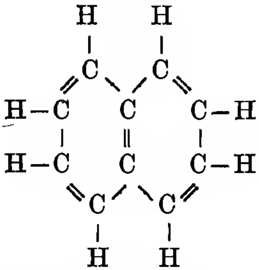


CHAPTER XVII.

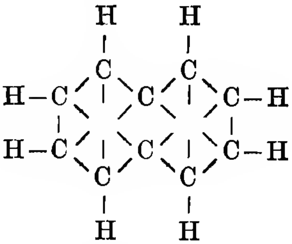
NAPHTHALENE AND ANTHRACENE. THE COAL-TAR INDUSTRY.

Naphthalene.

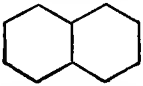
One of the most important hydrocarbons in the coal-tar distillate is naphthalene. This is a colorless, crystalline solid which melts at 79° and boils at 218°. It possesses a fatty luster and feel, it can be readily sublimed, and is volatile with steam. Naphthalene has the empirical formula $C_{10}H_8$, and a study of its constitution has led to the conviction that it consists essentially of two benzene rings which have two carbon atoms in common. This may find expression in either of the two formulæ given below:



or

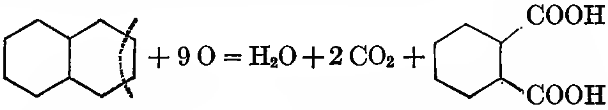


Disregarding these minor differences, the formula is usually abbreviated to



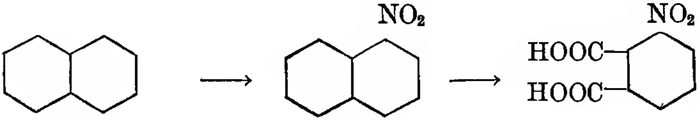
in which the two hexagons have practically the same significance as that in the familiar symbol for benzene.

The presence of one benzene ring in naphthalene is experimentally established by the ease and smoothness with which it yields phthalic acid on oxidation:

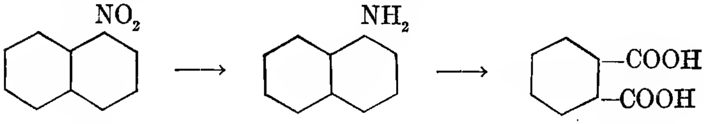


For the existence of two such nuclei, the following interesting proof is usually presented.

The nitration of naphthalene leads to the formation of a mono-nitro-compound which on oxidation yields the nitrophthalic acid whose formula is given in the scheme below:

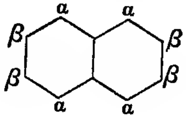


This establishes the presence of one benzene ring, and the position of the nitro-group. The latter, however, is not essential for the argument. The same nitronaphthalene when reduced yields an amine which, on the basis of all known analogous cases, must have the amino-group in the same position as the nitro-group in the compound from which it was derived. This compound when oxidized does not yield an aminophthalic acid but phthalic acid itself:



The disappearance of the amino-group is evidence that the benzene ring which contained it has been destroyed by oxidation, while a second one must have existed in the original naphthalene; otherwise no phthalic acid could have been formed.

The constitution of naphthalene just derived is supported by several syntheses and by the number of substitution products. Even a superficial examination of the formula,



will suffice to show that all the hydrogen atoms cannot be equivalent. The four marked α will, however, be mutually equivalent, and the same is true of the four marked β. As a matter of fact, two series of monosubstitution products are known, and they are regularly distinguished as α and β compounds. In individual cases the constitution is determined in a manner analogous to that employed in the case of the nitro-compound just cited. The compound is oxidized, and constitution of the resulting substituted phthalic acid determined. A more careful study of the naphthalene formula will reveal the fact that ten di-substitution products are possible according to the theory. As a matter of fact ten dichloronaphthalenes are known, and it has been found possible to assign to each a constitutional formula.

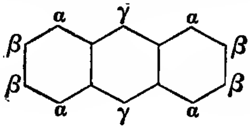
Naphthalene is essentially aromatic in chemical behavior. Its derivatives are in general analogous to those of benzene. Few of them have enough individual importance to detain us long. The phenols of this series, known as naphthols, and the amines called (naphthylamines), as well as several other derivatives, are manufactured on a large scale chiefly for use as components of azo-dyes. The consideration of these various applications would, however, teach little that is new in principle.

Naphthalene itself is sometimes employed as a cheap substitute for camphor as a protection for clothing against moths. Probably more naphthalene is oxidized for the preparation of phthalic anhydride than is used for any other single purpose. This is really the first step in the indigo synthesis, and until recently it was usually carried out by the action of chromic acid. Were it necessary, however, to use this oxidizing agent on the large scale, the cost of production of phthalic anhydride would have been prohibitive for the economical manufacture of indigo. Fortunately it was discovered that the oxidation could be carried out smoothly and successfully by means of highly concentrated sulphuric acid if mercury salts were added as catalytic agents.

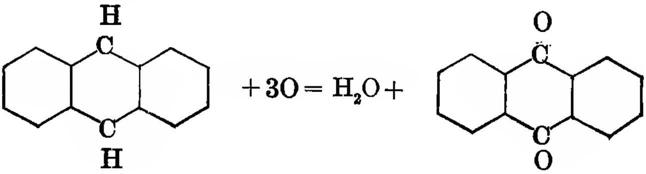
Anthracene.

Another of the higher-boiling constituents of coal-tar is anthracene. This is a crystalline solid which melts at 213° and boils at 351°. When pure it is colorless, although the commercial product has a marked yellow shade. The perfectly pure substance shows a fine blue fluorescence.

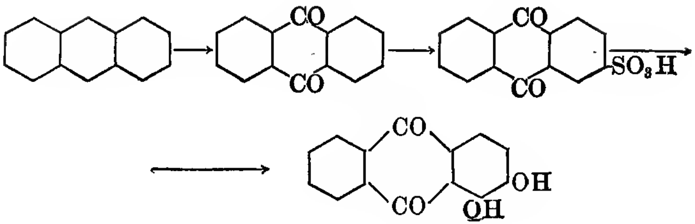
Having fixed the formula for naphthalene, that of anthracene requires no prolonged discussion. Anthracene is believed to have three benzene rings connected in a similar manner to those in naphthalene. Here, also, there are alternative possibilities with reference to the arrangement of the individual carbon valencies. For all practical purposes we may confine ourselves to the abbreviated formula.



Here it will readily be seen that three kinds of mono-substitution products must be possible according as hydrogen atoms in the α, β, or γ positions are replaced. This corresponds to the number actually existing. It is worthy of note that the hydrogens in the γ position are especially reactive. When anthracene is treated with bromine, for example, these two hydrogens are readily substituted. When anthracene is treated with oxidizing agents, it is again the γ hydrogens which are acted upon:



The product is called *anthraquinone.* It is a yellow, crystalline substance which melts at 285° and boils at 382°. It may be considered as the mother substance of an important group of dyes called the *alizarins.* The most important of these is that found in the madder root. This plant, *Rubia tinctorum,* was long cultivated in France on a very large scale for the production of this dye. In the course of a chemical investigation of the latter, it was found that when distilled over zinc dust, it yielded anthracene. This gave the key to its constitution which, on further study, was found to be that of dihydroxyanthraquinone. Soon after, it was found possible to synthesize it from anthracene. For that purpose, the latter is first oxidized to anthraquinone and that substance sulphonated. The product is a monosulphonic acid of the formula indicated below. When this is fused with caustic potash, the sulpho-group is replaced by hydroxyl, and, oxidation taking place at the same time, alizarin is formed:



This method of preparation soon proved so much more economical than the production of the dye from madder, that the latter product was driven from the market, and the land which had been used for its cultivation again became available for the production of other crops. This achievement has with justice been looked upon as one of the greatest industrial triumphs of Organic Chemistry. With it, of course, must now rank the production of synthetic indigo.

Alizarin proper, the dyestuff whose preparation has just been described, sublimes in orange-red needles which melt at 290°. A less pure product is the yellowish alizarin paste, — the form in which the dye is usually applied. Most of the dyes heretofore considered were capable of dyeing at least wool and silk directly. With the alizarins the use of a mordant is always necessary, and the color imparted to the fiber depends upon the nature of the mordant.

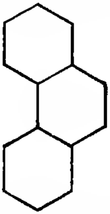
If alizarin is dissolved in alkali, and to this solution there is added the salts of various metals, precipitates are thrown down which have different colors according to the metal employed; thus aluminium salts yield a red precipitate, iron a violet black, chromium a violet brown. These precipitates may be regarded as alizarin salts. They are commonly called 'lakes,' and find use as pigments.

This makes clear the action of metallic salts as mordants. In practice, easily hydrolyzed salts, such as the acetates of aluminium, chromium, or iron, are usually employed. The cloth to be dyed is impregnated with these, and then boiled with alizarin paste, when the resulting precipitates are fixed in the fibers of the fabric. In practical dyeing with alizarin, more brilliant results are obtained by the use of 'turkey red oil.' This is a substance obtained by the action of sulphuric acid either upon castor oil or some cheaper substitute. It is an aliphatic sulphur compound of somewhat complex structure, and the chemistry of its use as a mordant is apparently not very well understood. It seems to bind both the dye and the metallic mordants. In calico printing the various portions of the design are frequently printed upon the cloth in different mordants, and then the colors brought out by a single dye.

There is quite a large group of dyes to which the class-designation of alizarins is applied. This consists of anthraquinone derivatives containing at least two hydroxyl groups and their various substitution products. The different compounds would not repay detailed consideration here.

Phenanthrene.

Isomeric with anthracene is the hydrocarbon phenanthrene. It also is found in coal tar, but has as yet no such wide application as anthracene or naphthalene. It is a colorless solid which melts at 99° and boils at 340°. The following formula represents its accepted constitution:



The only point of general interest which now attaches to this substance is the fact that the opium bases, morphine, codeine, and thebaine are to be numbered among its derivatives. Since the constitutions of these important alkaloids have not yet been fixed with certainty, no good purpose would be served by suggesting possible formulæ.

The Coal-tar Industry.

Soft coal seems to have been distilled in comparatively early times for the preparation of coke. In the latter part of the seventeenth century, Johann Joachim Becher took out a patent for the preparation of tar by this method. He recommended the use of this material as a substitute for wood-tar in the treatment of cordage and for similar purposes. He also noted that inflammable vapors were given off in the process, and pointed out that these could be made use of for smelting, as they produced "a flame ten feet long."

Little further advance seems to have been made until coal came to be distilled for the manufacture of illuminating gas. This was first done in England on a small scale by William Murdoch in 1792, but gas was first used generally for the illumination of cities about 1813. From this time on, the gas-making industry progressed rapidly, and the question of what to do with the by-products, ammonia and tar, became a serious technical problem. The latter was regarded as a special nuisance, and was for a time burned under the retorts as fuel. Later, partial distillation was effected, the light distillate being sold for use as a solvent — for india-rubber and other materials — while the residue found some employment as a preservative for timber.

A new outlook was given to the industry by the discovery that the light oils contained benzene. This observation was made by A. W. Hofmann in 1845. Benzene itself had been discovered by Faraday twenty years earlier.

The first aniline dye, *mauve,* was brought upon the market by Sir William Perkin, a student of Hofmann, in 1856. The introduction of *fuchsine* followed in 1859. From this time the use of coal-tar for the preparation of dyes increased rapidly. New impetus was given to it in 1868 by the discovery that *alizarin* could be obtained commercially from anthracene. This gave an increased value to the anthracene oil. Meantime the researches of Griess on the diazo-reaction (1858–1866) made possible the production of the great multitude of azo-dyes and so found use for a large quantity of naphthalene. The employment of naphthalene for the production of indigo dates from about 1894.

Although the preparation of dyes has been the chief object in the distillation of coal-tar, the latter has served incidentally as the source of hundreds of other products of the most various qualities. Only explosives, perfumes, and medicines need be mentioned here.

The chief constituents of the tar are the hydrocarbons; benzene, toluene, xylene, naphthalene, and anthracene, together with several phenols, as well as pyridine and allied bases. It is needless to add that this is by no means a complete list.

It would be impracticable to attempt to give an account of the manner in which coal-tar is treated technically for the production of these substances, as the methods of treatment vary widely in different establishments as well as under varying commercial conditions. In general it may be stated that the refining process consists in fractional distillation alternated with treatment by chemical reagents. Of the latter, those chiefly used in treating the cruder portions of the tar are, first, dilute caustic soda for separating the phenols and other acidic materials from the hydrocarbons; second, dilute acid for removing pyridine and other bases; third, concentrated sulphuric acid, which attacks unsaturated compounds, thiophene derivatives, and miscellaneous impurities. In making the first distillation, the following temperature limits are commonly observed.

Below 150°. — Light oil. This makes up from 3 to 5% of the tar and is the source of the simple benzene derivatives.

150°–210°. — Middle oil, 6 to 10%.

210°–270°. — Heavy oil, 8 to 10%. These two portions contain much naphthalene.

270°–400°. — Anthracene oil. From this product the anthracene is removed by chilling and consequent crystallization. The mother liquor is known as 'dead oil,' and serves for the preservation of timber.

In the retorts there still remains a quantity of pitch amounting to rather more than 50% of the original tar. This is used for such purposes as the preparation of stovepipe varnish, asphalting, and the manufacture of waterproof roofing materials.

The yields of purified products obtained from the original tar amount roughly to:

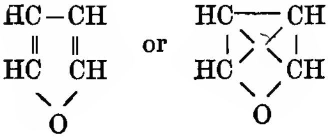
	Per Cent
Benzene and toluene	1.0 - 1.5
Phenol	0.5
Anthracene	0.25- 0.45
Naphthalene	6.0 -10.0

CHAPTER XVIII.

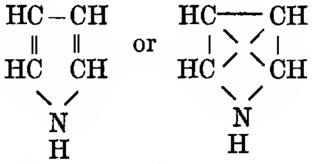
HETEROCYCLIC AND ALICYCLIC COMPOUNDS.

Heterocyclic Aromatic Compounds.

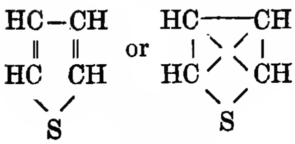
THE aromatic substances hitherto studied may all be regarded as derivatives of benzene. There exist, however, many compounds whose aromatic character is undoubted, which nevertheless are not derivatives of benzene, and indeed possess other elements besides carbon in the nucleus. All are cyclic compounds: that is, the constitutional formula of each contains a closed ring of some sort, but this is not to be regarded as the essential source of the aromatic properties. It will be seen later on that there are many cyclic compounds which are not aromatic. Those which are, however, show a certain curious similarity in structure. For each of them it is possible to write two formulæ which stand to each other in the same relation as the Kekulé and Baeyer formulæ for benzene. A few examples will illustrate this:



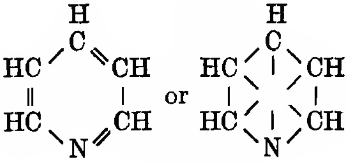
Furan



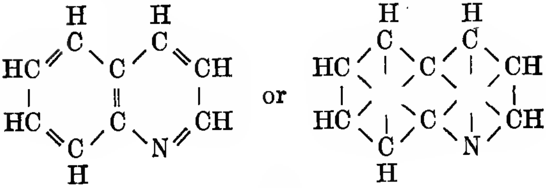
Pyrrole



Thiophene



Pyridine



Quinoline

Compounds like the above which contain other elements besides carbon as components of the ring are commonly classed as *heterocyclic.* Two or three of them deserve at least passing notice.

Thiophene occurs in small quantities associated with benzene in coal-tar. It remained undiscovered, however, for many years on account of the fact that not only thiophene itself but also most of its derivatives so closely resemble the corresponding derivatives of benzene that separation or distinction was hardly practicable. How remarkable is the resemblance may be suggested by the following table which compares the boiling-points of several benzene derivatives with those of the corresponding compounds of thiophene.

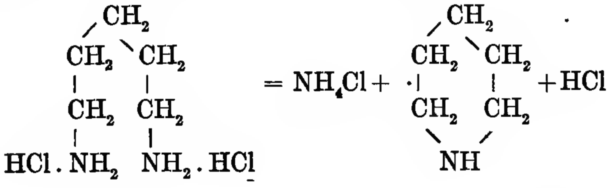
	Boiling-Pt.		Boiling-Pt.
Benzene,	80°	Thiophene,	84°
p-Dimethylbenzene,	138°	Dimethylthiophene,	135°
Isopropylbenzene,	153°	Isopropylthiophene,	154°
Diphenylmethane,	261°	Dithienylmethane,	267°
Chlorobenzene,	132°	α-Chlorothiophene,	130°
p-Dichlorobenzene,	172°	Dichlorothiophene,	170°
Tetrabromobenzene,	324°	Tetrabromothiophene,	326°

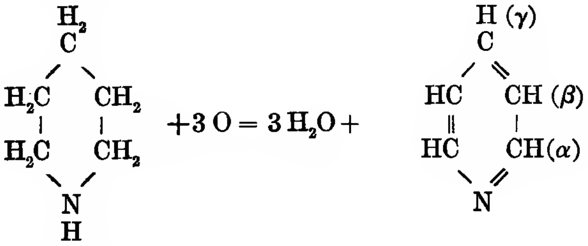
Such a parallelism is remarkable evidence that the properties of a chemical compound depend upon something else besides the identity of the elements which compose it.

Pyridine. This substance, whose formula is given above, occurs in small quantities in coal-tar, as well as in the oil obtained by the distillation of bones. It is a colorless liquid miscible in all proportions with water, as well as with most organic solvents. It has a peculiar, heavy, disgusting odor, and a depressing influence upon the nervous system. It boils at 115°. The constitution of pyridine is apparent from the following synthesis: There is an aliphatic compound, pentamethylenediamine,

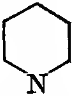
$$H_2N\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot NH_2,$$

commonly called cadaverine on account of its occurrence in decaying corpses. When the hydrochloride of this substance is distilled, a molecule of ammonium chloride is formed and a cyclic compound called piperidine is produced. The latter substance derives its name from the fact that it occurs in pepper. On oxidation it yields pyridine:

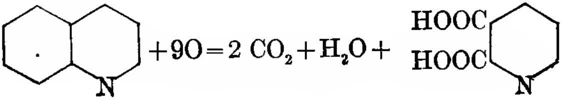




The constitution thus derived is confirmed by the number of substitution products. There are, for example, three series of mono-substitution products according to the position which the substituent assumes relative to the ring nitrogen. As indicated in the formula above, these positions are designated α, β, and γ. The formula of pyridine is commonly abbreviated as follows:



Quinoline like pyridine occurs in coal-tar and in bone-oil. It is a liquid boiling at 239°, and chemically it stands in the same relation to pyridine that naphthalene does to benzene. As a single illustration may be mentioned the fact that upon oxidation quinoline yields pyridinedicarboxylic acid. This is entirely analogous to the formation of phthalic acid by the oxidation of naphthalene:

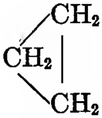


The Alkaloids.

Atomic complexes like those found in pyridine, quinoline and pyrrol make up important fragments of the molecule of several important alkaloids; such, for example, as coniine, atropine, nicotine, and quinine. Although much study has been devoted to compounds of this class, only a few have been synthesized, and while the general character of most of them is quite well understood, there is still some disagreement with regard to minor details of structure. A word may not be out of place here concerning the meaning of the term 'alkaloid.' In practice, substances of the most diverse chemical constitution are included under this designation. As the name indicates, they are all of a basic character. Other ideas commonly associated with the term include an animal or vegetable origin and the possession of marked physiological action. It has just been stated that many of these substances are associated chemically with pyridine and quinoline. Morphine and codeine, however, are derivatives of phenanthrene, caffeine is closely associated with uric acid, and cadaverine is a simple aliphatic diamine; yet all are commonly spoken of as alkaloids, and these illustrations serve to indicate the ill-defined character of the term. No attempt will be made here to treat in detail the chemical properties of these substances. For these the student must be referred to special treatises.

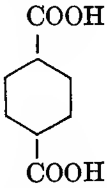
The Alicyclic Compounds.

The above designation is now commonly applied to the compounds which contain a closed ring of carbon atoms, and yet are not aromatic in character. The simplest of these is trimethylene:

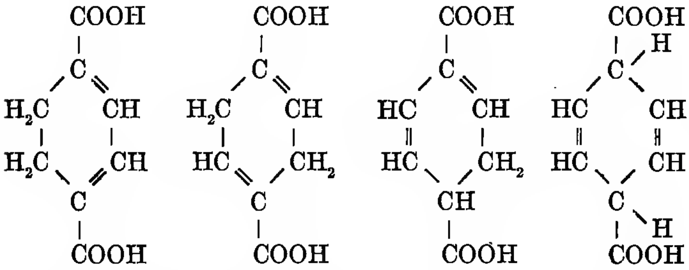


Without writing the formulæ of all possible rings of this type, it is sufficient to state that all the cyclic polymethylenes up to octomethylene $(CH_2)_8$ are known, and some of these have a great number of homologues and other derivatives, so that the total number of substances included in this branch of Organic Chemistry is already very large. Only those substances of this class will be alluded to here whose formulæ contain at least one ring of six carbon atoms. It is clear that such compounds may be regarded as reduction products of benzene derivatives, and, as a matter of fact, many of them can in practice be obtained in this manner. They are frequently referred to as *hydroaromatic* compounds.

A case of this kind which has been studied with exceptional thoroughness is that of *p*-phthalic, or, as it is more commonly called, terephthalic acid:

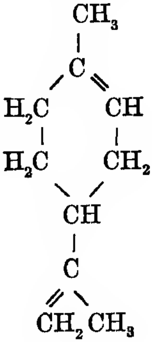


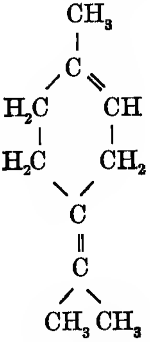
This substance adds hydrogen with far greater ease than does benzene itself, and at the first step in the reduction a marked difference in chemical properties is noticeable between the products and the parent substance. Disregarding possibilities of stereoisomerism, it will be observed that four dihydroterephthalic acids are possible, in accordance with the following formulæ:

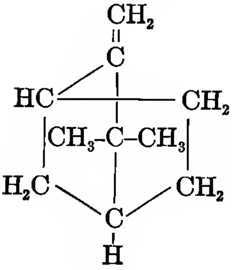


All of these substances are known and none of them are aromatic in character. The double bonds now show the properties usually associated with this type of structure in the aliphatic series. The compounds add halogen and are readily susceptible to the action of reducing agents, while oxidation frequently results in rupture of the ring at the point occupied by the double bond. The products of oxidation thus furnish the most important means of fixing the constitution of such substances. Those hydroaromatic compounds which occur in nature are, for the most part, allied to the terpenes. A strict interpretation of the latter word restricts its application to certain important hydrocarbons of the general formula, $C_{10}H_{16}$, which are hydroaromatic in character. Many of them are more or less closely allied to cymene (page 235). These substances occur in the sap of conifera and in many essential oils. They usually possess agreeable, refreshing odors. Their constitution and mutual genetic relationships have been the objects of thorough investigations for the past twenty years, and though, at one time, this was considered one of the ill-developed divisions of the science, it is now one of the most fruitful fields of investigation. The study offers some exceptional difficulties, as the products are particularly liable to molecular rearrangement and to polymerization. New material is all the time being contributed, and some of the constitutional formulæ which were once considered definitely established have recently been again called in question.

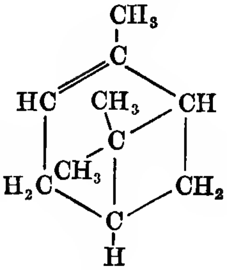
A list containing a few names and formulæ follows:


Limonene


Terpinolene



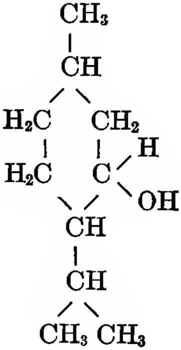
Camphene



Pinene

One compound, pinene, deserves more than passing notice, since it is the chief constituent of American oil of turpentine. This product is obtained by distilling the sap of conifera with steam. It is a colorless liquid of characteristic odor boiling at 155°. It finds its principal use as a component of paints, in which it is used as a 'thinning' material and also doubtless acts as a carrier of oxygen (page 146). Chemically it has served as a starting point in the commercial production of synthetic camphor.

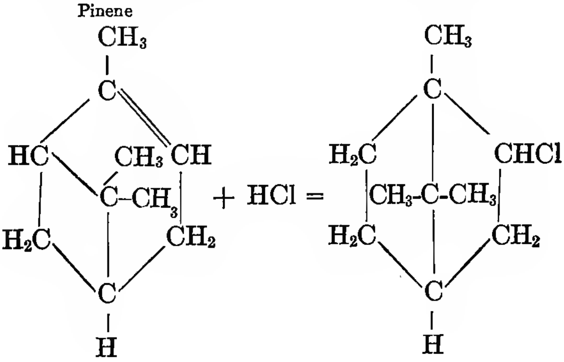
Closely allied with the hydrocarbons just alluded to are certain alcohols and ketones which are familiar substances. One example is menthol,

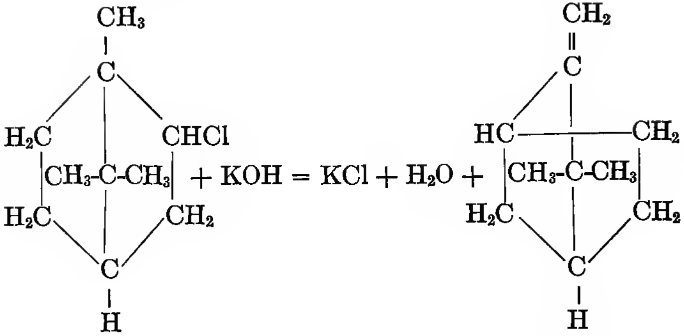


the chief and characteristic constituent of oil of peppermint. It is a crystalline solid melting at 42° and boiling at 212°. Its characteristic odor and cooling taste are well known.

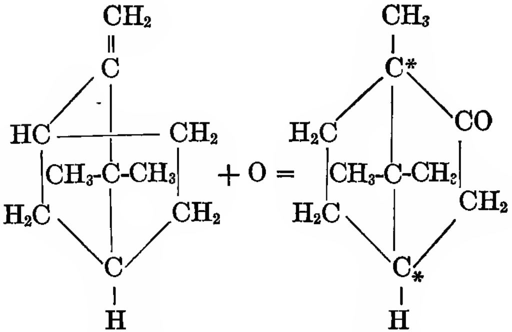
Camphor. The natural product is a gum obtained from certain trees growing mostly in Japan. It is purified by distillation with steam. It melts at 175° and boils at 204°. Camphor is used extensively for combating the ravages of moths and similar pests. Larger quantities are probably used in the manufacture of celluloid (page 179).

Some years ago the price of natural camphor rose temporarily to such a point as to stimulate efforts to prepare the substance chemically from turpentine. Two or three processes were devised and for a time they met with sufficient success to meet a considerable proportion of the commercial demand. One of the methods mentioned may be carried out as follows: Pinene is first treated with hydrochloric acid. This results in the addition of one molecule of the latter. The product is next treated with alcoholic potash, which removes a molecule of hydrochloric acid. This is, however, split off in such a way that not pinene, but an isomeric hydrocarbon, camphene, is produced. To the latter is usually ascribed the formula given in the equations below. Camphene readily yields camphor on oxidation:





Camphene



Camphene Camphor

The product is optically inactive, whereas natural camphor rotates the plane of polarized light to the right. Its optical activity can be easily accounted for in the usual way. It will be noticed that the formula given shows the presence of two asymmetric carbon atoms.

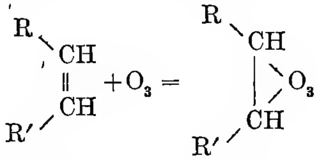
India-rubber.

An important substance whose chemical constitution has been much in doubt is india-rubber or caoutchouc. This is obtained from the sap of certain trees grown chiefly in countries near the equator. Until recently rubber was collected almost exclusively by the natives in the crudest way from the wild trees of the tropical forests, and the product was, on this account uneven in quality and relatively expensive. In recent years extensive plantations have sprung up in Ceylon and other parts of the East Indies where rubber cultivation is carried on in a scientific manner.

The sap of the rubber tree is a milky emulsion which can be coagulated by heat or better by the addition of acetic acid. The product is washed thoroughly, kneaded mechanically and finally pressed out in sheets and dried. The elasticity and amorphous character of india-rubber are well known. It dissolves readily in several organic solvents, but the solutions are colloidal. The results of analysis correspond to the formula, $C_{10}H_{16}$, but the true formula must be some large multiple of this, as there is every reason to think that the substance is a high polymer. India-rubber has the curious property of uniting directly with sulphur, and this union — known technically as *vulcanization* — adapts the rubber to its various technical uses, the hardness of the product being roughly proportional to the amount of sulphur chemically combined. In addition to this 'sulphur of vulcanization,' most commercial rubbers also contain a good deal of sulphur which is not chemically combined, as well as numerous other substances added for one purpose or another. Sometimes these additions serve a useful purpose in fitting the rubber for its use in certain articles, and sometimes they are added only for purposes of adulteration. Their presence often makes the complete analysis of rubber articles a very complicated matter.

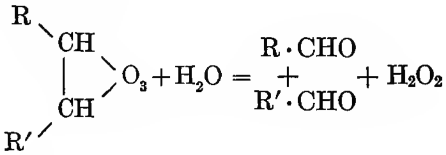
On account of its percentage composition and also because some substances allied to the terpenes are formed when rubber is destructively distilled, it had until recently been assumed that caoutchouc was itself a polymerized terpene, and that it probably contained a ring of six carbon atoms. Recent investigations have gone to show, however, that it is more probably the polymerization product of a compound containing a ring of eight carbon atoms.

The evidence upon which this conclusion is based is extremely interesting. A wide study of the action of ozone upon unsaturated compounds has revealed the fact that most substances containing a double bond react with this reagent in the manner indicated below:

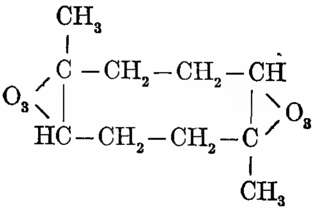


Three atoms of oxygen attach themselves to each double bond.

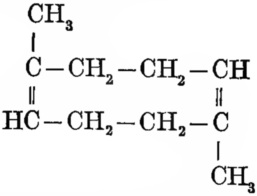
These ozonides, when treated with water, usually react vigorously in such a way that the carbons to which the ozone was attached are separated, while some of the oxygen remains with each. The product may be an acid, aldehyde, ketone, or peroxide, according to circumstances. The following equation is typical:



Now when india-rubber is treated with ozone in a dry chloroform solution, such an ozonide is formed quantitatively, six oxygens being added to each ten atoms of carbon. The molecular weight of this substance has been determined and the results yield the simple formula, $C_{10}H_{16}O_6$. By water this ozonide is readily decomposed into levulic acid, $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot COOH$, and the corresponding aldehyde peroxide, substances of well-known constitution. This result makes probable for the ozonide the constitution,



and for the original hydrocarbon that expressed by the formula,



*

Gutta percha is apparently isomeric with india-rubber, and is obtained from similar sources.

In recent years numerous attempts have been made to synthesize rubber, and while none of them have as yet proved commercially successful, results of much scientific interest have been obtained. A substance called isoprene is found among the products when rubber is destructively distilled. This substance has the empirical formula C_5H_8 and readily undergoes polymerization back to true rubber. This may be effected by heat alone or treatment with acids under

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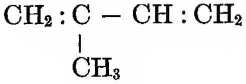
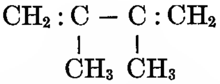
* Since the above was first printed serious doubt has been thrown upon the molecular weight of the ozonide. This makes it possible that in india rubber the isoprene fragments may be grouped in larger rings.

fixed conditions, and sometimes takes place spontaneously. Treatment with metallic sodium also causes polymerization to a substance which is practically equivalent to rubber in physical properties, but not chemically identical with it. The constitution of isoprene is



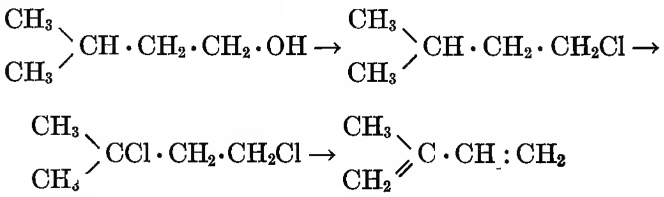
$$\begin{array}{l} CH_2 : \underset{\displaystyle CH_3}{\underset{|}{C}} - CH : CH_2 \end{array}$$

and it is interesting to note that other substances of similar structure such as butadiene $CH_2 : CH \cdot CH : CH_2$ and its dimethyl derivative



$$CH_2 : \underset{\displaystyle CH_3}{\underset{|}{C}} - \underset{\displaystyle CH_3}{\underset{|}{C}} : CH_2$$

can also be polymerized to substances which are scarcely distinguishable from caoutchouc. A practical rubber synthesis, therefore, involves the economical preparation of unsaturated hydrocarbons like those just mentioned. Several interesting processes have been worked out, but a discussion of their details would lie beyond the scope of this book. It may not be out of place, however, to indicate the steps in one synthesis of isoprene from the iso-amyl alcohol found in fusel-oil.



CHAPTER XIX.

THE STRUCTURE THEORY.

IN the foregoing pages, chemical phenomena have been discussed from the point of view of the structure theory. This assumes that the properties of chemical compounds depend upon two factors: the nature and proportions of the constituent elements, and the arrangement of the atoms of the latter within the molecules of the compounds. This arrangement is itself determined by a fixed or slightly variable saturation capacity for each element. It is further assumed that from the synthesis of a compound and its chemical behavior, it is possible to determine this structural arrangement.

The student can hardly have progressed thus far in the study of the subject without having asked himself more than once whether — however logical the various constitutional proofs might appear — such a mechanical conception of the nature of matter is in any case justifiable; and whether it is possible that minute particles of matter can exist with such complicated structures as, for example, that suggested on page 205.

It is believed that in a book of this kind such questions should receive frank discussion, but it has seemed better to place this at the end, in order that the student might approach it with some knowledge of the theory and with some ability to think in its terms. As a general principle, too, it is always advisable that a sympathetic insight into a subject should precede a critical examination of it.

At the outset it must be pointed out that the fundamental conceptions with which the structure theory deals — atoms, molecules, and valencies — contain much which is purely hypothetical. A few years ago it would have been necessary to go further and to concede that these conceptions were all pure hypothesis. Recent progress, however, in radioactivity and allied subjects has now placed almost beyond dispute the objective reality of the atom and even fixed quite definitely its mass and volume. Nevertheless, it is still true that the complex arrangements of atoms in molecules assumed by the structural formulæ of Organic Chemistry are as yet entirely hypothetical. This makes it desirable to emphasize the difference between hypothesis and fact, since the young student — and unfortunately the more venerable investigator as well — is too often apt to disregard the gulf which separates the two.

From the point of view of science, a fact is a natural phenomenon observed by the senses either directly or by means of instruments, such observation being then corrected for all sources of error known to be present in the media employed, including the sense organs themselves. The truth and validity of such a fact are obviously not absolute, since it cannot be certain, in a given case, that all sources of error are known or have been properly corrected; nevertheless, it represents the maximum of truth concerning a given phenomenon which is obtainable by the senses. A hypothesis stands upon an entirely different footing. It is a statement of something inaccessible to direct observation which, if it were a fact, would serve to coördinate and 'explain' a number of other facts. It is hardly admissible to say that a given hypothesis is 'true,' for in that case it would be a fact and no hypothesis. On the other hand, a hypothesis is obviously false if there exists any perfectly well-established fact which contradicts it. In such a case, the hypothesis must be given up or modified to fit the fact.

Such modifications have frequently resulted in the great strengthening of theories. As a rule, however, the continued necessity of making subordinate hypotheses to keep an original one afloat must be regarded as a sign of weakness.

To account for the stability of the earth in space, certain of the ancients asserted that it rested upon the back of an elephant. The difficulties caused by the elephant and his burden soon exceeded those of the original fact, and a hypothetical tortoise had to be introduced for him to stand upon. This only transferred the difficulty to the tortoise, and so a score of other hypothetical beasts had to be invented. This is an example of an especially crude and useless hypothesis, whose falsity no one has found it worth while to demonstrate.

On the other hand, the assumption that that form of energy which, acting upon the human retina, produces the impression of light, consists essentially of vibrations in an imponderable frictionless medium called the 'luminiferous ether,' — this assumption has served to satisfactorily coördinate and explain practically all the complicated phenomena of optics. The ether itself, however, remains as hypothetical a material as ever.

In the truth or falsity of a hypothesis, the scientist does not — or rather should not — have too great an interest. The question which should concern him is that of its utility. A hypothesis is useful if it coördinates facts otherwise isolated, and if it offers a stimulus for the discovery of new facts. A good hypothesis thus helps the teacher by making a subject easier to demonstrate, the student by relieving the memory of the load of many isolated details, and the investigator by suggesting experiments which test the validity of the hypothesis itself.

Having stated the advantages of a good hypothesis, what are the disadvantages? Like the advantages, these lie in the nature of the human mind. We acquire a personal interest in those hypotheses in whose terms we are accustomed to think, and a kind of blindness for those facts which lie beyond its limitations. It has frequently occurred that important facts, necessary and valuable for the progress of science, have been for long periods brushed aside and discredited because they failed to accord with dominant hypotheses, and the healthy progress of human knowledge has been much retarded in this way. Furthermore it is in the nature of every hypothesis to gradually wear out. Sooner or later a time comes when all attempts at patching fail, and the theory must be put aside and replaced by a more suitable generalization. There then frequently arises a long and often bitter controversy between the supporters of the old and those of the new. Whether such controversies are on the whole helpful to science or the reverse is a moot point. They often prove no mean stimulus to investigation, and bring out valuable facts. On the other hand, doubt may well be expressed whether the search for arguments in a desperate attempt to support one side of a passionate controversy produces the best frame of mind in which an investigator can approach the study of the truth. For these reasons many scientists believe that hypotheses have done nearly as much harm as good and some would go so far as to eliminate them altogether from the sciences. Instead, there should only be permitted such generalizations from the facts as contain terms capable of being directly measured. These should preferably be put in mathematical form.

Turning back to Organic Chemistry as we know it, there remain two questions to be asked: (1) Is the valence or structure theory a good hypothesis? (2) Is all hypothesis so objectionable that to banish it from Organic Chemistry would be for the good of that science?

There can be no doubt that the structure theory is a good hypothesis. It has coördinated quantities of apparently unrelated facts in a manner which has certainly not been excelled by any scientific generalization. It has brought these into a system. It is constantly giving the stimulus to new and profitable researches on practical as well as scientific lines, and it has again and again enabled chemists not only to imitate the products of nature, but to predict with surprising accuracy the properties of compounds "when as yet there was none of them." Into these advantages of the theory, students must have derived some insight from the foregoing pages. In an elementary work of this kind, these have perhaps been made more prominent than the weak points. The fact should not be glossed over that weak points exist. In certain cases, there seem to be more isomers than the theory can very conveniently account for. There are substances whose present formulæ seem very inadequate expressions of their chemical behavior. There are numerous chemical reactions for which the current explanations seem particularly lame and forced. Still throughout the history of the science such apparent exceptions have always existed, and in the majority of cases further experimentation has finally turned them into brilliant confirmations of the theory. There is every reason to hope that the present difficulties may be overcome in a similar manner.

For those who would tolerate in the science no hypothesis however good, the case may perhaps be fairly stated as follows: The properties of a chemical compound depend upon two factors. One of these is its elementary composition and the other its energy content. With these two non-hypothetical quantities as a basis, it should be possible to formulate expressions which should give all the information now furnished by our graphic formulæ, and not burden our minds with a quantity of hypothetical material which must sooner or later be sacrificed. As a matter of fact, no such mathematical formulæ as those suggested have ever been set up, nor has any adequate hint been offered by the opponents of the valence theory as to how this should be done. In the absence of such suggestions, it may be conceded that such formulæ might give valuable quantitative information, yet it is difficult to see how they could ever provide those valuable hints as to the qualitative behavior of substances which constitute so important a part of what can be learned from a graphic formula.

While the organic chemist will hardly be induced to forsake a hypothesis which has so wonderfully justified itself by its results, certain profitable lessons can be derived from the discussion. One of these is the undesirability of using hypotheses when non-hypothetical generalizations are equally serviceable and available. Organic chemists are perhaps too prone to forget that graphic formulæ are a means and not an end. They represent not a system of molecular architecture, but an epitome of chemical relationships and behavior.

In conclusion the student is advised to use hypotheses and not to be abused by them; to distinguish in his study, and to keep carefully separate in his mind, that which is fact and that which is hypothesis; and finally to maintain so impartial a mental attitude that when the time comes, he will be ready to replace the old forms by new and more appropriate symbols.

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